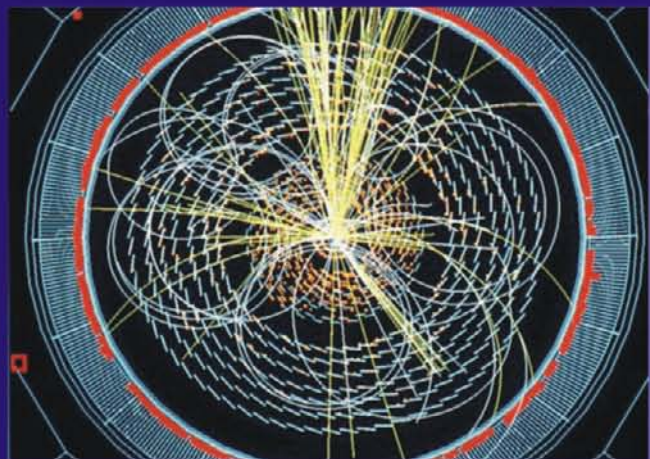


NEW AGE

SECOND EDITION

Introduction to **MODERN PHYSICS** VOLUME I



R.B. Singh



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Introduction to
**MODERN
PHYSICS**

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Introduction to **MODERN PHYSICS**

VOLUME I
(Second Edition)

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PUBLISHING FOR ONE WORLD

NEW AGE INTERNATIONAL (P) LIMITED, PUBLISHERS

New Delhi • Bangalore • Chennai • Cochin • Guwahati • Hyderabad
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ISBN (13) : 978-81-224-2922-0

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NEW AGE INTERNATIONAL (P) LIMITED, PUBLISHERS

4835/24, Ansari Road, Daryaganj, New Delhi - 110002

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PREFACE TO THE SECOND EDITION

The standard undergraduate programme in physics of all Indian Universities includes courses on *Special Theory of Relativity, Quantum Mechanics, Statistical Mechanics, Atomic and Molecular Spectroscopy, Solid State Physics, Semiconductor Physics and Nuclear Physics*. To provide study material on such diverse topics is obviously a difficult task partly because of the huge amount of material and partly because of the different nature of concepts used in these branches of physics. This book comprises of self-contained study materials on Special Theory of Relativity, Quantum Mechanics, Statistical Mechanics, Atomic and Molecular Spectroscopy. In this book the author has made a modest attempt to provide standard material to undergraduate students at one place. The author realizes that the way he has presented and explained the subject matter is not the only way; possibilities of better presentation and the way of better explanation of intrigue concepts are always there. The author has been very careful in selecting the topics, laying their sequence and the style of presentation so that student may not be afraid of learning new concepts. Realizing the mental state of undergraduate students, every attempt has been made to present the material in most elementary and digestible form. The author feels that he cannot guess as to how far he has come up in his endeavour and to the expectations of esteemed readers. They have to judge his work critically and pass their constructive criticism either to him or to the publishers so that they can be incorporated in further editions. To err is human. The author will be glad to receive comments on conceptual mistakes and misinterpretation if any that have escaped his attention.

A sufficiently large number of solved examples have been added at appropriate places to make the readers feel confident in applying the basic principles.

I wish to express my thanks to Mr. Saumya Gupta (Managing Director), New Age International (P) Limited, Publishers, as well as the editorial department for their untiring effort to complete this project within a very short period.

In the end I await the response this book draws from students and learned teachers.

R.B. Singh

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PREFACE TO THE FIRST EDITION

This book is designed to meet the requirements of undergraduate students preparing for bachelor's degree in physical sciences of Indian universities. A decisive role in the development of the present work was played by constant active contact with students at lectures, exercises, consultations and examinations. The author is of the view that it is impossible to write a book without being in contact with whom it is intended for. The book presents in elementary form some of the most exciting concepts of modern physics that has been developed during the twentieth century. To emphasize the enormous significance of these concepts, we have first pointed out the shortcomings and insufficiencies of classical concepts derived from our everyday experience with macroscopic system and then indicated the situations that led to make drastic changes in our conceptions of how a microscopic system is to be described. The concepts of modern physics are quite foreign to general experience and hence for their better understanding, they have been presented against the background of classical physics.

The author does not claim originality of the subject matter of the text. Books of Indian and foreign authors have been freely consulted during the preparation of the manuscript. The author is thankful to all authors and publishers whose books have been used.

Although I have made my best effort while planning the lay-out of the text and the subject matter, I cannot guess as to how far I have come up to the expectations of esteemed readers. I request them to judge my work critically and pass their constructive criticisms to me so that any conceptual mistakes and typographical errors, which might have escaped my attention, may be eliminated in the next edition.

I am thankful to my colleagues, family members and the publishers for their cooperation during the preparation of the text.

In the end, I await the response, which this book draws from the learned scholars and students.

R.B. Singh

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UNIT

I

SPECIAL THEORY OF RELATIVITY

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THE SPECIAL THEORY OF RELATIVITY

1.1 INTRODUCTION

All natural phenomena take place in the arena of space and time. A natural phenomenon consists of a sequence of events. By event we mean *something* that happens at some point of space and at some moment of time. Obviously the description of a phenomenon involves the space coordinates and time. The oldest and the most celebrated branch of science –*mechanics*– was developed on the concepts space and time that emerged from the observations of bodies moving with speeds very small compared with the speed of light in vacuum. Guided by intuitions and everyday experience Newton wrote about space and time: *Absolute space, in its own nature, without relation to anything external, remains always similar and immovable. Absolute, true and mathematical time, of itself, and from its own nature, flows equally without relation to anything external and is otherwise called duration.*

In Newtonian (classical) mechanics, it assumed that the space has three dimensions and obeys Euclidean geometry. Unit of length is defined as the distance between two fixed points. Other distances are measured in terms of this standard length. To measure time, any periodic process may be used to construct a clock. Space and time are supposed to be independent of each other. This implies that the space interval between two points and the time interval between two specified events do not depend on the state of motion of the observers. Two events, which are simultaneous in one frame, are also simultaneous in all other frames. Thus the *simultaneity* is an absolute concept. In addition to this, the space and time are assumed to be *homogeneous and isotropic*. *Homogeneity* means that all points in space and all moments of time are identical. The space and time intervals between two given events do not depend on *where* and *when* these intervals are measured. Because of these properties of space and time, we are free to select the origin of coordinate system at any convenient point and conduct experiment at any moment of time. *Isotropy* of space means that all the directions of space are equivalent and this property allows us to orient the axes of coordinate system in any convenient direction.

The description of a natural phenomenon requires a suitable frame of reference with respect to which the space and time coordinates are to be measured. Among all conceivable frames of reference, the most convenient ones are those in which the laws of physics appear simple. *Inertial frames* have this property. *An inertial frame of reference is one in which Newton's first law (the law of inertia) holds.* In other words, an inertial frame is one in which a body moves *uniformly* and *rectilinearly* in

absence of any forces. All frames of reference moving with constant velocity relative to an inertial frame are also inertial frames. A frame possessing acceleration relative to an inertial frame is called non-inertial frame. Newton's first law is not valid in non-inertial frame. Reference frame with its origin fixed at the center of the sun and the three axes directed towards the stationary stars was supposed to be the fundamental inertial frame. In this frame, the motion of planets appear simple. Newton's laws are valid in this heliocentric frame. Let us see whether the earth is an inertial frame or not. The magnitude of acceleration associated with the orbital motion of earth around the sun is 0.006 m/s^2 and that with the spin motion of earth at equator is 0.034 m/s^2 . For all practical purposes these accelerations are negligibly small and the earth may be regarded as an inertial frame but for precise work its acceleration must be taken into consideration. The entire classical mechanics was developed on these notions of space and time it worked efficiently. No deviations between the theoretical and experimental results were noticed till the end of the 19th century. By the end of 19th century particles (electrons) moving with speed comparable with the speed of light c were available; and the departures from classical mechanics were observed. For example, classical mechanics predicts that the radius r of the orbit of electron moving in a magnetic field of strength B is given by $r = mv/qB$, where m , v and q denote mass, velocity and charge of electron. The experiments carried out to measure the orbit radius of electron moving at low velocity give the predicted result; but the observed radius of electron moving at very high speed does not agree with the classical result. Many other experimental observations indicated that the laws of classical mechanics were no longer adequate for the description of motion of particles moving at high speeds.

In 1905 Albert Einstein gave new ideas of space and time and laid the foundation of *special theory of relativity*. This new theory does not discard the classical mechanics as completely wrong but includes the results of old theory as a special case in the limit $(v/c) \rightarrow 0$. i.e., all the results of special theory of relativity reduce to the corresponding classical expressions in the limit of low speed.

1.2 CLASSICAL PRINCIPLE OF RELATIVITY: GALILEAN TRANSFORMATION EQUATIONS

The Galilean transformation equations are a set of equations connecting the space-time coordinates of an event observed in two inertial frames, which are in relative motion. Consider two inertial frames S (unprimed) and S' (primed) with their corresponding axes parallel; the frame S' is moving along the common x - x' direction with velocity v relative to the frame S . Each frame has its own observer equipped with identical and compared measuring stick and clock. Assume that when the origin O of the frame S' passes over the origin O of frame S , both observers set their clocks at zero i.e., $t = t' = 0$. The event to be observed is the motion of a particle. At certain moment, the S -observer registers the space-time coordinates of the particle as (x, y, z, t) and S' -observer as (x', y', z', t') . It is evident that the primed coordinates are related to unprimed coordinates through the relationship

$$x' = x - vt, \quad y' = y, \quad z' = z, \quad t' = t \quad \dots(1.2.1)$$

The last equation $t' = t$ has been written on the basis of the assumption that time flows at the same rate in all inertial frames. This notion of time comes from our everyday experiences with slowly moving objects and is confirmed in analyzing the motion of such objects. Equations (1.2.1) are called Galilean transformation equations. Relative to S' , the frame S is moving with velocity v in negative

direction of x -axis and therefore inverse transformation equations are obtained by interchanging the primed and unprimed coordinates and replacing v with $-v$. Thus

$$x = x' + vt', \quad y = y', \quad z = z', \quad t = t' \quad \dots(1.2.2)$$

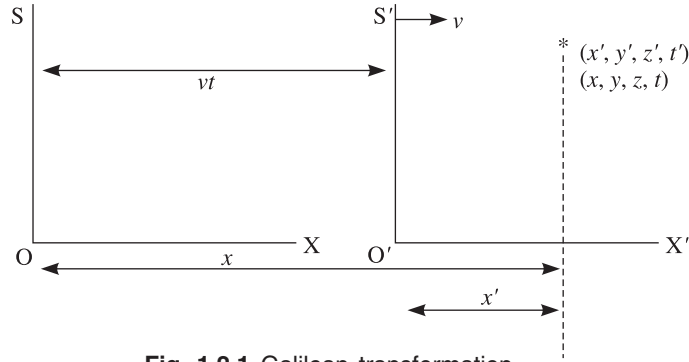


Fig. 1.2.1 Galilean transformation

Transformation of Length

Let us see how the length of an object transforms on transition from S to S'. Consider a rod placed in frame S along its x -axis. The length of rod is equal to the difference of its end coordinates: $l = x_2 - x_1$. In frame S', the length of rod is defined by the difference of its end coordinates measured simultaneously. Thus:

$$l' = x'_2 - x'_1$$

Making use of Galilean transformation equations we have

$$l' = (x_2 - vt) - (x_1 - vt) = x_2 - x_1 = l$$

Thus the distance between two points is invariant under Galilean transformation.

Transformation of Velocity

Differentiating the first equation of Galilean transformation, we have

$$\begin{aligned} \frac{dx'}{dt'} &= \frac{dx}{dt} - v \\ u'_x &= u_x - v \end{aligned} \quad \dots(1.2.3)$$

where u_x and u'_x are the x -components of velocity of the particle measured in frame S and S' respectively. Eqn. (1.2.3) is known as the classical law of velocity transformation. The inverse law is

$$u_x = u' + v \quad \dots(1.2.4)$$

These equations show that *velocity is not invariant*; it has different values in different inertial frames depending on their relative velocities.

Transformation of Acceleration

Differentiating equation (1.2.3) with respect to time, we have

$$\frac{du'_x}{dt} = \frac{du_x}{dt} \Rightarrow a'_x = a_x \quad \dots(1.2.5)$$

where a_x and a'_x are the accelerations of the particle in S and S'. Thus we see that *the acceleration is invariant with respect to Galilean transformation.*

Transformation of the Fundamental Law of Dynamics (Newton's Law)

The fundamental law of mechanics, which relates the force acting on a particle to its acceleration, is

$$m\mathbf{a} = \mathbf{F} \quad \dots(1.2.6)$$

In classical mechanics, the mass of a particle is assumed to be independent of velocity of the moving particle. The well known position dependent forces—gravitational, electrostatic and elastic forces and velocity dependent forces—friction and viscous forces are also invariant with respect to Galilean transformation because of the invariance of length, relative velocity and time. Hence *the fundamental law of mechanics is also invariant under Galilean transformation.* Thus

$$\begin{aligned} m\mathbf{a} &= \mathbf{F} && \text{in frame } S \\ m'\mathbf{a}' &= \mathbf{F}' && \text{in frame } S' \end{aligned}$$

The invariance of the basic laws of mechanics ensures that all mechanical phenomena proceed identically in all inertial frames of reference consequently no mechanical experiment performed wholly within an inertial frame can tell us whether the given frame is at rest or moving uniformly in a straight line. In other words all inertial frames are absolutely equivalent, and none of them can be preferred to others. This statement is called the classical (Galilean) principle of relativity.

The Galilean principle of relativity was successfully applied to the mechanical phenomena only because in Galileo's time mechanics represented the whole physics. The classical notions of space, time and matter were regarded so fundamental that nobody ever felt necessity to raise any doubts about their truth. The Galilean principle of relativity did not worry physicists too much by the middle of the 19th century. By the middle of 19th century other branches of physics—electrodynamics, optics and thermodynamics—were developing and each of them required its own basic laws. A natural question arose: does the Galilean principle of relativity cover all physics as well? If the principle of relativity does not apply to other branches of physics then non-mechanical phenomena can be used to distinguish inertial frames thereby choosing a preferred frame. The basic laws of electrodynamics—*Maxwell's field equations*—predicted that light was an electromagnetic phenomenon. The light propagates in vacuum with speed $c = (\mu_0\epsilon_0)^{-1/2} = 3 \times 10^8$ m/s. The wave nature of light compelled the then physicists to assume a medium for the propagation of light and hypothetical medium *luminiferous ether* was postulated to meet this requirement. *Ether* was regarded *absolutely at rest* and light was supposed to travel with speed c relative to the ether. If a certain frame is moving with velocity v relative to the ether; the speed of light in that frame, according to Galilean transformation, is $c \pm v$; the plus sign when c and v are oppositely directed and minus sign when c and v have the same direction. Making us of this result that the light has different speed in different frames; the famous Michelson-Morley experiment was set up to detect the motion of the earth with respect to the ether.

When Galilean transformation equations were applied to the newly discovered laws of electrodynamics, the *Maxwell's equations*, it was found that they change their shape on transition from one inertial frame to another. At first the validity of Maxwell's equations was questioned and attempts were made to modify them in a way to make them consistent with the Galilean principle of

relativity. But such attempts predicted new phenomenon, which could not be verified experimentally. It was then realized that Maxwell's equations need no modifications.

1.3 MICHELSON-MORLEY EXPERIMENT (1881)

The purpose of the experiment was to detect the motion of the earth relative to the hypothetical medium ether, which was supposed to be at rest. The instrument employed was the Michelson interferometer, which consists of two optically plane mirrors M_1 and M_2 fixed on two mutually perpendicular arms PM_1 and PM_2 . At the point of intersection of the two arms, a glass plate P semi-silvered at its rear end is fixed. The glass plate P is inclined at 45° to each mirror. Monochromatic light from an extended source is allowed to fall on the plate P , which splits the incident beam into two beams—beam 1 that travels along the arm PM_1 and beam 2 that travels along the arm PM_2 . The beam 1 is reflected back from mirror M_1 and comes to the rear surface of the plate P where it suffers partial reflection and finally goes into the telescope T . The beam 2 also suffers reflection at the mirror M_2 and is received into the telescope. These interfering beams produce interference fringes, which are observed in the telescope.

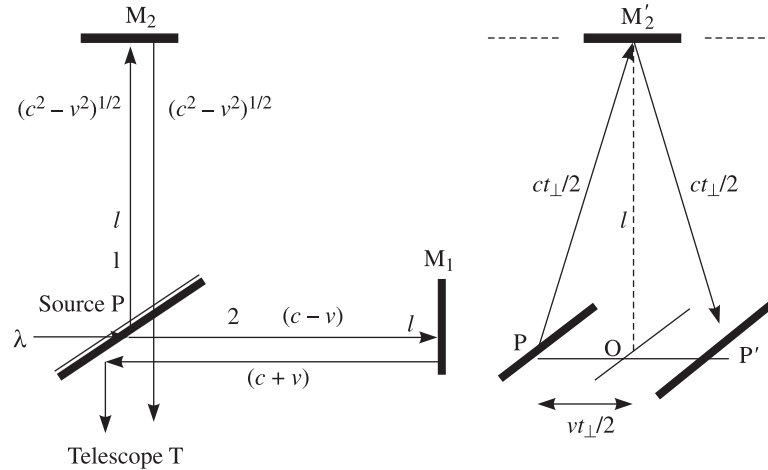


Fig. 1.3.1 Michelson's interferometer

Now suppose that at the moment of the experiment the apparatus moves together with the earth with velocity v ($= 3 \times 10^4$ m/s) in its orbit along the arm PM_1 . Relative to the apparatus the light traveling along the path PM_1 has speed $c - v$ and that traveling along the path M_1P has speed $c + v$. If l is the length of the arm PM_1 then the time spent by light to traverse the path PM_1P is equal to

$$t_{\parallel} = \frac{l}{c - v} + \frac{l}{c + v} = \frac{2l}{c} \frac{1}{1 - v^2/c^2} = \frac{2l}{c} \left(1 - \frac{v^2}{c^2}\right)^{-1} = \frac{2l}{c} \left(1 + \frac{v^2}{c^2}\right) \quad \dots(1.3.1)$$

Since $v/c \ll 1$, higher order terms in binomial expansion have been omitted.

For an observer stationed in ether frame the beam 2 to return to the plate P after suffering reflection at the mirror M_2 it must traverse the angular path PM'_2P' . Let $t_\perp$ be the time taken by the beam 2 to cover the distance PM'_2P' . During this time the plate covers a distance $PP' = v t_\perp$. From the geometry of the Fig. (1.3.1), we have

$$PM'_2{}^2 = PO^2 + OM'_2{}^2 \quad \text{or,} \quad (ct_\perp/2)^2 = (vt_\perp/2)^2 + l^2$$

whence

$$t_\perp = \frac{2l}{\sqrt{c^2 - v^2}} = \frac{2l}{c} \left(1 - \frac{v^2}{c^2} \right)^{-1/2} = \frac{2l}{c} \left(1 + \frac{v^2}{2c^2} \right) \quad \dots(1.3.2)$$

Comparing the expressions for $t_\parallel$ and $t_\perp$, we see that light beams 1 and 2 takes different times to cover the round trips. The time difference is

$$\Delta t = t_\parallel - t_\perp = \frac{2l}{c} \frac{v^2}{2c^2} \quad \dots(1.3.3)$$

This time difference is equivalent to path difference

$$\Delta x = c \Delta t = \frac{lv^2}{c^2}$$

Now the whole apparatus is rotated through 90° , the paths of the beams are interchanged. The rotation causes a change in path difference

$$(\Delta x)_{\text{rot}} = \frac{2lv^2}{c^2} \quad \dots(1.3.4)$$

A change of path difference λ produces a fringe shift of unity. Therefore the expected fringe shift resulting from the rotation of the apparatus is

$$\Delta n = \frac{2lv^2}{\lambda c^2} \quad \dots(1.3.5)$$

By using the technique of multiple reflections, Michelson and Morley made l as large as 11m. In one experiment a light source of wavelength $5900 \text{ \AA}$ was used. Substituting the values of l , λ , v and c we find

$$\Delta n = \frac{2 \times 11 \text{ m} \times (3 \times 10^4 \text{ m/s})^2}{5.9 \times 10^{-7} \text{ m} \times (3 \times 10^8 \text{ m/s})} = 0.37$$

The instrument was capable of measuring a fringe shift of the order of 0.01, but during the rotation of the apparatus the expected fringe shift did not appear. The experiment was repeated many times with greater accuracy during the different parts of the day and different seasons of the year. Every time no fringe shift was detected. The result of the experiment was called **null** or **negative**. Had there been a measurable fringe shift, we could calculate the velocity of the earth relative to

ether. The negative result of the experiment contradicted the Galilean law of addition of velocity. All attempts to explain the negative result of the Michelson experiment in terms of classical mechanics turned out to be unsatisfactory in the final analysis. The Michelson-Morley experiment showed that all inertial frames are equivalent for the description of physical phenomena. More experiments of the same kind performed later perfectly confirmed the validity of the principle of relativity for *all phenomena*.

1.4 EINSTEIN'S SPECIAL THEORY OF RELATIVITY

After making a profound analysis of the experimental and theoretical results of physics, particularly of electrodynamics, a virtually unknown clerk of the Swiss federal Patent Office, Albert Einstein (1879–1955) arrived at the conclusions that the very concepts of space and time over which the entire edifice of classical physics stood were no longer true. He realized that the Newtonian notions of space and time, that emerged from the observation of bodies moving with speeds very small compared with the speed of light and hence their extrapolation to bodies moving at speeds, comparable to the speed of light c in empty space, had no claim to be right. In 1905 Einstein in his epoch making paper ‘on the electrodynamics of moving bodies’ created the Special Theory of Relativity, which is essentially a physical theory of space and time. The special theory of relativity is based on two postulates, which have been confirmed by experimental tests.

1. The Principle of Relativity

This postulate is an extension of the Newtonian principle of relativity to all phenomena of nature. It states that *the laws of physics and the equations describing them are invariant, i.e., keep their form on transitions from one inertial frame to another. In other words: all inertial frames are equivalent in their physical properties and therefore they are equally suitable for the description of physical phenomena..* This postulate rejects the idea of absolute space and absolute motion. No experiment whatever can distinguish one inertial frame from the other.

2. The Universal Speed of Light

The speed of light in vacuum is the same in all inertial frames of reference, regardless of their relative motion. Thus the speed of light holds a unique position. In contrast to all other speeds, which change on transition from one reference frame to another, the speed of light in vacuum is an invariant quantity.

The postulates of special theory of relativity lead to a number of important conclusions, which are in drastic conflicts with the dictates of common sense. In Newtonian mechanics space and time were assumed to be absolute and independent of each other. According to the special theory of relativity space and time are not absolute, they depend on the state of motion and are inseparable from each other.

In order to correlate the observations carried out in different inertial frames of reference we need transformation equations, which must be consistent with the postulates of the special theory of relativity. Certainly they cannot be the Galilean transformations because they contradict the second postulate—the constancy of speed of light. Moreover, Galilean transformation equations change the

appearance of Maxwell's equations on transition from one inertial frame to another. We need transformation equations, which preserve not only the form of Maxwell's equations but also all the laws of physics. It was Hendrik Lorentz (1853–1928) who guessed empirically the correct form of transformation equations but Einstein gave their theoretical basis. The new transformation equations are called *relativistic or Lorentz transformation equations, which are derived in the following section.*

1.5 LORENTZ TRANSFORMATIONS

Derived on the basis of the postulates of special theory of relativity, the Lorentz transformations are a set of equations, which connect the space-time coordinates of an event measured in two inertial frames that are in relative motion. Consider two inertial frames S and S' with their corresponding axes parallel and the primed frame moving relative to unprimed frame with velocity v along the common x - x' direction. Each frame has its own observer equipped with measuring stick and synchronized clocks. Let the observers set their clocks at $t = 0 = t'$ when their origins coincide.

Suppose that the observer in the frame S records the space-time coordinates of a particle as x, y, z, t and S'-observer records them as x', y', z', t' . Our task is to seek relations of the type

$$\begin{aligned}x' &= f_1(x, y, z, t), \\y' &= f_2(x, y, z, t), \\z' &= f_3(x, y, z, t), \\t' &= f_4(x, y, z, t)\end{aligned}\quad \dots(1.5.1)$$

Since the frames have relative velocity only along x -direction, the y and z coordinates remain unchanged.

$$y' = y, \quad z' = z \quad \dots(1.5.2)$$

In addition to the postulates of special relativity we shall assume that the space and time are homogeneous and isotropic. This means that the length interval measured in a frame is independent of the position where it is measured and the time interval is independent of the instant when it is measured. A linear transformation satisfies this criterion.

In Fig. 1.5.1 a linear and a non-linear transformation are shown. A rod of length l placed along x -axis with end coordinates x_1 and x_2 in the frame S is transformed by linear transformation to a length l' with end coordinates x'_1 and x'_2 in the frame S'. The same rod placed between points x_3 and x_4 in frame S is transformed to a length l' with its end coordinates x'_3 and x'_4 . A linear transformation ensures that if $x_2 - x_1 = x_4 - x_3 = l$ then $x'_2 - x'_1 = x'_4 - x'_3 = l$. Whereas for non-linear transformation this criterion is not satisfied *i.e.*, if $x_2 - x_1 = x_4 - x_3 = l$ then $x'_2 - x'_1 \neq x'_4 - x'_3$. This is obvious from the Fig. (1.5.1).

Thus the transformations must be linear and we can write them as

$$\begin{aligned}x' &= a_{11}x + a_{12}t \\y' &= y \\z' &= z \\t' &= a_{21}x + a_{22}t\end{aligned}\quad \dots(1.5.3)$$

where a 's are constants. If the particle traverses a distance dx along x -axis in time dt in frame S , then the corresponding distance dx' and time dt' are given by

$$dx' = a_{11} dx + a_{12} dt \quad \dots(1.5.4)$$

$$dt' = a_{21} dx + a_{22} dt \quad \dots(1.5.5)$$

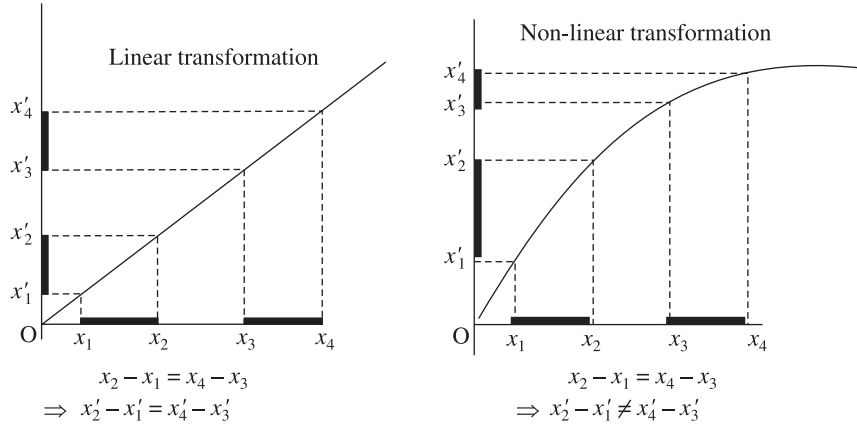


Fig. 1.5.1 Transformation of length by a linear and non-linear transformation

The velocity of the particle in frame S and S' are

$$u = dx/dt, \quad u' = dx'/dt' \quad \dots(1.5.6)$$

respectively. Dividing Eqn. (1.5.4) by Eqn. (1.5.5), we get

$$\frac{dx'}{dt'} = \frac{a_{11}dx + a_{12}dt}{a_{21}dx + a_{22}dt} = \frac{a_{11}(dx/dt) + a_{12}}{a_{21}(dx/dt) + a_{22}}$$

or

$$u' = \frac{a_{11}u + a_{12}}{a_{21}u + a_{22}} \quad \dots(1.5.7)$$

Now let us determine the constants a_{11} , a_{12} , a_{21} and a_{22} .

(i) Suppose that the particle under study is at rest in frame S then $u = 0$ and $u' = -v$. Substituting these values in Eqn. (1.5.7), we have

$$-v = \frac{a_{12}}{a_{22}} \therefore a_{12} = -a_{22}v \quad \dots(1.5.8)$$

(ii) If the particle is at rest in frame S' then $u' = 0$ and $u = v$. Substituting these values in Eqn. (1.5.7), we have

$$0 = \frac{a_{11}v + a_{12}}{a_{21}v + a_{22}} \therefore a_{12} = -a_{11}v = -a_{22}v \Rightarrow a_{11} = a_{22} \quad \dots(1.5.9)$$

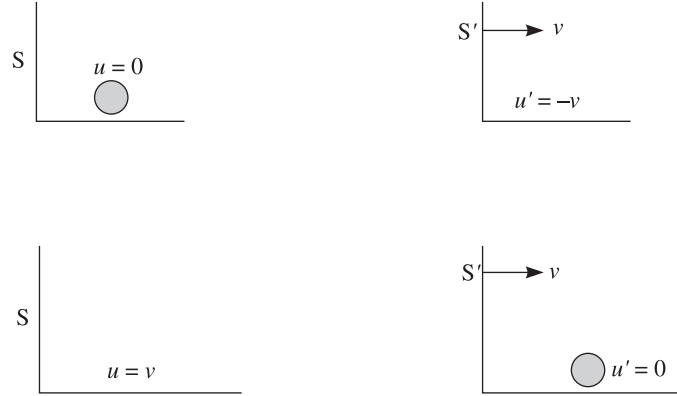


Fig. 1.5.2

(iii) Instead of mechanical particle, let the observers *see* photon or light wave front. According to the second postulate (the constancy of the speed of light in vacuum) the observers in both the frames find the speed of photon to be the same *i.e.*, $u = u' = c$. Hence from Eqn. (1.5.7), we have

$$c = \frac{a_{11}c + a_{12}}{a_{21}c + a_{22}} = \frac{a_{11}c - a_{11}v}{a_{21}c + a_{11}}$$

$$a_{21} = -\frac{v}{c^2} a_{11} \quad \dots(1.5.10)$$

Substituting the values of constants a_{12} , a_{22} and a_{21} in Eqn. (1.5.3), we have

$$x' = a_{11} (x - vt)$$

$$y' = y$$

$$z' = z$$

$$t' = a_{11} (t - vx/c^2) \quad \dots(1.5.11)$$

(iv) According to the first postulate both the frames S and S' are equally suitable for the description of physical phenomena. Relative to frame S', the frame S is moving with velocity $-v$, hence the inverse transformations must look as

$$x = a_{11} (x' + vt')$$

$$y = y'$$

$$z = z'$$

$$t = a_{11} (t' + vx'/c^2) \quad \dots(1.5.12)$$

Substituting the values of x' and t' from Eqn. (1.5.11) in (1.5.12), we find

$$a_{11} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \dots(1.5.13)$$

When the value of a_{11} is substituted in Eqns. (1.5.11) and (1.5.12), we get the Lorentz transformations as

$$x' = \frac{x - vt}{\sqrt{1 - v^2/c^2}}, \quad y' = y, \quad z' = z, \quad t' = \frac{t - vx/c^2}{\sqrt{1 - v^2/c^2}} \quad \dots(1.5.14)$$

The inverse transformations are obtained by mutual interchange of primed and unprimed coordinates and replacing v by $-v$. Thus

$$x = \frac{x' + vt'}{\sqrt{1 - v^2/c^2}}, \quad y = y', \quad z = z', \quad t = \frac{t' + vx'/c^2}{\sqrt{1 - v^2/c^2}} \quad \dots(1.5.15)$$

It is more convenient to write Lorentz transformations in terms of $\beta = v/c$ and

$$\gamma = \frac{1}{\sqrt{1 - \beta^2}} \text{ as shown in the table.}$$

Lorentz Transformation	Inverse Transformation
$x' = \frac{x - \beta ct}{\sqrt{1 - \beta^2}} = \gamma(x - \beta ct)$	$x = \frac{x' + \beta ct'}{\sqrt{1 - \beta^2}} = \gamma(x' + \beta ct')$
$y' = y$	$y = y'$
$z' = z$	$z = z'$
$t' = \frac{t - \beta x/c}{\sqrt{1 - \beta^2}} = \gamma(t - \beta x/c)$	$t = \frac{t' + \beta x'/c}{\sqrt{1 - \beta^2}} = \gamma(t' + \beta x'/c)$

It is remarkable feature of Lorentz transformations that they reduce to Galilean transformations in the limit of low velocity ($\beta = v/c \rightarrow 0$). Therefore Lorentz transformations are more general and Galilean transformations are special case of these equations.

When $v > c$, the Lorentz transformations for x and t become imaginary; this means that motion with speed greater than that of speed of light is impossible.

One of the thought-provoking features of the Lorentz transformations is that the time transformation equation contains spatial coordinate, which suggests that the space and time are inseparable. In other words, we should not speak separately of space and time but of unified *space-time* in which all phenomena take place.

1.6 VELOCITY TRANSFORMATION

Consider an inertial frame S' moving relative to frame S with velocity v along the common $x-x'$ direction. The space-time coordinates of a particle measured by S and S' observers are (x, y, z, t)

and (x', y', z', t') respectively. Let the particle move through a distance dx in time dt in frame S; the corresponding quantities measured by S' observer are obtained by differentiating the Lorentz-transformation equations

$$\begin{aligned}x' &= \gamma (x - vt), \quad y' = y, \quad z' = z \\t' &= \gamma (t - vx/c^2)\end{aligned}$$

From these equations, we have

$$dx' = \gamma (dx - vdt), \quad dy' = dy, \quad dz' = dz \quad \dots(1.6.1)$$

$$dt' = \gamma (dt - vdx/c^2) \quad \dots(1.6.2)$$

Dividing Eqn. (1.6.1) by (1.6.2), we have

$$\begin{aligned}\frac{dx'}{dt'} &= \frac{dx - vdt}{dt - vdx/c^2} = \frac{(dx/dt) - v}{1 - (v/c^2)(dx/dt)} \\u'_x &= \frac{u_x - v}{1 - vu_x/c^2} \quad \dots(1.6.3)\end{aligned}$$

$$\begin{aligned}\frac{dy'}{dt'} &= \frac{dy}{\gamma(dt - vdx/c^2)} = \frac{(dy/dt)}{\gamma(1 - (v/c^2)dx/dt)} \\u'_y &= \frac{u_y \sqrt{1 - \beta^2}}{1 - vu_x/c^2} \quad \dots(1.6.4)\end{aligned}$$

$$\begin{aligned}\frac{dz'}{dt'} &= \frac{dz}{\gamma(dt - vdx/c^2)} = \frac{(dz/dt)}{\gamma(1 - (v/c^2)dx/dt)} \\u'_z &= \frac{u_z \sqrt{1 - \beta^2}}{1 - vu_x/c^2} \quad \dots(1.6.5)\end{aligned}$$

Inverse velocity transformation equations are

$$u_x = \frac{u'_x + v}{1 + vu'_x/c^2}, \quad u_y = \frac{u'_y \sqrt{1 - \beta^2}}{1 + vu'_x/c^2}, \quad u_z = \frac{u'_z \sqrt{1 - \beta^2}}{1 + vu'_x/c^2} \quad \dots(1.6.6)$$

Let us apply the transformation equation to the speed of light. If a photon moves with velocity $u_x = c$ in frame S, then its velocity in frame S' will be

$$u'_x = \frac{u_x - v}{1 - vu_x/c^2} = \frac{c - v}{1 - vc/c^2} = c$$

It can easily be seen that the relativistic formulae for transformation of velocity reduce to the Galilean transformation equations in the limit of low speed $(v/c) \rightarrow 0$.

1.7 SIMULTANEITY

In relativity the concept of simultaneity is not *absolute*. Two events occurring simultaneously in one inertial frame may not be simultaneous, in general, in other. Assume that the event 1 occurs at point x_1, y_1, z_1 and at time t_1 and event 2 occurs at point x_2, y_2, z_2 and at time t_2 in frame S. The space-time coordinates of these two events as measured in frame S', which is moving relative to S with velocity v in the common x - x' direction, can be obtained from Lorentz transformations

$$\begin{aligned}x'_1 &= \gamma (x_1 - vt_1), & x'_2 &= \gamma (x_2 - vt_2) \\t'_1 &= \gamma (t_1 - vx_1/c^2), & t'_2 &= \gamma (t_2 - vx_2/c^2)\end{aligned}$$

The difference of space coordinates and time coordinates are in frame S' are

$$x'_2 - x'_1 = \gamma \{(x_2 - x_1) - v(t_2 - t_1)\} \quad \dots(1.7.1)$$

$$t'_2 - t'_1 = \gamma \{(t_2 - t_1) - (v/c^2)(x_2 - x_1)\} \quad \dots(1.7.2)$$

Eqn. (1.7.2) gives the time interval between the events as measured in frame S'. It is evident that if the two events are simultaneous (*i.e.*, $t_2 - t_1 = 0$) in frame S, they are *not simultaneous* (*i.e.*, $t'_2 - t'_1 \neq 0$) in frame S'. In fact

$$t'_2 - t'_1 = -(\gamma v/c^2)(x_2 - x_1) \quad \dots(1.7.3)$$

The events are simultaneous in S' only if they occur at the same point in S (*i.e.*, $x_2 - x_1 = 0$). Thus simultaneity is a relative concept.

If $t'_2 - t'_1 > 0$, the events occur in frame S' in the same sequence as they occur in frame S. This always happens for events, which are related by *cause* and *effect*. That is, cause precedes the effect, which is known as the *causality principle*.

If $t'_2 - t'_1 < 0$, the events occur in reverse sequence in S'. Such events cannot be related by *cause* and *effect*.

It is important to point out that the relativity of simultaneity follows from the finiteness of the speed of light. In the limit $c \rightarrow \infty$ (classical assumption), simultaneity is an absolute concept *i.e.*, $t'_2 - t'_1 = t_2 - t_1$.

1.8 LORENTZ CONTRACTION

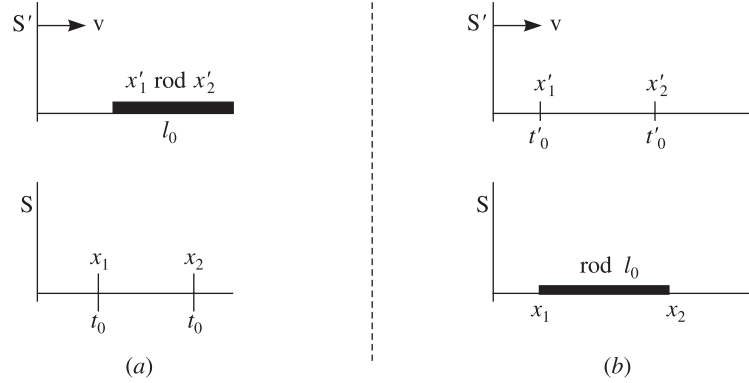
A moving body appears to be contracted in the direction of its motion. This phenomenon is called **Lorentz** (or **Fitzgerald**) contraction. Let us consider a rod arranged along the x' -axis and at rest relative to the frame S'. The length of the rod in frame S' is $l_0 = x'_2 - x'_1$ where x'_1 and x'_2 are the coordinates of the rod ends. The length l_0 is called the *proper length* of the rod. Now consider a frame S relative to which the frame S' is moving with velocity v along x - x' direction. To determine the length of rod in frame S, we must note the coordinates of the ends x_1 and x_2 at the same moment of time, say t_0 . The length of rod in frame S is $l_0 = x_2 - x_1$. From Lorentz transformations, we have

$$x'_1 = \gamma(x_1 - vt_0), \quad x'_2 = \gamma(x_2 - vt_0)$$

$$\therefore \quad l_0 = x'_2 - x'_1 = \gamma(x_2 - x_1) = \gamma l$$

$$l = (l_0/\gamma) = l_0 \sqrt{1-\beta^2} \quad \dots(1.8.1)$$

Evidently $l < l_0$. Thus the moving rod appears to be contracted.



(a) The rod is placed in frame S'

(b) The rod is placed in frame S

Fig. 1.8.1 Transformation of length

If the rod is placed in frame S then its proper length is $l_0 = x_2 - x_1$. Its length l in frame S' is equal to the difference of ends coordinates x'_1 and x'_2 measured at the same moment of time, say t'_0 .

$$l_0 = x_2 - x_1 = \gamma\{(x'_2 + vt'_0) - (x'_1 + vt'_0)\} = \gamma(x'_2 - x'_1) = \gamma l$$

$$\therefore l = l_0 / \gamma = l_0 \sqrt{1-\beta^2}$$

Thus the length contraction is reciprocal. The rod in either frame appears to be shortened to the observer in the other frame.

1.9 TIME DILATION

According to relativity there is no such thing as universal time. The rate of flow of time actually depends on the state of motion of the observer. Let us see how the time interval between two events measured in one inertial frame is related to that measured in another inertial frame, which is moving relative to the first one. Assume that an event 1 occurs at point x'_0 at time t'_1 in the frame S' and another event 2 also occurs at the same point but at time t'_2 . The interval between the two events is $\Delta t' = t'_2 - t'_1$. This time interval is measured on a single clock located at the point of occurrence of the events and is called the *proper time interval* and is usually denoted by $\Delta \tau$. The same two events are observed from a reference frame S relative to which the frame S' is moving with velocity v . Let t_1 and t_2 be the time of occurrence of the same events registered on the clocks of the frame S. Of course these times will be recorded on the clocks located at different points. The time interval

$\Delta t = t_2 - t_1$ measured in the frame S is called *non-proper or improper time interval*. From Lorentz transformations

$$\begin{aligned}
 t_1 &= \gamma(t'_1 + vx'_0/c^2), & t_2 &= \gamma(t'_2 + vx'_0/c^2) \\
 \therefore t_2 - t_1 &= \gamma(t'_2 - t'_1) \\
 \Delta t &= \gamma \Delta \tau \\
 \Delta t &= \frac{\Delta \tau}{\sqrt{1-\beta^2}}, \quad \beta = v/c
 \end{aligned}
 \tag{1.9.1}$$

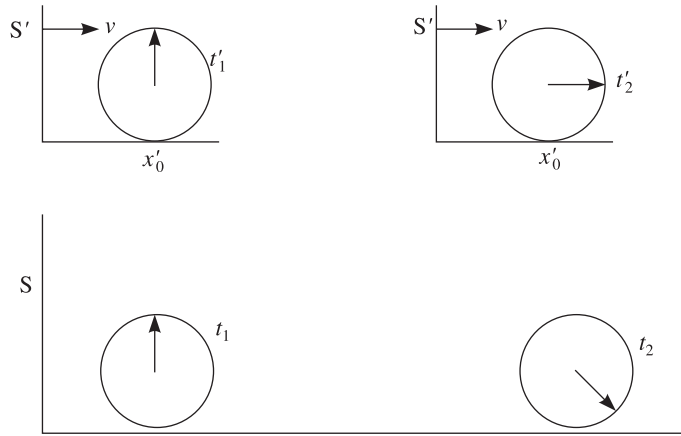


Fig. 1.9.1 Transformation of time interval

Thus the time interval between two events has different values in different inertial frames, which are in relative motion. The time interval is least in the reference frame in which the events take place at the same point and hence registered on the same clock. Since the non-proper time is greater than the proper time, *a moving clock appears to go slow*. This phenomenon is called *dilation of time*. The variation of Δt with velocity v is shown in Fig 1.9.2.

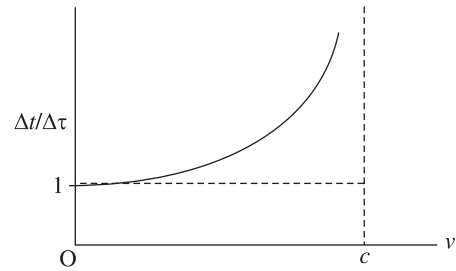


Fig. 1.9.2 Time dilation

1.10

EXPERIMENTAL VERIFICATION OF LENGTH CONTRACTION AND TIME DILATION

The conclusions of the special theory of relativity find direct experimental verification in many of the phenomena of particle physics. We shall illustrate this by an example. *Muons* are unstable sub-atomic particles, which decay into electron and neutrino. Their mean lifetime in a frame in which they are at rest is 2 μ s. They are created in the upper atmosphere at a height 5 to 6 kms during the

interaction of primary cosmic rays with the atmosphere. They are also found in considerable number at the sea level. The speed of muons is $v = 0.998 c$.

Classical calculation shows that muons can travel in their lifetime a distance

$$d = v t = (3 \times 10^8 \text{ m/s}) (2 \times 10^{-6} \text{ s}) = 600 \text{ m}$$

This distance is much smaller than the height where the muons are born. Let us explain this paradox by relativistic calculation. The lifetime of muons is their *proper life* measured in their own frame. In laboratory frame their life is $t = \tau / \sqrt{1 - \beta^2} = 31.7 \times 10^{-6} \text{ s}$. In this time muons can travel a distance $d = v t = (0.998 c) (31.7 \times 10^{-6} \text{ s}) = 9.5 \text{ km}$. Thus muons can reach the sea level in their lifetime.

We can arrive at the same conclusion by considering the length contraction formula. In muons frame the distance between the birthplace of muons and the sea level appears to be contracted to

$$d = d_0 \sqrt{1 - \beta^2} = (6 \times 10^3 \text{ m}) \sqrt{1 - (0.998)^2} = 379 \text{ m}$$

The time required to traverse this distance $t = d/v = 379 \text{ m} / (0.998 \times 3 \times 10^8 \text{ m/s}) = 1.26 \mu\text{s}$. This time is less than the proper lifetime of muons.

1.11 INTERVAL

An event in a frame is characterized by space-time coordinates. Assume that an event 1 occurs at point x_1, y_1, z_1 and at time t_1 . The corresponding coordinates for another event 2 are x_2, y_2, z_2, t_2 . The quantity s_{12} defined by

$$s_{12}^2 = c^2 (t_2 - t_1)^2 - (x_2 - x_1)^2 - (y_2 - y_1)^2 - (z_2 - z_1)^2 \quad \dots(1.11.1)$$

is called the *interval* between the events. If the events are infinitesimally close together, the interval is defined by

$$ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2 \quad \dots(1.11.2)$$

In frame S' the interval is defined by

$$(ds')^2 = c^2 (dt')^2 - (dx')^2 - (dy')^2 - (dz')^2 \quad \dots(1.11.3)$$

A remarkable property of interval is that it is *invariant* with respect to Lorentz transformations *i.e.*,

$$ds^2 = ds'^2$$

From Lorentz transformations, we have

$$dx' = \frac{dx - \beta c dt}{\sqrt{1 - \beta^2}}, \quad dy' = dy, \quad dz' = dz \quad \text{and}$$

$$dt' = \frac{dt - (\beta/c) dx}{\sqrt{1 - \beta^2}} \quad \dots(1.11.4)$$

Substituting these values in Eqn. (1.11.3), we find

$$\begin{aligned}(ds')^2 &= c^2 \frac{\{dt - (\beta/c)dx\}^2}{1-\beta^2} - \frac{(dx - \beta c dt)^2}{1-\beta^2} - dy^2 - dz^2 \\ &= c^2 dt^2 - dx^2 - dy^2 - dz^2 \\ &= ds^2\end{aligned}$$

1.12 DOPPLER'S EFFECT

The apparent change in frequency of a wave due to relative motion between the source of the wave and the observer receiving it, is called the Doppler's effect. Let a monochromatic source placed at the origin of frame S' emit a plane wave in xy -plane in the direction making an angle θ' with x' -axis. The equation of the wave in this frame is

$$\psi' = a' \cos[\omega' t' - k'_x x' - k'_y y']$$

where

$$k'_x = k' \cos \theta', \quad k'_y = k' \sin \theta', \quad k' = \frac{2\pi}{\lambda'}$$

$$\therefore \quad \psi' = a' \cos[\omega' t' - k' x' \cos \theta' - k' y' \sin \theta'] \quad \dots(1.12.1)$$

The equation of the same wave in the frame S will be written as

$$\psi = a \cos[\omega t - kx \cos \theta - ky \sin \theta] \quad \dots(1.12.2)$$

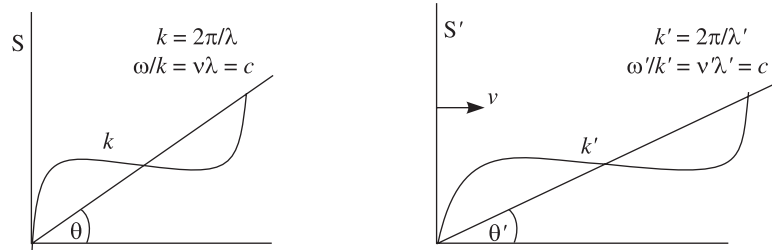


Fig. 1.12.1 Doppler's effect

The phase of a wave is invariant quantity *i.e.*, $\phi' = \phi$. On transition from S' to S , the phase of the wave (1.12.1) becomes

$$\begin{aligned}\phi &= [\omega' \gamma(t - vx/c^2) - k' \gamma(x - vt) \cos \theta' - k' y \sin \theta'] \\ &= \left[\gamma(\omega' + k' v \cos \theta') t - \gamma \left(\frac{\omega' v}{c^2} + k' \cos \theta' \right) x - k' y \sin \theta' \right] \quad \dots(1.12.3)\end{aligned}$$

Comparing Eqn. (1.12.3) with the phase of the wave (1.12.2), we have

$$\omega = \gamma(\omega' + k' v \cos \theta') \quad \dots(1.12.4)$$

$$k \cos \theta = \gamma \left(\omega' \frac{v}{c^2} + k' \cos \theta' \right)$$

$$\text{or,} \quad k \cos \theta = \gamma(k' \beta + k' \cos \theta') \quad \dots(1.12.5)$$

$$k \sin \theta = k' \sin \theta' \quad \dots(1.12.6)$$

The first two equations give relativistic Doppler's effect. Equation (1.12.4) can be transformed into a more convenient form as follows.

$$\omega = \gamma \left(\omega' + \frac{\omega'}{c} v \cos \theta' \right) \quad \text{since } k' = \omega'/c$$

$$\text{or} \quad \omega = \gamma(1 + \beta \cos \theta') \omega' \quad \dots(1.12.7)$$

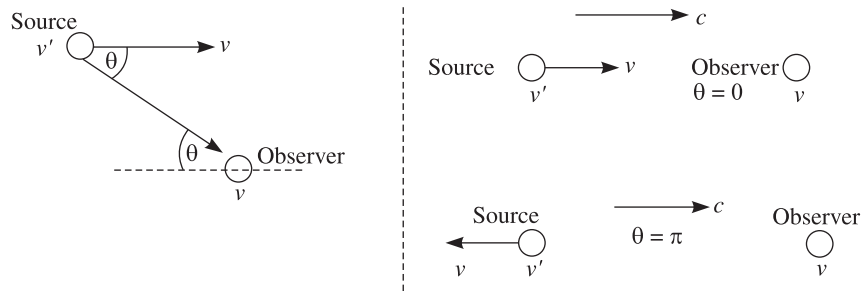
Inverse transformation of Eqn. (1.12.7) is

$$\omega' = \gamma(1 - \beta \cos \theta) \omega \quad \dots(1.12.8)$$

$$\therefore \quad \omega = \frac{\omega'}{\gamma(1 - \beta \cos \theta)} = \frac{\omega' \sqrt{1 - \beta^2}}{1 - \beta \cos \theta}$$

$$\text{or} \quad \nu = \frac{\nu' \sqrt{1 - \beta^2}}{1 - \beta \cos \theta} \quad \dots(1.12.9)$$

Eqn. (1.12.9) gives relativistic Doppler's shift.



ν' = proper frequency, ν = observed frequency

Fig. 1.12.2 Relativistic Doppler's effect

For $\theta = 0$ (velocity of source coincides with that of velocity of light)

$$\nu = \frac{\nu' \sqrt{1 - \beta^2}}{1 - \beta} = \nu' \frac{\sqrt{1 + \beta}}{\sqrt{1 - \beta}} \quad \dots(1.12.10)$$

Thus $\nu > \nu'$. Thus the observed frequency is greater than the emitted frequency

For $\theta = \pi$ (velocity of source is opposite to that of light)

$$\nu = \nu' \frac{\sqrt{1 - \beta}}{\sqrt{1 + \beta}} \quad \dots(1.12.11)$$

In this case $v < v'$. Observed frequency is less than that emitted by source.

For $\theta = \pi/2$, the relative velocity between the source and the observer is zero. However, even in this case there is a shift in frequency; the apparent frequency differs from the true frequency by a factor $\sqrt{1 - \beta^2}$. This is called *transverse Doppler's effect*. In this case the observed frequency is always lower than the proper frequency. The transverse Doppler's shift is a second order effect and does not exist in classical theory.

Classical Doppler's Effect

Retaining the terms up to first order in β in relativistic expression for Doppler's shift we get classical Doppler's effect. Thus

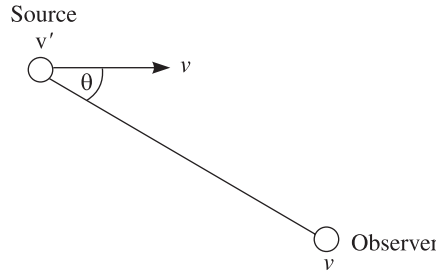
$$v = \frac{v' \sqrt{1 - \beta^2}}{1 - \beta \cos \theta} \xrightarrow{\text{neglecting } \beta^2} \frac{v'}{1 - \beta \cos \theta} = v'(1 + \beta \cos \theta) \quad \dots(1.12.12)$$

For $\theta = 0$

$$v = v'(1 + \beta) \quad \text{or} \quad \frac{\lambda - \lambda'}{\lambda'} = -\frac{v}{c} \quad (\text{violet shift}) \quad \dots(1.12.13)$$

and for $\theta = \pi$

$$v = v'(1 - \beta) \quad \text{or} \quad \frac{\lambda - \lambda'}{\lambda'} = \frac{v}{c} \quad (\text{red shift}) \quad \dots(1.12.14)$$



$$v = v' \left(\frac{1}{1 - \beta \cos \theta} \right) = v'(1 + \beta \cos \theta)$$

Fig. 1.12.3 Classical Doppler's effect

Aberration of Light

Dividing Eqn. (1.12.5) by (1.12.6), we obtain

$$\begin{aligned} \tan \theta &= \frac{k' \sin \theta'}{\gamma(k' \beta + k' \cos \theta')} \\ &= \frac{\sin \theta' \sqrt{1 - \beta^2}}{\cos \theta' + \beta} \end{aligned} \quad \dots(1.12.15)$$

The inverse transformation is

$$\tan \theta' = \frac{\sin \theta \sqrt{1-\beta^2}}{\cos \theta - \beta} \quad \dots(1.12.16)$$

Eqns. (1.12.15) and (1.12.16) connect the directions of light propagation θ and θ' as seen from two inertial frames S and S'. These are the relativistic equations for the aberration of light.

1.13 RELATIVISTIC MECHANICS

In Newtonian mechanics the momentum of a particle is defined as the product of its mass and velocity.

$$\mathbf{p} = m \mathbf{v} \quad (\text{classical})$$

Here m is regarded as independent of velocity of particle. Newton's laws are invariant with respect to the Galilean transformation but not with respect to the Lorentz transformation. If momentum is defined in a classical way then the law of conservation of momentum is found to be invariant under Galilean transformation but not under Lorentz transformation. The law of conservation of momentum is more fundamental than the Newton's laws. To make this law invariant under Lorentz transformation, momentum must be redefined.

1.14 RELATIVISTIC EXPRESSION FOR MOMENTUM: VARIATION OF MASS WITH VELOCITY

Let us consider inelastic collision of two identical balls. In frame S' the two balls approach each other with velocity u' along x -axis and after collision the stick together and the composite ball comes to rest. The same collision is observed from a frame S, which is fixed to one of the balls, say ball 2. Evidently the frame S' is moving with velocity $v = u'$ relative to S. The second ball is at rest in the frame S. The velocity of the first ball in the frame S can be obtained from the relativistic law of addition of velocity

$$u = \frac{u' + u'}{1 + u'^2/c^2} = \frac{2u'}{1 + u'^2/c^2} \quad \dots(1.14.1)$$

This equation can be written as

$$u'^2 - \frac{2c^2}{u} u' + c^2 = 0 \quad \dots(1.14.2)$$

whence

$$u' = \frac{c^2}{u} \pm \left[\left(\frac{c^2}{u} \right)^2 - c^2 \right]^{1/2}$$

or

$$u' = \frac{c^2}{u} \pm \frac{c^2}{u} \sqrt{1 - \frac{u^2}{c^2}} \quad \dots(1.14.3)$$

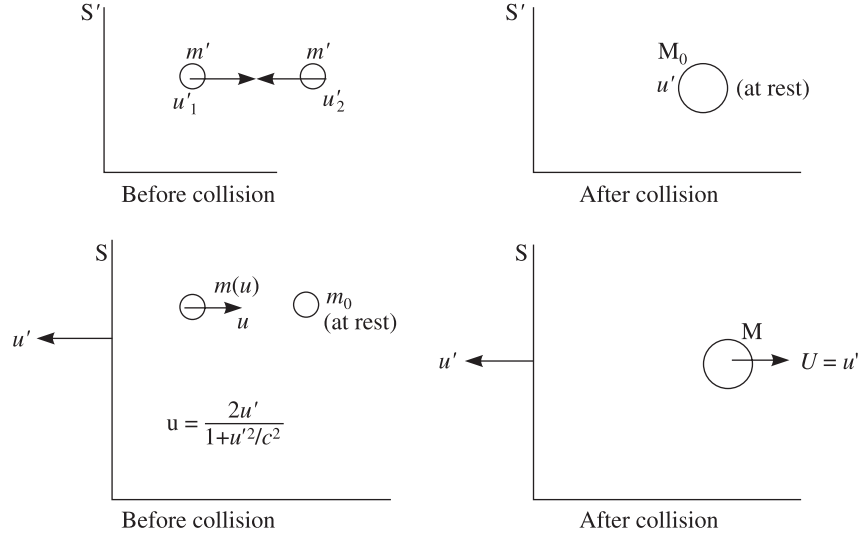


Fig. 1.14.1 Collision of two identical particles as viewed from two inertial frames

We must choose the negative sign before the radical because it gives the classical result ($u = 2u'$) in the limit $u/c \rightarrow 0$. Hence

$$u' = \frac{c^2}{u} - \frac{c^2}{u} \sqrt{1 - u^2/c^2} \quad \dots(1.14.4)$$

and

$$\begin{aligned} u - u' &= u - \left[\frac{c^2}{u} - \frac{c^2}{u} \sqrt{1 - u^2/c^2} \right] \\ &= \frac{c^2}{u} \left[\left(\frac{u^2}{c^2} - 1 \right) + \sqrt{1 - u^2/c^2} \right] \\ &= \frac{c^2}{u} \sqrt{1 - u^2/c^2} \left[1 - \sqrt{1 - u^2/c^2} \right] \quad \dots(1.14.5) \end{aligned}$$

Now let us apply the law of conservation of mass and momentum in frame S. Let m be the mass of the ball 1 before collision. Since the ball 2 is at rest in this frame, we denote its mass by m_0 . After collision the composite ball comes to at rest in frame S' and hence it appears to move with velocity u' . In frame S, we have

$$mu = Mu'$$

$$m_0 + m = M$$

Eliminating M from these equations, we have

$$\frac{m}{m_0} = \frac{u'}{u - u'}$$

Making use of Eqns. (1.14.4) and (1.14.5), we get

$$\frac{m}{m_0} = \frac{\frac{c^2}{u} \left[1 - \sqrt{1 - u^2/c^2} \right]}{\frac{c^2}{u} \sqrt{1 - u^2/c^2} \left[1 - \sqrt{1 - u^2/c^2} \right]} = \frac{1}{\sqrt{1 - u^2/c^2}}$$

$$\therefore m = \frac{m_0}{\sqrt{1 - u^2/c^2}} = \gamma m_0 \quad \dots(1.14.6)$$

In general if particle with rest mass m_0 moves with velocity v relative to an observer, its effective mass (or moving mass) is given by

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}} = \frac{m_0}{\sqrt{1 - \beta^2}} = \gamma m_0 \quad \dots(1.14.7)$$

The relativistic momentum is defined by

$$p = mv = \frac{m_0 v}{\sqrt{1 - \beta^2}} = \gamma m_0 v \quad (1.14.8)$$

The variation of Newtonian momentum and relativistic momentum of a particle with velocity v is shown in the Fig. (1.14.2).

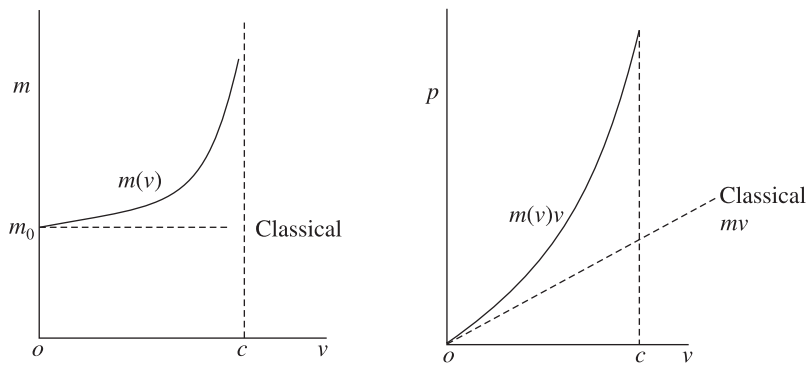


Fig. 1.14.2 Variation of mass and momentum with velocity

1.15 THE FUNDAMENTAL LAW OF RELATIVISTIC DYNAMICS

The fundamental equation of classical mechanics (Newton's laws) formulated in the form

$$m \frac{dv}{dt} = \mathbf{F}$$

is not invariant under Lorentz transformation. The correct law must, therefore, be formulated in

such a way that it must be Lorentz invariant and should transform to the classical law in the limit $v/c \rightarrow 0$. If Newton's law is formulated in the form

$$\frac{d}{dt} \left(\frac{m_0 \mathbf{v}}{\sqrt{1 - v^2/c^2}} \right) = \mathbf{F} \quad \dots(1.15.1)$$

it meets both the requirements. The formula $\mathbf{F} = m\mathbf{a}$ cannot be used in relativistic case because the acceleration vector $\mathbf{a}$ of a particle does not coincide in the general case with the direction of the force $\mathbf{F}$. In the relativistic case, we have

$$\begin{aligned} \frac{d}{dt}(m\mathbf{v}) &= \mathbf{F} \\ \frac{dm}{dt}\mathbf{v} + m\frac{d\mathbf{v}}{dt} &= \mathbf{F} \end{aligned} \quad \dots(1.15.2)$$

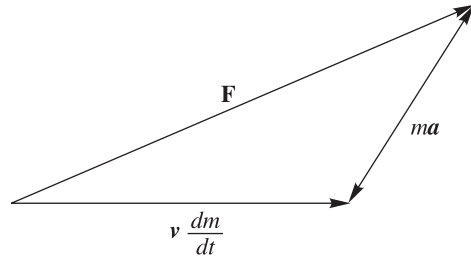


Fig. 1.15.1

This equation has been graphically illustrated in the Fig. (1.15.1). The acceleration vector $\mathbf{a}$ is not collinear with the force vector $\mathbf{F}$ in the general case. The direction of acceleration vector $\mathbf{a}$ coincides with that of $\mathbf{F}$ only in the two cases:

(i) $\mathbf{F}$ is perpendicular to $\mathbf{v}$. In this case $|\mathbf{v}| = \text{constant}$ and therefore the equation of motion becomes

$$\begin{aligned} \frac{d}{dt} \left(\frac{m_0 \mathbf{v}}{\sqrt{1 - v^2/c^2}} \right) &= \mathbf{F} \\ \frac{m_0}{\sqrt{1 - v^2/c^2}} \frac{d\mathbf{v}}{dt} &= \mathbf{F} \\ \frac{m_0}{\sqrt{1 - v^2/c^2}} \mathbf{a} &= \mathbf{F} \\ \mathbf{a} &= \frac{\mathbf{F} \sqrt{1 - v^2/c^2}}{m_0} \end{aligned} \quad \dots(1.15.3)$$

(ii) $\mathbf{F}$ is parallel to $\mathbf{v}$. In this case the equation of motion may be written in the scalar form as

$$\begin{aligned} \frac{d}{dt} \left(\frac{m_0 v}{\sqrt{1 - v^2/c^2}} \right) &= F \\ \frac{m_0 \left[\frac{dv}{dt} \sqrt{1 - v^2/c^2} + \frac{v^2}{c^2 \sqrt{1 - v^2/c^2}} \frac{dv}{dt} \right]}{1 - v^2/c^2} &= F \end{aligned}$$

$$m_0 \left[\frac{1}{\sqrt{1 - v^2/c^2}} + \frac{v^2/c^2}{(1 - v^2/c^2)^{3/2}} \right] \frac{dv}{dt} = \mathbf{F}$$

$$\therefore \quad a = \frac{\mathbf{F}(1 - v^2/c^2)^{3/2}}{m_0} \quad \dots(1.15.4)$$

1.16 MASS-ENERGY EQUIVALENCE

The work done by unbalanced force acting on a particle appears as increment in kinetic energy. The increment in kinetic energy dT due to the force $\mathbf{F}$ acting over the elementary path $d\mathbf{r}$ ($= \mathbf{v} dt$) is given by

$$\begin{aligned} dT &= \mathbf{F} \cdot d\mathbf{r} = \mathbf{F} \cdot \mathbf{v} dt = \frac{d}{dt}(m\mathbf{v}) \cdot \mathbf{v} dt = d(m\mathbf{v}) \cdot \mathbf{v} \\ &= dm \mathbf{v} \cdot \mathbf{v} + m d\mathbf{v} \cdot \mathbf{v} \\ &= v^2 dm + m \mathbf{v} \cdot d\mathbf{v} \\ &= v^2 dm + m v dv \end{aligned} \quad \dots(1.16.1)$$

The mass of the particle varies with velocity as

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

whence

$$m^2 c^2 = m^2 v^2 + m_0^2 c^2$$

Taking differential of this equation we have

$$2mc^2 dm = 2mv^2 dm + 2m^2 v dv$$

Canceling the common factors we have

$$c^2 dm = v^2 dm + m v dv \quad \dots(1.16.2)$$

Making use of Eqn. (1.16.2), we can write the expression for increment in kinetic energy as

$$dT = c^2 dm \quad \dots(1.16.3)$$

The total kinetic energy of the particle at the instant it acquires velocity v is given by

$$\int_0^T dT = c^2 \int_{m_0}^m dm$$

$$T = (m - m_0)c^2 = (\gamma - 1)m_0 c^2 \quad \dots(1.16.4)$$

$$T = m_0 c^2 \left(\frac{1}{\sqrt{1 - v^2/c^2}} - 1 \right) \quad \dots(1.16.5)$$

This is the expression for the *relativistic kinetic energy* of a particle. For small velocities ($v/c \rightarrow 0$) Eqn. (1.16.5) reduces to the classical formula.

$$\begin{aligned} T &= m_0 c^2 \left[\left(1 - \frac{v^2}{c^2} \right)^{-1/2} - 1 \right] \\ &= m_0 c^2 \left[\left(1 + \frac{1}{2} \frac{v^2}{c^2} + \frac{3}{8} \frac{v^4}{c^4} + \dots \right) - 1 \right] \\ &= \frac{1}{2} m_0 v^2 \quad (\text{classical result}) \end{aligned}$$

The variation of relativistic and classical energy with velocity is shown in the figure. The expression (1.16.4) for kinetic energy can be written as

$$mc^2 = T + m_0 c^2 \quad \dots(1.16.6)$$

Einstein interpreted the term mc^2 on the left hand side as the *total energy* E of the particle. Thus

$$E = mc^2 = T + m_0 c^2 \quad \dots(1.16.7)$$

If the particle is at rest, its kinetic energy T is zero but it still possesses energy equal to $m_0 c^2$. This energy is called the *rest energy*. In relativistic physics total energy of a particle means the sum of kinetic energy and rest energy. The expression

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} = \gamma m_0 c^2 \quad \dots(1.16.8)$$

is one of the most fundamental laws of nature expressing the relationship between the total energy E of a particle and its mass. Equation (1.16.8) states that a change in total energy of a particle by amount ΔE is equivalent to change in mass by amount $\Delta m = \Delta E/c^2$ and vice-versa.

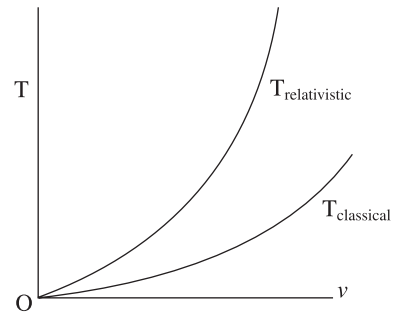


Fig. 1.16.1 Variation of kinetic energy with velocity

1.17 RELATIONSHIP BETWEEN ENERGY AND MOMENTUM

The total energy E and momentum p of a particle are

$$E = \gamma m_0 c^2 \quad \dots(1.17.1)$$

$$p = \gamma m_0 v \quad \therefore pc = \gamma m_0 vc \quad \dots(1.17.2)$$

Now

$$\begin{aligned} E^2 - p^2 c^2 &= \gamma^2 m_0^2 (c^4 - v^2 c^2) \\ &= \gamma^2 m_0^2 c^4 (1 - v^2 / c^2) \\ &= (m_0 c^2)^2 \end{aligned} \quad \dots(1.17.3)$$

This equation gives relation between energy and momentum. The quantities on the right hand side are invariant. Therefore $E^2 - (pc)^2$ is also invariant.

1.18 MOMENTUM OF PHOTON

The momentum of a particle moving with velocity v is given by

$$p = mv = \frac{E}{c^2} v \quad \dots(1.18.1)$$

Photon is a quantum of light with energy $E = h\nu$ and velocity c . Its momentum is

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{h}{\lambda} \quad \dots(1.18.2)$$

or

$$E = pc \quad \dots(1.18.3)$$

From Eqn. (1.17.3), we see that the rest mass of photon is zero. In fact all particles moving with speed of light c have zero rest mass. Photon and neutrino are such particles. Converse is also true *i.e.*, particles having zero rest mass always move with speed of light.

1.19 TRANSFORMATION OF MOMENTUM AND ENERGY

The total energy E and momentum p of a particle are velocity dependent and hence are not invariant. In this section we shall obtain transformation equations for energy and momentum.

Let a particle move from point (x, y, z) to point $(x + dx, y + dy, z + dz)$. The distance dl covered in time dt is $dl^2 = (dx)^2 + (dy)^2 + (dz)^2$. The velocity of the particle is $v = dl/dt$. The elementary interval between the initial and the final point is

$$\begin{aligned} ds &= [(cdt)^2 - (dl)^2]^{1/2} \\ &= cdt \left(1 - \frac{v^2}{c^2} \right)^{1/2} \\ &= \frac{cdt}{\gamma} \end{aligned}$$

whence

$$dt = \frac{\gamma ds}{c} \quad \dots(1.19.1)$$

Now the x -component of momentum of a particle is

$$p_x = \gamma m_0 v_x = \gamma m_0 \frac{dx}{dt} = \left(\frac{m_0 c}{ds} \right) dx \quad \dots(1.19.2)$$

Similarly

$$\begin{aligned} p_y &= \left(\frac{m_0 c}{ds} \right) dy \\ p_z &= \left(\frac{m_0 c}{ds} \right) dz \end{aligned} \quad \dots(1.19.3)$$

The energy of the particle is given by

$$E = \gamma m_0 c^2 = \gamma m_0 c^2 \frac{dt}{ds} = \left(\frac{m_0 c}{ds} \right) c^2 dt \quad \dots(1.19.4)$$

or

$$\frac{E}{c^2} = \left(\frac{m_0 c}{ds} \right) dt$$

Since m_0 , c and ds are invariants, from Eqns. (1.19.2–1.19.4) it follows that p_x , p_y , p_z and E/c^2 transform like dx , dy , dz and dt when we pass over from one inertial frame to another. Thus the transformation equations for the components of momentum and energy, together with those for coordinates and time are

$$p'_x = \gamma(p_x - vE/c^2), \quad x' = \gamma(x - vt) \quad \dots(1.19.5)$$

$$p'_y = p_y \quad y' = y$$

$$p'_z = p_z \quad z' = z$$

$$\frac{E'}{c^2} = \gamma \left(\frac{E}{c^2} - \frac{vp_x}{c^2} \right), \quad t' = \gamma \left(t - \frac{vx}{c^2} \right) \quad \dots(1.19.6)$$

Remembering the following correlations

$$p_x \Leftrightarrow x, p_y \Leftrightarrow y, p_z \Leftrightarrow z, (E/c^2) \Leftrightarrow t$$

we can write out the transformation equations for energy and momentum if we know the corresponding equations for time and space coordinates.

1.20 VERIFICATION OF MASS-ENERGY EQUIVALENCE FORMULA

There are many phenomena in which Einstein's formula $E = mc^2$ gets its experimental verification. Of these we shall discuss only two.

Pair production: In this phenomenon a gamma ray photon while passing nearby an atomic nucleus materializes into an *electron-positron* pair. The presence of third particle, such as nucleus in the present case, is necessary to conserve linear momentum. According to the law of mass-energy equivalence the minimum energy of photon for pair production must be equal to the sum of the rest energies of the created particles. The rest mass energy of electron-positron pair is $2m_0c^2 = 1.02 \text{ MeV}$. Indeed this has been verified. A gamma ray photon with energy less than 1.02 MeV cannot produce electron-positron pair whereas that having energy greater than 1.02 MeV creates electron-positron pair and the excess energy goes into the kinetic energies of the particles. The *threshold* wavelength of gamma ray photon is given by

$$\begin{aligned}
 h\nu &= \frac{ch}{\lambda} = 2m_0c^2 \\
 \lambda &= \frac{ch}{2m_0c^2} \\
 &= \frac{12.4 \times 10^{-3} \text{ MeV} \cdot \text{\AA}}{1.02 \text{ MeV}} = 0.012 \text{ \AA}
 \end{aligned}$$

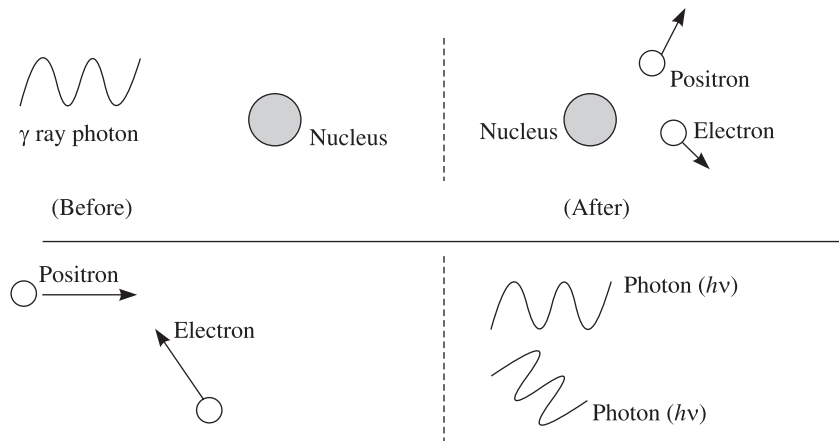


Fig. 1.20.1 Pair production and pair annihilation

When electron and positron meet, they annihilate each other creating at least two photons. This phenomenon is called *pair annihilation*.



1.21 NUCLEAR BINDING ENERGY

When nucleons (protons and neutrons) combine to form an atomic nucleus, the mass of the resulting nucleus is always less than the sum of masses of the constituent nucleons. The mass that disappears is called the mass defect and is liberated as binding energy of the nucleus. For a nucleus with mass number A (number of nucleons) and atomic number Z (number of protons) the mass defect is given by

$$\Delta m = [Zm_p + (A - Z)m_n - M_{\text{nuc}}] \quad \dots(1.21.1)$$

and the binding energy of the nucleus

$$B = (\Delta m) c^2 \quad \dots(1.21.2)$$

Let us calculate the binding energy of ${}^4_2\text{He}$, which consists of two protons and two neutrons.

Mass of protons = 2 (1.00815) amu = 2 (938.7) MeV

Mass of neutrons = 2 (1.0080) amu = 2 (939.5) MeV

Mass of nucleus = 4.00260 amu = 3728.0 MeV

Binding energy = (1877.4 + 1879.0 – 3728.0) MeV = 28.5 MeV

Binding energy per nucleon = 28.5/4 = 7.1 MeV

SOLVED EXAMPLES

Ex. 1. Verify that the law of conservation of linear momentum is invariant under Galilean transformation.

Sol. Consider the collision two balls of masses m_1 and m_2 moving with velocities u_1 and u_2 relative to ground. After the collision the balls move with velocities v_1 and v_2 . The statement of the law of conservation of linear momentum in frame S fixed to the ground reads

$$m_1 u_1 + m_2 u_2 = m_1 v_1 + m_2 v_2 \quad \dots(1)$$

The same collision is observed from a frame S' , which is moving relative to S with velocity v . In frame S' the velocities of the balls before and after collision are

$$u'_1 = u_1 - v, \quad u'_2 = u_2 - v, \quad v'_1 = v_1 - v, \quad v'_2 = v_2 - v \quad \dots(2)$$

In frame S' the law of conservation of linear momentum is

$$m_1 u'_1 + m_2 u'_2 = m_1 v'_1 + m_2 v'_2 \quad \dots(3)$$

Making use of (2) we can transform (3) as

$$m_1 (u_1 - v) + m_2 (u_2 - v) = m_1 (v_1 - v) + m_2 (v_2 - v)$$

$$m_1 u_1 + m_2 u_2 = m_1 v_1 + m_2 v_2$$

which is the law of conservation in frame S .

Ex. 2. Show that the law of conservation of kinetic energy in elastic collision of two particles is invariant under Galilean transformation.

Sol. In frame S , let us consider perfectly elastic collision of two particles of masses m_1 and m_2 moving with velocities u_1 and u_2 in x direction. After collision their velocities are v_1 and v_2 . The

law of conservation of kinetic energy in frame reads as:

$$\frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2 = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 \quad \dots(1)$$

The same collision is observed from frame S' , which moves with velocity v in x direction. The initial and final velocities of the particles in this frame are:

$$u'_1 = u_1 - v, \quad u'_2 = u_2 - v, \quad v'_1 = v_1 - v, \quad v'_2 = v_2 - v$$

Substituting the values of u_1, u_2, v_1, v_2 from above equations in (1), we have

$$\frac{1}{2}m_1(u'_1 + v)^2 + \frac{1}{2}m_2(u'_2 + v)^2 = \frac{1}{2}m_1(v'_1 + v)^2 + \frac{1}{2}m_2(v'_2 + v)^2 \quad \dots(2)$$

Subtracting (1) from (2) and making use of the law of conservation of momentum in the resulting equation, we find

$$\frac{1}{2}m_1u_1'^2 + \frac{1}{2}m_2u_2'^2 = \frac{1}{2}m_1v_1'^2 + \frac{1}{2}m_2v_2'^2 \quad \dots(3)$$

which is the law of conservation of kinetic energy in frame S' .

Ex. 3. An event occurs at $x = 50$ m, $y = 20$ m, $z = 10$ m, and $t = 5 \times 10^{-8}$ s in frame S . What are the space-time coordinates of the event as measured by an observer stationed in frame S' , which is moving relative to S with velocity $0.6c$ along the common x - x' axis.

Sol. Lorentz transformations are

$$x' = \gamma(x - vt), \quad y' = y, \quad z' = z, \quad t' = \gamma(t - vx/c^2)$$

$$\gamma = 1/\sqrt{1 - \beta^2} = 1/\sqrt{1 - 0.36} = 1.25$$

$$x' = 1.25(50 \text{ m} - 0.6 \times 3 \times 10^8 \text{ m/s} \times 5 \times 10^{-8} \text{ s}) = 51.25 \text{ m}$$

$$y' = 20 \text{ m}, \quad z' = 10 \text{ m}$$

$$t' = 1.25(5 \times 10^{-8} \text{ s} - 10 \times 10^{-8} \text{ s}) = -6.25 \times 10^{-8} \text{ s}.$$

Ex. 4. An event 1 occurs at $x_1 = 20$ m, $t_1 = 2 \times 10^{-8}$ s and event 2 occurs at $x_2 = 60$ m, $t_2 = 3 \times 10^{-8}$ s in frame S . A frame S' moves relative to S with velocity $0.6c$ along the common axis x - x' . (i) What is the spatial separation of the events in frame S' ? (ii) What is the time interval between the two events?

Sol. (i) The spatial separation of the events in frame S' is

$$\begin{aligned} x'_2 - x'_1 &= \gamma[(x_2 - x_1) - v(t_2 - t_1)] \\ &= 1.25[(60 - 20) \text{ m} - 0.6 \times 3 \times 10^8 \text{ m/s} (3 - 2) \times 10^{-8} \text{ s}] \\ &= 47.75 \text{ m}. \end{aligned}$$

(ii) The time interval between the events in frame S' is

$$\begin{aligned} t'_2 - t'_1 &= \gamma[(t_2 - t_1) - v(x_2 - x_1)/c^2] \\ &= 1.25[1 \times 10^{-8} \text{ s} - (0.6 \times 40)/(3 \times 10^8)] \\ &= -8.75 \times 10^{-8} \text{ s}. \end{aligned}$$

Ex. 5. The space-time coordinates of two events 1 and 2 in a frame S are $x_1 = 24 \text{ m}$, $t_1 = 8 \times 10^{-8} \text{ s}$ and $x_2 = 48 \text{ m}$, $t_2 = 4 \times 10^{-8} \text{ s}$. Find the velocity of the frame S' in which both the events occur simultaneously.

Sol. The time interval between the events in frame S' is

$$(t'_2 - t'_1) = \gamma [(t_2 - t_1) - v(x_2 - x_1)/c^2]$$

For the events to occur simultaneously in frame S' , $t'_2 - t'_1 = 0$. Hence

$$\frac{v}{c} = \frac{c(t_2 - t_1)}{x_2 - x_1} = \frac{3 \times 10^8 \text{ m/s} (-4 \times 10^{-8} \text{ s})}{48 \text{ m} - 24 \text{ m}} = -0.5$$

$$v = -0.5c.$$

Ex. 6. Two events occur at the same place in a frame S and are separated by a time interval of 1 s. The same events are separated by a time interval of 4 s in frame S' . What is the spatial separation of the events in frame S' ?

Sol. The spatial separation of events in frame S' is

$$x'_2 - x'_1 = \gamma [(x_2 - x_1) - v(t_2 - t_1)]$$

Given that: $x_2 - x_1 = 0$, $t_2 - t_1 = 1 \text{ s}$, $t'_2 - t'_1 = 4 \text{ s}$

$$\Rightarrow x'_2 - x'_1 = -\gamma v \quad \dots(1)$$

The time interval between the events in frame S' is

$$t'_2 - t'_1 = \gamma [(t_2 - t_1) - v(x_2 - x_1)/c^2]$$

$$4 = \gamma \quad \therefore \beta = \frac{\sqrt{15}}{4} \quad \dots(2)$$

From (1) and (2), we have $x'_2 - x'_1 = -2\left(\sqrt{\gamma^2 - 1}\right)c = -2c\sqrt{15}$.

Ex. 7. In a frame S , two events occur at the same time and are separated by a distance x_0 . In another frame S' , which is moving along the common x - x' axis with constant velocity, the events have spatial separation $2x_0$. What is the time interval between the events in frame S ?

Sol. Given that: $t_2 - t_1 = 0$, $x_2 - x_1 = x_0$, $x'_2 - x'_1 = 2x_0$

Now spatial separation between events in frame S'

$$x'_2 - x'_1 = \gamma [(x_2 - x_1) - v(t_2 - t_1)]$$

$$2x_0 = \gamma x_0$$

$$\gamma = 2 \Rightarrow v = c\sqrt{3}/2$$

$$t'_2 - t'_1 = \gamma [(t_2 - t_1) - v(x_2 - x_1)/c^2] = -\frac{\sqrt{3}}{c}x_0.$$

Ex. 8. How fast should a rocket ship move for its length to be contracted to 99% of its rest length?

Sol.

$$l = l_0 \sqrt{1 - \beta^2} \quad \text{whence} \quad \beta = \sqrt{1 - \left(\frac{l}{l_0}\right)^2} = \sqrt{1 - (0.99)^2} = 0.141$$

$$v = 0.141 \, c.$$

Ex. 9. A rod of proper length 1.00 m makes an angle of 45° with x -axis. Determine the length of the rod and its inclination with x -axis in a frame with respect to which the rod is moving with velocity $v = 0.5c$ along the common x - x' direction.

Sol. Let l_0 be the proper length of the rod and θ' its inclination with x' -axis in frame S' . The corresponding quantities in frame S are l and θ . Then

$$l_x = l'_x \sqrt{1 - \beta^2} \quad \text{or} \quad l \cos \theta = l' \cos \theta' \sqrt{1 - \beta^2} \quad \dots(1)$$

$$l_y = l'_y \quad \text{or} \quad l \sin \theta = l' \sin \theta'. \quad \dots(2)$$

Squaring and adding (1) and (2), we have

$$\begin{aligned} l^2 &= l'^2 [\sin^2 \theta' + (1 - \beta^2) \cos^2 \theta'] \\ &= 1.00 \left[\frac{1}{2} + \left(1 - \frac{1}{4}\right) \frac{1}{2} \right] = 0.875 \\ l &= 0.94 \, m \end{aligned}$$

From (1) and (2), we have

$$\begin{aligned} \tan \theta &= \frac{\tan \theta'}{\sqrt{1 - \beta^2}} = \frac{1}{\sqrt{1 - 1/4}} = 1.19 \\ \theta &= 49^\circ. \end{aligned}$$

Ex. 10. A piece of metal in the form of a rectangular bloc of dimensions a, b, c is placed with its edges parallel to the coordinate axes of a frame S . Its density is defined as the ratio of the rest mass to the volume. Find the velocity of the reference frame S' moving parallel to the edge a in which the density of bloc is 25% greater.

Sol. The density of the bloc in frame S

$$\rho_0 = \frac{m_0}{abc}$$

Let v be the velocity of frame S' relative to S . Its volume in frame S' is $abc\sqrt{1 - \beta^2}$. The density of the bloc in S' is

$$\rho = \frac{m_0}{abc\sqrt{1 - \beta^2}} = \frac{\rho_0}{\sqrt{1 - \beta^2}}.$$

Given that: $\rho = (1 + 0.25) \rho_0$

$$\therefore 1.25 = \frac{1}{\sqrt{1-\beta^2}}$$

$$\beta = 0.6.$$

Ex. 11. A clock keeps correct time. With what speed should it move relative to an observer so that it may seem to lose 4 min in 24 hours?

Sol. Proper time $\Delta\tau = 1436$ min, non-proper time $\Delta t = 1440$ min. Time dilation formula is

$$\Delta t = \frac{\Delta\tau}{\sqrt{1-\beta^2}} \quad \therefore \sqrt{1-\beta^2} = \frac{1436}{1440} = 1 - \frac{4}{1440}$$

$$1-\beta^2 = \left(1 - \frac{1}{360}\right)^2 = 1 - \frac{2}{360}$$

$$\beta = \frac{1}{\sqrt{180}}.$$

Ex. 12. A particle with mean proper lifetime of 1μ s moves through laboratory at 2.7×10^8 m/s.
(i) What is the lifetime of the particle as measured in the laboratory frame? (ii) How far does it go in the laboratory before disintegration?

Sol. (i) The lifetime of the particle in the lab frame is given by

$$\Delta t = \frac{\Delta\tau}{\sqrt{1-\beta^2}} = \frac{1 \times 10^{-6} \text{ s}}{\sqrt{1-(0.9)^2}} = 2.29 \times 10^{-6} \text{ s}$$

(ii) The distance traversed in the lab frame

$$d = v \Delta t = 2.7 \times 10^8 \text{ m/s} \times 2.29 \times 10^{-6} \text{ s} = 62 \times 10^3 \text{ m}.$$

Ex. 13. In a frame S , a muon moving with velocity $v = 0.99 c$ travels through a distance 3.0 km from its birthplace to the point where it decays. Find (i) proper lifetime of the muon (ii) the distance travelled by muon in the frame in which it is at rest.

Sol. The proper lifetime of muon

$$\Delta\tau = \Delta t \sqrt{1-\beta^2} = \frac{d}{v} \sqrt{1-v^2/c^2}$$

$$= \frac{3 \times 10^3 \text{ m}}{0.99 \times 3 \times 10^8 \text{ m/s}} \sqrt{1-(0.99)^2} = 1.4 \times 10^{-6} \text{ s}.$$

In muon's frame the distance travelled by it is

$$d' = d \sqrt{1-\beta^2} = (3 \times 10^3 \text{ m}) \sqrt{1-(0.99)^2} = 0.423 \times 10^3 \text{ m}.$$

Ex. 14. Two β particles are observed to be moving with speeds $0.6c$ and $0.8c$ in opposite directions in the laboratory frame. Calculate the speed of one β particle relative to the other.

Sol. In the lab frame S , the speeds of the β particles are

$$u_1 = 0.6c \text{ and } u_2 = -0.8c.$$

Let us consider a frame S' attached to the first β particle. Obviously the frame S' is moving with velocity $v = 0.6c$. In S' the first β particle is at rest. Let the velocity of the second β particle in S' be u'_2 . Then according to the relativistic transformation of velocity

$$u'_2 = \frac{u_2 - v}{1 - u_2 v / c^2} = \frac{-0.8c - 0.6c}{1 - (-0.8c)(0.6c)/c^2} = -0.946c.$$

Ex. 15. At what speed must a particle move for its mass be trebled?

Sol. Given that: $m = 3m_0$. From the formula $m = \frac{m_0}{\sqrt{1-\beta^2}}$ we have

$$\beta = \sqrt{1 - \frac{m_0}{m}} = \sqrt{1 - \frac{1}{3}} = \frac{2\sqrt{2}}{3} \quad \therefore v = \frac{2\sqrt{2}}{3}c.$$

Ex. 16. At what speed the total energy of a particle is n times its rest energy?

Sol. Given that $mc^2 = n m_0 c^2$, $m = n m_0$. From the formula $m = \frac{m_0}{\sqrt{1-\beta^2}}$ we have

$$\beta = \sqrt{\frac{n^2 - 1}{n^2}} = \sqrt{1 - \frac{1}{n^2}} \quad \therefore v = c \sqrt{1 - \frac{1}{n^2}}.$$

Ex. 17. At what speed the kinetic energy of a particle is n times its rest energy?

Sol. Given that $T = n m_0 c^2$
 $(m - m_0) c^2 = n m_0 c^2$

$$m = (n + 1) m_0$$

$$\frac{m_0}{\sqrt{1-\beta^2}} = (n+1)m_0 \quad \therefore \beta = \frac{\sqrt{n(n+2)}}{n+1}.$$

Ex. 18. If the total energy of a particle is n times its rest energy, what is its momentum?

Sol. Given that $E = n m_0 c^2$. We know that the total energy of a particle is given by

$$E^2 = (pc)^2 + (m_0 c^2)^2$$

$$pc = \sqrt{E^2 - (m_0 c^2)^2} = \sqrt{(n m_0 c^2)^2 + (m_0 c^2)^2}$$

$$p = m_0 c \sqrt{n^2 - 1}.$$

Ex. 19. At what momentum the kinetic energy of a particle equals n times its rest energy?

Sol. Given that: $T = n m_0 c^2$

We know that

$$E^2 = [T + m_0 c^2]^2 = (pc)^2 + (m_0 c^2)^2$$

$$\therefore pc = m_0 c^2 \sqrt{n(n+2)}$$

$$p = m_0 c \sqrt{n(n+2)}.$$

Ex. 20. Show that the velocity of a particle having total energy E is given by

$$v = c \left[1 - \left(\frac{m_0 c^2}{E} \right)^2 \right]^{1/2}.$$

Sol. We know that,

$$E^2 = (pc)^2 + (m_0 c^2)^2 \quad \dots(1)$$

$$p = \frac{E}{c^2} v. \quad \dots(2)$$

Substituting the value of p from (2) in (1), we get

$$E^2 = \frac{v^2}{c^2} E^2 + (m_0 c^2)^2$$

$$\therefore v = c \left[1 - (m_0 c^2 / E)^2 \right]^{1/2}.$$

Ex. 21. Show that the momentum p of a particle can be expressed in terms of kinetic energy T as

$$pc = \sqrt{T(T + 2m_0 c^2)}$$

Calculate the momentum of proton having kinetic energy of 500 MeV.

Sol. Since $E^2 = (T + m_0 c^2)^2 = (pc)^2 + (m_0 c^2)^2$

$$(pc)^2 = (T + m_0 c^2)^2 - (m_0 c^2)^2$$

$$pc = \sqrt{T(T + 2m_0 c^2)}.$$

Ex. 22. Show that the velocity of a particle having momentum p is given by

$$v = pc \left[p^2 + m_0^2 c^2 \right]^{-1/2}.$$

Sol. Squaring the equation $p = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$ and rearranging, we get

$$\left(1 - \frac{v^2}{c^2}\right)p^2 = m_0^2 v^2$$

$$v = \frac{pc}{\sqrt{p^2 + m_0^2 c^2}}.$$

Ex. 23. Calculate the momentum of electron having kinetic energy equal to 2 BeV.

Sol. Total energy

$$E^2 = (T + m_0 c^2)^2 = (pc)^2 + (m_0 c^2)^2.$$

If the rest energy is very small in comparison to the kinetic energy, then we can write the above formula as

$$E = T = pc.$$

The rest energy of electron is $m_0 c^2 = 0.51$ MeV. So we can neglect the rest energy of electron in comparison to its kinetic energy (2 BeV). Thus the momentum of electron is

$$p = T/c = 2 \text{ BeV}/c.$$

Ex. 24. At what velocity does the Newtonian momentum of a particle differ from its relativistic value by 1%?

Sol. Classical momentum $p_c = m_0 v$ and relativistic momentum $p_r = \frac{m_0 v}{\sqrt{1 - \beta^2}}.$

$$\frac{p_r - p_c}{p_r} = 1 - \sqrt{1 - \beta^2}$$

$$n = 1 - \sqrt{1 - \beta^2} \quad \text{where } n \text{ is fractional increase in momentum.}$$

From above equation, we get

$$\beta = \sqrt{n(2 - n)}$$

Putting $n = 0.01$, we have $\beta = 0.14$.

Ex. 25. Find the velocity at which the relativistic momentum of a particle exceeds its Newtonian momentum by n fold.

Sol. $\frac{p_r}{p_c} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{n}{1} \therefore v = \frac{c\sqrt{n^2 - 1}}{n}.$

Ex. 26. An electron is accelerated through a potential difference of 1 million volts. What is the speed of electron?

Sol. Kinetic energy of electron

$$T = m_0 c^2 \left(\frac{1}{\sqrt{1-\beta^2}} - 1 \right)$$

$$\therefore \beta = \sqrt{1 - \left(\frac{m_0 c^2}{T + m_0 c^2} \right)^2}$$

Putting $m_0 c^2 = 0.51 \text{ MeV}$ and $T = 1 \text{ MeV}$, we get

$$\beta = 0.9988.$$

Ex. 27. An electron is accelerated to energy of 2 BeV. Calculate (i) the effective mass of electron in terms of its rest mass, (ii) the speed of electron in terms of the speed of light.

Sol. Total energy of electron

$$mc^2 = T + m_0 c^2$$

Dividing throughout by $m_0 c^2$, we have

$$\frac{m}{m_0} = 1 + \frac{T}{m_0 c^2} = 1 + \frac{2000 \text{ MeV}}{0.51 \text{ MeV}} = 3915$$

From the relation $m = \frac{m_0}{\sqrt{1-\beta^2}}$, we have

$$\beta = \sqrt{1 - \left(\frac{m_0}{m} \right)^2} = \sqrt{1 - \left(\frac{1}{3915} \right)^2}$$

Ex. 28. What work has to be done in order to increase the velocity of a particle of rest mass m_0 from $0.60 c$ to $0.80 c$? Obtain the result classically and relativistic

Sol. (i) Classically, the work done equals the increase in kinetic energy of the particle

$$W = \frac{1}{2} m_0 v_0^2 - \frac{1}{2} m_0 v_1^2 = 0.5 m_0 [(0.8c)^2 - (0.6c)^2] = 0.14 m_0 c^2$$

(ii) On the basis of relativistic calculation, the required work W

$$= E_2 - E_1 = m_2 c^2 - m_1 c^2$$

$$= m_0 c^2 \left(\frac{1}{\sqrt{1 - \frac{v_2^2}{c^2}}} - \frac{1}{\sqrt{1 - \frac{v_1^2}{c^2}}} \right) = 0.417 m_0 c^2.$$

Ex. 29. Calculate the effective mass of photon of wavelength (i) 5000 Å (ii) 0.1 Å

Sol. (i) The relativistic energy of photon is $E = mc^2$ and in terms of quantum picture photon's energy is $E = h\nu = hc/\lambda$. Thus

$$mc^2 = \frac{hc}{\lambda} \quad \therefore m = \frac{h}{\lambda c} = \frac{6.63 \times 10^{-34} \text{ Js}}{(5000 \times 10^{-10} \text{ m}) (3 \times 10^8 \text{ m/s})} = 4.42 \times 10^{-36} \text{ kg}$$

(ii) The effective mass of photon of wavelength $\lambda = 0.1 \text{ Å}$

$$m = \frac{h}{\lambda c} = \frac{6.63 \times 10^{-34} \text{ Js}}{0.1 \times 10^{-10} \text{ m} \times 3 \times 10^8 \text{ m/s}} = 2.21 \times 10^{-31} \text{ kg}.$$

Ex. 30. Calculate the minimum energy of a gamma ray photon, which can produce an electron positron pair.

Sol. In pair production a gamma ray photon materializes into two particles electron and positron. For pair production to take place the energy of gamma ray photon must at least be equal to the sum of the rest energies of the electro and positron. Thus

$$E = 2 m_0 c^2 = 2 (0.51 \text{ MeV}) = 1.02 \text{ MeV}.$$

Ex. 31. A nucleus of mass m emits a gamma ray photon of frequency ν . Show that the loss of internal energy of the nucleus is given by

$$\Delta E = h\nu \left[1 + \frac{h\nu}{2m_0 c^2} \right].$$

Sol. The momentum of emitted photon is $p = h\nu/c$. To conserve linear momentum the nucleus recoils in opposite direction with equal momentum. If v is the recoil velocity of the nucleus then

$$mv = \frac{h\nu}{c}. \quad \dots(1)$$

The loss of internal energy of nucleus equals the sum of kinetic energy of recoil of the nucleus and the energy of photon. Thus

$$\begin{aligned} \Delta E &= h\nu + \frac{1}{2}mv^2 \\ &= h\nu + \frac{1}{2} \frac{(h\nu)^2}{mc^2} \end{aligned}$$

$$= h\nu \left[1 + \frac{h\nu}{2mc^2} \right].$$

Ex. 32. A particle of mass m_0 is subjected to a force F acting along x -axis. The particle starts moving from rest at $x = 0$ at $t = 0$. Find the position x as function of time.

Sol. The equation of motion of the particle is

$$\frac{dp}{dt} = F$$

$$\frac{d}{dt} \left(\frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}} \right) = F \quad \dots(1)$$

Integrating and using the initial condition: at $t = 0$, $v = 0$, we have

$$\frac{m_0 v}{\sqrt{1 - v^2/c^2}} = Ft$$

Solving for v , we find

$$v = \frac{dx}{dt} = \frac{(F/m_0) t}{\sqrt{1 + (Ft/m_0 c)^2}} \quad \dots(2)$$

Integrating (2), we have

$$x = \frac{F}{m_0} \int_0^t \frac{tdt}{\sqrt{1 + (Ft/m_0 c)^2}}$$

$$= \frac{m_0 c^2}{F} \left[\sqrt{1 + \left(\frac{Ft}{m_0 c} \right)^2} - 1 \right].$$

Ex. 33. The earth receives solar energy about $\sigma = 1.4 \times 10^3 \text{ J/m}^2\text{s}$ over an area held normal to the sun-rays. Calculate the fractional loss of mass of the sun per sec. The mean radius of the earth orbit is $R = 1.5 \times 10^{11} \text{ m}$ and the mass of sun is $M = 1.97 \times 10^{30} \text{ kg}$.

Sol. The amount of energy radiated per sec by the sun

$$\Delta E = 4 \pi R^2 \sigma$$

This energy is equivalent to mass $\Delta m = \Delta E/c^2$. The fractional loss of mass is

$$\begin{aligned}\frac{\Delta m}{M} &= \frac{E}{Mc^2} = \frac{4\pi R^2 \sigma}{Mc^2} = \frac{4 \times 3.14 \times (1.5 \times 10^{11} \text{ m})^2 (1.4 \times 10^3 \text{ J m}^{-2} \text{ s}^{-1})}{(1.97 \times 10^{30} \text{ kg})(3 \times 10^8 \text{ m/s})^2} \\ &= 2 \times 10^{-21} \text{ s}^{-1}.\end{aligned}$$

Ex. 34. A particle moves relative to frame S with velocity u in xy -plane at angle θ to the x -axis. Find the corresponding velocity u' at angle θ' in the frame S' which moves with velocity v relative to S along the common x - x' direction

Sol. The x and y components of velocity in frame S are

$$u_x = u \cos \theta, \quad u_y = u \sin \theta.$$

Let the velocity u' of the particle make angle θ' with x' -axis in frame S' . The x and y components of u' can be obtained from velocity transformation formula.

$$u'_x = \frac{u_x - v}{1 - u_x v / c^2} = \frac{u \cos \theta - v}{1 - (u \cos \theta) v / c^2} \quad \dots(1)$$

$$u'_y = \frac{u_y \sqrt{1 - \beta^2}}{1 - u_x v / c^2} = \frac{u \sin \theta \sqrt{1 - \beta^2}}{1 - (u \cos \theta) v / c^2} \quad \dots(2)$$

From (1) and (2)

$$\tan \theta' = \frac{u'_y}{u'_x} = \frac{u \sin \theta \sqrt{1 - \beta^2}}{u \cos \theta - v} = \frac{\sin \theta \sqrt{1 - \beta^2}}{\cos \theta - (v/u)} \quad \dots(3)$$

Inverse transformation is

$$\tan \theta = \frac{\sin \theta' \sqrt{1 - \beta^2}}{\cos \theta' + (v/u')} \quad \dots(4)$$

The velocity u' is given by

$$u'^2 = u_x'^2 + u_y'^2 = \frac{u^2 + v^2 - 2uv \cos \theta - \beta^2 u^2 \sin^2 \theta}{[1 + (vu \cos \theta) / c^2]^2}. \quad \dots(5)$$

Ex. 35. Acceleration transformation: A particle moves with acceleration a in frame S . Find the acceleration a' of the particle in the frame S' which moves with velocity v in the positive direction of x -axis of frame S .

Sol. The x -component of acceleration in frame S' is given by

$$a'_x = \frac{du'_x}{dt'} = \frac{du'_x}{dt} \frac{1}{dt'/dt} \quad \dots(1)$$

Velocity transformation is

$$u'_x = \frac{u_x - v}{1 - u_x v / c^2}. \quad \dots(2)$$

Differentiating (2) with respect to t , we have

$$\begin{aligned} \frac{du'_x}{dt} &= \frac{\frac{du_x}{dt}(1 - u_x v / c^2) - (u_x - v)\left(-\frac{du_x}{dt} \frac{v}{c^2}\right)}{(1 - u_x v / c^2)^2} \\ &= \frac{(1 - v^2 / c^2) a_x}{(1 - u_x v / c^2)^2} \end{aligned} \quad \dots(3)$$

The Lorentz transformation for time is

$$\begin{aligned} t' &= \frac{t - vx / c^2}{\sqrt{1 - v^2 / c^2}} \\ \therefore \frac{dt'}{dt} &= \frac{1 - u_x v / c^2}{\sqrt{1 - v^2 / c^2}} \end{aligned} \quad \dots(4)$$

The acceleration in frame S' is

$$a'_x = \frac{du'_x}{dt'} = \frac{du'_x}{dt} \frac{dt}{dt'} = \frac{(1 - v^2 / c^2)^{3/2}}{(1 - u_x v / c^2)^3} a_x. \quad \dots(5)$$

Ex. 36. Derive the relativistic aberration formula from the velocity transformation equations.

Sol. Consider a frame S' moving relative to S with velocity v along the common x - x' direction. A source at origin of S' emits a light wave in the direction θ' with x -axis. In frame S' , we have

$$u'_x = c \cos \theta', \quad u'_y = c \sin \theta'$$

In frame S

$$\begin{aligned} u_x &= \frac{u'_x + v}{1 + u'_x v / c^2} = \frac{c \cos \theta' + v}{1 + (v/c) \cos \theta'} \\ u_y &= \frac{u'_y \sqrt{1 - \beta^2}}{1 + u'_x v / c^2} = \frac{c \sin \theta' \sqrt{1 - \beta^2}}{1 + (v/c) \cos \theta'} \\ \tan \theta &= \frac{u_y}{u_x} = \frac{\sin \theta' \sqrt{1 - \beta^2}}{\cos \theta' + \beta}. \end{aligned}$$

QUESTIONS

1. What do Galilean Transformation and Galilean invariance principle mean? Show that whereas the length and acceleration are invariant this transformation, velocity is not.
2. What are Galilean transformations? Discuss the Galilean invariance of Newton's equation of motion. What is the significance of Michelson–Morley experiment?
3. Discuss the theoretical background of M.M experiment. Briefly describe the experimental set up and what conclusions of importance have been obtained from this experiment.
4. Describe the essential features of M.M. experiment and discuss the significance of this result in the development of special theory of relativity.
5. What are Lorentz transformations? Show that two events, which are simultaneous in one frame of reference, are not simultaneous in other frame of reference in relative motion with the first.
6. Write down the Lorentz transformation equations. Explain the phenomenon of time dilation and length contraction.
7. State the postulates of special theory of relativity and show how Lorentz transformations have been obtained from them.
8. (a) Assuming the invariance of equation of light wave front in two inertial frames of reference with uniform relative velocity, derive the Lorentz transformations.
(b) Show that the length of a moving rod appears to be contracted.
9. Write Lorentz transformation equations. Show that two successive Lorentz transformations in the same direction are equivalent to a single transformation. Find the equivalent velocity.
10. Prove that the equation of a spherical pulse of light starting from origin at $t = t' = 0$, $x^2 + y^2 + z^2 - c^2 t^2 = 0$ is invariant under Lorentz transformation.
11. Show that the differential equation $dx^2 + dy^2 + dz^2 - c^2 dt^2 = ds^2$ is invariant under a Lorentz transformations.
12. A light pulse is emitted at the origin of a frame of reference s at time $t' = 0$. Its distance x' from the origin after a time t' is given by $(x')^2 = c^2 t'^2$. Use the Lorentz transformation to transform this equation to an equation in x and t and show that the result is $x^2 = c^2 t^2$. Discuss the implications of this result.
13. State Lorentz transformation equations and use them to obtain Einstein's addition theorem of velocities. Discuss the physical significance of the theorem.
14. Derive Einstein's law for the addition of two velocities. What happens if one of the particles moves with the velocity of light?
15. Derive the formula $m = m_0 \frac{1}{\sqrt{1-\beta^2}}$ where $\beta = v/c$.
16. Derive the Einstein's formula expressing the equivalence of mass and energy.
17. Obtain the relativistic expression for kinetic energy of a body and show that for small speeds it reduces to the classical expression.
18. Derive the following relations:

$$(i) \ E = mc^2, \quad (ii) \ E^2 = (pc)^2 + (m_0 c^2)^2 \quad (iii) \ T = m_0 c^2 \left[\frac{1}{\sqrt{1-\beta^2}} - 1 \right]$$

$$(iv) \ T = c\sqrt{p^2 + (m_0 c)^2} - m_0 c^2, \ p = \frac{1}{c} \sqrt{T(T + 2m_0 c^2)}, \quad (v) \ m_0 = \frac{1}{c} \sqrt{E^2 - p^2 c^2}$$

PROBLEMS

[Lorentz Transformation, Space Contraction and Time Dilation]

1. An event occurs at $x' = 60$ m, $t' = 5 \times 10^{-8}$ s in frame S' . The frame s' moves with velocity $0.6 C$ along the common x - x' direction with respect to the frame s . The origins of s and s' coincide at $t' = t = 0$. Find the space time coordinates of the event in frame s .
[Ans. $x = 86.25$ m, $t = 21.25 \times 10^{-8}$ s]
2. A rocket was found to be of length 100 m when measured on the earth. It then leaves the earth and moves away at a constant speed 2×10^8 m/s. What will be its length now as measured from the earth $C = 3 \times 10^8$ m/s.
3. A rod has length 100 cm when the rod is in a satellite moving with velocity $0.8 C$ relative to the laboratory. What is the length of the rod as determined by an observer in the laboratory?
4. A rod 1 metre long is moving with a velocity $0.6 C$. Calculate its length as it appears to (a) a stationary observer (b) an observer moving with the rod itself.
[Ans. (a) 0.8 m (b) 1 m]
5. A rocket is 100 m long on the ground. When it is in the flight its length is 99 m to an observer on the ground. Calculate its speed.
[Ans. $v = 0.14 c$]
6. Calculate the percentage contraction of a rod moving with velocity $0.8 c$ in a direction inclined at 60° to its own length.
[Ans. 8.0%]

Hint: The component of length parallel to the direction of motion is $L_0 \cos 60^\circ = 1/2 L_0$. Only this component changes in length. The length of parallel component measured by an observer with respect to which the rod is

moving with velocity $0.8 c$ is $L_x = \frac{1}{2} L_0 \sqrt{1 - (0.8)^2} = 0.3 L_0$.

The component of length perpendicular to the direction of motion is $L_y = L_0 \sin 60^\circ = \frac{\sqrt{3}}{2} L_0$ and this length remains unchanged.

The moving length of rod $L = \sqrt{(0.3 L_0)^2 + (0.866 L_0)^2} = 0.92 L_0$.

Percentage contraction $\left(\frac{L_0 - 0.92 L_0}{L_0} \right) \times 100 = 8\%$.

7. With what velocity a spaceship fly so that everyday spent on it may correspond to 3 days on earth's surface.

Hint: $\Delta t_0 = 1$ day, $\Delta t = 3$ days. $\Delta t = \frac{\Delta t_0}{\sqrt{1 - \beta^2}}$ gives $\beta = \frac{\sqrt{8}}{3} C$.

8. What is the mean life of π^+ mesons traveling with a velocity of $0.73 C$. The mean life-time for π^+ mesons at rest is 2.5×10^{-8} sec.
[Ans. 3.7×10^{-8} sec]
9. The mean life-time of pions in the laboratory is 2.5×10^{-7} sec. Calculate its velocity if the proper mean life-time is 2.5×10^{-8} sec.
10. The mean life-time of a muon at rest is about 2×10^{-8} sec. It is moving with velocity $v = 0.99 C$. What is its mean life to a laboratory observer and what distance does it traverse before decaying.
[Ans. $\Delta t = 14.18 \times 10^{-8}$ s, $d = v.A t = 42$ m]
11. Half life-time of pions is 1.8×10^{-8} sec. A beam of pions is produced with speed $v = 0.8 c$. Calculate the distance traversed by the beam during which its intensity reduces to half its original value.
[Ans. $d = 7.2$ m]

[Addition of Velocities]

12. Two electrons, each of velocity $0.8c$ move towards each other. Find the relative velocity of one electron with respect to other.
13. One β -particle is moving east with a velocity of $0.95c$ and a second β -particle is moving west with a velocity $0.85c$. Find the relative velocity of the two β -particles.

$$\left[\text{Ans. } u_x = \frac{u'_x + v}{1 + \frac{vu'_x}{c^2}} = \frac{0.85c + 0.95c}{1 + 0.85 \times 0.95} = 0.99c \right]$$

14. In the laboratory two β -particles are observed to travel in opposite directions with speed 2.8×10^8 m/sec. Deduce the velocity of one particle relative to each other?
15. An observer in a laboratory 'sees' two particles coming towards him from opposite directions at speeds of $0.8c$ and $0.9c$ respectively. What is the relative speed of the two particles as measured by an observer moving with either one. [Ans. $0.98c$]
16. An experimenter observes a radio-active atom moving with a velocity of $c/4$. The atom emits a beta particle which has a velocity of $0.9c$ relative to the atom in the direction of its motion. What is the velocity of the beta particle as observed by the experimenter. [Ans. $0.9c$]

[Variation of Mass with Velocity : Mass-energy Equivalence]

17. A relativistic particle whose rest mass is m_0 , is moving with a velocity of $0.9c$. Determine its kinetic energy. [Ans. $T = (m - m_0)c^2 = (2.3m_0 - m_0)c^2 = 1.3m_0c^2$]
18. Calculate the speed of a particle of rest mass 3.33×10^{-27} g whose energy is estimated to be 2 MeV.
19. A particle moves at a speed such that its kinetic energy is equal to its rest mass energy. What is the speed of the particle?
20. Calculate the mass and speed of (i) 1 GeV (=1000 MeV) proton (ii) 2 MeV electron. Calculate the momentum of a photon of energy 1×10^{-12} erg.
21. An x-rays beam has a wavelength of $1\text{\AA}$. Calculate (i) the energy of x-ray photon (ii) the momentum of photon (iii) mass of photon (iv) rest mass of photon.
22. A γ -ray photon of wavelength $0.0045\text{\AA}$ materializes into an electron-positron pair in the neighbourhood of a heavy nucleus. What is the kinetic energy of the pair in MeV. [Ans. 1.73 MeV]
23. Calculate the binding energy in MeV for deuteron. $m_n = 1.008962$ amu, $m_p = 1.008142$ amu, $m_d = 2.01470$ amu.
24. The rest mass of hydrogen atom is 1.00727 amu and that of proton and electron are $m_p = 1.00727$ amu and $m_e = 0.005486$ amu. Calculate the binding energy of the hydrogen atom.
25. A 0.50 MeV electron enters normally a region of magnetic field of 5×10^{-3} Weber/m². Calculate the radius of the trajectory classically and relativistically. [Ans. 47.8 cm, 58.2 cm]
26. Deuterium is the isotope of hydrogen consisting of deuteron nucleus (containing a proton and a neutron) and an electron revolving around it in an orbit. The ionization potential of deuterium is 13.6 eV and the energy required to separate the neutron and proton is 2.23 MeV. Determine the mass of the deuterium atom if the masses of neutron, proton and electron are 1.6748×10^{-27} kg, 1.6728×10^{-27} kg and 9.1×10^{-31} kg respectively.
27. Calculate the threshold wavelength for pair production.

Hint: $\frac{ch}{\lambda} = 2m_0c^2$.

UNIT

II

QUANTUM MECHANICS

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ORIGIN OF QUANTUM CONCEPTS

1.1 INTRODUCTION

The observation of the phenomena of interference, diffraction and polarization led to the developments of the wave theory of light. The negation of the concept of ether through the development of special theory of relativity raised serious questions regarding the nature of light waves. A large number of experimental evidences conclusively demonstrated that light was an electromagnetic phenomenon. The understanding of the emission and absorption of radiation by matter posed some difficulties. However this difficulty was partially resolved by making some ad-hoc assumptions regarding the structure of matter. It was assumed that atoms and molecules, which constitute matter, consist of electron oscillators, begin to oscillate under the influence of some external source of excitation. Since the oscillating electron is an accelerated charged particle, it radiates electromagnetic radiation. Therefore, when electromagnetic wave is incident on such an atomic oscillator, electrons are set into forced oscillations, which in turn emit electromagnetic waves of frequency equal to that of the incident wave. To explain the phenomenon of absorption it was assumed that some kind of dissipative force of viscous type, whose exact origin was not known at that time, act on atomic oscillator. The transformation of incident electromagnetic energy into other form on account of dissipative forces causes loss of energy. At the end of 19th century, like classical mechanics, the electromagnetic theory of radiation was regarded as the ultimate theory of radiation. At this time when the classical physics was at the zenith of its accomplishments, some physicists were facing problems that could not be understood within the framework of classical physics. The most outstanding problems among them were (i) the explanation of line spectrum emitted by elements in gaseous state (ii) the emission of electrons when metals are exposed to high frequency radiation—the photoelectric effect, (iii) the distribution of energy in the spectrum of a black body. Probably, the understanding of these phenomena indicated a different aspect of the nature of radiation. In other words, the understanding of phenomena associated with interaction of radiation with matter requires a fundamental change in our concepts regarding the nature of radiation and the structure of matter. In this chapter we shall restrict ourselves to the study of those phenomena, which have direct bearing to the nature of light. We shall see that the explanation of these phenomena requires that the radiation should be regarded as a stream of particles rather than waves. The theory, which regards radiation as stream of particles (called quanta) is called *quantum theory of radiation*.

Historically the quantum theory originated in an attempt to explain the spectral distribution of thermal energy radiated by a black body. We shall, therefore, begin our study with a brief description of characteristic features of the distribution of thermal energy in black body radiation.

1.2 BLACK BODY RADIATION

The thermal radiation emitted by a hot body, in general, depends on the composition and the temperature of the body. However, there is a class of bodies, called *black bodies*, which emit thermal radiation whose quantity and quality depend only on their temperature. For this reason the radiation emitted by such bodies is called the thermal radiation. Such bodies are named black bodies because they absorb all the radiation that falls on it. Lamp black and platinum black are nearest to ideal black bodies. When a black body is maintained at constant high temperature, the emitted radiation is called the black body radiation. For experimental purposes a cavity having a small hole can be regarded as a perfect black body because of its identical behavior with that of the perfectly black body. If radiation is allowed to enter such a cavity, it is reflected back and forth at the inner walls of the cavity and at each reflection some portion of energy is absorbed. After suffering a large number of reflections at the walls it is completely absorbed in the cavity. Therefore at lower temperature the hole appears black. When the cavity is maintained at higher temperature the radiation that comes out of the hole is similar to that emitted by a black body at the same temperature. Thus, a cavity with a small hole acts like a black body.

Radiant Emittance

The power emitted by unit area of a black body in all directions (within the limit of a solid angle 2π) is called *radiant emittance* and is denoted by R . The emitted radiation consists of waves having different frequencies (wavelengths). The power emitted by unit area of a black body within the frequency interval $d\omega$ (wavelength interval $d\lambda$) is called the *spectral radiant emittance* E_ω or E_λ and is defined such that

$$R = \int_0^\infty E_\omega d\omega = \int_0^\infty E_\lambda d\lambda \quad \dots(1.2.1)$$

The *spectral emittance* $E(\omega, T)$ or $E(\lambda, T)$ is function of frequency (wavelength) and temperature and describes the spectral composition of the thermal radiation.

The black body radiation is characterized by spectral energy density $u(\omega, T)$ or $u(\lambda, T)$ which is defined such that the total energy density $u(T)$ at a temperature T for all frequencies (wavelengths) is given by

$$u(T) = \int_0^\infty u(\omega, T) d\omega = \int_0^\infty u(\lambda, T) d\lambda \quad \dots(1.2.2)$$

It can be shown that the radiant emittance of a black body is related to energy density u as

$$R = (1/4) c u(\omega, T)$$

This relation holds for all frequencies. Hence

$$R = \frac{c}{4} \int_0^\infty u(\omega, T) d\omega = \frac{c}{4} \int_0^\infty u(\lambda, T) d\lambda \quad (1.2.3)$$

1.3 SPECTRAL DISTRIBUTION OF ENERGY IN THERMAL RADIATION

The experimental study of thermal radiation emitted from a black body was initiated by an excellent group of German spectroscopists Lummer, Pringsheim, Rubens and Karlbaum. The spectral energy density u_λ or u_ω was measured at different temperatures with special spectrograph. The energy density was plotted against the wavelength at different temperatures. The results obtained may be summarized as follows:

1. At a particular temperature the spectral energy density increases with wavelength and attains a maximum value and then falls to zero for longer wavelengths.
2. As the temperature is increased, the wavelength $\lambda_{\max}$ corresponding to maximum energy density shifts towards the shorter wavelength region. It was experimentally found by Wein that

$$\lambda_{\max} T = b = 2.898 \times 10^{-3} \text{ m-K}$$

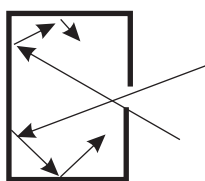
This relation is known as Wein's displacement law.

3. As the temperature is increased the total energy density u for all wavelengths increases. It was found that the total energy density, which is equal to the area under the curve is proportional to the fourth power of the temperature *i.e.*,

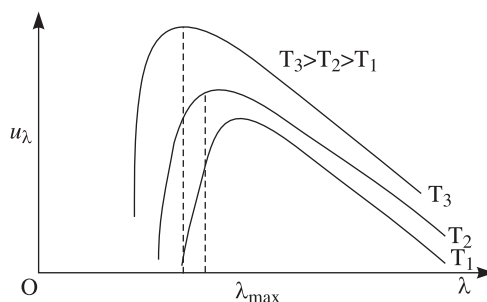
$$R = \frac{c}{4} u = \frac{c}{4} \int_0^\infty u_\lambda d\lambda = \sigma T^4, \quad \sigma = \text{constant}$$

which is the Stefan's law.

In order to explain the dependence of spectral energy density on wavelength and temperature it was realized that certain assumptions regarding the structure of black body on atomic level and its interaction with radiation were necessary.



A cavity with a small hole in it acts like a black body



Distribution of energy among wavelengths

Fig. 1.3.1 Black body

Fig. 1.3.2 Spectral distribution of energy

1.4 CLASSICAL THEORIES OF BLACK BODY RADIATION

Wein's Law : Wein, in 1893, from thermodynamic reasoning alone showed that energy density in black body radiation is given by

$$u(\lambda, T) d\lambda = \frac{c_1}{\lambda^5} e^{-c_2/\lambda T} d\lambda \quad \dots(1.4.1)$$

where c_1 and c_2 are empirical constants. By proper choice of these constants Wein's law can be made to fit the experimental curve in the shorter wavelength region alone but fails in the longer wavelength region.

Rayleigh and Jeans Law

The British physicists Lord Rayleigh (1842–1919) and James Jeans (1877–1946) made an attempt to derive a better radiation law on the basis of the following assumptions.

1. The radiation in a cavity is electromagnetic in nature. In a metallic cavity whose walls are perfectly reflecting, the superposition of incident and reflected waves of each frequency results in the formation of standing waves with nodes at the walls. The number of standing waves (or modes) per unit volume in the frequency range ω and $\omega + d\omega$ is given by

$$N(\omega) d\omega = \frac{\omega^2}{\pi^2 c^3} d\omega \quad \dots(1.4.2)$$

Making use of the relations $\omega = \frac{2\pi c}{\lambda}$ and $|d\omega| = \frac{2\pi c}{\lambda^2} d\lambda$, Eqn.(1.4.2) can be written in terms of wavelength as

$$N(\lambda) d\lambda = \frac{8\pi}{\lambda^4} d\lambda \quad \dots(1.4.3)$$

Notice that the number of modes is proportional to the square of the frequency of the radiation.

2. The theorem of equipartition of energy is also valid for electromagnetic waves. According to this theorem the average contribution of each degree of freedom to the total energy of a system is $\frac{1}{2} kT$ where k is Boltzmann constant and T is the temperature of the system. A standing wave is a system of two degrees of freedom, one corresponding to the electric field and the other to the magnetic field. Hence the average energy of each standing wave (or mode) is kT .

The energy density of radiation in the frequency range ω and $\omega + d\omega$ in a cavity maintained at temperature T is

$$u(\omega, T) d\omega = \frac{\omega^2}{\pi^2 c^3} kT d\omega \quad \dots(1.4.4)$$

In terms of wavelength this relation is expressed as

$$u(\lambda, T) d\lambda = \frac{8\pi}{\lambda^4} kT d\lambda \quad \dots(1.4.5)$$

Eqns. (1.4.4) and (1.4.5) represent the Rayleigh-Jeans formula for black body radiation. A glance at the Rayleigh-Jeans formula, which is a rigorous consequence of classical physics, reveals that it fails to explain the experimental results in the higher frequency (lower wavelength) region. Instead of finite energy density, it predicts infinite energy density at extremely short wavelengths ultraviolet, X-rays and gamma rays. This discrepancy between the theory and the experiment was dramatically called *ultraviolet catastrophe*.

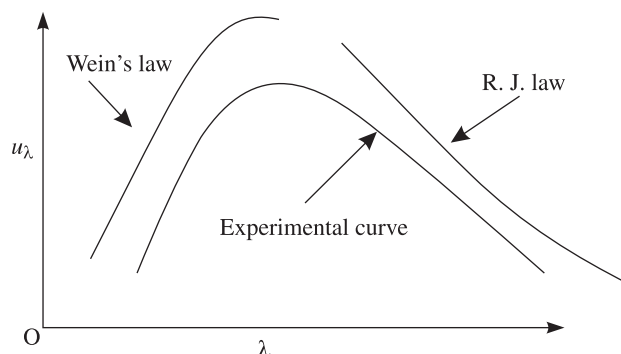


Fig. 1.4.1 Comparison of theoretical radiation laws with experimental curve

The failure of Rayleigh-Jeans law was taken more seriously because it was the only possible law that could be derived on the basis of the then known laws of classical physics. The failure of Rayleigh-Jeans law means the failure of the basic assumptions derived from the well-established laws of classical physics. This situation compelled the German physicist Max Planck to look beyond the framework of classical physics. He proposed a revolutionary hypothesis, according to which the emission and absorption of electromagnetic energy takes place in the form of *packets (bundles)*, called *quanta*. This concept of quantisation of energy is foreign to the classical physics.

Max Planck (1858–1947)

Max Planck was born in Germany and studied at Munich and *Berlin* and obtained his doctoral degree in 1879. After holding position at the university of Kiel he was appointed professor of theoretical physics at Berlin university in 1899 where he became acquainted with the experimental work on black body radiation carried out by Lummer, Pringsheim, Rubens and Karlbaum and devoted himself to the task of deriving a correct radiation formula. Before deriving the radiation law he first guessed the correct form of the law and announced it at the meeting of German Physical Society on October 14, 1900. The formula was checked by Rubens, Lummer and Pringsheim and was found to be in good agreement with the experimental results. After about eight weeks of strenuous labor Planck was able to derive the radiation law theoretically and presented his findings to the German Physical Society on December 14, 1900. The scientific world was not ready to accept Planck's discovery that destroyed one of the most fundamental principle of classical physics—the continuous emission, absorption and distribution of energy. Planck's theory was strongly recognized only after Einstein successfully explained the phenomenon of photoelectric effect in 1905. Planck was awarded Nobel Prize for his discovery in 1919.

1.5 PLANCK'S RADIATION LAW

The failure of Rayleigh-Jeans law led Planck to think that it was not possible to obtain a correct radiation law within the framework of classical physics. Planck assumed that the walls of the cavity consist of microscopic oscillators. In thermal equilibrium the absorption and emission of radiation by these oscillators take place at equal rate. According to Planck's hypothesis the emission and absorption of radiation by an oscillator take place in the form of discrete packets of energy called photons, whose energy is proportional to the frequency of radiation. The energy ε of a photon of frequency ω is

$$\varepsilon = \hbar\omega$$

where $\hbar = h/2\pi$, $h = 6.625 \times 10^{-34}$ Js, is now known as Planck's constant. Since an oscillator can absorb whole number of photons, the allowed values of energy of oscillator are

$$0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots, n\varepsilon$$

$$0, \hbar\omega, 2\hbar\omega, 3\hbar\omega, \dots, n\hbar\omega$$

Let $N_0, N_1, N_2, N_3, \dots, N_n, \dots$, be the number of oscillators with energy $0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots, n\varepsilon, \dots$. Obviously, the total number of oscillators N and the total energy E of the system are given by

$$N = N_0 + N_1 + N_2 + N_3 + \dots + N_n + \dots = \sum_{n=0}^{\infty} N_n$$

$$E = 0 N_0 + \varepsilon N_1 + 2\varepsilon N_2 + 3\varepsilon N_3 + \dots + n\varepsilon N_n + \dots = \sum_{n=0}^{\infty} n\varepsilon N_n$$

The number of modes of standing waves in the cavity is equal to the number of oscillators in the walls and the average energy per mode of a standing wave is equal to the average energy of an oscillator. According to Maxwell-Boltzmann statistics the number of oscillators with energy ε is proportional to factor $\exp(-\varepsilon/kT)$. Therefore the number of oscillators with energy $n\varepsilon$ is given by

$$N_n = C e^{-n\varepsilon/kT}$$

where C is a constant.

The average energy of oscillator is given by

$$\begin{aligned} \langle \varepsilon \rangle &= \frac{E}{N} = \frac{\sum_n n\varepsilon N_n}{\sum_n N_n} = \frac{\sum_n n\varepsilon e^{-n\varepsilon/kT}}{\sum_n e^{-n\varepsilon/kT}} = \frac{\sum_n n\hbar\omega e^{-n\hbar\omega/kT}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/kT}} \\ &= \hbar\omega \frac{\sum_{n=0}^{\infty} n e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}}, \quad \text{where } x = \frac{\hbar\omega}{kT} \end{aligned}$$

$$\begin{aligned}
&= -\hbar\omega \frac{d}{dx} \left(\ln \sum_{n=0}^{\infty} e^{-nx} \right) \\
&= -\hbar\omega \frac{d}{dx} \left[\ln \left(1 + e^{-x} + e^{-2x} + \dots \dots \infty \right) \right] \\
&= -\hbar\omega \frac{d}{dx} \left(\ln \frac{1}{1 - e^{-x}} \right) \\
&= \hbar\omega \frac{d}{dx} \ln (1 - e^{-x}) \\
&= \hbar\omega \left(\frac{e^{-x}}{1 - e^{-x}} \right) \\
&= \hbar\omega \left(\frac{1}{e^x - 1} \right) \\
&= \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \quad \dots(1.5.1)
\end{aligned}$$

The number of oscillators in the frequency range ω and $\omega + d\omega$ is

$$N(\omega)d\omega = \frac{\omega^2}{\pi^2 c^3} d\omega \quad \dots(1.5.2)$$

The energy density $u(\omega, T)$ in the frequency range ω and $\omega + d\omega$ is

$$u(\omega, T)d\omega = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} d\omega \quad \dots(1.5.3)$$

This relation can be written in terms of wavelength as

$$u(\lambda, T) = \frac{16\pi^2 \hbar c}{\lambda^5} \frac{1}{e^{2\pi\hbar c/\lambda kT} - 1} d\lambda \quad \dots(1.5.4)$$

Equations (1.5.3) and (1.5.4) are called Planck's radiation laws. It agrees well with the experimental observations for all wavelengths and at all temperatures.

In the limit $\hbar \rightarrow 0$, the average value of energy of oscillator becomes kT , which is the classical result.

$$\langle \epsilon \rangle = \lim_{\hbar \rightarrow 0} \left(\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right)$$

$$\begin{aligned}
&= \lim_{\hbar \rightarrow 0} \frac{\hbar\omega}{\left(1 + \frac{\hbar\omega}{kT} + \frac{1}{2}\left(\frac{\hbar\omega}{kT}\right)^2 + \dots\right) - 1} \\
&= \lim_{\hbar \rightarrow 0} \frac{\hbar\omega}{\hbar\omega/kT} \\
&= kT
\end{aligned}$$

Thus, the finite value of Planck's constant saves the Planck's formula from its failure and its smallness forbids the discontinuity or discreteness in energy to be observed in our everyday experience.

Limiting cases of planck's radiation law: In the lower frequency (higher wavelength) range the Planck's radiation law reduces to Rayleigh-Jeans law. In the limit $\hbar\omega/kT \ll 1$.

$$\begin{aligned}
u(\omega)d\omega &= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{1 + \frac{\hbar\omega}{kT} + \dots - 1} d\omega \\
&= \frac{\omega^2}{\pi^2 c^3} kT d\omega
\end{aligned}$$

which is the Rayleigh-Jeans law.

In the limit of high frequencies (low wavelengths) $\hbar\omega/kT \gg 1$.

$$\begin{aligned}
u(\omega)d\omega &= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT}} d\omega = c_1 \omega^3 e^{-c_2/\lambda T} d\omega \\
&= \frac{c_1}{\lambda^5} [\exp(-c_2/\lambda T)] d\lambda
\end{aligned}$$

which is the Wien's law.

1.6 DEDUCTION OF STEFAN'S LAW FROM PLANCK'S LAW

The radiant emittance (energy emitted per unit area per unit time for all wavelengths) of a black body is given by

$$\begin{aligned}
R &= \frac{cu}{4} \\
R &= \frac{c}{4} \int_0^\infty u(\omega, T) d\omega
\end{aligned}$$

$$\begin{aligned}
&= \int_0^\infty \frac{\hbar \omega^3}{4\pi^2 c^2} \frac{d\omega}{e^{\hbar\omega/kT} - 1} \\
&= \frac{\hbar}{4\pi^2 c^2} \left(\frac{kT}{\hbar} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx, \quad \text{where } x = \frac{\hbar\omega}{kT} \\
&= \frac{\hbar}{4\pi^2 c^2} \left(\frac{kT}{\hbar} \right)^4 \left(\frac{\pi^4}{15} \right) \\
&= \left(\frac{\pi^2 k^4}{60 c^2 \hbar^3} \right) T^4 \\
&= \sigma T^4
\end{aligned}$$

where the constant σ has the value

$$\sigma = \frac{\pi^2 k^4}{60 c^2 \hbar^3} = 5.57 \times 10^{-8} \frac{\text{watt}}{\text{m}^2 \text{K}^4}.$$

1.7 DEDUCTION OF WIEN'S DISPLACEMENT LAW

The wavelength λ_{max} corresponding to the maximum energy density is the solution of the equation

$$\frac{d}{d\lambda} u(\lambda, T) = 0$$

$$\frac{d}{d\lambda} \left[\frac{16\pi^2 \hbar c}{\lambda^5} \frac{1}{e^{2\pi\hbar c/\lambda kT} - 1} \right]_{\lambda=\lambda_{\text{max}}} = 0$$

$$\frac{d}{d\lambda} \left[\frac{x^5}{e^x - 1} \right] = 0, \quad \text{where } x = \frac{2\pi\hbar c}{\lambda kT}$$

$$\frac{d}{dx} \left[\frac{x^5}{e^x - 1} \right] \frac{dx}{d\lambda} = 0$$

$$\left(\frac{5x^4(e^x - 1) - x^5 e^x}{(e^x - 1)^2} \right) x^2 = 0$$

$$5(e^x - 1) - xe^x = 0$$

$$1 - e^{-x} = \frac{x}{5} \quad \dots(1.7.1)$$

The solution of this equation is the point of intersection of curves

$$y = 1 - e^{-x} \quad \text{and} \quad y = \frac{x}{5}.$$

At the point of intersection $x = 4.96$ i.e.,

$$\left(\frac{2\pi\hbar c}{\lambda kT} \right)_{\lambda_{\max}} = 4.96$$

$$\lambda_{\max} T = \frac{2\pi\hbar c}{4.96k} = b \quad \dots(1.7.2)$$

where b is a constant called Wien's constant and has value

$$b = 2.898 \times 10^{-3} \text{ m-K.}$$

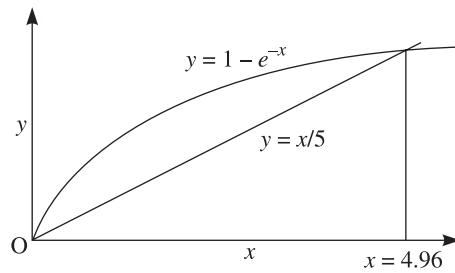


Fig. 1.7.1 Graphical solution of $y = 1 - e^{-x}$ and $y = x/5$

SOLVED EXAMPLES

Ex. 1.(a) Calculate the average energy of Planck's oscillator for $(\hbar\omega/kT) = 0.01, 0.1, 1.0, 10$.

(b) Using Planck's radiation law, find the power radiated by a unit area of a black body within a narrow wavelength interval $\Delta\lambda = 1.0 \text{ nm}$ close to the maximum of spectral radiation density at a temperature $T = 3000^\circ \text{ K}$.

Sol. (a) The average energy of Planck's oscillator is

$$\langle \epsilon \rangle = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} = \frac{(\hbar\omega/kT)}{e^{\hbar\omega/kT} - 1} kT$$

Putting the values of $(\hbar\omega/kT)$ given in the problem we find

$$\langle \epsilon \rangle = kT, 0.95 kT, 0.58 kT, 0.00045 kT.$$

(b) Making use of Wien's law $\lambda T = b$ we can write the formula for the spectral energy density as

$$u(T) = \frac{16\pi^2 \hbar c T^5}{b^5} \frac{1}{e^{2\pi \hbar c / b\lambda} - 1}$$

The power radiated per unit area in the wavelength interval $\Delta\lambda$ is

$$P = \frac{cu}{4} = \frac{4\pi^2 \hbar c^2 T^5}{b^5} \frac{1}{e^{2\pi \hbar c / b\lambda} - 1} \Delta\lambda$$

Substituting the given values, we get

$$P = 3100 \text{ W/m}^2.$$

Ex. 2. Calculate the number of modes in a cube of side 2 cm in the wavelength range 4995 Å and 5005 Å. What is the total radiant energy in the cavity in this wavelength interval? The cavity is maintained at a temperature of 1500 K.

Sol. Number of modes

$$\begin{aligned} dN &= \frac{8\pi}{\lambda^4} V d\lambda = \frac{8 \times 3.14 \times (2 \times 10^{-2} \text{ m})^3 (10 \times 10^{-10} \text{ m})}{(5000 \times 10^{-10} \text{ m})^4} \\ &= 3.215 \times 10^{11}. \end{aligned}$$

Energy density is given by

$$\begin{aligned} U(\lambda, T) &= dN kT d\lambda \\ &= (3.215 \times 10^{11})(1.38 \times 10^{-23} \text{ JK}^{-1})(1500 \text{ K}) \\ &= 6.65 \times 10^{-9} \text{ J}. \end{aligned}$$

Ex. 3. A spring mass system has a mass equal to 0.10 kg and a spring constant equal to 10 N/m. The system oscillates with amplitude of 0.10 m.

- If the energy of the oscillator is quantized what is the quantum number n associated with this energy?
- If the quantum number n changes by unity, what is the fractional change in energy?
- What conclusion do you draw from this example?

Sol. (a) Frequency of the oscillator is

$$\omega = \sqrt{k/m} = 10 \text{ rad/s}.$$

Energy of oscillator

$$E = (1/2)kA^2 = 0.05 \text{ J}.$$

The quantum number n associated with this energy is given by

$$E = n\hbar\omega$$

where

$$n = E/(\hbar\omega) = 10^{31} \text{ a very large number}.$$

(b) If n changes by unity, the fractional change in energy is given by

$$\frac{\Delta E}{E} = \frac{\Delta n \hbar \omega}{n \hbar \omega} = \frac{\Delta n}{n} = \frac{1}{n} = 10^{-31} \text{ a very small number}.$$

(c) This example illustrates that the energy levels of macroscopic oscillators are so close together that even most delicate instruments cannot reveal the quantized nature of energy levels. All this is due to smallness of Planck's constant $\hbar$. In the limit $\hbar \rightarrow 0$, the energy levels become continuous.

1.8 PHOTOELECTRIC EFFECT

The emission of electrons by a substance under the action of light is called the *photoelectric effect*. This phenomenon was discovered in 1887 by the German physicist Heinrich Hertz. It is an irony of fate that Hertz, who demonstrated the existence of electromagnetic waves, discovered photoelectric effect that could not be understood in terms of the wave model of light.

The phenomenon of photoelectric effect can be studied with the help of an apparatus schematically shown in the Fig. (1.8.1). Within an evacuated glass jacket two electrodes A and B are enclosed and the light radiation is allowed to enter the jacket through a quartz window. The radiation falls on the electrode A, called cathode. The electrode B can be kept at positive or negative potential with respect to the cathode. A sensitive ammeter is put in the circuit to record the current resulting from the photoelectrons. The potential difference between the cathode and the anode can be measured by voltmeter. The experimental observations of photoelectric effect may be summarized as follows:

1. For a constant potential difference between the cathode and anode, the number of electrons emitted from cathode (and hence the photoelectric current) increases with increasing intensity of radiation.
2. For a constant intensity and frequency of incident radiation the photoelectric current varies with the potential difference V between the cathode and anode and reaches a constant value beyond which further increase of potential difference does not effect the photoelectric current, on the other hand, if the plate B is made more and more negative with respect of the photocathode surface the current decreases. This negative potential (with respect to cathode) of the plate is called *retarding potential*. For a particular value of retarding potential, the photoelectric current becomes zero. This potential is called *cut-off or stopping potential* V_0 and is measure of maximum kinetic energy of photoelectrons and we can write

$$T_{\max} = eV_0$$

where $T_{\max}$ is the maximum kinetic energy of the ejected electron.

3. The stopping potential V_0 and hence the maximum kinetic energy $T_{\max}$ of photoelectrons is independent of the intensity of incident radiation and depends only on the frequency ω of radiation.
4. For each substance there exists a characteristic frequency ω_0 such that for radiation with frequency below ω_0 the photoelectrons are not ejected from the surface. This frequency is called the *threshold frequency* and the corresponding wavelength is called *threshold wavelength*, λ_0 .
5. It has been observed that as soon as the light is incident on the substance, the electrons are emitted *i.e.*, there is no time lag between the incidence of radiation and the ejection of electron.

Failure of classical physics: The phenomenon of photoelectric effect cannot be understood in terms of wave model of radiation. According to classical theory, light consists of oscillating electric and magnetic fields; the intensity of radiation is proportional to the square of the electric vector E . The force on electron exerted by incident radiation is eE and hence the kinetic energy of ejected electron should depend on the intensity of the radiation but the experimental results are contrary to the prediction.

Further the existence of threshold frequency has no explanation at all in the classical theory. Also according to classical theory there should be considerable time lag between the arrival of the radiation and the ejection of electron, which is contrary to the observation. Therefore, any attempt to explain the photoelectric effect within the framework of classical physics is an impossible task.

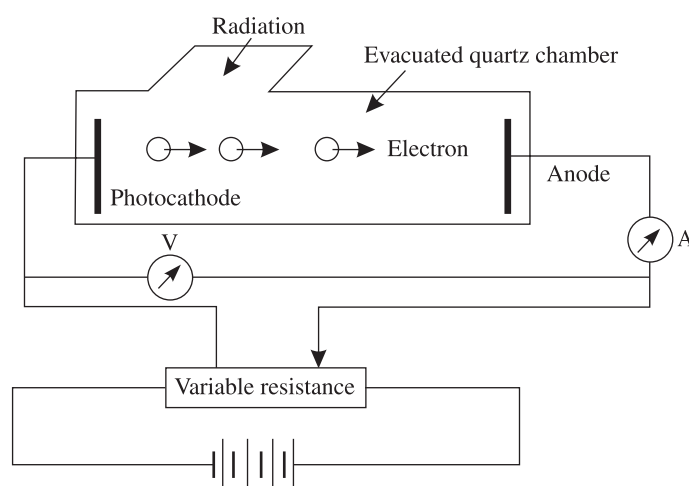


Fig. 1.8.1 Schematic arrangement of the apparatus used for the study of photoelectric effect

Einstein's explanation of photoelectric effect: A satisfactory explanation of photoelectric effect was first proposed by Albert Einstein in 1905. According to Einstein, electromagnetic radiation of frequency ω consists of small packets, called photons, each of energy $\hbar\omega$. When a photon of energy $\hbar\omega$ ($= 2\pi\hbar c/\lambda$) is incident on the surface of a material, some of its energy is spent in making the electron free and the rest appears as kinetic energy of the electron. The electrons at the surface of the material are most loosely bound and require minimum energy for their liberation. This energy is called the *work function* ϕ of the material. The maximum kinetic energy of photoelectrons, ejected from the surface, is given by

$$T_{\max} = \hbar\omega - \phi = (2\pi\hbar c/\lambda) - \phi \quad \dots(1.8.1)$$

The electrons, which are more tightly bound, are ejected with less kinetic energies. Thus the kinetic energy of ejected electron depends on the fact whether it is on the surface of the material or it is deeper inside the material. If ω_0 is the frequency of the incident radiation such that the photon energy $\hbar\omega_0$ is just sufficient to make the electron free from the material the ejected electron has zero kinetic energy. This happens when

$$\hbar\omega_0 = \phi \quad \text{or} \quad 2\pi\hbar c/\lambda_0 = \phi$$

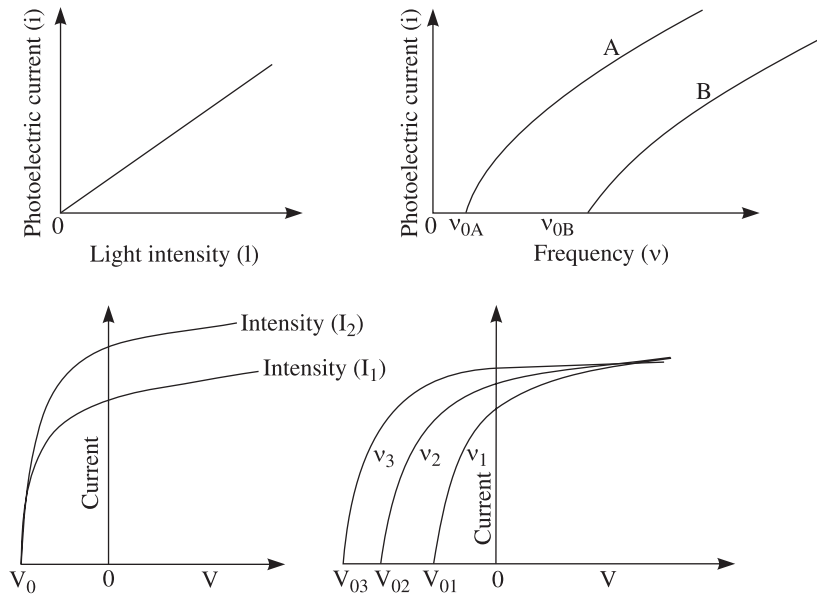


Fig. 1.8.2 Variation of photoelectric current with intensity, frequency and accelerating potential

The frequency ω_0 is the *threshold or cut-off frequency* and the corresponding wavelength λ_0 is called *threshold wavelength*. Thus the threshold frequency ω_0 (wavelength λ_0) is a measure of the work function of the material. In terms of photon frequency ω and threshold frequency ω_0 , Einstein's photoelectric equation can be written as

$$\begin{aligned} T_{\max} &= \hbar\omega - \hbar\omega_0 \\ &= 2\pi\hbar c \left[(1/\lambda) - (1/\lambda_0) \right] \end{aligned} \quad \dots(1.8.2)$$

If V_0 is the stopping potential corresponding to incident radiation of wavelength λ then

$$T_{\max} = eV_0 = 2\pi\hbar c \left[(1/\lambda) - (1/\lambda_0) \right] \quad \dots(1.8.3)$$

The frequency (wavelength) dependence of maximum kinetic energy of photoelectrons is evident from above equation. By increasing the *intensity* of the incident radiation, we merely increase the number of photons and not the energy of the photons. The increase in intensity increases the probability of photon electron collision and hence the number of ejected photoelectrons; this explains the dependence of photoelectric current on the intensity of incident radiation. Since the energy of photon is concentrated in a small region and photon is moving at very high speed (c), the energy of photon is instantaneously transferred to electron and consequently there is no appreciable time lag between the incidence of light and the emission of electron.

Millikan's verification of Einstein equation: The linear relation between the frequency ω of incident radiation and the maximum kinetic energy $T_{\max}$ or eV_0 of ejected electron was verified by R. A. Millikan. Using different materials as target, he illuminated them with light of different frequencies (wavelengths) and measured the corresponding stopping potentials. In accordance with the expectations, a graph between ω and eV_0 was found to be a straight line. The slope of the line gives the value of Planck's constant $\hbar$ and the intercept on energy axis gives the work function of the target material.

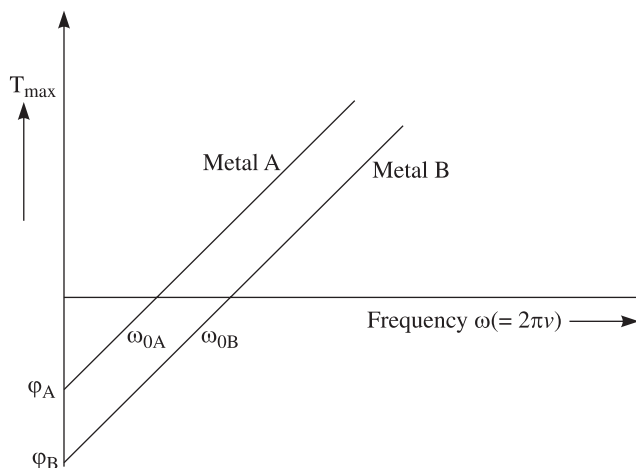


Fig. 1.8.3 Variation of kinetic energy of photoelectrons with frequency of incident radiation

SOLVED EXAMPLES

Ex. 4. Show that $ch = 2\pi\hbar c = 12400 \text{ eV } \text{\AA} = 1240 \text{ eV nm}$

$$\begin{aligned} \text{Sol. } ch = 2\pi\hbar c &= \frac{(6.625 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s})}{1.6 \times 10^{-19} \text{ J/eV}} \\ &= 12421 \times 10^{-10} \text{ eV m} \\ &= 12400 \text{ eV } \text{\AA} = 1240 \text{ eV nm.} \end{aligned}$$

Ex. 5. Light of wavelength $2000 \text{ \AA}$ falls on aluminium surface, which has work function of 4.2 eV . Calculate

- maximum kinetic energy of photoelectrons.
- minimum kinetic energy of photoelectrons.
- cut-off wavelength.
- stopping potential.

Sol. (a) Maximum kinetic energy of photoelectrons

$$\begin{aligned} T_{\max} &= \hbar\omega - \phi = (2\pi\hbar c/\lambda) - \phi \\ &= \frac{12400 \text{ eV } \text{\AA}}{2000 \text{ \AA}} - 4.2 \text{ eV} = 2.0 \text{ eV} \end{aligned}$$

(b) $T_{\min} = 0$

(c) Threshold wavelength

$$\lambda_0 = \frac{2\pi\hbar c}{\phi} = \frac{12400 \text{ eV } \text{\AA}}{4.2 \text{ eV}} = 5950 \text{ \AA}$$

(d) Stopping potential = 2 volt.

Ex. 6. In a photoelectric effect, it was observed that for light of wavelength $4000 \text{ \AA}$, a stopping potential of 2.0 volt is needed and for light of wavelength $6000 \text{ \AA}$, a stopping potential of 1.0 volt . From these data, calculate the work function of the material and the Planck's constant.

Sol. Let $\lambda_1 = 4000 \text{ \AA}$, $V_1 = 2.0 \text{ volt}$
 $\lambda_2 = 6000 \text{ \AA}$, $V_2 = 1.0 \text{ volt}$

Einstein's photoelectric equations for the two observations are

$$eV_1 = \frac{2\pi\hbar c}{\lambda_1} - \phi \quad \dots(1)$$

$$eV_2 = \frac{2\pi\hbar c}{\lambda_2} - \phi \quad \dots(2)$$

From these two equations we have

$$e(V_1 - V_2) = 2\pi\hbar c \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

$$\therefore 2\pi\hbar c = \frac{e(V_1 - V_2)}{c} \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}$$

Substituting the given values in above equation, we get

$$h = 2\pi\hbar = 6.4 \times 10^{-34} \text{ J-s}$$

The work function of the material

$$\phi = \frac{2\pi\hbar c}{\lambda_1} - eV_1 = \frac{12400 \text{ eV \AA}}{4000 \text{ \AA}} - 2.0 \text{ eV} = 1.1 \text{ eV}.$$

Ex. 7. Which of the following materials can be used for designing photocell operable with visible light?

Tantalum ($\phi = 4.2 \text{ eV}$), *Tungsten* ($\phi = 4.5 \text{ eV}$), *Aluminium* ($\phi = 4.2 \text{ eV}$), *Barium* ($\phi = 2.5 \text{ eV}$), *Lithium* (2.3 eV).

Sol. For photoelectric effect to occur $\lambda \leq \lambda_0 = 2\pi\hbar c/\phi$.

$$\text{For tantalum } \lambda_0 = 2\pi\hbar c/\phi = (12400 \text{ eV \AA})/4.2 \text{ eV} = 2952 \text{ \AA}$$

$$\text{Tungsten } \lambda_0 = 2755 \text{ \AA}$$

$$\text{Aluminium } \lambda_0 = 2952 \text{ \AA}$$

$$\text{Barium } \lambda_0 = 4960 \text{ \AA}$$

$$\text{Lithium } \lambda_0 = 5391 \text{ \AA}$$

The wavelength interval of visible light is $4000 \text{ \AA}$ to $8000 \text{ \AA}$. The threshold wavelength for barium and lithium lies in the visible range and hence they can be used in photocell.

1.9 COMPTON'S EFFECT

Planck's theory of blackbody radiation provided an indirect evidence of the quantum nature of radiation, which became more explicit in Einstein's explanation of photoelectric effect. The most clear-cut and conclusive evidence in favour of particle nature of radiation came in 1922 from Compton's discovery. In 1922, the American physicist Arthur Compton, investigating the scattering of X-rays by different substances, observed that the scattered rays, in addition to radiation of the initial wavelength λ , contain also rays of a greater wavelength λ' . This phenomenon is known as *Compton effect*. The difference $\Delta\lambda = \lambda' - \lambda$, called Compton shift, was found to depend only on the angle θ made by the direction of the scattered radiation with that of the initial beam. The value of $\Delta\lambda$ does not depend on the wavelength λ and the nature of the scattering material. Since the scattered radiation contains wavelength other than the incident one, the phenomenon is also called *incoherent scattering*.

According to classical model of radiation, it consists of oscillating electric and magnetic fields. When such a radiation is incident on matter, loosely bound electrons begin to oscillate with frequency equal to that of the incident radiation and in doing so they radiate electromagnetic waves of the same frequency as that of the incident one. Thus the classical picture of radiation predicts the presence of only *unmodified radiation*. The presence of radiation of longer wavelength, called *modified radiation*, in the scattered radiation can never be understood on the basis of wave model of radiation.

Quantum theory of radiation, on the other hand, provides clear-cut understanding of the basic feature of Compton scattering. According to quantum theory, a monochromatic beam of X-ray of frequency ω (wavelength λ) consists of photons each of energy $\hbar\omega$ and momentum $\hbar k$, ($k = 2\pi/\lambda$). The Compton scattering is explained by considering it as a process of elastic collision of X-ray photons with almost free electrons. During the collision, the photon transfers some of its energy to the electron and therefore the scattered photon has less energy (that is, lower frequency or higher wavelength) and the electron recoils in some other direction. Suppose that the energy and momentum of scattered photon are $\hbar\omega'$ and $\hbar k'$. The energy and momentum of electron before collision are m_0c^2 and zero. (The electron is assumed to be at rest.) If the electron possesses momentum p_e after collision then its energy will be $[(p_e c)^2 + (m_0 c^2)^2]^{1/2}$.

Applying the principle of conservation of energy we have

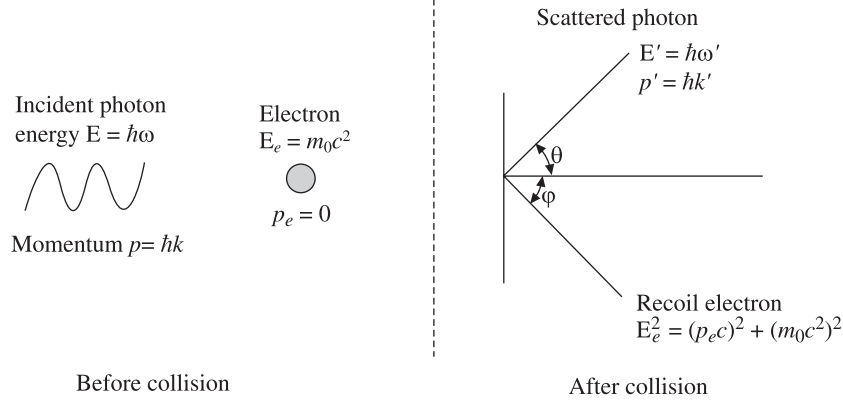
$$\hbar\omega + m_0c^2 = \hbar\omega' + c\sqrt{p_e^2 + m_0^2c^2} \quad \dots(1.9.1)$$

The law of conservation of momentum in vector form is

$$\hbar k = p_e + \hbar k' \quad \dots(1.9.2)$$

The first equation can be arranged as

$$\begin{aligned} p_e^2 + m_0^2c^2 &= \left[\left(\frac{\hbar\omega}{c} - \frac{\hbar\omega'}{c} \right) + m_0c \right]^2 \\ &= [\hbar k - \hbar k' + m_0c]^2 \\ p_e^2 &= \hbar^2(k^2 - 2kk' + k'^2) + 2m_0c\hbar(k - k') \quad \dots(1.9.3) \end{aligned}$$

**Fig. 1.9.1** Compton scattering

The second equation can be written as

$$p_e^2 = \hbar^2 (\vec{k} - \vec{k}')^2 = \hbar^2 (k^2 - 2kk' \cos \theta + k'^2) \quad \dots(1.9.4)$$

From Eqns. (1.9.3) and (1.9.4), we obtain

$$m_0 c (k - k') = \hbar k k' (1 - \cos \theta)$$

$$\frac{k - k'}{kk'} = \frac{\hbar}{m_0 c} (1 - \cos \theta)$$

$$\frac{1}{k'} - \frac{1}{k} = \frac{\hbar}{m_0 c} (1 - \cos \theta)$$

$$\lambda' - \lambda = \frac{2\pi\hbar}{m_0 c} (1 - \cos \theta) = \frac{h}{m_0 c} (1 - \cos \theta)$$

$$\Delta\lambda = \lambda_c (1 - \cos \theta) \quad \dots(1.9.5)$$

where

$$\lambda_c = \frac{h}{m_0 c} = \frac{2\pi\hbar}{m_0 c} = 0.0243 \text{ \AA} \quad \dots(1.9.6)$$

The quantity λ_c is called the Compton wavelength of electron. The Compton wavelength of an electron is the wavelength of radiation whose photon has energy equal to the rest energy of the electron.

Equation (1.9.5) shows that the Compton shift $\Delta\lambda$ is independent of the wavelength of the incident radiation and the nature of the target material. It depends only on the angle of scattering. In the forward direction ($\theta = 0$), the Compton shift is zero. In the direction $\theta = \pi/2$, $\Delta\lambda = (\hbar/m_0 c) = \lambda_c$ and in the backward direction ($\theta = \pi$), Compton shift is maximum equal to $2\lambda_c$.

When photons of the incident radiation collide with tightly bound electrons of the target atom, the energy and momentum are exchanged with the atom as a whole. Since the mass of an atom is much greater than that of an electron, the Compton shift in this case is negligible, and λ' practically coincides with λ . This explains the existence of *unmodified radiation* at all angles of scattering.

Energy of Scattered Photon

The Compton shift is given by

$$\lambda' - \lambda = \frac{2\pi\hbar}{m_0c}(1 - \cos\theta)$$

$$\frac{2\pi\hbar c}{E'} - \frac{2\pi\hbar c}{E} = \frac{2\pi\hbar}{m_0c}(2\sin^2\theta/2)$$

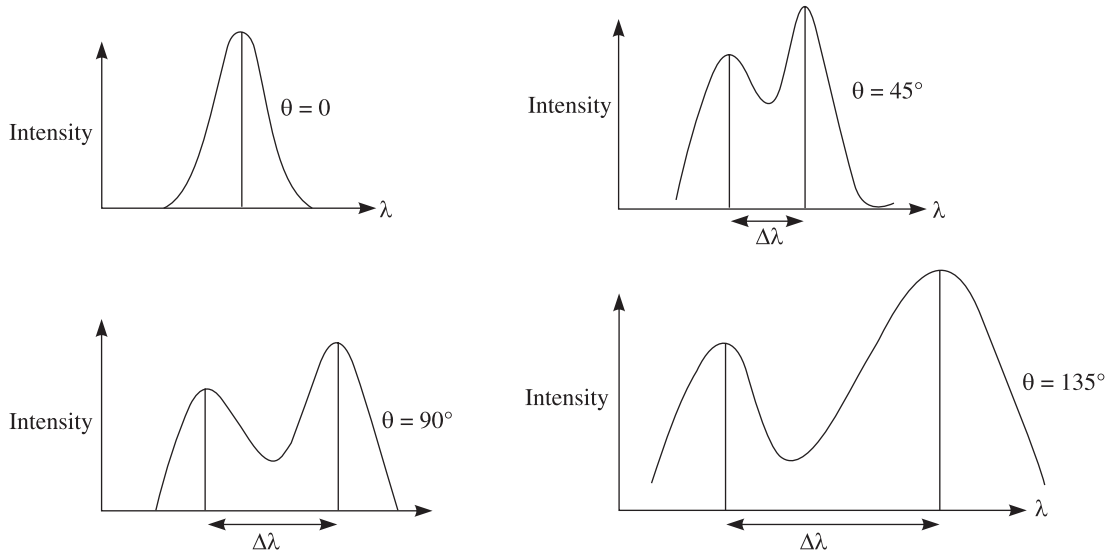


Fig. 1.9.2 Variation of Compton's shift with angle of scattering θ

$$E' = \frac{E}{1 + \left(\frac{2E}{m_0c^2} \right) \sin^2 \frac{\theta}{2}} \quad \dots(1.9.7)$$

The scattered photon will have minimum energy for $\theta = 180^\circ$. Thus

$$E'_{\min} = \frac{E}{1 + \left(\frac{2E}{m_0c^2} \right)} \quad \dots(1.9.8)$$

For

$$\theta = 0, \quad E'_{\max} = E.$$

Kinetic energy of compton electron: The kinetic energy imparted to the recoil electron is given by

$$T = \hbar\omega - \hbar\omega' = \frac{2\pi\hbar c}{\lambda} - \frac{2\pi\hbar c}{\lambda'} = 2\pi\hbar c \left(\frac{\lambda' - \lambda}{\lambda\lambda'} \right) = hc \frac{\Delta\lambda}{\lambda(\lambda + \Delta\lambda)} \quad \dots(1.9.9)$$

In terms of initial energy E of photon, the kinetic energy of electron can be expressed as

$$T = E - E' = E - \frac{E}{1 + \left(\frac{2E}{m_0 c^2} \sin^2 \frac{\theta}{2} \right)}$$

$$T = \frac{\frac{2E^2}{m_0 c^2} \sin^2 \frac{\theta}{2}}{1 + \frac{2E}{m_0 c^2} \sin^2 \frac{\theta}{2}} \quad \dots(1.9.10)$$

The Compton electron acquires maximum kinetic energy when photon is scattered at angle $\theta = 180^\circ$. Hence

$$T_{\max} = \frac{\left(\frac{2E}{m_0 c^2} \right)}{1 + \left(\frac{2E}{m_0 c^2} \right)}, \quad \theta = 180^\circ \quad \dots(1.9.11)$$

$$T_{\min} = 0 \text{ for } \theta = 0.$$

Recoil direction of electron: If the Compton electron moves in the direction making angle ϕ with the direction of incident photon, the law of conservation of x and y components momentum permits us to write

$$p_e \cos \phi + p' \cos \theta = p$$

$$p_e \sin \phi = p' \sin \theta$$

Hence
$$\tan \phi = \frac{p' \sin \theta}{p - p' \cos \theta} = \frac{E' \sin \theta}{E - E' \cos \theta}$$

SOLVED EXAMPLES

Ex. 8. X-rays of wavelength $1.0 \text{ \AA}$ are scattered by a carbon block. The scattered radiations are observed at 60° , 90° and 180° . Find (a) Compton shift (b) kinetic energy imparted to the recoil electron.

Sol. (a) Compton shift $\Delta\lambda = \lambda_c(1 - \cos \theta)$

$$\Delta\lambda_{60} = \lambda_c (1 - \cos 60^\circ) = 0.5\lambda_c = 0.012 \text{ \AA}$$

$$\Delta\lambda_{90} = \lambda_c (1 - \cos 90^\circ) = \lambda_c = 0.024 \text{ \AA}$$

$$\Delta\lambda_{180} = \lambda_c (1 - \cos 180^\circ) = 2\lambda_c = 0.048 \text{ \AA}$$

(b) Kinetic energy imparted to the electron

$$T = E - E' = ch \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right) = \frac{ch}{\lambda} \left(\frac{\Delta\lambda}{\lambda + \Delta\lambda} \right)$$

$$(i) \quad T = \frac{12400 \text{ eV\AA}}{1.00 \text{ \AA}} \left(\frac{0.012 \text{ \AA}}{1.012 \text{ \AA}} \right) = 147 \text{ eV}$$

$$(ii) \quad T = 290 \text{ eV}$$

$$(iii) \quad T = 568 \text{ eV}$$

Ex. 9. For what wavelength of incident photon it shows Compton scattering in which the energy of scattered photon is one-half that of incident photon at a scattering angle of 45° ? In what region of the electromagnetic spectrum does such a photon lie?

Sol. Given that $E = E/2$, therefore $\lambda' = 2\lambda$ and $\Delta\lambda = \lambda$

Now

$$\Delta\lambda = \lambda_c (1 - \cos 45^\circ)$$

$$\lambda = \lambda_c (1 - 1/\sqrt{2}) = 0.0071 \text{ \AA} \text{ (gamma ray)}$$

Ex. 10. A photon with energy 1.00 MeV is scattered by a stationary free electron. Find the kinetic energy of electron if the photon's wavelength changed by $\eta = 25\%$ due to scattering.

Sol. Given that $\Delta\lambda/\lambda = \eta = 0.25$

Kinetic energy of recoil electron

$$T = \frac{ch}{\lambda} \left(\frac{\Delta\lambda}{\lambda + \Delta\lambda} \right) = E \frac{\eta}{1 + \eta} = (1.00 \text{ MeV}) \left(\frac{0.25}{1 + 0.25} \right) = 0.20 \text{ MeV.}$$

Ex. 11. A photon of energy 250 keV is scattered at an angle $\theta = 120^\circ$ by a stationary free electron. Find the energy of the scattered photon.

Sol. Energy of scattered photon

$$E' = \frac{E}{1 + \left(\frac{E}{m_0 c^2} \right) (1 - \cos \theta)}$$

Putting $E = 0.250 \text{ MeV}$, $m_0 c^2 = 0.510 \text{ MeV}$ and $\cos 120^\circ = -0.50$ we get $E' = 0.143 \text{ MeV}$.

Ex. 12. A photon with momentum $p = 1.02 \text{ MeV/c}$ is scattered by a stationary free electron. Its momentum on scattering becomes $p' = 0.255 \text{ MeV/c}$. At what angle is the photon scattered?

Sol. Compton shift $\lambda' - \lambda = \lambda_c (1 - \cos \theta)$

$$\frac{h}{p'} - \frac{h}{p} = \lambda_c \left(2 \sin^2 \frac{\theta}{2} \right)$$

$$\begin{aligned}
\sin^2 \frac{\theta}{2} &= \frac{h}{2\lambda_c} \left(\frac{p - p'}{pp'} \right) \\
&= \frac{1}{2} m_0 c \left(\frac{p - p'}{pp'} \right) \\
&= \frac{1}{2} \left(0.51 \frac{\text{MeV}}{c} \right) \left(\frac{0.765 \text{ MeV}/c}{1.02 \text{ MeV}/c \times 0.255 \text{ MeV}/c} \right) \\
&= 0.7502 \\
\sin \frac{\theta}{2} &= 0.86 = \sin 60 \\
\theta &= 120^\circ.
\end{aligned}$$

Ex. 13. A photon is scattered at an angle $\theta = 120^\circ$ by a stationary free electron. As a result the electron acquires a kinetic energy $T = 0.45 \text{ MeV}$. Find the energy of the incident photon.

Sol. The energy of the scattered photon is given by

$$E' = \frac{m_0 c^2 E}{m_0 c^2 + 2E \sin^2 \theta/2}$$

Kinetic energy of electron

$$T = E - E' = E - \frac{m_0 c^2 E}{m_0 c^2 + 2E \sin^2 \theta/2}$$

$$T = \frac{2E^2 \sin^2 \theta/2}{m_0 c^2 + 2E \sin^2 \theta/2}$$

This is quadratic equation in E. When solved for E, we get

$$E = \frac{T}{2} \left[1 + \sqrt{1 + \frac{2m_0 c^2}{T \sin^2 \theta/2}} \right]$$

Substituting $T = 0.45 \text{ MeV}$, $m_0 c^2 = 0.51 \text{ MeV}$, $\theta = 60^\circ$, we find $E = 0.67 \text{ MeV}$

1.10 BREMSSTRAHLUNG

The quantum nature of radiation is also confirmed by the existence of a short wavelength limit of the *bremsstrahlung* X-ray spectrum. The *bremsstrahlung* is the radiation produced by deceleration of the electrons and is also called *braking radiation*. X-rays are produced when solid targets are bombarded with fast electrons. An X-ray tube is an evacuated bulb with several electrodes. The electrons are produced by thermionic emission. These electrons are accelerated under high potential difference and then directed to fall on anode (anticathode) made of heavy metals (W, Cu, Pt etc.). Almost all energy of electrons is liberated on the anticathode in the form of heat and only from 1 to 3% of

energy of electrons is transformed into X-rays. For this reason arrangements are made for cooling the anticathode. The distribution of X-rays intensity at various wavelengths, with molybdenum and tungsten as targets, are shown in the Fig. (1.10.1). The important features of the curves are as follows:

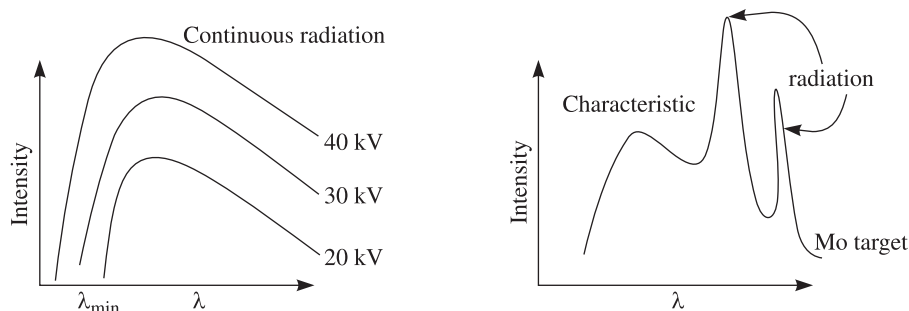


Fig. 1.10.1

- (1) For each accelerating potential there exists a short wavelength limit $\lambda_{\min}$ below which no radiation is produced. The value of $\lambda_{\min}$ depends only on the magnitude of the accelerating voltage and not on the nature of the target material. Duane and Hunt (1915) observed that $\lambda_{\min}$ is inversely proportional to the accelerating voltage. The exact relationship between $\lambda_{\min}$ and the accelerating voltage V is given by

$$\lambda_{\min} = \frac{12400}{V} \text{ \AA}$$

where λ is in Angstrom and V in volt.

- (2) X-ray energy is continuously distributed among all wavelengths from $\lambda_{\min}$ to infinity. For this reason the braking radiation is called *continuous* or *white radiation*. For each target when the accelerating voltage is increased beyond a certain value, which is the characteristic of the target, the intensity-wavelength curve shows several peaks. The wavelengths at which these peaks are observed are the characteristic properties of the target material and the radiation itself is called *characteristic radiation*.

The X-rays are produced from catastrophic encounters of fast electrons with atomic nuclei. If this process is analyzed quantum mechanically, it turns out that there is a certain probability that electron-nuclear encounter will result only in deflection of the electron with *no emission* of radiation. This is called an elastic Rutherford scattering. Besides this, there is also a probability that electron-nuclear encounter will result in the emission of photon as well as deflection of electron. This is called an *inelastic* or *radiative* collision. When a fast electron interacts with the target nucleus via Coulomb field, it transfers momentum to the nucleus and a photon is emitted in the process. If T' is the kinetic energy of the outgoing electron then the energy of the emitted photon is given by

$$\hbar\omega = T - T'$$

The incoming electrons lose different amount of energy in such nuclear encounters and suffer many encounters before coming to rest. The emitted radiation, therefore, forms a continuous spectrum.

The X-ray photon of shortest wavelength is produced when the incoming electron loses its entire kinetic energy in a single encounter ($T' = 0$). Thus

$$\hbar\omega_{\max} = T = eV$$

$$\frac{2\pi\hbar c}{\lambda_{\min}} = eV$$

where

$$\lambda_{\min} = \frac{2\pi\hbar c/e}{V} = \frac{12400}{V} \text{ \AA}$$

The value of $\hbar$ obtained making use this formula is considered to be the most accurate. In the limit $\hbar \rightarrow 0$, $\lambda_{\min} \rightarrow 0$. This means that the existence of short wavelength limit is a quantum mechanical-phenomenon. The *Bremsstrahlung* process is sometimes called an *inverse photoelectric effect*. In a photoelectric effect, a photon is absorbed and its energy and momentum are transferred to an electron. In *bremsstrahlung* process, a photon is created and its energy and momentum are derived from the collision of electron with nucleus.

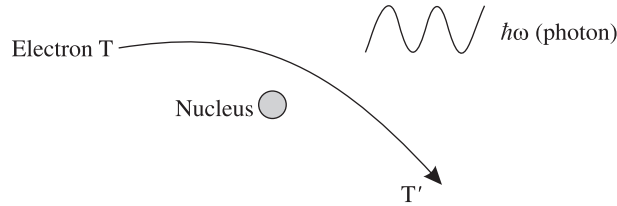


Fig. 1.10.2 Continuous and characteristic x-ray radiation

1.11 RAMAN EFFECT

In 1927 C.V. Raman and K.S. Krishnan were investigating the scattering of light by molecules of transparent liquids, gases and solids. They found that in addition to the frequency of incident light, the scattered radiation had a number of other frequencies higher and lower than the incident one. This phenomenon is called Raman effect. The lower frequencies in the scattered light are called Stokes' frequencies (red satellites) and those of higher frequencies are called antistokes' frequencies (violet satellites). These extra frequencies are independent of the frequency of the incident light and are characteristic of the scattering substance. It is also found that the red satellites have greater intensity than the violet satellites. The intensity of the violet satellites rapidly grows with rise of temperature of the scattering substance.

The quantum physics of atoms and molecules and the quantum theory of radiation provide a simple explanation of Raman effect. This phenomenon can be considered as the inelastic collision of photon of the incident light with the molecule of the scatterer. Let us consider the collision of a photon of frequency ω_0 with a molecule, which is initially in the energy state E_i . During the process of collision, the photon either gives up its energy to the molecule or receives energy from the molecule and the molecule goes to the energy state E_f . If the scattered photon has frequency ω then the law of conservation of energy requires that

$$\hbar\omega_0 + E_i = \hbar\omega + E_f$$

$$\omega = \omega_0 + \left(\frac{E_i - E_f}{\hbar} \right)$$

$$\omega = \omega_0 + \Delta\omega \quad \dots(1.11.1)$$

where $\Delta\omega = (E_i - E_f)/\hbar \quad \dots(1.11.2)$

Now two cases arise:

1. If $E_i < E_f$, $\Delta\omega$ is negative and the frequency of the scattered is given by

$$\omega = \omega_0 - |\Delta\omega| \quad (\text{Stokes' lines}) \quad \dots(1.11.3)$$

This happens when the molecule is initially in the ground state and the photon transfers its energy to the molecule. The photon energy (and hence frequency) diminishes and the molecule jumps to the excited state. This explains the origin of Stokes' lines. Since there are a large number of excited states, the transitions of molecules from the ground state to the excited states are accompanied by many spectral lines.

At ordinary temperature, the number of molecules in the ground state exceeds those in the excited states, the probability of upward transitions is greater than the downward transitions. Hence the intensities of red satellites are greater than those of violet satellites.

2. $E_i > E_f$, $\Delta\omega$ is positive and the frequency of scattered photon is given by

$$\omega = \omega_0 + |\Delta\omega| \quad (\text{Antistokes' line}) \quad \dots(1.11.4)$$

This happens when the molecule is initially in one of its excited state. The incident photon causes it to jump to the ground state. During this process the photon receives energy from the molecule and hence the scattered photon has higher energy (frequency). This process causes the violet satellites to appear.

At ordinary temperature, the number of molecules in the excited states is smaller than those in the ground state and hence the number of downward transitions from the excited states to the ground state is smaller. That is why the violet satellites are weaker in intensity. On heating the scattering substance, the number of molecules in the excited states increases and so does the number of downward transitions. Thus an increase in temperature of the scattering substance causes an increase in intensity of the violet companions.

In terms wave numbers $\left(\bar{\nu} = \frac{1}{\lambda} = \frac{\omega}{2\pi c} \right)$, the Raman shift is expressed as

$$\bar{\nu} = \bar{\nu}_0 \pm \Delta\bar{\nu} \quad \dots(1.11.5)$$

where positive sign stands for antistokes' lines and negative sign for stokes' lines.

Experimental arrangement: The experimental arrangement for studying Raman effect is schematically shown in the Fig. (1.11.1). The scattering substance is taken in a tube whose one end is flat and the other end extends into a horn shape. The latter is blackened and filled with mercury to provide dark background. A spectrograph is mounted in front of the flat face of the tube. The tube

is surrounded by a jacket in which water is circulated to keep the temperature of the liquid constant. A monochromatic source with suitable filters is used to illuminate the experimental liquid. After suffering scattering, the light enters spectrograph through slits. The Raman lines are recorded on a photographic plate.

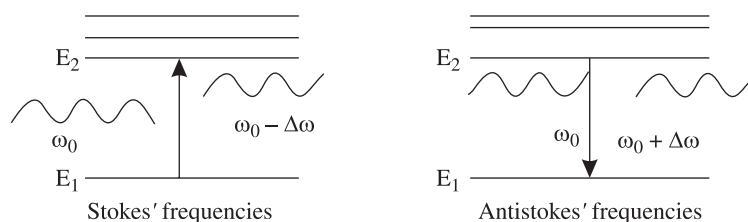


Fig. 1.11.1 Origin of Raman lines

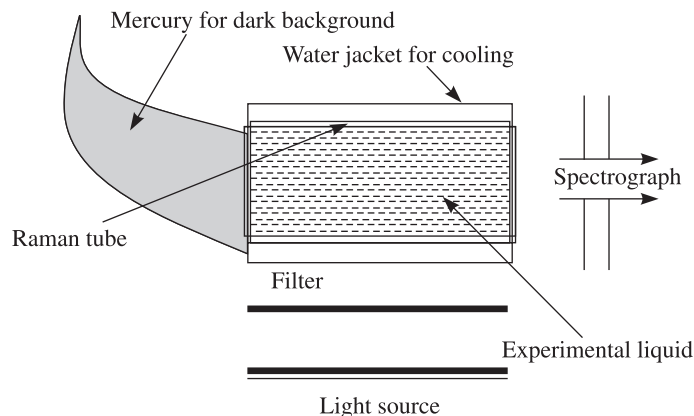


Fig. 1.11.2 Schematic arrangement of Raman apparatus

The Raman effect is characteristic of molecules and hence it is widely used in the determination of structure of molecules. It also provides a proof in favour of quantum nature of radiation. Raman was awarded Nobel Prize for this discovery in 1930.

SOLVED EXAMPLES

Ex. 14. With exciting line $2536 \text{ \AA}$, a Raman line for a sample is found at $2612 \text{ \AA}$. Calculate the Raman shift in m^{-1} .

$$\text{Sol. } \bar{\nu}_0 = \frac{1}{\lambda_0} = \frac{1}{2536 \times 10^{-10} \text{ m}} = 3943000 \text{ m}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2612 \times 10^{-10} \text{ m}} = 3828000 \text{ m}^{-1}$$

Raman shift $\Delta\bar{\nu} = \bar{\nu}_0 - \bar{\nu} = 115000 \text{ m}^{-1}$.

Ex. 15. Excited by a radiation of wavelength $5000 \text{ \AA}$, a sample gives a Raman line at $5050.5 \text{ \AA}$. Calculate the Raman frequency in m^{-1} and the position of the corresponding antistokes' line in $\text{\AA}$.

Sol. $\bar{\nu}_0 = 2 \times 10^6 \text{ m}^{-1}$ and $\bar{\nu} = 1.98 \times 10^6 \text{ m}^{-1}$

Raman shift $\Delta\bar{\nu} = 0.02 \times 10^6 \text{ m}^{-1}$

Frequency of antistoke's line

$$\bar{\nu} = \bar{\nu}_0 + \Delta\bar{\nu} = 2.02 \times 10^6 \text{ m}^{-1}$$

Wavelength of antistokes' line $\lambda = \frac{1}{\bar{\nu}} = 4950.05 \text{ \AA}$.

1.12 THE DUAL NATURE OF RADIATION

The discovery of photoelectric effect, Compton's effect etc. posed a serious dilemma before the contemporary physicists. The phenomenon of interference and diffraction of light could be explained on the basis of wave model of radiation whereas the phenomenon involving interaction of radiation with matter viz photoelectric effect, Compton's effect could only be understood on the basis of particle nature of radiation. In the particle picture of radiation, photon energy is expressed as $\hbar\omega$. It is very difficult to assign a meaningful significance to the frequency ω associated with a particle. In order to determine photon energy ($\hbar\omega = 2\pi\hbar c/\lambda$) we determine the speed of light and the wavelength. The determination of wavelength is based on the wave nature of light. This paradoxical situation is most forcefully encountered in Compton's scattering experiment where X-ray wavelength is determined with crystal spectrometer, the interpretation and the analysis of the measurement is based on the wave model and the scattering of X-ray can only be understood in terms of particle model. The particle and the wave aspect of radiation are not revealed simultaneously in the same experiment. In experiments involving propagation of radiation including interference and diffraction, the wave aspect is shown while in experiments where radiation interacts with matter, its particle aspect is manifested. This situation has an interesting analogy, as described by Arthur Schawlow: *It (the complex behaviour of light) be likened to the elephant, as blind men in fable; to one who touched the tail, the elephant was like a rope; to another who touched a leg, it was like a tree; to others it was like a wall.*

In 1928 N. Bohr suggested that the wave and the particle properties of radiation are complementary. It is not possible to apply both descriptions at the same time. When wave behaviour is observed easily, the particle behaviour is hardly observed and vice-versa. This idea is known as the Bohr's complementary principle.

The wave and the particle properties of radiation are linked by Planck's constant $\hbar$, which is product of two variables; one is characteristic of a wave and the other is characteristic of a particle, viz.

$$\hbar = \frac{E}{\omega} = \frac{ET}{2\pi}$$

where E is energy of photon, ω is frequency of photon and T is time period of the wave (radiation). Here E represents particle characteristic and ω or T wave characteristic. If the magnitude of one property is larger, the magnitude of the other will be smaller and vice-versa. Meaning thereby, if the particle property is dominant, the wave property will hardly be observable. If the wave property is more pronounced, it will be difficult to detect particle property. In case of short X-rays and gamma rays, the photon energy is very high and therefore their particle property is more dominating; it is difficult to establish their wave behaviour. On the other hand, the wavelength of radio waves very large and therefore their particle behaviour can hardly be demonstrated.

QUESTIONS AND PROBLEMS

1. Show that the average energy of a Planck's oscillator is given by

$$\bar{\epsilon} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

Discuss the variation of ϵ with temperature and frequency of the oscillator.

2. Deduce Planck's for the spectral distribution of energy in black body radiation. From Planck's law, obtain (i) Wien's displacement law (ii) Stefan's law.
3. Derive Planck's radiation law. Show that it reduces to Wien's law and Rayleigh-Jeans law in appropriate limit.
4. Describe the experimental results obtained in the study of photoelectric effect. Give Einstein's explanation photoelectric effect.
5. What is Compton's effect? Derive an expression for Compton's shift. Discuss the dependence of Compton's shift on the angle of scattering. Explain the existence of unmodified radiation in the scattered radiation.
6. An X-ray photon of energy E undergoes Compton scattering in the direction θ with the initial direction. Show that the energy of the scattered photon is given by

$$E' = \frac{E}{1 + \frac{2E}{m_0c^2} \sin^2 \theta/2}$$

and hence

$$E'_{\min} = \frac{E}{1 + \frac{2E}{m_0c^2}}$$

7. Show that the kinetic energy of the Compton electron is given by

$$T = \frac{\left(\frac{2E^2}{m_0c^2} \right) \sin^2 \theta/2}{1 + \left(\frac{2E^2}{m_0c^2} \right) \sin^2 \theta/2}$$

and hence

$$(T_e)_{\max} = \frac{\left(\frac{2E}{m_0c^2}\right)}{1 + \left(\frac{2E}{m_0c^2}\right)}$$

8. Show that the direction of recoil of Compton electron is given by

$$\tan \phi = \frac{E' \sin \theta}{E - E' \cos \theta}$$

where the symbols have their usual meanings.

9. The energy required to remove an electron from sodium is 2.3 eV. Does sodium show photoelectric effect for light of wavelength 6500 Å.
10. The stopping potential for photoelectrons emitted from a surface illuminated by light of wavelength 5000 Å is 0.70 volt. When the incident wavelength is changed, the stopping potential is found to be 1.50 volt. What is the new wavelength?
11. In an experiment of photoelectric effect, it is observed that for a light of wavelength 3000 Å, the stopping potential is 1.85 volt and for light of wavelength 4000 Å, the stopping potential is 0.82 volt. From these data determine (i) Planck's constant (ii) work function of the substance (iii) threshold wavelength for the substance.
12. What is the frequency, wavelength and momentum of a photon whose energy is equal to the rest energy of an electron?
13. An X-ray is found to have its wavelength doubled on being scattered through 90°. What is the wavelength of the X-ray?
14. If the Compton shift in an experiment is found to be 0.0121 Å. Find the scattering angle.
15. A 300 keV photon undergoes a Compton scattering. The kinetic energy of recoil electron is 250 keV. Calculate the wavelength of the scattered photon.
16. An X-ray quantum having a wavelength of 0.15 Å undergoes a Compton collision and is scattered through an angle of 37°. (i) What are the energies of the incident and scattered photon and of the ejected electron (ii) what is the momentum of each photon?
17. Using the conservation laws, demonstrate that a free electron cannot absorb a photon completely.

Hint: The laws of conservation of energy and momentum permit us to write:

$$E + m_0c^2 = E_e \quad (1) \text{ and } (E/c) = p_e \quad \dots(1)$$

The relativistic energy of electron is

$$E_e^2 = (p_e c)^2 + (m_0c^2)^2 \quad \dots(2)$$

In view of the conservation laws, we can write (2) as

$$(E + m_0c^2)^2 = E^2 + (m_0c^2)^2$$

$$\Rightarrow 2m_0c^2E = 0 \text{ which is meaningless.}$$

WAVE NATURE OF MATERIAL PARTICLES

2.1 INTRODUCTION

The remarkable success of Bohr's theory in providing interpretation of hydrogen spectrum stimulated the imagination of physicists to extend his ideas with some modifications to account for the finer details of complex spectra of multi-electron atoms. Sommerfeld's theory, for instance, was an attempt of this nature. Although Sommerfeld's theory with relativistic correction, provided an explanation for the existence of the fine structure of H_{α} line in the hydrogen spectrum, it could not be carried further in the interpretation of spectra of multi-electron atoms. Using instruments of higher and higher resolving power many puzzling features of the atomic spectra were recorded. The behaviour of atoms in electric and magnetic field—electro-optic and magneto-optic phenomena posed a serious challenge to theoreticians. In early days of the development of atomic physics the usual methods of understanding these complex features of atomic spectra were to introduce empirical rules with several types of quantum numbers without any theoretical basis. The hypothesis of spinning electron, proposed by Uhlenbeck and Goudsmit (1925), was an attempt of this kind. During this period, it was realized that a mere patch-works on the classical principles was no longer adequate in the understanding of atomic phenomena. The state of affairs indicated the need for drastic changes in our concepts of microscopic systems. In 1924 a young French graduate Louis de Broglie in his doctoral thesis suggested such a radical change in our concepts of micro-systems.

2.2 de BROGLIE HYPOTHESIS

The reasoning that led de Broglie to put forward his revolutionary hypothesis runs as follows. The entire physical universe is composed of matter and radiation. In quantum theory of radiation a fragment or quantum of energy ε is assigned a frequency, ω ($=2\pi\nu$) such that $\varepsilon = \hbar\omega$. Although there is no physical sense of frequency ω , nevertheless the theory based on this assumption works well. From this notion de Broglie speculated that material particles, which are also fragments of energy (e.g., $\varepsilon = mc^2$), might be assigned some characteristic frequency. A material particle of rest mass m_0 is equivalent to energy m_0c^2 , therefore, according to de Broglie's idea we can write

$$m_0c^2 = \hbar\omega \quad \dots(2.2.1)$$

where ω is the frequency of some intrinsic periodic process associated with the material particle. Let us see what this periodic process appears to an observer with respect to which it is moving.

Let us consider a frame S' , which is moving with the particle. The frequency of the internal process associated with the particle is

$$\omega = m_0 c^2 / \hbar$$

The vibratory motion associated with this periodic internal process can be represented by

$$\psi'(x', t') = \exp(-i\omega t') = \exp\left(-i \frac{m_0 c^2}{\hbar} t'\right) \quad \dots(2.2.2)$$

Let S be the observer's frame with respect to which the particle is moving along x -axis with velocity v . Making use of Lorentz transformation for time, the equation of the periodic process associated with the particle transforms on transition from S' to S as

$$\psi(x, t) = \exp\left(-i \frac{m_0 c^2}{\hbar} \left(\frac{t - vx/c^2}{\sqrt{1 - \beta^2}} \right)\right), \quad \beta = v/c \quad \dots(2.2.3)$$

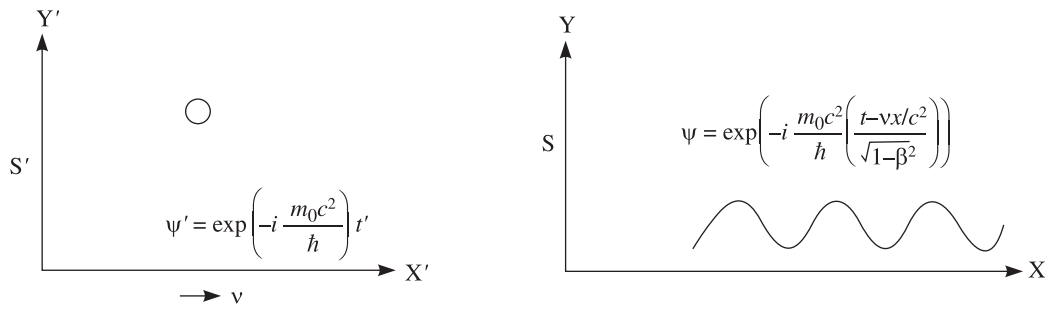


Fig. 2.2.1

The above equation represents a progressive wave with propagation constant k given by

$$\begin{aligned} k &= \frac{m_0 c^2}{\hbar} \frac{v/c^2}{\sqrt{1 - \beta^2}} \\ &= \frac{1}{\hbar} \frac{m_0 v}{\sqrt{1 - \beta^2}} \\ &= \frac{p}{\hbar} \end{aligned} \quad \dots(2.2.4)$$

$$\text{or} \quad p = \hbar k \quad \dots(2.2.5)$$

$$\text{or} \quad \lambda = \frac{h}{\sqrt{2mT}} \quad \dots(2.2.6)$$

where T = kinetic energy of the particle.

Equations (2.2.4–2.2.6) determined the wavelength of the de Broglie wave representing the particle.

2.3 EXPERIMENTAL VERIFICATION OF de BROGLIE HYPOTHESIS

Although de Broglie speculated about the wave nature of material particles, yet none of the theoretical physicist of that time could think of a way to establish the physical existence of such waves. It was Elasser who in 1925 pointed out that the existence of such waves could be demonstrated by their diffraction by an appropriate grating. Two American physicists C.J. Davisson and L.H. Germer carried out an experiment, which definitely showed the existence of de Broglie waves and verified the relation between wavelength and momentum. The schematic arrangement of their experiment is shown in the Figure 2.3.1. A beam of electrons was accelerated through a potential difference and then it was allowed to fall on a nickel target. A detector D received the scattered electrons. The entire arrangement was placed in an evacuated chamber. To electrons the nickel is not a smooth surface and hence they will be scattered in all directions. From the view point of classical physics the intensity of the scattered beam should be independent of the direction of observation and the energy of primary electrons. These predictions were verified in the experiment.

However, in the midst of the experiment, air leaked into the chamber accidentally and the nickel surface got oxidized. In order to reduce the oxide layer of the target, it was taken out and was heated strongly in a high temperature oven. After this treatment the target was again placed in the apparatus and the experiment was repeated. The experimental results were surprising. *At certain angles the scattered electron intensity showed maxima and minima. Furthermore the angular positions of maxima and minima depended on the energy of primary electrons.*

The angular variation of scattered electron intensity for different accelerating potentials is shown in the Figure 2.3.2. The intensity at any angle is proportional to the distance of the curve at that angle from the point of scattering.

The experimental results may be interpreted as follows. Initially, the nickel target was a polycrystalline material, which after heating became a single crystal due to arrangement of atoms in a regular lattice. According de Broglie hypothesis, the electron waves are diffracted by atomic planes in the same way as X-rays are diffracted from crystal planes.

In one particular arrangement, a beam of 54 eV electrons was allowed to be incident on a single nickel target and the diffracted beam was observed to have maximum intensity in the direction $\phi = 50^\circ$ from the incident beam. This diffracted beam arises from the crystal planes shown in the Figure 2.3.1. Evidently the angle of incidence relative to the crystal planes is $\theta = 65^\circ$. From X-rays measurements the spacing of these planes is found to be $d = 0.91 \text{ \AA}$. The Bragg's equation for maximum in the diffraction pattern is

$$2d \sin \theta = m\lambda; \quad m = 1, 2, \dots$$

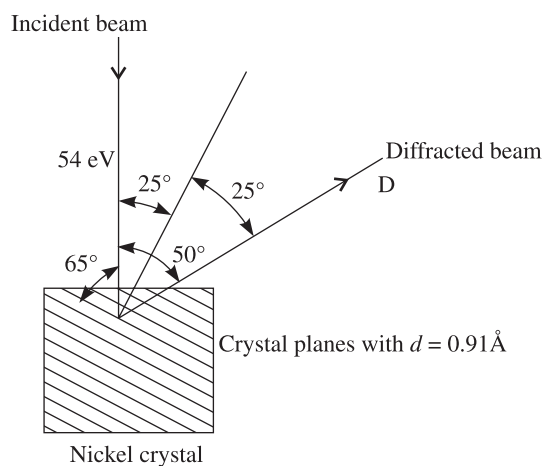


Fig. 2.3.1 Schematic diagram of Davisson-Germer experiment

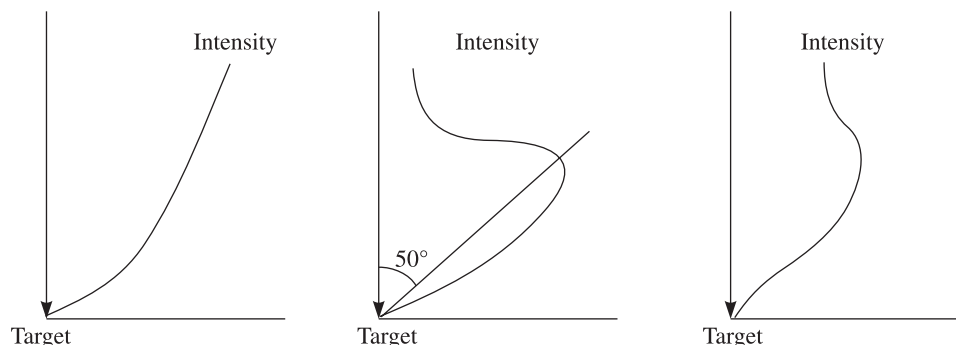


Fig. 2.3.2 Variation of intensity of the diffracted electron beam with energy of the electron

The wavelength of electron waves calculated from this equation (for $m = 1$) comes out to be

$$\lambda = 2d \sin \theta = 2 \times (0.91 \text{ \AA}) \sin 65 = 1.65 \text{ \AA}$$

On the other hand the wavelength of electron beam from de Broglie hypothesis comes out to be

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2 \text{ meV}}} = \frac{6.625 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 9.1 \times 10^{-31} \text{ kg} \times 1.6 \times 10^{-19} \text{ C} \times 54 \text{ V}}} \\ &= 1.66 \times 10^{-10} \text{ m} = 1.66 \text{ \AA} \end{aligned}$$

The excellent agreement between the value obtained from diffraction experiment and that from de Broglie relation provides experimental proof for the validity of wave nature of electrons.

G. P. Thomson's experiment: Another verification of de Broglie hypothesis came from the G.P. Thomson's experiment (1927). In this experiment a narrow beam of electrons was allowed to pass through a thin film of polycrystalline material. The transmitted beam was received on a photographic film.

The diffraction pattern obtained from electron beam was similar to the *powder diffraction pattern of X-rays*. This experiment independently confirmed the de Broglie hypothesis.

Not only electrons, but all material objects exhibit wave properties under appropriate conditions. In fact neutron diffraction technique is widely used in the determination of crystal structure.

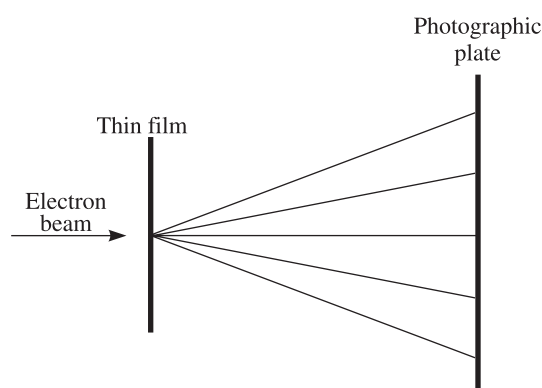


Fig. 2.3.3 G.P. Thomson arrangement for getting electron diffraction pattern

2.4 WAVE BEHAVIOR OF MACROSCOPIC PARTICLES

It is a well-known fact that the diffraction effects of waves are more pronounced if the dimensions of the diffracting objects are of the order of the wavelengths of the waves. For instance, if light waves are incident on an aperture, the diffraction effects become more and more observable when the aperture is progressively reduced. In case of electromagnetic waves, as we move from higher wavelength region (radio waves) to the lower wavelength region (gamma rays), the manifestation of wave nature is gradually reduced and the particle nature becomes more and more pronounced. For gamma rays particle properties become so dominant that it is very difficult to demonstrate wave-like behavior. Moreover, the difficulty also arises because of the unavailability of diffracting element of the dimensions comparable to the wavelength of gamma rays.

The de Broglie wavelength of a macroscopic object moving with common velocity is so small that its particle property dominates the wave behavior and so the latter is not observable. (The wavelength of a body of mass 100 g moving with velocity 1000 m/s is $\lambda = h/mv = 6.6 \times 10^{-36}$ m). On the other hand the wavelength of microscopic particles like electrons, protons, neutrons etc., are of the order of spacing of atoms and molecules in solids and therefore solids themselves offer as natural diffraction gratings. Indeed the first experimental verification of wave nature of material particles was established by using crystal as diffracting element.

2.5 HISTORICAL PERSPECTIVE

It is instructive to recall that the particle nature of radiation was discovered in 1905, and its converse i.e., wave nature of particle was conceived in 1924 i.e., two decades later. In order to gain some insight into the chronological order of the discoveries, we can ask why did physicists not speculate the converse idea in the year 1905? It must be noted that Einstein proposed his revolutionary idea of quantum nature of radiation for explaining certain experimentally observed phenomena, which could not otherwise be explained. On the other hand, one must admire the boldness of Louis de Broglie from the fact that he proposed his idea in the absence of any suggestive experimental observation. The intellectual climate at the time of de Broglie was more receptive to new ideas than the time when Einstein published his famous paper on photoelectric effect, which was given a cold reception. However, the de Broglie notion received immediate and respectful attention at least in the minds of an influential minority. The acceptability of de Broglie concept was facilitated as Einstein who was at the peak of his fame, became his strong advocate.

When de Broglie's paper for doctoral thesis was sent to Einstein, he commented, "**de Broglie lifted a corner of the great veil**". The publication of de Broglie's idea stimulated a great deal of discussion among theoretical physicists. In Zurich, the well-known chemist Peter Debye suggested a young German physicist Erwin Schrodinger to make a careful study of de Broglie's theory. In the course of this study Schrodinger presented a wave equation which when applied to atomic and molecular problems, proved to be a successful attempt in understanding the behavior of microscopic system.

The experimental verification of de Broglie concept was established after a year when Schrodinger presented his new system of mechanics, **wave mechanics**. The electron diffraction experiment of Davisson and Germer had its origin in a famous suit; the parties in the suit were the General Electric Company

and Western Electric Company. The work on electron scattering continued for several years (1919–1927). Up to 1926 Davisson and Germer were unaware of the de Broglie notion. When Davisson came to Oxford, there he heard the new theory and realized that the results of electron bombardment in his experiment was similar to that of X-rays diffraction. Thus de Broglie hypothesis got accidental experimental verification.

It is more interesting to notice the fact that J.J. Thomson, who in 1897 discovered electron and showed that it was a negatively charged particle, received Nobel Prize in 1906 and his son G. P. Thomson, who in 1927 discovered that electron is a wave, received Nobel Prize (with Davisson and Germer). In 1937, Max Jammer says, “The father was awarded the Nobel Prize for having shown that the electron is a particle, and the son for having shown that electron is a wave.”

2.6 THE WAVE PACKET

From what has been discussed in the preceding sections we come to conclusion that as the wavelength of electromagnetic radiation is progressively reduced, its particle nature becomes more and more dominant. On the other hand as the mass of a body is reduced, its wave nature is manifested. Therefore, it is apparent that the wave nature and the particle nature are the two aspects of the same physical reality. Although it appears that the two aspects are so different that it is difficult to reconcile them. The most obvious difference between particle and wave is that the former is localized whereas the wave is extensive in time and space. Consequently the only way in which we can reconcile the two concepts is to localize waves. The concept of wave packet has this characteristic.

The concept of wave packet is of great importance in quantum mechanics because it provides a means of reconciling the apparently incompatible wave and particle aspects of the behavior of matter and radiation. In fact, wave packet is a wave, which extends over a limited region. It is formed by superposition of a large number of waves of different wave numbers and amplitudes. On account of its limited extension it resembles with particle and the wave behavior is implicit in its very structure. Thus the representation of a particle by a wave packet is logical.

Let us consider the superposition of two waves

$$\psi_1 = A \cos(\omega_1 t - k_1 x)$$

$$\psi_2 = A \cos(\omega_2 t - k_2 x)$$

The phase velocity of the first wave is $v_1 = \omega_1/k_1$ and that of the second wave is $v_2 = \omega_2/k_2$. The resultant wave is given by

$$\begin{aligned} \psi &= \psi_1 + \psi_2 \\ &= A \cos(\omega_1 t - k_1 x) + A \cos(\omega_2 t - k_2 x) \\ &= 2A \cos\left\{\left(\frac{\omega_1 - \omega_2}{2}\right)t - \left(\frac{k_1 - k_2}{2}\right)x\right\} \cos\left\{\left(\frac{\omega_1 + \omega_2}{2}\right)t - \left(\frac{k_1 + k_2}{2}\right)x\right\} \\ &= 2A \cos\left\{\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right\} \cos\{(\bar{\omega}t - \bar{k}x)\} \quad \dots(2.6.1) \end{aligned}$$

where $\Delta\omega = \omega_1 - \omega_2, \Delta k = k_1 - k_2, \bar{\omega} = \frac{\omega_1 + \omega_2}{2}, \bar{k} = \frac{k_1 + k_2}{2}$

The slowly varying first term of eqn. (2.6.1) represents *amplitude modulated wave* traveling with velocity

$$v_g = \Delta\omega/\Delta k$$

The dotted curve in Fig. (2.6.1) represents the modulated wave. It is evident that resultant wave is divided in groups. The velocity with which these groups travel is called group velocity v_g . If a very large number of waves, differing in frequencies and propagation constants by infinitesimally small amount, are superposed, the resulting modulated wave moves with group velocity given by

$$v_g = \left(\frac{d\omega}{dk} \right)_{k_0} \quad \dots(2.6.2)$$

where the derivative is to be evaluated at the central value of k_0 .

If the component waves move with equal velocity, the groups also move with the same velocity. If the component waves have different speeds, the group velocity is different from those of component waves.

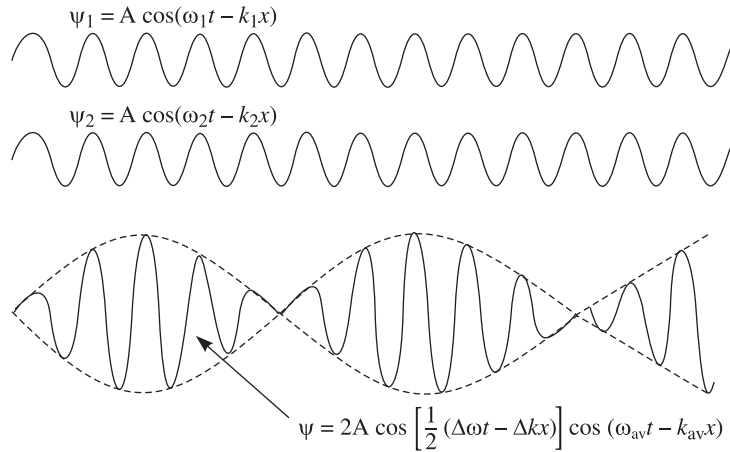


Fig. 2.6.1 Superposition of two waves of slightly different frequencies give rise to a resultant wave which consists of wave groups

In order that a group of waves may appear as a particle, it is necessary that only one group be formed. To obtain such a single group, an infinite number of waves, whose frequencies and propagation constants differ infinitesimally from one another, are required. A more general superposition of several sinusoidal waves is represented by

$$\psi(x, t) = \sum_n A_n e^{i(k_n x - \omega_n t)} \quad \dots(2.6.3)$$

If the component waves have continuous distribution of frequencies and propagation constants the above sum becomes an integral *i.e.*,

$$\psi(x, t) = \int A(k) e^{i(kx - \omega t)} dk \quad \dots(2.6.4)$$

Representation of functions as superposition of sinusoidal functions is called the Fourier's series. Eqn. (2.6.3) represents the Fourier's series of function $\psi(x, t)$ and Eqn. (2.6.4) represents the Fourier's integral of function $\psi(x, t)$. The amplitude function $A(k)$ represents the amplitude of the component wave having propagation constant k . By appropriate choice of amplitude function $A(k)$, a wave group of any desired shape may be constructed. In Fig. (2.6.2) some wave packets along with their amplitude function $A(k)$ are shown. The amplitude function $A(k)$ is called the *Fourier's transform* of the wave packet. Notice that a wave packet having larger extension in space corresponds to a sharply peaked amplitude function and vice versa. If Δx is the extension of a wave packet and Δk is the range of propagation constants in which amplitudes are distributed, then it can be shown that

$$\Delta x \cdot \Delta k = 1 \quad \dots(2.6.5)$$

It is obvious that when Δk is large, the corresponding Δx is small and vice versa. This reciprocal relationship is very important and forms the basis of the famous Heisenberg's uncertainty principle.

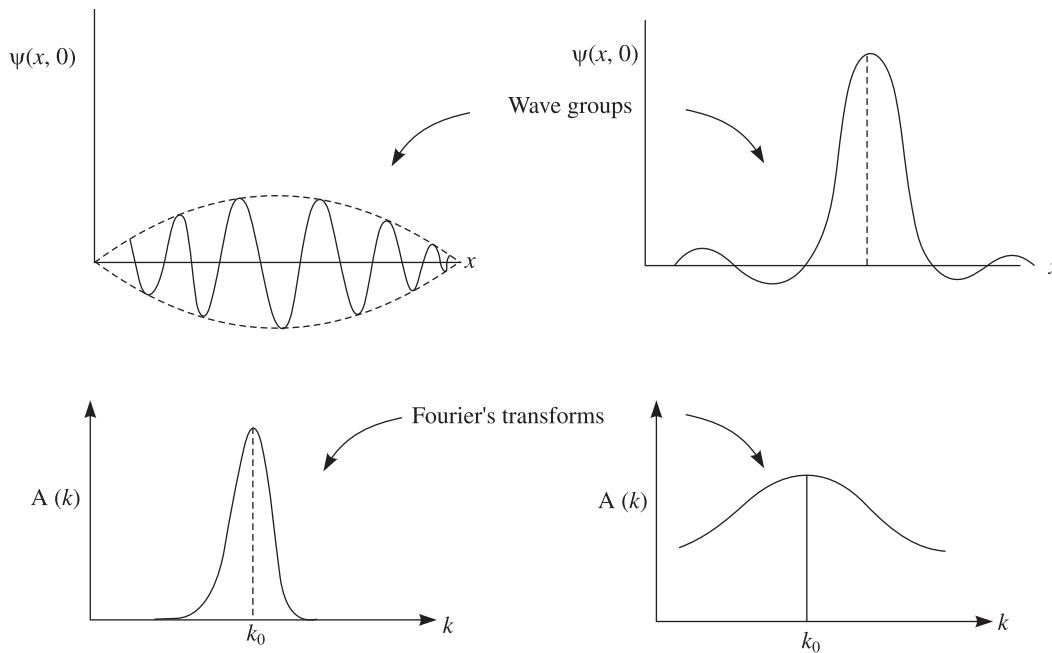


Fig. 2.6.2 Some wave groups and their Fourier's transforms

2.7 PARTICLE VELOCITY AND GROUP VELOCITY

According to de Broglie's hypothesis the momentum p of a particle is related to its wavelength λ ($k = 2\pi/\lambda$) as

$$p = \hbar k$$

and according to Einstein, the energy E of a particle is related to its mass and intrinsic frequency ω as

$$E = mc^2 = \hbar\omega$$

The phase velocity of de Broglie waves representing the particle is

$$u = \frac{\omega}{k} = \frac{mc^2/\hbar}{p/\hbar} = \frac{mc^2}{p} = \frac{mc^2}{mv} = \frac{c^2}{v} \quad \dots(2.7.1)$$

Since particle velocity v is less than the speed of light c , the phase velocity u is greater than the speed of light c . Thus the particle and the phase waves would not accompany. Although the phase velocity is greater than the speed of light, it does not contradict the special relativity because phase waves do not carry energy.

Now we shall show that the velocity of the particle is equal to the group velocity of the corresponding wave packet.

The velocity of the particle is

$$v = \frac{p}{m} = \frac{pc^2}{mc^2} = \frac{pc^2}{E} \quad \dots(2.7.2)$$

Making use of the relations $p = \hbar k$ and $E = \hbar\omega$ we have $dp = \hbar dk$ and $dE = \hbar d\omega$. Therefore $(dE/dp) = (d\omega/dk)$

The group velocity of the wave packet is

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp} \quad \dots(2.7.3)$$

The relativistic energy of a particle is

$$E^2 = (pc)^2 + (m_0c^2)^2$$

$$\therefore \frac{dE}{dp} = \frac{pc^2}{E} \quad \dots(2.7.4)$$

From Eqns. (2.7.2), (2.7.3) and (2.7.4)

$$v_g = \frac{pc^2}{E} = v \quad \dots(2.7.5)$$

Thus the representation of a particle by wave packet gets logical support.

2.8 HEISENBERG'S UNCERTAINTY PRINCIPLE OR THE PRINCIPLE OF INDETERMINACY

The dual nature of matter and radiation requires profound changes in our concepts built on the basis of common sense and everyday experience. The formulation of classical mechanics implies that the position and momentum of a particle are assumed to have well defined values and can be determined simultaneously with perfect accuracy. But the wave particle duality compels us to abandon the idea of simultaneous determination of position and momentum with perfect accuracy. In 1927 Werner Heisenberg, a German physicist, enunciated that *it is impossible to determine both position and momentum simultaneously with perfect accuracy. If Δx is the uncertainty in position and Δp_x is the uncertainty in the corresponding momentum then*

$$\Delta p_x \cdot \Delta x \geq \hbar \quad \dots(2.8.1)$$

Similarly if ΔE is the uncertainty in energy and Δt is uncertainty in time then

$$\Delta E \cdot \Delta t \geq \hbar \quad \dots(2.8.2)$$

From Eqn. (2.8.1) it is evident that if we try to measure the position of particle with utmost accuracy i.e., $\Delta x \rightarrow 0$, the corresponding uncertainty in momentum becomes very large i.e., $\Delta p_x \rightarrow \infty$ and vice versa.

Let us illustrate the above assertion. Consider a particle having well-defined momentum $p_x (= \hbar k)$. Such a particle has well defined k or λ and is represented by a sinusoidal (monochromatic wave). A monochromatic wave has no beginning and end i.e., it is infinitely long; its amplitude is constant for all values space coordinates x and therefore the particle may be anywhere between $x = -\infty$ to $+\infty$. Thus the position of the particle is completely uncertain ($\Delta x \rightarrow \infty$).

Now consider a particle having well-defined position ($\Delta x \rightarrow 0$). A wave packet having very small extension in space describes such a particle. Fourier's transform of this wave packet shows that it is formed by superposition of a very large number of waves having continuous distribution of k or λ within a large range of Δk . Thus the uncertainty in k or p is very large ($\Delta k \rightarrow \infty$).



Fig. 2.8.1 A particle with well-defined momentum p is described by a sinusoidal wave extending from $x = -\infty$ to $+\infty$. Here $\Delta p \rightarrow 0$ but $\Delta x \rightarrow \infty$

Thus a particle with relatively small uncertainty in momentum has large uncertainty in position.

A sinusoidal wave has well defined frequency and so is its energy ($E = \hbar\omega$). A particle described this wave also has well-defined energy E and therefore $\Delta E = 0$. In order to see the constancy of amplitude of such a sinusoidal wave, which exists from $t = -\infty$ to $+\infty$, we have to look for a very long time. Therefore, the uncertainty in time is infinite ($\Delta t \rightarrow \infty$).

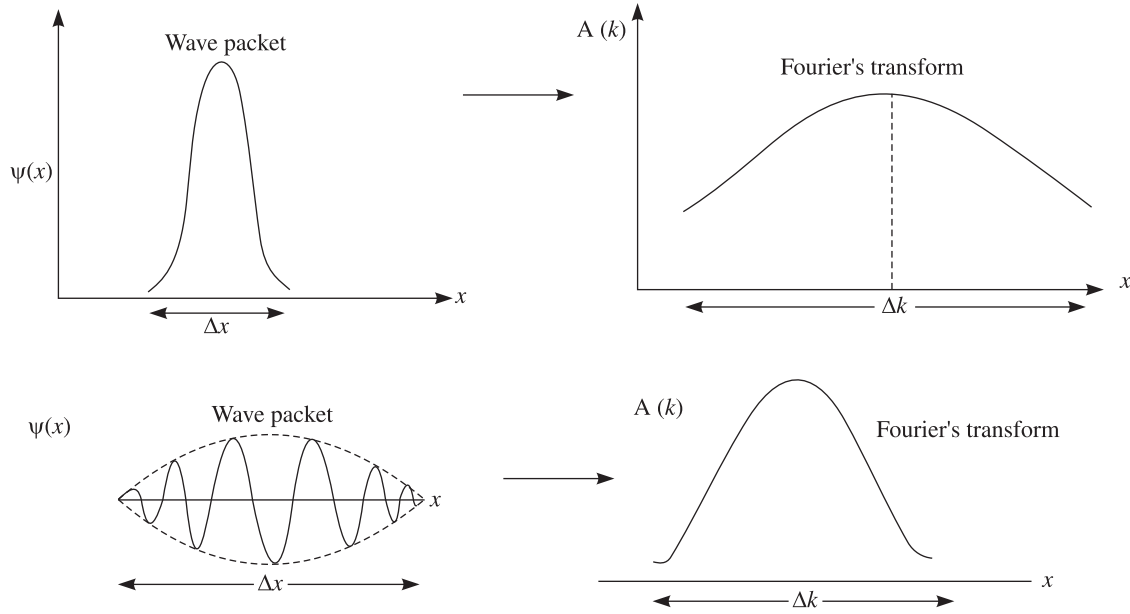


Fig. 2.8.2 Some wave packets and their Fourier's transforms, $\Delta x \Delta k \cong 1$

Consider a particle, which is described by a wave packet as shown in the Fig. (2.8.2). The Fourier's transform of the wave packet is also shown adjacent to it. Let Δx be the spread of the wave packet in space and Δk the spread in propagation constant. It can be shown by standard mathematical technique that

$$\Delta x \Delta k \geq 1 \quad \dots(2.8.3)$$

Since $p = \hbar k$ and $\Delta p = \hbar \Delta k$ we have

$$\Delta p_x \Delta x \geq \hbar \quad \dots(2.8.4)$$

which is the uncertainty relation.

It should be carefully noted that the uncertainties in measurement of position and momentum are not because of inadequacies in our measuring instruments. Even with ideal instrument we can never in principle do better. This principle is the fundamental law of nature. The indeterminism is inherent in the very structure of matter. The momentum and position don't assume well-defined values simultaneously.

Notice that it is the smallness of Planck's constant that makes the uncertainty principle insignificant in macroscopic world. In microscopic world the consequences of uncertainty principle cannot be ignored.

SOLVED EXAMPLES

Ex. 1. Show that the wavelength of electron accelerated through a potential difference V is given by

$$\lambda = \frac{h}{\sqrt{2m eV}} = \frac{12.3}{\sqrt{V(\text{volt})}} \text{ \AA}.$$

Sol. The kinetic energy of electron $T = \frac{p^2}{2m} = eV$

and

$$p = \sqrt{2mT} = \sqrt{2m eV}$$

Therefore
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mT}} = \frac{h}{\sqrt{2m eV}}$$

Substituting $m = 9.1 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C, $h = 6.6 \times 10^{-34}$ Js, we have

$$\lambda = \frac{12.3}{\sqrt{V}} \times 10^{-10} \text{ m} = \frac{12.3}{\sqrt{V}} \text{ \AA}$$

For other charged particles appropriate values of m and charge q should be substituted in the above equation.

Ex. 2. Obtain expression for the wavelength of a particle moving with relativistic speed.

Sol. The relativistic momentum of a particle

$$p = \frac{m_0 v}{\sqrt{1 - v^2/c^2}}$$

$$\therefore \lambda = \frac{h}{p} = \frac{h(1 - v^2/c^2)^{1/2}}{m_0 v} = \frac{h}{m_0 c} \frac{(1 - v^2/c^2)^{1/2}}{(v/c)}$$

The momentum p of a relativistic particle can also be expressed as follows.

$$E^2 = p^2 c^2 + (m_0 c^2)^2 = (T + m_0 c^2)^2$$

$$p = \frac{\sqrt{T(T + 2m_0 c^2)}}{c}$$

Hence

$$\begin{aligned} \lambda &= h/p \\ &= \frac{hc}{\sqrt{T(T + 2m_0 c^2)}} = \frac{h}{\sqrt{2m_0 T}} \frac{1}{\sqrt{1 + T/2m_0 c^2}} \end{aligned}$$

$$= \frac{h}{\sqrt{2m_0 T}} \left(1 + \frac{T}{2m_0 c^2} \right)^{-1/2}$$

If the particle under consideration is an electron accelerated through a potential difference of V volt, its de Broglie wavelength is given by

$$\lambda = \frac{h}{\sqrt{2m_0 eV}} \left(1 + \frac{eV}{2m_0 c^2} \right)^{-1/2}$$

Ex. 3. Find the de Broglie wavelength of (i) electron moving with velocity 1000 m/s (ii) an object of mass 100 gram moving with the same velocity.

Sol. (i) de Broglie wavelength of electron

$$\begin{aligned} \lambda &= \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(1000 \text{ m/s})} = 7285 \times 10^{-10} \text{ m} \\ &= 7285 \text{ \AA} \end{aligned}$$

(ii) de Broglie wavelength of object

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ Js}}{(0.1 \text{ kg})(1000 \text{ m/s})} = 8.63 \times 10^{-36} \text{ m}$$

Owing to extremely short wavelength of the object its wave behavior cannot be demonstrated.

Ex. 4. Find the de Broglie wavelength of electron, proton and α -particle all having the same kinetic energy of 100 eV.

Sol. For electron

$$\begin{aligned} \lambda &= \frac{h}{\sqrt{2mT}} = \frac{6.63 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (9.1 \times 10^{-31} \text{ kg})(100 \times 1.6 \times 10^{-19} \text{ J})}} \\ &= 1.23 \times 10^{-10} \text{ m} = 1.23 \text{ \AA} \end{aligned}$$

For proton $m = 1.67 \times 10^{-27} \text{ kg}$,

$$\therefore \lambda = 0.028 \text{ \AA}$$

For α -particle $m = 4 \times 1.67 \times 10^{-27} \text{ kg}$

$$\therefore \lambda = 0.014 \text{ \AA}$$

Ex. 5. At what kinetic energy would an electron have the wavelength equal to that of yellow spectral line of sodium, $\lambda = 5896 \text{ \AA}$?

Sol. Since $\lambda = \frac{h}{\sqrt{2mT}}$

$$\therefore T = \frac{h^2}{2m\lambda^2}$$

Substituting $h = 6.63 \times 10^{-34}$ Js, $m = 9.1 \times 10^{-31}$ kg, $\lambda = 5896 \times 10^{-10}$ m, we have
 $T = 6.93 \times 10^{-25}$ J = 4.3×10^{-6} eV

Ex. 6. What is the wavelength of thermal neutron at 300 K?

Sol. Kinetic energy of thermal neutron $E = \frac{3}{2}kT = \frac{3 \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}}{2} = 6.2 \times 10^{-21}$ J

$$\therefore \lambda = \frac{h}{\sqrt{2mE}} = \frac{6.63 \times 10^{-34} \text{ Js}}{\sqrt{2 \times 1.67 \times 10^{-27} \text{ kg} \times 6.2 \times 10^{-21} \text{ J}}} = 1.45 \text{ \AA}$$

Ex. 7. Find the de Broglie wavelength of hydrogen molecules, which corresponds to their most probable speed at room temperature 27°C.

Sol. The most probable speed of hydrogen molecule at temperature T is

$$v = \sqrt{\frac{2kT}{m}}$$

Momentum of molecule $p = mv = \sqrt{2mkT}$

$$\begin{aligned} \therefore \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2mkT}} \\ &= \frac{6.63 \times 10^{-34} \text{ Js}}{\sqrt{2 \times (3.34 \times 10^{-27} \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}} \\ &= 1.26 \times 10^{-10} \text{ m} = 1.26 \text{ \AA}. \end{aligned}$$

Ex. 8. At what value of kinetic energy is the de Broglie wavelength of an electron equal to its Compton wavelength?

Sol. Energy of electron $E = T + m_0c^2 = \sqrt{(pc)^2 + (m_0c^2)^2}$

$$\therefore p = \frac{\sqrt{T^2 + 2m_0c^2T}}{c}$$

de Broglie wavelength of electron

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{T^2 + 2m_0c^2T}}$$

Given that $\lambda = \lambda_c = \frac{h}{m_0c}$

$$\frac{h}{m_0 c} = \frac{hc}{\sqrt{T^2 + 2m_0 c^2 T}}$$

$$T = -m_0 c^2 \pm \sqrt{2} m_0 c^2 \quad (- \text{ sign is meaningless})$$

$$T = m_0 c^2 (\sqrt{2} - 1) = (0.51 \text{ MeV})(0.414) = 0.21 \text{ MeV}.$$

Ex. 9. Find the de Broglie wavelength of relativistic electrons reaching the anticathode of an X-ray tube if the short wavelength limit of continuous X-ray spectrum is equal to $0.10 \text{ \AA}$.

Sol. Short wavelength limit of X-ray spectrum

$$\lambda_0 = \frac{hc}{\text{eV}} \quad \therefore \text{eV} = \frac{hc}{\lambda_0}$$

Kinetic energy of electron $T = \text{eV} = hc/\lambda_0$

$$\text{Momentum of electron } p = \frac{\sqrt{T(T + 2m_0 c^2)}}{c}$$

de Broglie wavelength of electron

$$\lambda = \frac{h}{p} = \frac{hc}{\sqrt{T(T + 2m_0 c^2)}}$$

$$\lambda = \frac{hc}{\sqrt{\frac{hc}{\lambda_0} \left(\frac{hc}{\lambda_0} + 2m_0 c^2 \right)}} = \frac{\lambda_0}{\sqrt{1 + \frac{(2m_0 c^2)\lambda_0}{hc}}}$$

For electron $m_0 c^2 = 0.51 \text{ MeV}$, $hc = 0.0124 \text{ MeV \AA}$.

$$\lambda = \frac{0.10 \text{ \AA}}{\sqrt{1 + \frac{1.02 \times 0.10}{0.0124}}} = 0.033 \text{ \AA}.$$

Ex. 10. Find the de Broglie wavelength of electron traveling along the first Bohr orbit in hydrogen atom.

Sol. The angular momentum of electron in the first Bohr orbit

$$mvr = \frac{nh}{2\pi}$$

$$\therefore mv = \frac{h}{2\pi r}$$

de Broglie wavelength of electron

$$\lambda = \frac{h}{mv} = 2\pi r = 2 \times 3.14 \times 0.53 \text{ Å} = 3.3 \text{ Å}.$$

Ex. 11. Describe the Bohr's quantum condition in terms of de Broglie wave.

Sol. A stationary Bohr orbit must accommodate whole number of de Broglie wavelengths. If r is the radius of electron orbit then

$$2\pi r = n\lambda \quad \dots(1)$$

According to de Broglie hypothesis

$$\lambda = \frac{h}{mv} \quad \dots(2)$$

Eliminating λ from these equations we have

$$2\pi r = \frac{nh}{mv}$$

$$\text{or} \quad mvr = \frac{nh}{2\pi}$$

which is the Bohr's quantum condition.

Ex. 12. An object has a speed of 10000 m/s accurate to 0.01%. With what fundamental accuracy can we locate its position if the object is (a) a bullet of mass of 0.05kg (b) an electron?

Sol. Momentum of bullet $p = mv = (0.05 \text{ kg})(1000 \text{ m/s}) = 50 \text{ kg m/s}$

Uncertainty in momentum $\Delta p = 50 \times 0.0001 = 5 \times 10^{-3} \text{ kg m/s}$

Minimum uncertainty in position

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.054 \times 10^{-34} \text{ Js}}{5 \times 10^{-3} \text{ kg m/s}} = 2.1 \times 10^{-31} \text{ m}$$

Momentum of electron

$$p = mv = (9.1 \times 10^{-31} \text{ kg})(1000 \text{ m/s}) = 9.1 \times 10^{-28} \text{ kg m/s}$$

Uncertainty in momentum

$$\Delta p = 9.1 \times 10^{-28} \times 0.0001 = 9.1 \times 10^{-32} \text{ kg m/s}$$

Uncertainty in position

$$\Delta x = \frac{\hbar}{\Delta p} = \frac{1.054 \times 10^{-34} \text{ Js}}{9.1 \times 10^{-32} \text{ kg m/s}} = 0.115 \text{ m}$$

The uncertainty in bullet's position is so small that it is far beyond the possibility of measurement. Thus, we see that for macroscopic objects like bullet, the uncertainty principle practically sets no limits to the measurement of conjugate dynamic variables position and momentum. For electron, the uncertainty in its position is very large, nearly 10^7 times the dimensions of atom. Thus for microscopic objects such as electrons, the uncertainty in their position is significant and cannot be overlooked.

Ex. 13. The position and momentum of 1 keV electrons are measured simultaneously. If its position is located within $1\text{\AA}$, what is the percentage uncertainty in its momentum? Is this consistent with the binding energy of electrons in atoms?

Sol. The uncertainty in position of electron

$$\Delta p \geq \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{10^{-10} \text{ m}} = 1.054 \times 10^{-24} \text{ kg m/s}$$

The momentum of electron inside the atom is at least equal to $p = 1.054 \times 10^{-24} \text{ kg m/s}$. The corresponding kinetic energy is

$$T = \frac{p^2}{2m} = \frac{(1.054 \times 10^{-24} \text{ kg m/s})^2}{2 \times 9.1 \times 10^{-31} \text{ kg}} = 0.061 \times 10^{-17} \text{ J} = 3.8 \text{ eV}$$

The ionization potential of atoms is of this order and hence the uncertainty in momentum is consistent with the binding energy of electrons in atoms.

Ex. 14. Imagine an electron to be somewhere in the nucleus whose dimension is 10^{-14} m . What is the uncertainty in momentum? Is this consistent with the binding energy of nuclear constituents?

Sol. If an electron were in the nucleus, its momentum would be uncertain by amount Δp given by

$$\Delta p \geq \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{10^{-14} \text{ m}} = 1.054 \times 10^{-20} \text{ kg m/s}$$

The momentum itself must be at least equal to $p = 1.54 \times 10^{-20} \text{ kg m/s}$. The corresponding kinetic energy of electron is many times greater than the rest energy $m_0 c^2$ of electron and therefore the kinetic energy of electron may be taken equal to pc .

$$T = pc = (1.054 \times 10^{-20} \text{ kg m/s})(3 \times 10^8 \text{ m/s}) = 3.3 \times 10^{-12} \text{ J} \\ = 20 \text{ MeV}$$

Experiments show that energy of electrons in nuclear disintegration (β decay) is very much less than 20 MeV. Hence the uncertainty principle rules out the possibility of electrons being a nuclear constituent.

Ex. 15. Consider a proton or neutron to be inside the nucleus. What is the uncertainty in momentum of electron? Is this consistent with the binding energy of nuclear constituents?

Sol. If a proton or neutron were inside the nucleus, the uncertainty in momentum would be

$$\Delta p \geq \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{10^{-14} \text{ m}} = 1.054 \times 10^{-20} \text{ kg m/s}$$

The corresponding kinetic energy $T \ll m_0 c^2$. Hence

$$T = \frac{p^2}{2m} = \frac{(1.054 \times 10^{-20} \text{ kg m/s})^2}{2 \times 1.67 \times 10^{-27} \text{ kg}} = 3.6 \times 10^{-14} \text{ J} = 0.23 \text{ MeV}$$

The binding energies of nuclei are of this order.

Ex. 16. The energy of a harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

where p is momentum and k is force constant. Using uncertainty principle, show that the minimum energy of the oscillator is $\hbar\omega_0$, where $\omega_0 = \sqrt{k/m}$.

Sol. According to uncertainty principle, $\Delta p \geq \frac{\hbar}{\Delta x}$. The momentum of oscillator is at least equal to p where $p = \hbar/x$. The energy of oscillator may be written as

$$E = \frac{\hbar^2}{2mx^2} + \frac{1}{2}kx^2 \quad \dots(1)$$

$$\text{For minimum energy } \frac{\partial E}{\partial x} = 0 = -\frac{\hbar^2}{mx^3} + kx \Rightarrow x^2 = \frac{\hbar}{\sqrt{mk}}$$

Substituting the value of x^2 in (1), we get

$$E = \hbar\sqrt{k/m} = \hbar\omega_0.$$

Ex. 17. A nucleus exists in excited state about 10^{-12} sec. What is uncertainty in energy of the gamma ray photon emitted by the nucleus?

Sol. The minimum uncertainty in energy is at least equal to ΔE , where

$$\Delta E \cdot \Delta t = \hbar$$

Therefore

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{1.054 \times 10^{-34} \text{ Js}}{10^{-12} \text{ s}} = 1.054 \times 10^{-22} \text{ J}.$$

Ex. 18. The average excited atom has a life-time of about 10^{-8} sec. During this period it emits a photon. What is the minimum uncertainty in the frequency of photon?

Sol. According to uncertainty principle

$$\Delta E \Delta t \geq \hbar$$

$$\hbar \Delta \omega \Delta t \geq \hbar$$

Minimum uncertainty in frequency of photon

$$\Delta \omega = \frac{1}{\Delta t} = 10^8 \text{ rad/s}.$$

Ex. 19. Making use of uncertainty principle give an estimate of radius and binding energy of electron in hydrogen atom in the ground state.

$$\text{Sol. Energy of electron } E = \frac{p^2}{2m} + \frac{-e^2}{4\pi\epsilon_0 r} \quad \dots(1)$$

Assuming that the uncertainties in momentum and energy are equal to the momentum and energy themselves, we can write the uncertainty principle as

$$pr = \hbar \quad \dots(2)$$

Eliminating p from these equations, we get

$$E = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad \dots(3)$$

In the ground state, energy is minimum. Therefore,

$$\frac{\partial E}{\partial r} = -\frac{2\hbar^2}{2mr^3} - \frac{e^2}{4\pi\epsilon_0 r^2} = 0$$

This gives
$$r = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \quad \dots(4)$$

This value of r , that is ground state radius of hydrogen atom, is called Bohr radius (a_0).

Substituting the value of r in (3) we get ground state energy of atom

$$E = -\frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^2}. \quad \dots(5)$$

QUESTIONS AND PROBLEMS

1. Give reasoning that led de Broglie to speculate the wave behavior of material particles. Derive de Broglie relation.
2. Show that the wavelength of an electron beam accelerated through a potential difference of V volt is
$$\lambda = \frac{12.3}{\sqrt{V(\text{volt})}} \text{ \AA}.$$
3. Describe Davisson-Germer experiment and interpret its results.
4. State and explain Heisenberg uncertainty principle. Use this principle to show that (i) electrons cannot reside inside the nucleus (ii) radius of the first orbit of hydrogen atom is $r = 4\pi\epsilon_0 \frac{\hbar^2}{me^2}$.
5. Show that the principle of indeterminacy can be expressed as $\Delta L \Delta \theta \geq \hbar$ where ΔL is uncertainty in angular momentum and $\Delta \theta$ is uncertainty in angular position of the particle under investigation.
6. (a) An electron beam of energy 100 eV is passed through a circular hole of radius 5×10^{-4} cm. What is the uncertainty introduced in the angle of emergence? (b) A lead ball of mass 200 gram is passed through a hole of radius 25 cm, calculate the uncertainty in the angle of emergence. The velocity of ball is 20 m/s.
7. According to uncertainty principle. A particle of momentum p cannot be confined by a central force to a circle of radius r less than $\hbar/p$. Assume that $pr = \hbar$, show that the total energy of electron in hydrogen atom is
$$E = \frac{\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$
 Show that for minimum value E , r has the value $r_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53 \text{ \AA}$ Bohr radius.
8. The accuracy in measurement of wavelength of photon is one part per million (i.e., $\Delta\lambda/\lambda = 10^{-6}$). What is the minimum uncertainty Δx in a simultaneous measurement of the position of the photon in the case of (a) a photon with $\lambda = 6000 \text{ \AA}$ and (b) an x-ray photon with $\lambda = 5 \text{ \AA}$.
9. The atoms in a solid possess a certain minimum zero-point energy even at 0 K. Using uncertainty principle, explain this statement.

SCHRÖDINGER EQUATION

3.1 INTRODUCTION

The laws governing the behaviour of microscopic systems are radically different from those of macroscopic systems. Our sensory organs can have direct perception of only macroscopic objects and the illustrative images of such objects are very useful in the description of behavior of macroscopic objects. But these images can no longer be transferred to the description of objects of micro-world. It is therefore best approach to discard from the very beginning any tendency to construct illustrative images of microscopic objects and the phenomena being studied. For example, the concept of electron being a negatively charged sphere performing orbital and spin motion is absolutely unrealistic. The quantum mechanics which, studies the behavior of objects of micro-world, employs abstract concepts and the entire structure of this system of mechanics is developed on few postulates. Werner Heisenberg and P.A.M. Dirac laid the foundation of abstract formalism of quantum mechanics. The mathematical language of quantum mechanics is very peculiar and the impossibility of visual representation and intricate mathematical language make quantum mechanics more difficult to understand.

The concept of **state** is the first basic thing on which the structure of quantum mechanics is built. In order to explain it, we may well take up an example of a simple system viz hydrogen atom in magnetic field. This system consists of a proton, an electron and the applied magnetic field. Each component of the system interacts with the other according to specific laws of interaction. There will be various possible motions of the constituents of the system consistent with the laws of interaction. Each such motion is called a state of the system. This state is denoted by a complex function ψ . All knowable information about the system can be derived from this function if we can obtain law describing the evolution of ψ with space and time coordinates.

The information about the state of a system is obtained by performing measurement *i.e.*, by making the system interact with an instrument (which is a macroscopic system). Consequently the results of the measurements performed on micro-system are necessarily expressed in terms of concepts developed for characterizing macroscopic objects (coordinates, momentum, energy, angular momentum etc.). These characteristics of the micro-system are called *dynamical variables* or *observables*. The abstract formalism of quantum mechanics is beyond the understanding of students for whom this book is intended. We, therefore, start with somewhat easier approach to quantum mechanics formulated by Erwin Schrödinger in 1926.

The wave like behaviour of material particles allows us to ascribe a wave associated with the moving particle, which can be called matter waves. The function describing the wave behavior of a moving particle is usually denoted by ψ and is analogous to the displacement function of mechanical waves or to the components of electric and magnetic fields of electromagnetic waves. The wave function of mechanical and electromagnetic waves of classical physics are the solution of the so-called *classical wave equation*

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} \quad \dots(3.1.1)$$

where the function ψ represents the displacement of the medium in case of mechanical waves and the components of electric and magnetic field in case of electromagnetic waves. It is natural to expect that the wave function describing the material particle be a solution of some kind of differential equation like Eqn. (3.1.1). It is well-known fact the wave equation for mechanical waves is derived from Newton's law of motion and the wave equation for electromagnetic waves is derived from Maxwell's electromagnetic field equations. Unfortunately there is no fundamental equation from which the wave equation for matter waves can be derived. It was Erwin Schrodinger who guessed the correct equation for matter waves. Schrödinger equation is a postulate in the same sense as the postulates of special theory of relativity and the laws of thermodynamics. None of these can be derived from other principle. This equation is a conjecture and it must stand or fall by the test of experiments. It has been found that the Schrodinger wave equation leads to the conclusions that are in complete agreement with experiments and therefore we may regard it as a valid postulate in the development of the story of quantum mechanics.

3.2 SCHRÖDINGER EQUATION

The wave function of a particle moving in x-direction is

$$\psi(x, t) = A e^{-i(\omega t - k_x x)} = A e^{i(k_x x - \omega t)} \quad \dots(3.2.1)$$

The wave attributes $k_x (= 2\pi/\lambda)$ and $\omega (= 2\pi\nu)$ are related to the particle attributes p_x and E as

$$p_x = \hbar k_x, \quad E = \hbar \omega \quad \dots(3.2.2)$$

In terms of p_x and E the wave function $\psi(x, t)$ can be expressed as

$$\psi(x, t) = A \exp \left\{ -i \left(\frac{Et}{\hbar} - \frac{p_x x}{\hbar} \right) \right\} \quad \dots(3.2.3)$$

From Eqn. (3.2.3)

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= -\frac{iE}{\hbar} \psi \\ i\hbar \frac{\partial \psi}{\partial t} &= E\psi \end{aligned} \quad \dots(3.2.4)$$

Similarly,

$$\begin{aligned}\frac{\partial \psi}{\partial x} &= \frac{ip_x}{\hbar} \psi \\ -i\hbar \frac{\partial \psi}{\partial x} &= p_x \psi\end{aligned}\quad \dots(3.2.5)$$

Differentiating Eqn. (3.2.5) again with respect to x , we have

$$\begin{aligned}-i\hbar \frac{\partial^2 \psi}{\partial x^2} &= p_x \frac{\partial \psi}{\partial x} = i \frac{p_x^2}{\hbar} \psi \\ -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} &= p_x^2 \psi\end{aligned}\quad \dots(3.2.6)$$

For a non-relativistic free particle the total energy E of the particle moving in x -direction is equal to its kinetic energy T .

$$E = T = \frac{p_x^2}{2m}$$

Multiplying both sides of above equation by ψ , we have

$$E\psi = \frac{p_x^2}{2m} \psi \quad \dots(3.2.7)$$

Making use of Eqns. (3.2.4) and (3.2.6) we can write Eqn. (3.2.7) as

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} \quad \dots(3.2.8)$$

This equation is known as *time-dependent Schrödinger for a free particle*.

If the particle is moving in a force field described by potential energy function V , its total energy is

$$E = \frac{p_x^2}{2m} + V(x)$$

and the Schrödinger equation is

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi} \quad \dots(3.2.9)$$

If the particle is free to in three dimensions, it is represented by wave function

$$\psi(x, y, z, t) = A \exp\left\{-i(\omega t - k_x x - k_y y - k_z z)\right\}$$

$$= A \exp \left\{ -\frac{i}{\hbar} (Et - p_x x - p_y y - p_z z) \right\} \quad \dots(3.2.10)$$

From Eqn. (3.2.10), we have

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi \quad \dots(3.2.11)$$

$$-i\hbar \frac{\partial \psi}{\partial x} = p_x \psi \quad \text{and} \quad -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = p_x^2 \psi \quad \dots(3.2.12)$$

$$-i\hbar \frac{\partial \psi}{\partial y} = p_y \psi \quad \text{and} \quad -\hbar^2 \frac{\partial^2 \psi}{\partial y^2} = p_y^2 \psi \quad \dots(3.2.13)$$

$$-i\hbar \frac{\partial \psi}{\partial z} = p_z \psi \quad \text{and} \quad -\hbar^2 \frac{\partial^2 \psi}{\partial z^2} = p_z^2 \psi \quad \dots(3.2.14)$$

Total energy of the particle is

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(x, y, z) \quad \dots(3.2.15)$$

Making use of Eqns. (3.2.11) and (3.2.12,13 and 14) we can write Eqn. (3.2.15) as

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V\psi$$

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

... (3.2.16)

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is Laplacian operator. Eqn. (3.2.16) is known as the **time-dependent**

Schrödinger equation of a particle in three dimensions.

Stationary state: Time-independent Schrödinger Equation: When the potential energy V is independent of time, the wave function $\psi(x, t)$ may be written as product of two wave functions, of which one is function of x and the other is function of t only.

$$\psi(x, t) = \psi(x)f(t) \quad \dots(3.2.17)$$

Substituting Eqn. (3.2.16) in (3.2.10) and dividing the resulting equation throughout by $\psi(x)f(t)$ we find

$$i\hbar \frac{1}{f(t)} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi}{dx^2} + V \quad \dots(3.2.18)$$

The left hand side of (3.2.18) is function of time t only and the right hand side is function of x only. Since x and t are independent of each other, this equality can hold only if each side is equal to the same constant. Each side has the dimensions of energy, so we write the separation constant as E . The separation constant E is number and represents the total energy of the particle. Therefore

$$i\hbar \frac{1}{f(t)} \frac{df}{dt} = E \quad \dots(3.2.19)$$

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{d^2\psi}{dx^2} + V = E \quad \dots(3.2.20)$$

Eqn. (3.2.19) can be expressed as

$$\frac{df}{dt} - \frac{E}{i\hbar} f = 0,$$

which integrates to

$$f(t) = C \exp\left(-\frac{iEt}{\hbar}\right) \quad \dots(3.2.21)$$

where C is constant of integration. A particle whose state is described by wave function

$$\psi(x, t) = \psi(x) \cdot e^{-iEt/\hbar}$$

is said to be in stationary state because its probability density $\Psi^*(x, t)\Psi(x, t)$ or $|\Psi(x, t)|^2$ is independent of time.

The time independent Schrödinger equation can be expressed as

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad \dots(3.2.22)$$

or

$$\boxed{\hat{H}\psi = E\psi} \quad \dots(3.2.23)$$

where

$$\hat{H} = \frac{\hat{p}^2}{2m} + V = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V$$

is *Hamiltonian operator*, an operator representing the total energy of the particle. Eqn. (3.2.22) can also be written as

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0} \quad \dots(3.2.24)$$

[For a system whose potential energy V is a function of coordinates only, the total energy remains constant with time i.e. E is conserved. For a conservative system, the classical mechanical Hamiltonian function turns out to be the total energy expressed in terms of coordinates and conjugate momenta.]

Eqn. (3.2.23) is an **eigen value equation**. Thus the time-independent Schrödinger wave equation is an *eigen value problem*.

The time-dependent Schrödinger equation can be written as

$$\hat{H}\psi(x, t) = \hat{E}\psi(x, t)$$

where
$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V} \quad \text{and} \quad \hat{E} = i\hbar \frac{\partial}{\partial t}.$$

3.3 PHYSICAL SIGNIFICANCE OF WAVE FUNCTION ψ

It is natural to ask the question regarding the physical significance of the wave function ψ . For a vibrating string, it represents the displacement of the string from equilibrium position; in case of electromagnetic waves it represents the electric or magnetic field at the point under consideration. But there is no physical quantity with which the wave function ψ of matter wave may be associated. Just as the concepts of electric and magnetic field are abstraction to explain the interaction between electrical charges, the concept of wave function ψ is an abstraction to describe the dynamics of microscopic particles. But such an interpretation of ψ is of little significance. In 1926 Max Born suggested a useful statistical interpretation of wave function, which was inspired by Einstein's concept of wave like behavior of particle like photons. According to Einstein the propagation of photon in space is described by Maxwell's equation involving electric field $E(x, y, z, t)$ and magnetic field $B(x, y, z, t)$. The magnitude of field E and B provides the probability of the location of the photon. In the region where E and B are large, the likelihood of finding the photon is also large and vice-versa. It is therefore reasonable to associate a probability function P with wave amplitude E . The probability function $P(x, y, z, t)$ expresses the likelihood of finding the photon and is related to the wave amplitude $E(x, y, z, t)$ as

$$P(x, y, z, t) = |E(x, y, z, t)|^2$$

According Born, the wave function $\psi(x, y, z, t)$ is analogous to the electric field E and Einstein's interpretation can be utilized to provide a physical meaning to the wave function associated with the material particles. *The probability of finding a particle at a point (x, y, z) at time t is given by $|\psi(x, y, z, t)|^2$ or $\psi\psi^*$ where ψ^* is complex conjugate of ψ . The probability of finding the particle in a volume element $dx dy dz$ centered around the point (x, y, z) is given by*

$$|\psi(x, y, z, t)|^2 dx dy dz \quad \text{or} \quad \psi\psi^* dx dy dz$$

Thus $|\psi|^2$ is **probability density** and ψ itself is called **probability amplitude**.

Since the probability of finding the particle somewhere in the universe is unity, we have

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi\psi^* dx dy dz = 1 \quad \dots(3.3.1)$$

The wave function, which satisfies the condition in Eqn. (3.3.1)), is said to be *normalized*.

The probabilistic interpretation of the wave function ψ asserts that the wave field generated by Schrödinger wave equation is a *probability field*. The microscopic entities retain their status as particles so far as the detecting devices are concerned but their distribution in space is governed by the wave field. The probability waves show all the characteristic properties of waves viz interference and diffraction in the same way as the waves of classical physics do.

Where do the probability waves come from? What mechanism generates them? These questions have no answers at present. Quantum physics as it now stands asserts the existence of probability waves. Richard Feynman, one of the principal contributors to the present day quantum electrodynamics has to say about the law of probability waves: “*one might still ask: how does it work? What is the machinery behind the law? No one has found any machinery behind the law. No one can explain any more than we have explained. No one will give any deeper representation of the situation. We have no idea about a more basic mechanism from which these results can be deduced.*”

3.4 INTERPRETATION OF WAVE FUNCTION ψ IN TERMS OF PROBABILITY CURRENT DENSITY

Consider a stream of particles moving in x -direction. Let ψ be the wave function of the particles in the beam. The product $\psi\psi^*$ represents the probability density of finding the particle at point x . In what follows we shall find relation between the probability density of the particles and the probability current density associated with the particle beam.

The time-dependent Schrödinger wave equation is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \quad \dots(3.4.1)$$

From this equation

$$\frac{\partial \psi}{\partial t} = -\frac{\hbar}{2mi} \nabla^2 \psi + \frac{V}{i\hbar} \psi \quad \dots(3.4.2)$$

The complex conjugate of above equation is

$$\frac{\partial \psi^*}{\partial t} = \frac{\hbar}{2mi} \nabla^2 \psi^* - \frac{V}{i\hbar} \psi^* \quad \dots(3.4.3)$$

Multiplying Eqn. (3.4.2) by ψ^* and Eqn. (3.4.3) by ψ and adding the resulting equations, we have

$$\begin{aligned} \psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} &= \frac{\hbar}{2mi} [\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi] \\ \frac{\partial (\psi^* \psi)}{\partial t} &= \frac{\hbar}{2mi} [\psi \nabla^2 \psi^* - \psi^* \nabla^2 \psi] \quad \dots(3.4.4) \end{aligned}$$

Making use of the vector identity

$$\nabla \cdot \phi \mathbf{A} = \nabla \phi \cdot \mathbf{A} + \phi \nabla \cdot \mathbf{A}$$

we have

$$\begin{aligned}
 \nabla \cdot (\psi^* \nabla \psi - \psi \nabla \psi^*) &= (\nabla \psi^* \cdot \nabla \psi + \psi^* \nabla^2 \psi) - \\
 &\quad (\nabla \psi \cdot \nabla \psi^* - \psi \nabla^2 \psi^*) \\
 &= \psi^* \nabla^2 \psi - \psi \nabla^2 \psi^*
 \end{aligned} \quad \dots(3.4.5)$$

In view of Eqn. (3.4.5) we can write Eqn. (3.4.4) as

$$\begin{aligned}
 \frac{\partial}{\partial t}(\psi^* \psi) &= \frac{\hbar}{2mi} \left[\nabla \cdot (\psi \nabla \psi^* - \psi^* \nabla \psi) \right] \\
 \frac{\partial}{\partial t}(\psi^* \psi) + \nabla \cdot \frac{\hbar}{2mi} (\psi^* \nabla \psi - \psi \nabla \psi^*) &= 0
 \end{aligned} \quad \dots(3.4.6)$$

This equation is similar to the equation of continuity in electrodynamics viz

$$\frac{\partial}{\partial t} \rho + \nabla \cdot \mathbf{J} = 0 \quad \dots(3.4.7)$$

where ρ is charge density and $\mathbf{J}$ is current density. A comparison of Eqns. (3.4.6) and (3.4.7) allows us to interpret $\psi^* \psi$ as probability density and $\frac{\hbar}{2mi}(\psi^* \nabla \psi - \psi \nabla \psi^*)$ as probability current density $\mathbf{J}$ where $\mathbf{J}$ represents the rate at which probability is streaming outward across a closed surface. The Cartesian components of $\mathbf{J}$ are

$$\begin{aligned}
 J_x &= \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right) \\
 J_y &= \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial y} - \psi \frac{\partial \psi^*}{\partial y} \right) \\
 J_z &= \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \psi^*}{\partial z} \right)
 \end{aligned}$$

For a beam of free particles moving in x -direction the wave function is

$$\psi = A \exp\{-i(Et - p_x x)/\hbar\}$$

$$\psi^* = A^* \exp\{i(Et - p_x x)/\hbar\}$$

and therefore the probability current density is given by

$$J_x = \frac{\hbar}{2mi} \left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right)$$

$$\begin{aligned}
&= \frac{p_x}{m} (\psi^* \psi) \\
&= \frac{p_x}{m} (A^* A) \\
&= v_x |A|^2
\end{aligned}$$

J_x represents the flux of particles (number of particles crossing per unit area per second). Recall that $|\psi|^2$ determines the probability density of finding a particle at a point where ψ is defined. The interpretation of ψ in terms of probability current density puts additional condition on ψ that it must have continuous and finite first derivative. It thus follows that

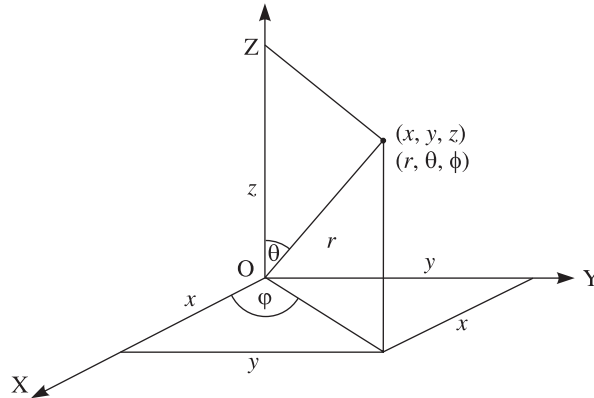
- (i) ψ must be finite and single valued.
- (ii) ψ and $\partial\psi/\partial x$ must be continuous, and
- (iii) ψ must be square integrable.

These conditions, which the wave function ψ must obey, are called the standard conditions and the wave function is said to be well behaved.

3.5 SCHRÖDINGER EQUATION IN SPHERICAL POLAR COORDINATES

In polar coordinates the Laplacian operator is expressed as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad \dots(3.5.1)$$



$$\{x = r \sin \theta \cos \phi, y = r \sin \theta \sin \phi, z = r \cos \theta, r^2 = x^2 + y^2 + z^2, \tan \phi = y/x\}$$

Fig. 3.5.1 Relationship between Cartesian and polar coordinates

The relationship between Cartesian coordinates and spherical polar coordinates is defined in the Fig. (3.5.1). The Schrodinger equation in spherical polar coordinates is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(3.5.2)$$

If the wave function ψ depends only on radial distance r then the Laplacian operator simplifies to

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$$

and the Schrodinger wave equation assumes the simple form

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \psi(r) + \frac{2m}{\hbar^2} (E - V(r)) \psi(r) = 0. \quad \dots(3.5.3)$$

3.6 OPERATORS IN QUANTUM MECHANICS

An operator is a rule or an instruction which transforms a function into another function. Linear operators play a very important role in quantum mechanics. If $\hat{Q}$ is an operator and $f(x)$ is an arbitrary function then the action of $\hat{Q}$ on $f(x)$ is represented as

$$\hat{Q}f(x) = \lambda g(x) \quad \dots(3.6.1)$$

where $g(x)$ is another function and λ is constant. A linear operator is one which satisfies the following two conditions:

$$\hat{Q}(f_1 + f_2 + \dots) = \hat{Q}f_1 + \hat{Q}f_2 + \dots \quad \dots(3.6.2)$$

$$\hat{Q}(cf) = c\hat{Q}f, \text{ where } c \text{ is an arbitrary constant.} \quad \dots(3.6.3)$$

A physically measurable property of a system is called an **observable (dynamical variable)**. Energy, momentum, angular momentum and position coordinates are examples of observables. In quantum mechanics every observable is represented by a linear operator.

Algebra of Operators

(i) The sum and difference of two operators $\hat{P}$ and $\hat{Q}$ are defined by equations

$$(\hat{P} + \hat{Q})f(x) = \hat{P}f(x) + \hat{Q}f(x)$$

$$(\hat{P} - \hat{Q})f(x) = \hat{P}f(x) - \hat{Q}f(x)$$

(ii) The product of two operators $\hat{P}$ and $\hat{Q}$ is defined by equations

$$\hat{P}\hat{Q}f(x) = \hat{P}[\hat{Q}f(x)]$$

In above equation, we first operate on $f(x)$ with the operator on the right of the operator product and then we take the resulting function and operate on it with the operator on the left of the operator product.

(iii) Two operators are said to be equal if

$$\hat{P}f(x) = \hat{Q}f(x).$$

(iv) The operator $\hat{1}$ (multiplication by 1) is the unit operator.

(v) The operator $\hat{0}$ (multiplication by 0) is the null operator.

(vi) The square of an operator is defined as the product of the operator with itself.

$$\hat{Q}^2 = \hat{Q}\hat{Q}$$

The n th power of an operator is defined to mean applying the operator n times in succession.

(vii) Operators obey associative law of multiplication.

$$\hat{P}(\hat{Q}\hat{R}) = (\hat{P}\hat{Q})\hat{R}$$

An important difference between operator algebra and ordinary algebra is that numbers obey commutative law of multiplication but operators do not necessarily do so. That is $\hat{P}\hat{Q}$ and $\hat{Q}\hat{P}$ are not necessarily equal operators.

(viii) We define the *commutator* $[\hat{P}, \hat{Q}]$ of operator $\hat{P}$ and $\hat{Q}$ as operator $\hat{P}\hat{Q} - \hat{Q}\hat{P}$.

$$[\hat{P}, \hat{Q}] = \hat{P}\hat{Q} - \hat{Q}\hat{P}$$

If $\hat{P}\hat{Q} = \hat{Q}\hat{P}$ then $[\hat{P}, \hat{Q}] = 0$ and we say that $\hat{P}$ and $\hat{Q}$ *commute*.

Operators of Some Dynamical Variables: The wave function of a free particle moving in three dimensional space is

$$\psi(x, y, z, t) = A \exp \left\{ -\frac{i}{\hbar} (Et - p_x x - p_y y - p_z z) \right\} \quad \dots(3.6.4)$$

Partial derivative of ψ with respect to x is

$$\frac{\partial \psi}{\partial x} = \frac{i}{\hbar} p_x \psi \quad \text{or} \quad -i\hbar \frac{\partial \psi}{\partial x} = p_x \psi$$

$$-i\hbar \frac{\partial \psi}{\partial y} = p_y \psi$$

$$-i\hbar \frac{\partial \psi}{\partial z} = p_z \psi$$

Similarly,

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi$$

...(3.6.5)

A close look at the above equations reveals that the dynamical variables p_x, p_y, p_z and E are in some sense related to the differential operators $-i\hbar \frac{\partial}{\partial x}, -i\hbar \frac{\partial}{\partial y}, -i\hbar \frac{\partial}{\partial z}$, and $i\hbar \frac{\partial}{\partial t}$ respectively. These symbols instruct what operation is to be carried out on the functions that follow. The operators of position coordinates x, y, z are the variables themselves. Similarly the operator of position dependent potential energy $V(x, y, z)$ is $V(x, y, z)$ itself. For convenience we rewrite the dynamical variables and their corresponding operators in tabular form.

<i>Dynamical Variables</i>	<i>Operators</i>
p_x	$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$
p_y	$\hat{p}_y = -i\hbar \frac{\partial}{\partial y}$
p_z	$\hat{p}_z = -i\hbar \frac{\partial}{\partial z}$
p	$\hat{p} = -i\hbar \nabla$
E	$\hat{E} = i\hbar \frac{\partial}{\partial t}$
Kinetic energy $T = \frac{p^2}{2m}$	$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$

The Hamiltonian (total energy) function of a mechanical system is given by

$$H = \frac{p^2}{2m} + V$$

and the corresponding operator is

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \quad \dots(3.6.6)$$

For a conservative system the total energy is represented by Hamiltonian function H expressed in terms of position coordinates and conjugate momenta. Therefore energy operator is Hamiltonian

operator $\hat{H} \rightarrow -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}$ and not $i\hbar \frac{\partial}{\partial t}$. Time is not an observable, but it is a parameter in quantum

mechanics. Hence there is no operator for time.

In view of Eqn. (3.6.5), the time independent Schrödinger equation can be written as

$$\hat{H}\psi = E\psi$$

or

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi}$$

which is an eigen value equation.

Angular momentum operator: In classical mechanics the angular momentum of a particle is given by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$\Rightarrow \quad L_x = yp_z - zp_y, L_y = zp_x - xp_z, L_z = xp_y - yp_x$$

The operators corresponding to these variables are

$$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad \dots(3.6.7)$$

$$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad \dots(3.6.8)$$

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad \dots(3.6.9)$$

Notice the kind of symmetry in the expression for operator $\hat{L}_x$. By carrying a cyclic permutation of x, y, z (*i.e.*, replacing x by y , y by z and z by x) we can get operator of $\hat{L}_y$ and $\hat{L}_z$.

In problems having spherical symmetry it is useful to express these operators in spherical coordinates, which are defined in the Figure 3.6.1. The relationships between the Cartesian and the polar coordinates are

$$x = r \sin \theta \cos \varphi \quad \dots(3.6.10)$$

$$y = r \sin \theta \sin \varphi \quad \dots(3.6.11)$$

$$z = r \cos \theta \quad \dots(3.6.12)$$

$$r^2 = x^2 + y^2 + z^2 \quad \dots(3.6.13)$$

$$\tan \varphi = y/x \quad \dots(3.6.14)$$

$$\tan^2 \theta = \frac{x^2 + y^2}{z^2} \quad \dots(3.6.15)$$

$$\cos \theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}} \quad \dots(3.6.16)$$

From Eqn. (3.6.13)

$$\frac{\partial r}{\partial x} = \frac{x}{r} = \sin \theta \cos \varphi \quad \dots(3.6.17)$$

$$\frac{\partial r}{\partial y} = \frac{y}{r} = \sin \theta \sin \varphi \quad \dots(3.6.18)$$

$$\frac{\partial r}{\partial z} = \frac{z}{r} = \cos \theta \quad \dots(3.6.19)$$

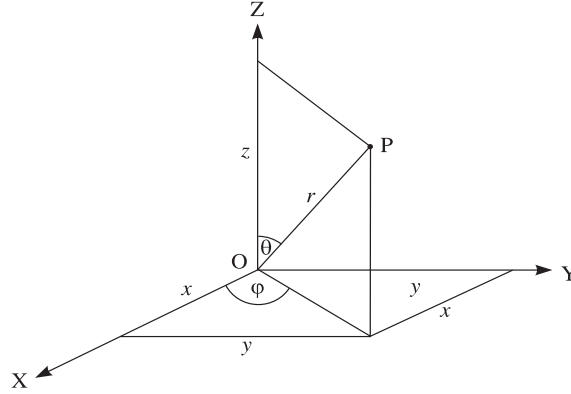


Fig. 3.6.1

Differentiating Eqn. (3.6.15) w.r.t. x , we have

$$2 \tan \theta \sec^2 \theta \frac{\partial \theta}{\partial x} = \frac{2x}{z^2} = \frac{2r \sin \theta \cos \phi}{r^2 \cos^2 \theta}$$

$$\therefore \frac{\partial \theta}{\partial x} = \frac{\cos \theta \cos \phi}{r} \quad \dots(3.6.20)$$

Similarly, $\frac{\partial \theta}{\partial y} = \frac{\cos \theta \sin \phi}{r}, \quad \frac{\partial \theta}{\partial z} = -\frac{\sin \theta}{r}$

Differentiating Eqn. (3.6.14) w.r.t. x , we have

$$\sec^2 \phi \frac{\partial \phi}{\partial x} = -\frac{y}{x^2} = -\frac{r \sin \theta \sin \phi}{r^2 \sin^2 \theta \cos^2 \phi}$$

$$\therefore \frac{\partial \phi}{\partial x} = -\frac{\sin \phi}{r \sin \theta} \quad \dots(3.6.21)$$

Similarly, $\frac{\partial \phi}{\partial y} = \frac{\cos^2 \phi}{r}, \quad \frac{\partial \phi}{\partial z} = 0$

Now

$$\begin{aligned} \frac{\partial \psi}{\partial x} &= \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} + \frac{\partial \psi}{\partial \theta} \frac{\partial \theta}{\partial x} + \frac{\partial \psi}{\partial \phi} \frac{\partial \phi}{\partial x} \\ &= \frac{\partial \psi}{\partial r} \sin \theta \cos \phi + \frac{\partial \psi}{\partial \theta} \frac{\cos \theta \cos \phi}{r} - \frac{\partial \psi}{\partial \phi} \frac{\sin \phi}{r \sin \theta} \end{aligned}$$

$$\therefore \frac{\partial}{\partial x} = \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \quad \dots(3.6.22)$$

Similarly,
$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial y} \frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial y} = \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\cos \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \quad \dots(3.6.23)$$

and

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z} \frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial z} \frac{\partial}{\partial \varphi}$$

$$\frac{\partial}{\partial z} = \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} \quad \dots(3.6.24)$$

Making use of above results we can write the operators corresponding to the Cartesian components of angular momentum.

$$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = -i\hbar \left[r \sin \theta \cos \varphi \left\{ \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \sin \varphi}{r} \frac{\partial}{\partial \theta} + \frac{\cos \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right\} - \right. \\ \left. r \sin \theta \sin \varphi \left\{ \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{\cos \theta \cos \varphi}{r} \frac{\partial}{\partial \theta} - \frac{\sin \varphi}{r \sin \theta} \frac{\partial}{\partial \varphi} \right\} \right]$$

$$= -i\hbar \frac{\partial}{\partial \varphi} \quad \dots(3.6.25)$$

Similarly,
$$\hat{L}_x = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad \dots(3.6.26)$$

$$\hat{L}_y = -i\hbar \left(\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad \dots(3.6.27)$$

Making use of the definitions

$$\hat{L}_x^2 = \hat{L}_x \hat{L}_x \quad \text{and} \quad \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

we can find $\hat{L}_z^2$

$$\hat{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial \varphi^2} \quad \dots(3.6.28)$$

$$\text{and} \quad \hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(3.6.29)$$

3.7 EIGEN VALUE EQUATION

In general, each physical quantity is represented by a linear operator and for each operator one can set up an equation of the type

$$\hat{Q}u_q = qu_q \quad \dots(3.7.1)$$

i.e., the effect of the operator is to multiply the function u_q by a constant factor q . Eqn. (3.7.1) is an **eigen value equation**. The solutions of above equation satisfying the set of conditions can be found not for all values but only for selected values of the parameter q . These special values of the parameter q are called the **eigen (characteristic) values** of the operator $\hat{Q}$ and the functions u_q , which satisfy the above equation, are called the **eigen (characteristic) functions** of the operator.

When a system is in an eigenstate u_q of $\hat{Q}$, the dynamical variable Q has a definite value equal to the eigen value q . That is, the uncertainty in the value of Q is zero if the system is in one of the eigen states of $\hat{Q}$ and the physical quantity Q is said to be quantized. The meaning of Eqn. (3.7.1) is that if the system is in the eigen state u_q , the measurement of the quantity Q will yield only one number q . The set of all eigen values of $\hat{Q}$ forms a spectrum, called eigen value spectrum. The spectrum may be discrete or continuous or partly discrete and partly continuous. If there exists only one eigen function belonging to a given eigen value, the eigen value is said to be **non-degenerate**. It may happen that several eigen functions may belong to a single eigen value. Then this eigen value is said to be degenerate. If u_q and v_q belong to the same eigen value q , then their linear combination $c_1u_q + c_2v_q$, for all values of c_1 and c_2 , is also an eigen function belonging to the same eigen value.

$$\hat{Q}(c_1u_q + c_2v_q) = c_1\hat{Q}u_q + c_2\hat{Q}v_q = q(c_1u_q + c_2v_q) \quad \dots(3.7.2)$$

Thus a degenerate eigen value corresponds to an infinite number of eigen functions. The totality of eigen functions belonging to a degenerate eigen value forms a linear space, called *eigen-space*. The set of all eigen functions belonging to a given degenerate eigen value is closed under linear combination. This implies that any linear combination of members of the set is also a member of the set. Not all the members of the set are linearly independent. From the members of the set of eigen functions, it is always possible to choose a subset of linearly independent eigen functions, say $u_{q1}, u_{q2}, \dots, u_{qr}$ such that any eigen function belonging to the eigen value q can be expressed uniquely as a linear combination of the type $(c_1u_{q1} + c_2u_{q2} + \dots + c_ru_{qr})$ with suitable coefficients $c_1, c_2, \dots, c_r$. The set of independent functions $u_{q1}, u_{q2}, \dots, u_{qr}$ is said to span the linear space and this set of functions is said to form the basis functions of the space. The number r is characteristic of the space. This means that out of infinite number of eigen functions belonging to a given degenerate eigen value there exists only a definite number, say r , of linearly independent functions. This number r is called the **degree of degeneracy** and the eigen value is said to be **r -fold degenerate**.

If the system is an arbitrary state ψ (*i.e.*, ψ is not an eigen function), and the measurement of physical quantity Q is made on a large number of identical systems (*i.e.*, all in the same state), the result is not a fixed value but the outcome has a range of values whose **average value** (also called **expectation value**) is given by

$$\langle q \rangle = \int \psi^* \hat{Q} \psi d\tau \quad \dots(3.7.3)$$

where ψ is normalized wave function of the state.

The foregoing discussion may be illustrated with an example. The eigen value equation for a free particle is

$$\begin{aligned} \hat{H}\psi &= E\psi \\ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} &= E\psi \\ \frac{d^2\psi}{dx^2} + k^2\psi &= 0, \quad k^2 = \frac{2mE}{\hbar^2} \end{aligned} \quad \dots(3.7.4)$$

The linearly independent solutions of Eqn. (3.7.4) are $\psi_1 = e^{ikx}$ and $\psi_2 = e^{-ikx}$. So the eigen value E is two-fold degenerate and the ψ_1 and ψ_2 are the basis functions. The following linear combinations of ψ_1 and ψ_2 are also the eigen functions of the operator $\hat{H}$.

$$\frac{e^{ikx} + e^{-ikx}}{2} = \cos kx, \quad \frac{e^{ikx} - e^{-ikx}}{2i} = \sin kx.$$

3.8 ORTHOGONALITY OF EIGEN FUNCTIONS

Two eigen functions ψ_m and ψ_n belonging to different eigen values ϵ_m and ϵ_n are said to be orthogonal if they satisfy the relation

$$\int \psi_m^* \psi_n d\tau = 0 \quad \dots(3.8.1)$$

The time-independent Schrödinger wave equation $\hat{H}\psi = \epsilon\psi$ is an eigen value equation. We shall show that the eigen functions of Hamiltonian operator are orthogonal.

The Schrödinger equation is

$$\frac{d^2\psi_m}{dx^2} + \frac{2m}{\hbar^2}(\epsilon_m - V)\psi_m = 0 \quad \dots(3.8.2)$$

The complex conjugate of Eqn. (3.8.2) is

$$\frac{d^2\psi_m^*}{dx^2} + \frac{2m}{\hbar^2}(\epsilon_m - V)\psi_m^* = 0 \quad \dots(3.8.3)$$

Schrodinger equation for the state ψ_n is

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}(\epsilon_n - V)\psi_n = 0 \quad \dots(3.8.4)$$

Multiplying Eqn. (3.8.3) by ψ_n and Eqn. (3.8.4) by ψ_m^* and subtracting and then integrating, we get

$$\int \left[\psi_m^* \frac{d^2\psi_n}{dx^2} - \psi_n \frac{d^2\psi_m^*}{dx^2} \right] dx + \frac{2m}{\hbar^2}(\epsilon_n - \epsilon_m) \int \psi_m^* \psi_n dx = 0$$

The quantity in the square bracket in the first term is derivative of $\{\psi_m^* d\psi_n/dx - \psi_n d\psi_m^*/dx\}$ with respect to x . Thus

$$\begin{aligned} \int_{-\infty}^{\infty} \frac{d}{dx} \left[\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right] dx &= \frac{2m}{\hbar^2}(\epsilon_m - \epsilon_n) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \\ \left[\psi_m^* \frac{d\psi_n}{dx} - \psi_n \frac{d\psi_m^*}{dx} \right]_{-\infty}^{\infty} &= \frac{2m}{\hbar^2}(\epsilon_m - \epsilon_n) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx \end{aligned}$$

Physically well-behaved wave function ψ and its derivative must vanish as $x \rightarrow \pm \infty$. So the left hand side vanishes at both the limits. Therefore

$$(\epsilon_m - \epsilon_n) \int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0$$

Since $\epsilon_m \neq \epsilon_n$, we have

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n dx = 0 \quad \dots(3.8.5)$$

Thus the eigen function belonging to different eigen values are orthogonal. The normalization condition for wave function $\psi(x)$ is

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1 \quad \dots(3.8.6)$$

The properties of wave function expressed by Eqns. (3.8.5) and (3.8.6) can be expressed by a single equation as

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n d\tau = \delta_{mn} \quad \dots(3.8.7)$$

where δ_{mn} is kronecker delta having the properties

$$\begin{aligned} \delta_{mn} &= 0 \text{ for } m \neq n \\ &= 1 \text{ for } m = n \end{aligned}$$

The property of wave function expressed by Eqn. (3.8.7) is known as *orthonormality* of wave function.

It should be noted that the orthonormality of eigen functions is not restricted to the eigen functions of Hamiltonian operator. In fact the wave functions of all *hermitian operators* satisfy the orthonormality condition.

3.9 COMPATIBLE AND INCOMPATIBLE OBSERVABLES

Two observables which can be measured simultaneously and precisely without influencing each other are called **compatible**. The operators of such observables commute *i.e.*, $[\hat{P}, \hat{Q}] = 0$. On the other hand, two observables are such that the determination of one observable introduces an uncertainty in the other, they are called **incompatible**. The operators of incompatible observables do not commute. That is, $[\hat{P}, \hat{Q}] \neq 0$.

Assume that two physical quantities Q and R can simultaneously have definite values when the system is in a common state ψ_n . The wave function ψ_n of the state in which the quantity Q has a value q_n and the quantity R, the value r_n , must satisfy following two equations simultaneously.

$$\hat{Q}\psi_n = q_n\psi_n \quad \dots(3.9.1)$$

$$\hat{R}\psi_n = r_n\psi_n \quad \dots(3.9.2)$$

The product of operators is determined by the condition

$$\Pi\psi_n = (\hat{Q}\hat{R})\psi_n = \hat{Q}(\hat{R}\psi_n) = q_n r_n \psi_n \quad \dots(3.9.3)$$

Making use of Eqns. (3.9.1) and (3.9.2), we find that

$$(\hat{R}\hat{Q})\psi_n = \hat{R}(\hat{Q}\psi_n) = \hat{R}(q_n\psi_n) = r_n q_n \psi_n \quad \dots(3.9.4)$$

From Eqns. (3.9.3) and (3.9.4), we see that

$$\Pi = \hat{Q}\hat{R} = \hat{R}\hat{Q} \quad \dots(3.9.5)$$

$$\hat{Q}\hat{R} - \hat{R}\hat{Q} = 0. \quad \dots(3.9.6)$$

Thus **if two quantities can simultaneously have definite values then (i) their operators have common eigen functions and (ii) their operators commute.**

In general, the product of operators is non-commuting *i.e.*,

$$\hat{Q}\hat{R} \neq \hat{R}\hat{Q}$$

This can be verified taking the example of the operators

$$\hat{Q} = \frac{\partial}{\partial x} \quad \text{and} \quad \hat{R} = x$$

$$(\hat{Q}\hat{R})\psi = \frac{\partial}{\partial x}(x\psi) = x \frac{\partial \psi}{\partial x} + \psi$$

$$(\hat{R}\hat{Q})\psi = x \frac{\partial \psi}{\partial x}$$

Operators $\hat{Q}$ and $\hat{R}$ for which the condition

$$\hat{Q}\hat{R} = \hat{R}\hat{Q} \quad \dots(3.9.7)$$

is observed are said to be *commutative operators*. If the condition Eqn. (3.9.7) is not observed, the operators are said to be non-commutative. Operators, which satisfy the condition

$$\hat{Q}\hat{R} = -\hat{R}\hat{Q} \quad \dots(3.9.8)$$

are called *anticommutative operators*.

3.10 COMMUTATOR

The operator $\hat{Q}\hat{R} - \hat{R}\hat{Q}$ formed from the operators $\hat{Q}$ and $\hat{R}$ is called the **commutator** of the given operators and is designated by the symbol $[\hat{Q}, \hat{R}]$ i.e.,

$$[\hat{Q}, \hat{R}] = \hat{Q}\hat{R} - \hat{R}\hat{Q} \quad \dots(3.10.1)$$

The commutator of commuting operators is zero.

Commutation relations: Linear operators obey following commutations rules:

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}]$$

Some commutation relations of quantum mechanical operators:

$$1. [\hat{x}, \hat{y}] = [\hat{y}, \hat{z}] = [\hat{z}, \hat{x}] = 0$$

$$[\hat{x}, \hat{y}] = \hat{x}\hat{y} - \hat{y}\hat{x} = xy - yx = 0$$

$$2. [\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$$

$$[\hat{x}, \hat{p}_x]\psi = (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi = -i\hbar \left(x \frac{\partial \psi}{\partial x} - \frac{\partial(x\psi)}{\partial x} \right)$$

$$= -i\hbar \left(x \frac{\partial \psi}{\partial x} - \psi - x \frac{\partial \psi}{\partial x} \right) = i\hbar \psi$$

$$3. [\hat{x}, \hat{p}_y] = [\hat{y}, \hat{p}_z] = [\hat{z}, \hat{p}_x] = 0$$

$$\begin{aligned} [\hat{x}, \hat{p}_y]\psi &= (\hat{x}\hat{p}_y - \hat{p}_y\hat{x})\psi = -i\hbar \left(x \frac{\partial \psi}{\partial y} - \frac{\partial (x\psi)}{\partial y} \right) \\ &= -i\hbar \left(x \frac{\partial \psi}{\partial y} - x \frac{\partial \psi}{\partial y} \right) = 0 \end{aligned}$$

$$4. [\hat{p}_x, \hat{p}_y] = [\hat{p}_y, \hat{p}_z] = [\hat{p}_z, \hat{p}_x] = 0$$

$$[\hat{p}_x, \hat{p}_y]\psi = (\hat{p}_x\hat{p}_y - \hat{p}_y\hat{p}_x)\psi = (-i\hbar)^2 \left(\frac{\partial}{\partial x} \frac{\partial \psi}{\partial y} - \frac{\partial}{\partial y} \frac{\partial \psi}{\partial x} \right) = 0$$

$$5. [\hat{H}, \hat{p}] = 0$$

$$\begin{aligned} [\hat{H}, \hat{p}]\psi &= (\hat{H}\hat{p} - \hat{p}\hat{H})\psi \\ &= \left\{ \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \left(-i\hbar \frac{\partial}{\partial x} \right) + i\hbar \frac{\partial}{\partial x} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \right\} \psi \\ &= i \frac{\hbar^3}{2m} \left(\frac{\partial^3 \psi}{\partial x^3} - \frac{\partial^3 \psi}{\partial x^3} \right) = 0 \end{aligned}$$

$$6. [\hat{L}_x, \hat{x}] = 0, [\hat{L}_y, \hat{y}] = 0, [\hat{L}_z, \hat{z}] = 0$$

$$\begin{aligned} [\hat{L}_x, \hat{x}]\psi &= (\hat{L}_x\hat{x} - \hat{x}\hat{L}_x)\psi = -i\hbar \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) x\psi - x \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi \right\} \\ &= 0 \end{aligned}$$

Inspection of above formulas shows that a component of the angular momentum and the corresponding coordinate can have simultaneously definite values.

$$7. [\hat{L}_x, \hat{y}] = i\hbar z, [\hat{L}_y, \hat{z}] = i\hbar x, [\hat{L}_z, \hat{x}] = i\hbar y$$

$$\begin{aligned} [\hat{L}_x, \hat{y}]\psi &= (\hat{L}_x\hat{y} - \hat{y}\hat{L}_x)\psi \\ &= -i\hbar \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) (y\psi) - y \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi \right\} \end{aligned}$$

$$\begin{aligned}
&= -i\hbar \left\{ y^2 \frac{\partial \psi}{\partial z} - zy \frac{\partial \psi}{\partial y} - z\psi - y^2 \frac{\partial \psi}{\partial z} + yz \frac{\partial \psi}{\partial y} \right\} \\
&= i\hbar z \psi
\end{aligned}$$

Inspection of these formulas shows that the component L_x and the coordinate y (or z) cannot be determined simultaneously. The same holds for L_y and the coordinate z (or x), and also for L_z and the coordinate x (or y).

8. $[\hat{L}_x, \hat{p}_x] = 0$, similar results hold for other similar commutators.

$$\begin{aligned}
[\hat{L}_x, \hat{p}_x]\psi &= (\hat{L}_x \hat{p}_x - \hat{p}_x \hat{L}_x)\psi \\
&= (-i\hbar)^2 \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x} \left(y \frac{\partial \psi}{\partial z} - z \frac{\partial \psi}{\partial y} \right) \right\} = 0
\end{aligned}$$

9. $[\hat{L}_x, \hat{p}_y] = i\hbar \hat{p}_z$ similar results hold for other components.

$$\begin{aligned}
[\hat{L}_x, \hat{p}_y]\psi &= (\hat{L}_x \hat{p}_y - \hat{p}_y \hat{L}_x)\psi \\
&= (-i\hbar)^2 \left\{ \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \frac{\partial \psi}{\partial y} - \frac{\partial}{\partial y} \left(y \frac{\partial \psi}{\partial z} - z \frac{\partial \psi}{\partial y} \right) \right\} \\
&= (-i\hbar)^2 \left\{ y \frac{\partial^2 \psi}{\partial y \partial z} - z \frac{\partial^2 \psi}{\partial y^2} - y \frac{\partial^2 \psi}{\partial z \partial y} - \frac{\partial \psi}{\partial z} + z \frac{\partial^2 \psi}{\partial y^2} \right\} \\
&= (-i\hbar)^2 \left(-\frac{\partial \psi}{\partial z} \right) \\
&= i\hbar \left(-i\hbar \frac{\partial \psi}{\partial z} \right) \\
&= i\hbar \hat{p}_z \psi.
\end{aligned}$$

10. $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$, $[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$, $[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$

$$\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = \hat{L}_x (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) - (\hat{z} \hat{p}_x - \hat{x} \hat{p}_z) \hat{L}_x \\
&= \hat{L}_x \hat{z} \hat{p}_x - \hat{L}_x \hat{x} \hat{p}_z - \hat{z} \hat{p}_x \hat{L}_x + \hat{x} \hat{p}_z \hat{L}_x
\end{aligned}$$

Since $\hat{L}_x$ commutes both with $\hat{x}$ and $\hat{p}_x$ we can interchange the operators $\hat{L}_x$ and $\hat{x}$ in the second term and also the operators $\hat{p}_x$ and $\hat{L}_x$ in the third term. The result is

$$[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{z} \hat{p}_x - \hat{x} \hat{L}_x \hat{p}_z - \hat{z} \hat{L}_x \hat{p}_x + \hat{x} \hat{p}_z \hat{L}_x$$

Let us combine the first term with the third one and the second term with the fourth one. Thus

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= (\hat{L}_x \hat{z} - \hat{z} \hat{L}_x) \hat{p}_x - \hat{x} (\hat{L}_x \hat{p}_z - \hat{p}_z \hat{L}_x) \\ &= (i\hbar y) \hat{p}_x - \hat{x} (i\hbar \hat{p}_y) \\ &= i\hbar (\hat{y} \hat{p}_x - \hat{x} \hat{p}_y) \\ &= i\hbar \hat{L}_z \end{aligned}$$

By carrying out two successive cyclic permutations on $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$, we can get the remaining two results.

$$11. [\hat{L}^2, \hat{L}_x] = 0, [\hat{L}^2, \hat{L}_y] = 0, [\hat{L}^2, \hat{L}_z] = 0$$

$$\begin{aligned} [\hat{L}^2, \hat{L}_x] &= (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \hat{L}_x - \hat{L}_x (\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2) \\ &= \hat{L}_x^3 + \hat{L}_y^2 \hat{L}_x + \hat{L}_z^2 \hat{L}_x - \hat{L}_x^3 - \hat{L}_x \hat{L}_y^2 - \hat{L}_x \hat{L}_z^2 \end{aligned}$$

Using the commutation relations $\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = i\hbar \hat{L}_z$, we transform the second and fifth term as follows:

$$\begin{aligned} \hat{L}_y^2 \hat{L}_x - \hat{L}_x \hat{L}_y^2 &= \hat{L}_y \hat{L}_y \hat{L}_x - \hat{L}_x \hat{L}_y \hat{L}_y \\ &= \hat{L}_y (\hat{L}_x \hat{L}_y - i\hbar \hat{L}_z) - (\hat{L}_y \hat{L}_x + i\hbar \hat{L}_z) \hat{L}_y \\ &= -i\hbar (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y) \end{aligned}$$

Using the relation $\hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z = i\hbar \hat{L}_y$, we can perform a similar transformation of the third and sixth terms:

$$\begin{aligned} \hat{L}_z^2 \hat{L}_x - \hat{L}_x \hat{L}_z^2 &= \hat{L}_z \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z \hat{L}_z \\ &= \hat{L}_z (\hat{L}_x \hat{L}_z + i\hbar \hat{L}_y) - (\hat{L}_z \hat{L}_x - i\hbar \hat{L}_y) \hat{L}_z \\ &= i\hbar (\hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z) \end{aligned}$$

Making use of these transformations, we get

$$[\hat{L}^2, \hat{L}_x] = 0$$

We conclude that only the square of the vector L and one of its projections onto the coordinate axes can be determined simultaneously. The other two projections are indeterminate (except when all three components are zero). Consequently, all that we can know about the vector L is its “length” and the angle it makes with a certain axis. The direction of the vector L , however, does not lend itself to determination. The operators, which commute, can have simultaneous eigen states.

3.11 COMMUTATION RELATIONS FOR LADDER OPERATORS

The ladder operators $\hat{L}_+$ and $\hat{L}_-$ are defined by

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad \dots(3.11.1)$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y \quad \dots(3.11.2)$$

$\hat{L}_+$ and $\hat{L}_-$ are also called raising and lowering operators respectively. The adjoint of $\hat{L}_+$ is $\hat{L}_-$ and that of $\hat{L}_-$ is $\hat{L}_+$.

$$\hat{L}_+^\dagger = \hat{L}_-, \hat{L}_-^\dagger = \hat{L}_+ \quad \dots(3.11.3)$$

The commutation relations for $\hat{L}_+$ and $\hat{L}_-$ are:

$$[\hat{L}_z, \hat{L}_+] = \hbar\hat{L}_+, [\hat{L}_z, \hat{L}_-] = -\hbar\hat{L}_-, [\hat{L}_+, \hat{L}_-] = 2\hbar\hat{L}_z, [\hat{L}^2, \hat{L}_\pm] = 0 \quad \dots(3.11.4)$$

These commutation relations can be proved as follows:

$$\begin{aligned} [\hat{L}_z, \hat{L}_+] &= [\hat{L}_z, \hat{L}_x + i\hat{L}_y] = [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y + \hbar\hat{L}_x \\ &= \hbar(\hat{L}_x + i\hat{L}_y) = \hbar\hat{L}_+ \end{aligned} \quad \dots(3.11.5)$$

$$\begin{aligned} [\hat{L}_z, \hat{L}_-] &= [\hat{L}_z, \hat{L}_x - i\hat{L}_y] = [\hat{L}_z, \hat{L}_x] - i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y - \hbar\hat{L}_x \\ &= -\hbar(\hat{L}_x - i\hat{L}_y) = -\hbar\hat{L}_- \end{aligned} \quad \dots(3.11.6)$$

$$\begin{aligned} [\hat{L}_+, \hat{L}_-] &= [\hat{L}_x + i\hat{L}_y, \hat{L}_x - i\hat{L}_y] \\ &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) - (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 - i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) - \{\hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x)\} \\ &= -2i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) \end{aligned}$$

$$= -2i[\hat{L}_x, \hat{L}_y] = 2\hbar\hat{L}_z \quad \dots(3.11.7)$$

$$\begin{aligned} [\hat{L}^2, \hat{L}_+] &= [\hat{L}^2, \hat{L}_x + i\hat{L}_y] = \hat{L}^2(\hat{L}_x + i\hat{L}_y) - (\hat{L}_x + i\hat{L}_y)\hat{L}^2 \\ &= \hat{L}^2\hat{L}_x + i\hat{L}^2\hat{L}_y - \hat{L}_x\hat{L}^2 - i\hat{L}_y\hat{L}^2 \\ &= \hat{L}^2\hat{L}_x - \hat{L}_x\hat{L}^2 + i(\hat{L}^2\hat{L}_y - \hat{L}_y\hat{L}^2) \\ &= [\hat{L}^2, \hat{L}_x] + i[\hat{L}^2, \hat{L}_y] = 0 \end{aligned} \quad \dots(3.11.8)$$

Similarly, we can prove that

$$[\hat{L}^2, \hat{L}_-] = 0 \quad \dots(3.11.9)$$

$$\begin{aligned} \hat{L}_+\hat{L}_- &= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 - i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) \\ &= \hat{L}_x^2 + \hat{L}_y^2 - i[\hat{L}_x, \hat{L}_y] = \hat{L}_x^2 + \hat{L}_y^2 + \hbar\hat{L}_z = \hat{L}^2 - \hat{L}_z^2 + \hbar\hat{L}_z \end{aligned}$$

Similarly

$$\hat{L}_-\hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar\hat{L}_z$$

Hence

$$\hat{L}^2 = \frac{1}{2}(\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+) + \hat{L}_z^2 \quad \dots(3.11.10)$$

In polar coordinates the ladder operators can be expressed as

$$\begin{aligned} \hat{L}_+ &= \hat{L}_x + i\hat{L}_y \\ &= i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cos\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) - \hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \sin\varphi\cot\theta\frac{\partial}{\partial\varphi}\right) \\ &= \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right) \end{aligned} \quad \dots(3.11.11)$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y = \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right) \quad \dots(3.11.12)$$

3.12 EXPECTATION VALUE

When the wave function Ψ of a system is not an eigen function of operator $\hat{Q}$ representing an observable Q of the system then the measurement of Q with identical systems will give various possible

values. The expectation value of observable Q is equal to the average value of the results of these measurements.

The expectation value of a physical quantity Q represented by operator $\hat{Q}$ is defined by

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi d\tau \quad \dots(3.12.1)$$

where ψ is the state of the system. If the wave function ψ is not normalized the expectation value is given by

$$\langle Q \rangle = \frac{\int \psi^* \hat{Q} \psi d\tau}{\int \psi^* \psi d\tau} \quad \dots(3.12.2)$$

The expectation values of the physical quantities x , p_x , p , E etc., with respect to the state ψ are calculated from the following equations respectively:

$$\langle x \rangle = \int \psi^* x \psi d\tau$$

$$\langle p_x \rangle = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi d\tau$$

$$\langle p \rangle = \int \psi^* (-i\hbar \nabla) \psi d\tau$$

$$\langle E \rangle = \int \psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \psi d\tau$$

$$\left\langle \frac{p^2}{2m} \right\rangle = \int \psi^* \left(\frac{-\hbar^2}{2m} \nabla^2 \right) \psi d\tau$$

$$\langle V \rangle = \int \psi^* V \psi d\tau$$

Since $\langle E \rangle = \left\langle \frac{p^2}{2m} \right\rangle + \langle V \rangle$ we have

$$\langle E \rangle = \int \psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \psi d\tau + \int \psi^* V \psi d\tau.$$

3.13 EHRENFEST THEOREM

The theorem states that the classical equations of motion viz

$$\frac{dx}{dt} = \frac{p_x}{m}, \quad \frac{dp_x}{dt} = -\frac{\partial V}{\partial x} = F_x$$

are valid in quantum mechanics if we replace the physical quantities (such as x, p_x) by their expectation values. Thus the quantum equations of motion are

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m} \quad \dots(3.13.1)$$

$$\frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{\partial V}{\partial x} \right\rangle$$

In other words, the expectation values of physical quantities obey the classical equations of motion.

Proof: The time derivative of expectation value of position coordinate x is

$$\begin{aligned} \frac{d}{dt}\langle x \rangle &= \frac{d}{dt} \int \psi^* x \psi d\tau \\ &= \int \psi^* x \frac{\partial \psi}{\partial t} d\tau + \int \frac{\partial \psi^*}{\partial t} x \psi d\tau \end{aligned} \quad \dots(3.13.2)$$

All changes in x with time is being determined by the change in ψ , therefore there is no term like $\frac{\partial x}{\partial t}$ in above equation. This is how Schrödinger mechanics works.

Substituting the values of $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$ obtained from Schrödinger equation in Eqn. (3.13.2) we have

$$\begin{aligned} \frac{d}{dt}\langle x \rangle &= \int \psi^* x \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi \right) d\tau + \int -\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \psi^* + V\psi^* \right) x \psi d\tau \\ &= \frac{1}{i\hbar} \int \frac{-\hbar^2}{2m} \left(\psi^* x \nabla^2 \psi - \nabla^2 \psi^* x \psi \right) d\tau \\ &= \frac{i\hbar}{2m} \int \left[\psi^* x \nabla^2 \psi - (\nabla^2 \psi^*) (x\psi) \right] d\tau \\ &= \frac{i\hbar}{2m} \int \psi^* x \nabla^2 \psi d\tau - I \end{aligned} \quad \dots(3.13.3)$$

$$\text{where} \quad I = \frac{i\hbar}{2m} \int (\nabla^2 \psi^*) (x\psi) d\tau \quad \dots(3.13.4)$$

Making use of the identity

$$\nabla \cdot (\phi \mathbf{A}) = \nabla \phi \cdot \mathbf{A} + \phi \nabla \cdot \mathbf{A}$$

we can write

$$\nabla \cdot (x\psi \nabla \psi^*) = \nabla x\psi \cdot \nabla \psi^* + x\psi \nabla^2 \psi^* \quad \dots(a)$$

Interchanging $x\psi$ and ψ^* , we obtain

$$\nabla \cdot (\psi^* \nabla x\psi) = \nabla \psi^* \cdot \nabla (x\psi) + \psi^* \nabla^2 (x\psi) \quad \dots(b)$$

In view of (a) we have

$$\begin{aligned} I &= \frac{i\hbar}{2m} \int \left\{ \nabla \cdot (x\psi \nabla \psi^*) - \nabla x\psi \cdot \nabla \psi^* \right\} d\tau \\ &= \frac{i\hbar}{2m} \left\{ \int (x\psi \nabla \psi^*) \cdot ds - \int \nabla x\psi \cdot \nabla \psi^* d\tau \right\} \end{aligned}$$

where use of divergence theorem has been made to transform the volume integral into surface integral. The surface integral vanishes because $\psi \rightarrow 0$ as $x \rightarrow \infty$. So

$$I = \frac{i\hbar}{2m} \int (-\nabla x\psi \cdot \nabla \psi^*) d\tau$$

Making use of (b), we have

$$\begin{aligned} I &= \frac{i\hbar}{2m} \int [\psi^* \nabla^2 (x\psi) - \nabla \cdot (\psi^* \nabla x\psi)] d\tau \\ &= \frac{i\hbar}{2m} \int \psi^* \nabla^2 (x\psi) d\tau - \frac{i\hbar}{2m} \int \psi^* \nabla (x\psi) \cdot ds \\ &= \frac{i\hbar}{2m} \int \psi^* \nabla^2 (x\psi) d\tau + 0 \quad (\text{The surface integral again vanishes}) \end{aligned}$$

Now Eqn. (3.13.3) becomes

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= \frac{i\hbar}{2m} \int [\psi^* x \nabla^2 \psi - \psi^* \nabla^2 x\psi] d\tau \\ &= \frac{i\hbar}{2m} \int \psi^* \left(x \frac{d^2 \psi}{dx^2} - \frac{d^2}{dx^2} (x\psi) \right) d\tau \\ &= \frac{i\hbar}{2m} \int \psi^* \left(x \frac{d^2 \psi}{dx^2} - x \frac{d^2 \psi}{dx^2} - 2 \frac{d\psi}{dx} \right) d\tau \\ &= \frac{i\hbar}{2m} \int \psi^* \left(-2 \frac{d\psi}{dx} \right) d\tau \\ &= \frac{1}{m} \int \psi^* \left(-i\hbar \frac{d}{dx} \right) \psi d\tau \end{aligned}$$

$$= \frac{1}{m} \langle p_x \rangle$$

Similarly,

$$\begin{aligned} \frac{d}{dt} \langle p_x \rangle &= \frac{d}{dt} \int \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right) d\tau \\ &= -i\hbar \int \left(\psi^* \frac{\partial}{\partial x} \frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x} \right) d\tau \end{aligned}$$

Substituting the value of $\frac{\partial \psi}{\partial t}$ and $\frac{\partial \psi^*}{\partial t}$ from Schrödinger equation, we obtain

$$\begin{aligned} \frac{d}{dt} \langle p_x \rangle &= \frac{\hbar^2}{2m} \int \left(\psi^* \frac{\partial}{\partial x} \nabla^2 \psi - \nabla^2 \psi^* \frac{\partial \psi}{\partial x} \right) d\tau - \int \left(\psi^* \frac{\partial}{\partial x} (V\psi) - V\psi^* \frac{\partial \psi}{\partial x} \right) d\tau \\ &= \frac{\hbar^2}{2m} \int \left(\psi^* \frac{\partial}{\partial x} \nabla^2 \psi - \psi^* \frac{\partial}{\partial x} \nabla^2 \psi \right) d\tau - \\ &\quad \int \left(\psi^* \frac{\partial}{\partial x} (V\psi) - V\psi^* \frac{\partial \psi}{\partial x} \right) d\tau \\ &= - \int \psi^* \left(\frac{\partial}{\partial x} (V\psi) - V \frac{\partial \psi}{\partial x} \right) d\tau \\ &= \int \psi^* \left(-\frac{\partial V}{\partial x} \right) \psi d\tau \\ &= \left\langle -\frac{\partial V}{\partial x} \right\rangle \end{aligned}$$

3.14 SUPERPOSITION OF STATES (EXPANSION THEOREM)

A physical quantity is represented by a linear (Hermitian) operator and for each operator one can set up an eigen value equation of the type

$$\hat{Q}\phi_m = q_m \phi_m \quad \dots(3.14.1)$$

q_m being the eigen value and ϕ_m the eigen function of the operator $\hat{Q}$ representing the physical quantity Q . The eigen values may form discrete or continuous or both kind of spectrum. In case of discrete spectrum, we denote the eigen values and the eigen functions as

$$\begin{array}{ccccccc} q_1 & q_2 & q_3 & q_4 & \dots\dots\dots q_m \dots\dots\dots \\ \varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \dots\dots\dots \varphi_m \dots\dots\dots \end{array}$$

An important property of eigen functions of the operator of a physical quantity is that they form a complete set. This implies that any arbitrary well-behaved state wave function ψ of the system, which obeys the same boundary conditions as the eigen functions, can be expanded as a linear combination (superposition) of the eigen functions φ_q . A superposition of eigen functions also represents a possible state of the system. In case of discrete spectrum of eigen values, this property of eigen functions permits us to write

$$\psi = \sum_m c_m \varphi_{qm} \quad \dots(3.14.2)$$

where c_m are constant coefficients, in general complex. Of course, it is understood that ψ 's and φ 's are all functions of the same set of variables.

(The particle-in-box stationary state eigen functions given by

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad 0 \leq x \leq L$$

and harmonic oscillator wave functions are well-known examples of complete orthonormal functions.)

Eqn. (3.14.2) may be viewed as expressing the state ψ as **superposition** of eigenstates φ_m . This equation also states that the measurement of the quantity Q represented by $\hat{Q}$ in the state ψ yields one of the eigen values $q_1, q_2, q_3, \dots, q_m$. In particular if all the coefficients except one, say c_m , are zero then Eqn. (3.14.2) becomes

$$\psi = c_m \varphi_{qm} \quad \dots(3.14.3)$$

which means that the measurement of quantity Q in the state ψ will yield only one value c_m . To have the significance of the expansion coefficients c_m we assume that the eigen functions φ_{qm} are normalized. If all c 's are not zero, then the measurement of quantity Q in the state ψ does not yield a definite value, the outcome has a range of values whose average or expectation value is given by

$$\begin{aligned} \langle Q \rangle &= \int \psi^* \hat{Q} \psi d\tau \\ &= \int \left(\sum_m c_m^* \varphi_m^* \right) \hat{Q} \left(\sum_n c_n \varphi_n \right) d\tau \\ &= \sum_m \sum_n c_m^* c_n \int \varphi_m^* \hat{Q} \varphi_n d\tau \\ &= \sum_m \sum_n c_m^* c_n q_n \int \varphi_m^* \varphi_n d\tau \\ &= \sum_m \sum_n c_m^* c_n q_n \delta_{mn} \end{aligned}$$

$$\begin{aligned}
&= \sum_n |c_n|^2 \cdot q_n \\
&= c_1^2 q_1 + c_2^2 q_2 + \dots
\end{aligned}
\quad \dots(3.14.4)$$

When the system is in state ψ , the result of any measurement of Q is one of the eigen values $q_1, q_2, \dots$, the expectation value of Q is weighted average of these eigen values. The probability of obtaining a particular value q_n equals the square of the magnitude of c_n . This gives the physical significance of the expansion coefficient c_n in the expression Eqn. (3.14.2). Of course, the sum of probabilities must be unity.

$$\sum_n |c_n|^2 = 1 \quad \dots(3.14.5)$$

The expansion coefficient c_n may be obtained by making use of the orthogonal property of eigen functions ϕ_m . The orthogonal property of eigen functions signifies that

$$\int \phi_m^* \phi_n d\tau = \delta_{mn}$$

or

$$\langle \phi_m | \phi_n \rangle = \delta_{mn}$$

where the integral is evaluated over the entire range of variables in which ϕ is defined. To determine c_n , we multiply Eqn. (3.14.2) scalarly with ϕ_n^* and integrate.

$$\begin{aligned}
\int \phi_n^* \psi d\tau &= \int \phi_n^* \sum_m c_m \phi_m d\tau \\
&= \sum_m c_m \int \phi_n^* \phi_m d\tau \\
&= \sum_m c_m \delta_{nm} \\
&= c_n \\
c_n &= \int \phi_n^* \psi d\tau = \langle \phi_n | \psi \rangle
\end{aligned}
\quad \dots(3.14.6)$$

In case of continuous spectrum we shall denote the eigen value and corresponding eigen function by q and ϕ_{qm} respectively.

3.15 ADJOINT OF AN OPERATOR

Let $\hat{Q}$ and $\hat{R}$ be two operators such that

$$\int \phi^* \hat{Q} \psi d\tau = \int (\hat{R} \phi)^* \psi d\tau \quad \text{or} \quad (\phi, \hat{Q} \psi) = (\hat{R} \phi, \psi) \quad \dots(3.15.1)$$

then $\hat{R}$ is said to be adjoint of $\hat{Q}$ and is denoted by $\hat{Q}^+$ i.e., $\hat{R} = \hat{Q}^+$. Eqn. (3.15.1) can be written as

$$\int \phi^* \hat{Q} \psi d\tau = \int (\hat{Q}^+ \phi)^* \psi d\tau \quad \dots(3.15.2)$$

or
$$\langle \phi | \hat{Q} \psi \rangle = \langle \hat{Q}^+ \phi | \psi \rangle \quad \dots(3.15.3)$$

In other words, as far as the value of the integral is concerned, it makes no difference whether $\hat{Q}$ acts on ψ or its adjoint $\hat{Q}^+$ acts on the other function ϕ .

3.16 SELF-ADJOINT OR HERMITIAN OPERATOR

An operator $\hat{Q}$ is said to be self-adjoint (or Hermitian) if $\hat{Q}^+ = \hat{Q}$. Dynamical variables are real quantities and therefore their operators must be Hermitian. Property of Hermitian operator is

or
$$\int \phi^* \hat{Q} \psi d\tau = \int (\hat{Q} \phi)^* \psi d\tau \quad \text{or} \quad (\phi, \hat{Q} \psi) = (\hat{Q} \phi, \psi) \quad \dots(3.16.1)$$

$$\langle \phi | \hat{Q} \psi \rangle = \langle \hat{Q} \phi | \psi \rangle \quad \dots(3.16.2)$$

where ϕ and ψ are two arbitrary functions.

3.17 EIGEN FUNCTIONS OF HERMITIAN OPERATOR BELONGING TO DIFFERENT EIGEN VALUES ARE MUTUALLY ORTHOGONAL

Let $\hat{Q}$ be a self-adjoint (Hermitian) operator and ϕ_m and ϕ_n be two eigen functions corresponding to different eigen values q_m and q_n . Then

$$\begin{aligned} \hat{Q} \phi_m &= q_m \phi_m \\ \hat{Q} \phi_n &= q_n \phi_n \end{aligned} \quad \dots(3.17.1)$$

The condition of self-adjointness is

$$\int \phi_m^* \hat{Q} \phi_n d\tau = \int (\hat{Q} \phi_m)^* \phi_n d\tau \quad \dots(3.17.2)$$

$$\int \phi_m^* q_n \phi_n d\tau = \int q_m^* \phi_m^* \phi_n d\tau$$

$$(q_n - q_m^*) \int \phi_m^* \phi_n d\tau = 0$$

Since $q_n \neq q_m$, we must have

$$\int \phi_m^* \phi_n d\tau = 0 \quad \dots(3.17.3)$$

Thus the eigen functions belonging to different eigen values are orthogonal.

3.18 EIGEN VALUE OF A SELF-ADJOINT (HERMITIAN OPERATOR) IS REAL

Let the eigen values of operator $\hat{Q}$ in the states ϕ_m and ϕ_n be q_m and q_n respectively. That is

$$\begin{aligned}\hat{Q}\phi_m &= q_m \phi_m \\ \hat{Q}\phi_n &= q_n \phi_n\end{aligned}\quad \dots(3.18.1)$$

Since $\hat{Q}$ is Hermitian, we must have

$$\int \phi_m^* \hat{Q} \phi_n d\tau = \int (\hat{Q} \phi_m)^* \phi_n d\tau \quad \dots(3.18.2)$$

$$\int \phi_m^* q_n \phi_n d\tau = \int q_m^* \phi_m^* \phi_n d\tau$$

$$(q_n - q_m^*) \int \phi_m^* \phi_n d\tau = 0$$

This relation holds for all values of m and n . In particular, it must be true for $m = n$ also. So

$$(q_n - q_n^*) \int \phi_n^* \phi_n d\tau = 0$$

Since the integral on the left hand side is not zero, we must have

$$q_n = q_n^* \quad \dots(3.18.3)$$

The eigen values of Hermitian operator are real.

SOLVED EXAMPLES

Ex. 1. Select the acceptable wave functions from the following functions:

- (i) $\psi = x^n$ (ii) $\psi = e^x$ (iii) $\psi = e^{-x}$ (iv) $\psi = \sin x$
(v) $\psi = \exp(-x^2)$ (vi) $\psi = \tan x$.

Sol. Acceptable function must be finite, continuous and single valued.

- (i) As $x \rightarrow \pm \infty$, $\psi \rightarrow \pm \infty$. Hence x^n is not an acceptable function.
(ii) As $x \rightarrow \infty$, $\psi \rightarrow \infty$. So e^x is not acceptable.
(iii) As $x \rightarrow -\infty$, $\psi \rightarrow \infty$. So e^{-x} is not acceptable.
(iv) $\sin x$ oscillates between -1 and $+1$, so it is acceptable.
(v) As $x \rightarrow \pm \infty$, $\psi \rightarrow 0$, so it is acceptable.
(vi) $\tan x$ blows at $x = \pi/2$, hence it is not acceptable.

Ex. 2. Obtain expressions for the following operators:

$$\left(\frac{d}{dx} + x\right)^2, \left(x \frac{d}{dx}\right)^2, \left(\frac{d}{dx}(x)\right)^2$$

Sol.

$$\begin{aligned}
 \left(\frac{d}{dx} + x\right)^2 \psi &= \left(\frac{d}{dx} + x\right) \left(\frac{d}{dx} + x\right) \psi \\
 &= \left(\frac{d}{dx} + x\right) \left(\frac{d\psi}{dx} + x\psi\right) \\
 &= \frac{d^2\psi}{dx^2} + 2x \frac{d\psi}{dx} + (x^2 + 1)\psi
 \end{aligned}$$

$$\therefore \left(\frac{d}{dx} + x\right)^2 = \frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 + 1$$

$$\begin{aligned}
 \left(x \frac{d}{dx}\right)^2 \psi &= \left(x \frac{d}{dx}\right) \left(x \frac{d}{dx}\right) \psi = \left(x \frac{d}{dx}\right) \left(x \frac{d\psi}{dx}\right) \\
 &= x \left(\frac{d\psi}{dx} + x \frac{d^2\psi}{dx^2}\right) \\
 &= x \frac{d\psi}{dx} + x^2 \frac{d^2\psi}{dx^2}
 \end{aligned}$$

$$\left(x \frac{d}{dx}\right)^2 = x^2 \frac{d^2}{dx^2} + x \frac{d}{dx}$$

$$\begin{aligned}
 \left(\frac{d}{dx} x\right)^2 \psi &= \left(\frac{d}{dx} x\right) \left(\frac{d}{dx} x\right) \psi = \left(\frac{d}{dx} x\right) \left(\frac{d}{dx} x\psi\right) \\
 &= \frac{d}{dx} x \left(\psi + x \frac{d\psi}{dx}\right) \\
 &= \frac{d}{dx} \left(x\psi + x^2 \frac{d\psi}{dx}\right) \\
 &= \psi + x \frac{d\psi}{dx} + 2x \frac{d\psi}{dx} + x^2 \frac{d^2\psi}{dx^2}
 \end{aligned}$$

$$\therefore \left(\frac{d}{dx} x\right)^2 = x^2 \frac{d^2}{dx^2} + 3x \frac{d}{dx} + 1$$

Ex. 3. A particle is moving in one dimension is represented by the wave function

$$\psi(x) = \left(\frac{\sqrt{2}}{\pi} \right)^{1/2} \frac{x + ix}{1 + ix^2}$$

Find the position probability density where the particle is most likely to be found.

Sol. Position probability density

$$P = \psi^* \psi = |\psi|^2 = \frac{2\sqrt{2}}{\pi} \cdot \frac{x^2}{1 + x^4}$$

$$\text{For maximum value of } P, \frac{dP}{dx} = 0 \Rightarrow \frac{2x(1 + x^4) - x^2 \cdot 4x^3}{(1 + x^4)^2} = 0 \Rightarrow x = \pm 1$$

Ex. 4. Find the value of constant A which makes the function $\exp(-\lambda x^2)$ an eigen function of the operator $\left(\frac{d^2}{dx^2} - Ax^2 \right)$. What is the corresponding eigen value?

Sol. Eigen value equation of the given operator is

$$\left(\frac{d^2}{dx^2} - Ax^2 \right) \exp(-\lambda x^2) = q \exp(-\lambda x^2), \quad q \text{ is eigen value.}$$

$$(-2\lambda + 4\lambda^2 x^2 - Ax^2) \exp(-\lambda x^2) = q \exp(-\lambda x^2)$$

The function $\exp(-\lambda x^2)$ will be an eigen function of the given operator if $(4\lambda^2 x^2 - Ax^2 - 2\lambda)$ is independent of x . That is, the coefficient of x^2 must vanish. Thus

$$4\lambda^2 - A = 0 \quad \text{or} \quad A = 4\lambda^2.$$

The expression for operator now becomes

$$\left(\frac{d^2}{dx^2} - 4\lambda^2 x^2 \right)$$

The eigen value equation is

$$\begin{aligned} \left(\frac{d^2}{dx^2} - 4\lambda^2 x^2 \right) \exp(-\lambda x^2) &= q \exp(-\lambda x^2) \quad \text{where } q \text{ is eigen value.} \\ &= -2\lambda \exp(-\lambda x^2) \end{aligned}$$

Therefore, -2λ is the eigen value of the given operator.

Ex. 5. Normalize the wave function

$$\begin{aligned}\psi(x) &= A \exp(-\lambda x), & \text{for } x > 0 \\ &= A \exp(\lambda x), & \text{for } x < 0\end{aligned}$$

Where λ is a positive constant.

Sol. The normalization condition is

$$\begin{aligned}\int_{-\infty}^{\infty} \psi^* \psi dx &= 1 \\ \int_{-\infty}^0 A^2 \exp(2\lambda x) dx + \int_0^{\infty} A^2 \exp(-2\lambda x) dx &= 1 \\ A &= \sqrt{\lambda}\end{aligned}$$

Normalized wave function is

$$\psi(x) = \sqrt{\lambda} \exp(-\lambda x) \text{ for } x > 0, \text{ and}$$

$$\psi(x) = \sqrt{\lambda} \exp(\lambda x) \text{ for } x < 0.$$

Ex. 6. The operator $x + \frac{d}{dx}$ has the eigen value λ . Obtain the corresponding eigen function.

Sol. Let ψ be the eigen function. The eigen value equation is

$$\begin{aligned}\left(x + \frac{d}{dx}\right)\psi &= \lambda\psi \\ x\psi + \frac{d\psi}{dx} &= \lambda\psi \\ \frac{d\psi}{\psi} &= -(x - \lambda)dx \\ \psi &= c \exp\left(-\frac{x^2}{2} + \lambda x\right)\end{aligned}$$

Ex. 7. Which of the following functions are eigen functions of operator $\frac{d^2}{dx^2}$? Find the eigen value in each state.

$$(i) \psi = A \sin mx \quad (ii) \psi = B \cos nx \quad (iii) \psi = Cx^2 \quad (iv) \psi = D/x \quad (v) \psi = A e^{-mx}$$

Sol.

$$(i) \frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2} A \sin mx = -m^2\psi$$

So $\psi = A \sin mx$ is eigen function and $-m^2$ is eigen value.

$$(ii) \quad \frac{d^2}{dx^2} (B \cos nx) = -n^2 (B \cos nx)$$

So $\psi = B \cos nx$ is eigen function and $-n^2$ is eigen value.

$$(iii) \quad \frac{d^2}{dx^2} Cx^2 = 2C$$

So $\psi = Cx^2$ is not an eigen function. No eigen value exists.

(iv) $\psi = D/x$ is not an eigen function.

$$(v) \quad \frac{d^2}{dx^2} (Ae^{-mx}) = m^2 (Ae^{-mx})$$

Hence $\psi = A e^{-mx}$ is eigen function and m^2 is the eigen value.

Ex. 8. Find the eigen function and eigen value of momentum operator

$$\hat{p} = -i\hbar \frac{d}{dx}.$$

Sol.

We need to solve the equation

$$-i\hbar \frac{d}{dx} \psi_n(x) = q_n \psi_n(x)$$

$$-i\hbar \frac{d\psi}{\psi} = q_n dx$$

$$-i\hbar \ln \psi = q_n x + \ln c$$

$$\psi = c \exp(iq_n x / \hbar)$$

The eigen value q_n can be any number. However, if we impose the boundary condition that $\psi_n(x)$ be a periodic in some distance L then

$$\exp(iq_n x / \hbar) = \exp(iq_n (x + L) / \hbar)$$

$$\exp(iq_n L / \hbar) = 1$$

$$\cos \frac{q_n L}{\hbar} = 1$$

$$q_n = \frac{2\pi n \hbar}{L}, \quad n \text{ is an integer.}$$

The eigen function is given by

$$\psi_n(x) = c \exp\left(\frac{i2\pi nx}{L}\right)$$

So the eigen values are discrete and real. This shows that the eigen values and the eigen functions depend not only on the nature of the operator but also on the boundary conditions.

Ex. 9. Find the eigen function and eigen values of the operator $\hat{L}_z = -i\hbar \frac{d}{d\phi}$.

Sol. Eigen value equation is

$$-i\hbar \frac{d\psi(\phi)}{d\phi} = q\psi(\phi)$$

$$\frac{d\psi}{\psi} = -\frac{q}{i\hbar} d\phi$$

$$\psi = c \exp\left(\frac{iq\phi}{\hbar}\right)$$

The function ψ is periodic function of variable ϕ with a period of 2π i.e., $\psi(\phi) = \psi(\phi + 2\pi)$. This condition implies that the eigen value q is an integral multiple of $\hbar$ and ψ given by the above formula is the eigen function.

Ex. 10. Show that $\hat{p}_x = -i\hbar \frac{d}{dx}$ is a Hermitian operator.

Sol. Let ψ and ϕ be orthogonal functions we have to prove that

$$\begin{aligned} \int_{-\infty}^{\infty} \psi^* \hat{p}_x \phi d\tau &= \int_{-\infty}^{\infty} \phi (\hat{p}_x \psi)^* d\tau \\ \text{LHS} &= \int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{d}{dx}\right) \phi d\tau = -i\hbar \left[\left(\psi^* \phi\right)_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \phi \frac{d\psi^*}{dx} d\tau \right] \\ &= 0 + i\hbar \int_{-\infty}^{\infty} \phi \frac{d\psi^*}{dx} d\tau \\ &= \int_{-\infty}^{\infty} \phi \left(i\hbar \frac{d\psi^*}{dx}\right) d\tau \\ &= \int_{-\infty}^{\infty} \phi \left(-i\hbar \frac{d\psi}{dx}\right)^* d\tau \end{aligned}$$

$$= \int_{-\infty}^{\infty} \varphi(\hat{p}_x \psi)^* d\tau$$

Ex. 11. If $\hat{A} = 3x^2$ and $\hat{B} = \frac{d}{dx}$. Show that $\hat{A}$ and $\hat{B}$ do not commute.

Sol.
$$\begin{aligned} [\hat{A}, \hat{B}] \psi &= \left[3x^2, \frac{d}{dx} \right] \psi = \left[3x^2 \frac{d}{dx} - \frac{d}{dx} (3x^2) \right] \psi = 3x^2 \frac{d\psi}{dx} - \frac{d}{dx} (3x^2 \psi) \\ &= -6x\psi \neq 0 \end{aligned}$$

Hence $\hat{A}$ and $\hat{B}$ do not commute.

Ex. 12. Show that $[\hat{A}, \hat{B}] = -[\hat{A}, \hat{B}]$.

Sol.
$$\begin{aligned} [\hat{A}, \hat{B}] \psi &= (\hat{A}\hat{B} - \hat{B}\hat{A}) \psi = \hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi \\ [\hat{B}\hat{A}] \psi &= (\hat{B}\hat{A} - \hat{A}\hat{B}) \psi = \hat{B}\hat{A}\psi - \hat{A}\hat{B}\psi = -(\hat{A}\hat{B}\psi - \hat{B}\hat{A}\psi) \\ &= -[\hat{A}, \hat{B}] \psi. \end{aligned}$$

Ex. 13. Show that $[x^n, \hat{p}_x] = i\hbar n x^{n-1}$.

Sol.
$$\begin{aligned} (\hat{x}^n \hat{p}_x - \hat{p}_x \hat{x}^n) \psi &= \left\{ x^n (-i\hbar \frac{d}{dx}) - (-i\hbar \frac{d}{dx} x^n) \right\} \psi \\ &= -i\hbar \left\{ x^n \frac{d\psi}{dx} - \frac{d}{dx} x^n \psi \right\} \\ &= i\hbar n x^{n-1} \psi. \end{aligned}$$

Ex. 14. Show that the function $\psi(x) = c x \exp\left(-\frac{1}{2}x^2\right)$ is an eigen function of the operator $\left(x^2 - \frac{d^2}{dx^2}\right)$. Find the eigen value, normalization constant c and the expectation value of x for the state described by the wave function, when x varies from $-\infty$ to $+\infty$.

$$\begin{aligned}\text{Sol. } \left(x^2 - \frac{d^2}{dx^2} \right) cx \exp\left(-\frac{1}{2}x^2\right) &= cx^3 \exp\left(-\frac{1}{2}x^2\right) - c \frac{d^2}{dx^2} x \exp\left(-\frac{1}{2}x^2\right) \\ &= 3cx \exp\left(-\frac{1}{2}x^2\right)\end{aligned}$$

Hence the eigen value is 3.

The normalization constant c is obtained by equation

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

$$c^2 \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 1$$

$$\left[\because \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \frac{1}{2\alpha} \left(\frac{\pi}{\alpha} \right)^{1/2} \right]$$

$$c^2 \left(\frac{\pi}{4} \right)^{1/2} = 1$$

$$c = \left(\frac{4}{\pi} \right)^{1/4}$$

The expectation value of x is given by

$$\langle x \rangle = \int_{-\infty}^{\infty} cxe^{-\frac{1}{2}x^2} x cxe^{-\frac{1}{2}x^2} dx = c^2 \int_{-\infty}^{\infty} x^3 e^{-x^2} dx = 0$$

(integrand is odd function)

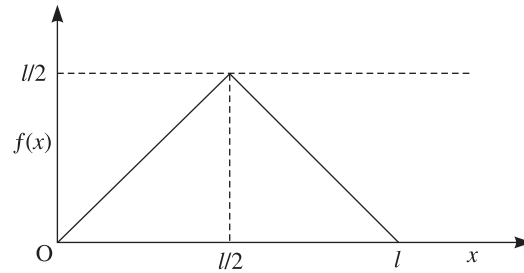
Ex. 15. Obtain the expansion of function

$$f(x) = x \quad 0 \leq x \leq l/2$$

$$f(x) = l - x \quad l/2 \leq x \leq l$$

in terms of one-dimensional particle in a box stationary state wave function.

Sol. The function is sketched in the figure.



Let
$$f(x) = \sum a_n \psi_n(x)$$

where

$$\begin{aligned} a_n &= \int_0^l \psi_n^*(x) f(x) dx = \sqrt{\frac{2}{l}} \int_0^l \sin \frac{n\pi x}{l} f(x) dx \\ &= \sqrt{\frac{2}{l}} \int_0^{l/2} x \sin \frac{n\pi x}{l} dx + \sqrt{\frac{2}{l}} \int_{l/2}^l (l-x) \sin \frac{n\pi x}{l} dx \\ &= \frac{(2l)^{3/2}}{n^2 \pi^2} \sin \frac{n\pi}{2}, \quad \text{where } \sin \frac{n\pi}{2} = 0 \text{ for even } n \\ &\quad = \pm 1 \text{ for odd } n \\ &= \frac{4l}{\pi^2} \left[\sin \frac{\pi x}{l} - \frac{1}{3^2} \sin \frac{3\pi x}{l} + \frac{1}{5^2} \sin \frac{5\pi x}{l} - \dots \right] \end{aligned}$$

The integrals can be evaluated making use of following result:

$$\int x \sin bx dx = \frac{1}{b^2} \sin bx - \frac{x}{b} \cos bx$$

Ex. 16. The ground state and the first excited state wave functions of an atom are ψ_0 and ψ_1 respectively, the corresponding energies being E_0 and E_1 . If the system has a 40% probability of being found in the ground state and 60% probability in the first excited state,

- (i) What is the wave function of the atom?
- (ii) What is the average energy of the atom?

Sol. Let the wave function of the atom be

$$\Psi = c_0 \psi_0 + c_1 \psi_1 \quad \dots(1)$$

Here the expansion coefficients c_0 and c_1 have the following meanings. c_0^2 represents the probability of finding system in the state ψ_0 with energy eigen value E_0 . Thus

$$c_0^2 = 0.40 \quad \therefore c_0 = \sqrt{0.40}$$

Similarly, the square of the coefficient c_1 viz. c_1^2 represents the probability of finding the system in the state ψ_1 with energy eigen value E_1 .

$$c_1^2 = 0.60 \quad \therefore c_1 = \sqrt{0.60} \quad \dots(2)$$

Of course, $c_0^2 + c_1^2 = 1$

Wave function of the state $\Psi = c_0 \psi_0 + c_1 \psi_1 = \sqrt{0.40} \psi_0 + \sqrt{0.60} \psi_1$

Average energy of the system in the state

$$\langle E \rangle = c_0^2 E_0 + c_1^2 E_1 = 0.40 E_0 + 0.60 E_1$$

Ex. 17. Show that the Hamiltonian must be Hermitian for conservation of probability.

Sol. The time dependent Schrodinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \quad \dots(1)$$

Its complex conjugate is

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \hat{H}^* \psi^* \quad \dots(2)$$

Multiplying (1) by ψ^* and (2) by ψ and then subtracting one equation from the other we have

$$i\hbar \left[\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t} \right] = \psi^* \hat{H}\psi - \psi \hat{H}^* \psi^*$$

$$\frac{\partial}{\partial t} (\psi^* \psi) = \frac{1}{i\hbar} [\psi^* \hat{H}\psi - \psi (\hat{H}\psi)^*]$$

Integrating over entire space

$$\frac{\partial}{\partial t} \int \psi^* \psi d\tau = \frac{1}{i\hbar} \left[\int \psi^* (\hat{H}\psi) d\tau - \int \psi (\hat{H}\psi)^* d\tau \right]$$

Conservation of probability demands that $\frac{\partial}{\partial t} \int \psi^* \psi d\tau = 0$. This is possible when

$$\int \psi^* (\hat{H}\psi) d\tau = \int (\hat{H}\psi)^* \psi d\tau$$

This is the condition for hermiticity for Hamiltonian operator.

Ex. 18. Show that (i) $[\hat{x}, \hat{H}] = \frac{i\hbar}{m} \hat{p}_x$ (ii) $[\hat{x}, \hat{p}_x^2] = 2\hbar^2 \frac{\partial}{\partial x}$

$$\text{Sol. } [\hat{x}, \hat{H}] = [\hat{x}, \hat{T} + \hat{V}] = [\hat{x}, \hat{T}] + [\hat{x}, \hat{V}] = [\hat{x}, \hat{T}] = \left[\hat{x}, \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} \right]$$

$$= \frac{1}{2m} [\hat{x}, \hat{p}_x^2] + \frac{1}{2m} [\hat{x}, \hat{p}_y^2] + \frac{1}{2m} [\hat{x}, \hat{p}_z^2] = \frac{1}{2m} \cdot 2\hbar^2 \frac{\partial}{\partial x} + 0 + 0 = \frac{i\hbar}{m} \hat{p}_x$$

$$[\hat{x}, \hat{p}_x^2] = [\hat{x}, \hat{p}_x] \hat{p}_x + \hat{p}_x [\hat{x}, \hat{p}_x] = i\hbar(-i\hbar \frac{\partial}{\partial x}) + (-i\hbar \frac{\partial}{\partial x}) \cdot i\hbar = 2\hbar^2 \frac{\partial}{\partial x}$$

Ex. 19. At $t = 0$, the Harmonic oscillator wave function in a state is given by

$$\psi(x, 0) = \frac{1}{\sqrt{3}} \psi_0(x) + i\sqrt{\frac{2}{3}} \psi_2(x)$$

Where ψ_0 is ground state wave function and ψ_2 is second excited state wave function.

(i) Write down the time evolution wave function.

(ii) Find the average energy of the oscillator.

Sol. Time evolution of wave function is

$$\Psi(x, t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right) = \frac{1}{\sqrt{3}} \psi_0(x) \exp\left(-\frac{1}{2}i\omega t\right) + i\sqrt{\frac{2}{3}} \psi_2(x) \exp\left(-\frac{5}{2}i\omega t\right)$$

[Energy of oscillator in ground state is $E_0 = \frac{1}{2} \hbar \omega$ and in state $n = 2$ is $E_2 = (5/2) \hbar \omega$].

According to the meaning of expansion coefficients, the probability of finding the oscillator in the ground state with energy $\frac{1}{2} \hbar \omega$ is $(1/\sqrt{3})^2 = 1/3$ and that in the state $n = 2$ with energy $(5/2) \hbar \omega$ is $[\sqrt{(2/3)}]^2 = 2/3$.

The average energy of the oscillator is

$$\langle E \rangle = c_0^2 E_0 + c_2^2 E_2 = \frac{1}{3} \left(\frac{1}{2} \hbar \omega \right) + \frac{2}{3} \left(\frac{5}{2} \hbar \omega \right) = \frac{11}{6} \hbar \omega$$

Ex. 20. Show that the average value of square of a Hermitian operator is positive.

Sol. Let $\hat{Q}$ be a Hermitian operator. The eigen value equation for $\hat{Q}^2$ is

$$\hat{Q}^2 \psi = \lambda^2 \psi$$

We have to show that λ^2 is positive. The average value of Q^2 is

$$\begin{aligned} \langle Q^2 \rangle &= \int \psi^* \hat{Q}^2 \psi d\tau = \int \psi^* \hat{Q} \hat{Q} \psi d\tau = \int (\hat{Q} \psi)^* (\hat{Q} \psi) d\tau = \int (\lambda \psi)^* (\lambda \psi) d\tau \\ &= \lambda^* \lambda \int \psi^* \psi d\tau = \lambda^* \lambda = |\lambda|^2 = \text{positive number.} \end{aligned}$$

Ex. 21. Show that complex conjugation is not a (i) linear operator (ii) Hermitian operator.

Sol. (i) Let us denote the complex conjugation by an operator $\hat{A}$. Then

$$\hat{A} \psi = \psi^* \quad \dots(1)$$

Let ψ be linear combination of ψ_1 and ψ_2 . Therefore,

$$\hat{A} \psi = \hat{A}(c_1 \psi_1 + c_2 \psi_2) = (c_1 \psi_1 + c_2 \psi_2)^* = c_1^* \psi_1^* + c_2^* \psi_2^* \quad \dots(2)$$

If $\hat{A}$, were linear operator, one would expect the following result.

$$\hat{A}(c_1 \psi_1 + c_2 \psi_2) = \hat{A}(c_1 \psi_1) + \hat{A}(c_2 \psi_2) = c_1 \hat{A} \psi_1 + c_2 \hat{A} \psi_2 = c_1 \psi_1^* + c_2 \psi_2^* \quad \dots(3)$$

Since (1) and (2) are not the same, $\hat{A}$ is not a linear operator.

(ii) A Hermitian operator satisfies the condition

$$\int \psi^* \hat{Q} \phi d\tau = \int (\hat{Q} \psi)^* \phi d\tau \quad \dots(1)$$

For operator $\hat{A}$,

$$\text{Left hand side} = \int \psi^* \hat{A} \phi d\tau = \int \psi^* \phi^* d\tau \quad \dots(2)$$

$$\text{Right hand side} = \int (\psi^*)^* \phi d\tau = \int \psi \phi d\tau \quad \dots(3)$$

Since $\int \psi^* \phi^* d\tau \neq \int \psi \phi d\tau$, complex conjugation is not Hermitian.

Ex. 22. If $\{\phi_1(x), \phi_2(x), \dots\}$ is a complete set of orthonormal functions, then show that the following closure relation is satisfied

$$\sum_{n=1}^{\infty} \phi_n^*(x') \phi_n(x) = \delta(x - x')$$

Sol. Let $\psi(x)$ be an arbitrary function. We can express this function in terms given orthonormal functions.

$$\psi(x) = \sum_{n=1}^{\infty} c_n \phi_n(x) \quad \dots(1)$$

$$\text{where} \quad c_n = \int \phi_n^*(x) \psi(x) dx \quad \dots(2)$$

Therefore,

$$\begin{aligned} \psi(x) &= \sum_{n=1}^{\infty} \left[\int \phi_n^*(x') \psi(x') dx' \right] \phi_n(x) \\ &= \int \psi(x') dx' \cdot \left[\sum_{n=1}^{\infty} \phi_n^*(x') \phi_n(x) \right] \\ &= \int \psi(x') \delta(x - x') dx' \quad \dots(3) \end{aligned}$$

where

$$\sum_{n=1}^{\infty} \phi_n^*(x') \phi_n(x) = \delta(x - x') \quad [\text{closure relation}]. \quad \dots(4)$$

Ex. 23. Show that the momentum p of a free particle is a constant of motion.

Sol. When the operator of a physical quantity commutes with Hamiltonian H , it remains conserved. For a free particle moving in x -direction,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad \text{and} \quad p_x = -i\hbar \frac{\partial}{\partial x}$$

Now
$$\hat{p}_x \hat{H} \psi(x) = -i\hbar \frac{\partial}{\partial x} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) \right] = -\frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3} \psi(x)$$

$$\hat{H} \hat{p}_x \psi(x) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \left(-i\hbar \frac{\partial}{\partial x} \right) \psi(x) = -\frac{i\hbar^3}{2m} \frac{\partial^3}{\partial x^3} \psi(x)$$

Therefore,
$$[\hat{p}_x, \hat{H}] = \hat{p}_x \hat{H} - \hat{H} \hat{p}_x = 0.$$

Ex. 24. The Hamiltonian of a harmonic oscillator is $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2$. Prove that

(i) $[\hat{x}, \hat{H}] = \frac{i\hbar p}{m}$ (ii) $[\hat{p}_x, \hat{H}] = -i\hbar m\omega^2 x$

Sol. (i)
$$[\hat{x}, \hat{H}] \psi = \frac{1}{2m} [\hat{x}, \hat{p}_x^2] \psi + \frac{1}{2} m\omega^2 [\hat{x}, x^2] \psi = \frac{1}{2m} \{x(-i\hbar \frac{\partial}{\partial x})^2 - (-i\hbar \frac{\partial}{\partial x})^2 x\} \psi + 0$$

$$= -\frac{\hbar^2}{2m} \left\{ x \frac{\partial^2}{\partial x^2} \psi - \frac{\partial^2}{\partial x^2} (x\psi) \right\}$$

$$= -\frac{\hbar^2}{2m} \left\{ -2 \frac{\partial \psi}{\partial x} \right\} = i\hbar \frac{p_x \psi}{m}$$

(ii)
$$[\hat{p}_x, \hat{H}] \psi = \left[\hat{p}_x, \frac{\hat{p}_x^2}{2m} \right] \psi + \left[\hat{p}_x, \frac{1}{2} m\omega^2 x^2 \right] \psi = 0 + \frac{1}{2} m\omega^2 [\hat{p}_x, x^2] \psi$$

$$= \frac{1}{2} m\omega^2 \left\{ (-i\hbar \frac{\partial}{\partial x})(x^2 \psi) - x^2 (-i\hbar \frac{\partial}{\partial x}) \psi \right\} = -i\hbar m\omega^2 x \psi$$

Ex. 25. Show that $i[A, B]$ will be Hermitian if A and B are Hermitian operators.

Sol. Let $\hat{Q} = i[\hat{A}, \hat{B}]$. Then

$$\hat{Q} = i(\hat{A}\hat{B} - \hat{B}\hat{A})$$

Suppose that $\hat{A}$ and $\hat{B}$ are Hermitian.

$$\begin{aligned}\hat{Q}^+ &= -i\{(\hat{A}\hat{B})^+ - (\hat{B}\hat{A})^+\} = -i\{\hat{B}^+\hat{A}^+ - \hat{A}^+\hat{B}^+\} = -i\{\hat{B}\hat{A} - \hat{A}\hat{B}\} \\ &= i\{\hat{A}\hat{B} - \hat{B}\hat{A}\} = i[\hat{A}, \hat{B}] = \hat{Q}.\end{aligned}$$

Thus $\hat{Q}$ or $i[\hat{A}, \hat{B}]$ is Hermitian.

Ex. 26. Show that Parity operator is Hermitian.

Sol. Let $\hat{P}$ be parity operator. Then

$$\hat{P}\psi(x) = \psi(-x)$$

If parity operator is Hermitian then

$$\int \psi(x)^* \hat{P} \phi(x) dx = \int (\hat{P}\psi)^* \phi dx$$

$$\text{or} \quad \int \psi^*(x) \phi(-x) dx = \int \psi^*(-x) \phi(x) dx \quad \dots(1)$$

Let us change the variable on the left hand side of (1) through the substitution $x = -x$.

$$\text{LHS} = \int \psi^*(-x') \phi(x') dx' = \int \psi^*(-x) \phi(x) dx = \text{RHS of Eqn. (1)}$$

Ex. 27. Show that every operator can be expressed as the combination of two operators, each of them is Hermitian.

Sol. Let $\hat{A}$ be an operator whose adjoint is $\hat{A}^+$. Now, let

$$\hat{A} = \left(\frac{\hat{A} + \hat{A}^+}{2} \right) + i \left(\frac{\hat{A} - \hat{A}^+}{2i} \right) = \hat{B} + i\hat{C}$$

$$\text{where} \quad \hat{B} = \frac{\hat{A} + \hat{A}^+}{2} \quad \text{and} \quad \hat{C} = \frac{\hat{A} - \hat{A}^+}{2i}$$

$$\text{Now,} \quad \hat{B}^+ = \frac{\hat{A}^+ + \hat{A}}{2} = \hat{B} \quad \text{and} \quad \hat{C}^+ = \frac{\hat{A}^+ - \hat{A}}{-2i} = \frac{\hat{A} - \hat{A}^+}{2i} = \hat{C}$$

Thus $\hat{B}$ and $\hat{C}$ are both Hermitian. So $\hat{A}$ can be expressed as $\hat{A} = \hat{B} + i\hat{C}$.

Ex. 28. If ϕ_1 and ϕ_2 are two degenerate eigen functions of the linear operator H , show that $\psi = c_1 \phi_1 + c_2 \phi_2$ is an eigen function of H with the same eigen value as that of ϕ_1 and ϕ_2 .

Sol. Given that $\hat{H}\phi_1 = \lambda\phi_1$ and $\hat{H}\phi_2 = \lambda\phi_2$

$$\text{Now} \quad \hat{H}\psi = \hat{H}(c_1\phi_1 + c_2\phi_2) = c_1\lambda\phi_1 + c_2\lambda\phi_2 = \lambda(c_1\phi_1 + c_2\phi_2) = \lambda\psi$$

Ex. 29. Find the solution of eigen value equation $\frac{d^2\psi}{dx^2} = \lambda\psi$. Discuss the conditions under which the eigen functions are well behaved and when λ is an eigen value.

Sol. Given equation is $\frac{d^2\psi}{dx^2} = \lambda\psi$.

For $\lambda \neq 0$, the solution of the equation is

$$\psi = c_1 \exp(\sqrt{\lambda} x) + c_2 \exp(-\sqrt{\lambda} x), \quad c_1 \text{ and } c_2 \text{ are arbitrary constants.}$$

(i) When $\lambda < 0$, let $\sqrt{\lambda} = im$.

The solution is

$$\psi = c_1 \exp(imx) + c_2 \exp(-imx)$$

When $|x| \rightarrow \infty$, $\psi \rightarrow \infty$. The solution is not well behaved.

(ii) When $\lambda > 0$, $\psi = c_1 \exp(\sqrt{\lambda} x) + c_2 \exp(-\sqrt{\lambda} x)$

For $x < 0$, the first term of the solution is finite for all negative values of x , but the second part blows up for $x \rightarrow -\infty$. Hence ψ is not well behaved.

For $x > 0$, the first term becomes infinite for $x \rightarrow \infty$ and the second term remains finite for all values of x . The solution ψ is not well behaved.

(iii) When $\lambda = 0$, $\psi = Cx + D$. The solution is well behaved for $C = 0$, and in this case $\psi = D$.

Ex. 30. Discuss the nature of solution of equation $\frac{d^2\psi}{dx^2} = \pm c\psi$, $-\infty < x < \infty$, c is positive constant

Sol. Case 1: Choose positive sign. The solution of the equation is

$$\psi = A \exp(\sqrt{c} x) \pm B \exp(-\sqrt{c} x)$$

For $x \rightarrow \pm\infty$, ψ is not well behaved.

However, if $A = 0$, $\psi = B \exp(-\sqrt{c} x)$ is well behaved for $0 < x < \infty$.

If $B = 0$, $\psi = A \exp(\sqrt{c} x)$ is well behaved for $x < 0$.

Case 2: Choose negative sign. The differential equation is

$$\frac{d^2\psi}{dx^2} = -c\psi$$

Solution of equation is

$$\psi = A \sin \sqrt{c} x + B \cos \sqrt{c} x$$

The solution is well behaved for all values of x . The eigen values $(-c)$ form continuous spectrum.

QUESTIONS AND PROBLEMS

1. State the physical significance of wave function. Explain the meaning of well-behaved function. Give the interpretation of wave function in terms of probability current density j associated with particle flux.
2. Obtain time dependent and time independent Schrodinger equation. What do you mean by normalization and orthogonality of wave function?
3. What do you mean by dynamical variable and expectation value of a dynamical variable? Obtain quantum mechanical operators corresponding to linear momentum, angular momentum, kinetic energy and Hamiltonian of a system.
4. State Ehrenfest's theorem. Prove that

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m}, \quad \frac{d}{dt}\langle p_x \rangle = -\left\langle \frac{dV}{dx} \right\rangle = \langle F_x \rangle$$

5. Explain the meaning of linear operator, adjoint of an operator and Hermitian operator. Show that (i) the eigen values of a Hermitian operator are real (ii) the eigen functions of Hermitian operator corresponding to different eigen values are orthogonal.
6. Explain expansion theorem. Give the meaning of expansion coefficients.
7. The wave function of a particle moving in a potential free region is given by $\psi(x) = A \cos kx$, where k and A are real constants. Is it an eigen state of the operator $\hat{H}, \hat{p}_x, \hat{p}_x^2$. If so, find the corresponding eigen values.

Ans. $\frac{\hbar^2 k^2}{2m}$, $\psi(x)$ is not an eigen state of $\hat{p}_x, \hbar^2 k^2$.

8. Show that $\frac{d}{dt}\langle p_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle$, where the symbols have their usual meanings. (All'd 1995)
9. (a) Show that the Hamiltonian must be Hermitian for conservation of probability.
 (b) Two operators P and Q are non-hermitian. Make a suitable linear combination which will be Hermitian.
 (c) If the operators P, Q and PQ are all Hermitian, show that $[P, Q] = 0$. (All'd 1995)
10. An operator $\hat{A}$ associated with a physical observable A satisfies the following eigen value equation

$$\hat{A}\phi_n(x) = a_n\phi_n(x)$$
 (a) What are the possible results of observation of A ?
 (b) What is the average value of repeated observations when the system is in a definite eigen state $\phi_n(x)$? (All'd 1996)
11. (a) Obtain the eigen functions of a one-dimensional momentum operator and normalize them by using delta-function technique.
 (b) A particle of mass m is confined to move in a two dimensional square of side L . Obtain the total number of allowed states for energy of the particle lying between E and $E + dE$ and calculate the density of states. (All'd 1996)
12. (a) Show that eigen vectors belonging to two different eigen values of a Hermitian operator are orthogonal.
 (b) Evaluate $[z^2, p_z]$ and $[xz, p_z]$ (1996)

13. (a) Discuss the postulates of quantum mechanics.
 (b) If O_1 and O_2 are two mathematical operators corresponding to two physical observations, write the physical significance of (i) $[\hat{O}_1, \hat{O}_2] \neq 0$, (ii) $[\hat{O}_1, \hat{O}_2] = 0$, (iii) $[\hat{O}_1, \hat{H}] = 0$, (iv) Give explicit examples of O_1 and O_2 that satisfy (i), (ii) and (iii) H is Hamiltonian operator. (All'd 1997)
14. (a) Prove Ehrenfest theorem and describe its significance.
 (b) What is meant by expectation value of a physical quantity? How is calculated? Calculate

$$\langle P \rangle \text{ if } \phi(x, t) = \frac{1}{\sqrt{2\pi}} \exp[i(kx - \omega t)]. \quad (\text{All'd 1997})$$

15. L and P are orbital angular momentum and parity operators respectively referred to the origin of a set of spherical coordinates. If P transforms (r, θ, ϕ) to $(r, \pi - \theta, \phi + \pi)$, show that $[P, L] = 0$. Hence prove that each spherical harmonic has a well defined parity dependent on l . (All'd 1997)

16. (a) Show that $\frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{\partial V}{\partial x} \right\rangle$.
 (b) If operators A and B are Hermitian show that $I[A, B]$ is also Hermitian.
 (c) Show that the eigen functions of a Hermitian operator having different eigen values must be orthogonal. (All'd 1998)

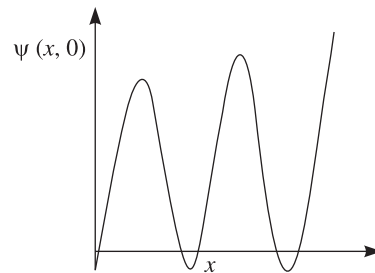
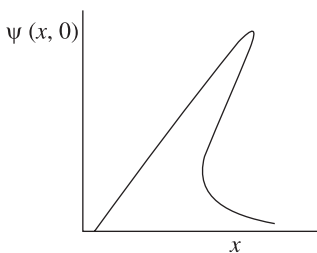
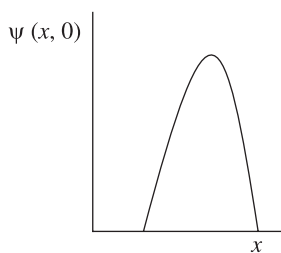
17. (a) Explain, in brief, the difference between Kroncker and Dirac delta functions.
 (b) If ψ_1 and ψ_2 are eigen functions of a linear operator, show that their linear combination will also be an eigen function of the operator.
 (c) For conservation of probability show that the Hamiltonian must be Hermitian.

18. (a) Evaluate $\left[\frac{d^2}{dx^2}, x \right]$

(b) Prove that $\hat{L}_z \hat{L}_+ = \hat{L}_+ (\hat{L}_z + \hbar)$ and $\hat{L}_z \hat{L}_- = \hat{L}_- (\hat{L}_z - \hbar)$. (All'd 2007)

19. (a) Test if the following are eigen functions of operator $\frac{d^2}{dx^2}$? What are the corresponding eigen values?
 (i) $\sin x$ (ii) $\log x$ (iii) $\exp(ax)$, where a is a constant?
 (b) Explain why Hamiltonian of a system is always Hermitian? (All'd 2007)

20. (a) Explain with reasons which of the following wave functions are acceptable and unacceptable in quantum mechanics?



(b) If the Hamiltonian can be written as following $H = \sum_{n,m} C_{nm} x^n p_x^m$, hence prove the Ehrenfest theorem

$$\frac{d}{dt} \langle x \rangle = \left\langle \frac{\partial H}{\partial p_x} \right\rangle \quad \text{and} \quad \frac{d}{dt} \langle p_x \rangle = \left\langle -\frac{\partial H}{\partial x} \right\rangle \quad (\text{All'd 2006})$$

21. (a) Find $[\hat{A}, \hat{B}]$ if $\hat{A} = \hat{x} + \frac{d}{dx}$ and $\hat{B} = \hat{x} - \frac{d}{dx}$. (All'd 2006)

22. (a) Write down the Schrodinger equation for a free particle confined to move in a plane and find out the allowed energy levels.

(b) Which of the following forms of the wave function are acceptable in quantum mechanics.

(i) $\sin x$ (ii) $\tan x$ (iii) $\exp(-x)$ (iv) $\exp(-x^2)$ (All'd 2005)

23. (a) When are the energy eigen values of a quantum particle discrete in nature? (All'd 2005)

24. (a) Write Hamiltonian of a particle of mass moving with velocity v along x direction with potential energy

$$V = \frac{A}{x^2} + Bv, \text{ where } A \text{ and } B \text{ are constants ?}$$

(b) Prove that (i) If two operators A and B are Hermitian and their product AB is also Hermitian. (ii) The operators A and B commute.

(c) If $T_a \psi(x) = \psi(x+a)$, prove that $T_a^\dagger = T_{-a}$ (All'd 2004)

25. (a) Show that momentum operator is Hermitian.

(b) Prove that $[x^n, p_x] = i\hbar n x^{n-1}$ and $[x, p_x^m] = i\hbar m p_x^{m-1}$ (All'd 2003)

26. (a) What is expectation value? Find expectation value of potential energy in the ground state of a linear harmonic oscillator.

(b) For operators A, B, C prove that $(ABC)^\dagger = C^\dagger B^\dagger A^\dagger$ hence show that for operators A and B to commute, A, B and AB should be Hermitian. (All'd 2002)

27. (a) What is meant by free and bound states of a quantum mechanical system?

(b) Consider the momentum operator $\hat{p}_x$ (i) obtain its eigen functions and eigen values, (ii) normalize the eigen functions using box normalization technique, (iii) compare the eigen values with those of a particle of mass m confined inside a box of length L . In what limit do they coincide? (All'd 2001)

28. (a) Define orthogonality and normalizability of Schrodinger wave function.

(b) Write down the Hamiltonian for a particle of mass m moving along x axis with potential energy $V(x) = Ax^2 + Bv$, where v is the velocity of the particle and A and B are constants. (All'd 2000)

29. (a) A wave function can be expanded in the form $\Psi = \sum_n a_n u_n$. What do u_n represent and what is the physical significance of $|a_n|^2$? Explain in short.

(b) Show that if operators A and B are Hermitian, the operator $\frac{i}{2}[A, B]$ is also Hermitian. (All'd 1999)

(c) If ψ_1 and ψ_2 are eigen functions of a linear operator, show that their linear combination will also be an eigen function of the operator. (All'd 1998)

POTENTIAL BARRIER PROBLEMS

4.1 POTENTIAL STEP OR STEP BARRIER

A potential step is described by

$$\begin{aligned} V(x) &= 0 & \text{for } x < 0 \\ &= V_0 & \text{for } x > 0 \end{aligned} \quad \dots(4.1.1)$$

This potential function is sketched in the Fig. (4.1.1).

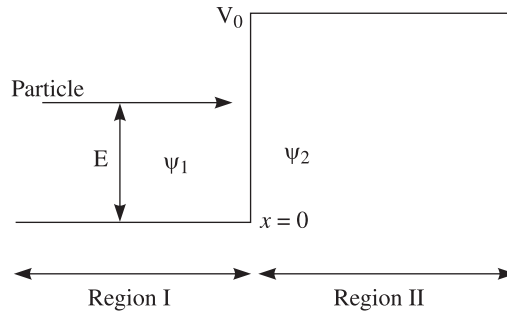


Fig. 4.1.1 A potential step: For $E < V_0$, region I is classically allowed and region II is forbidden

A particle with total energy E is incident on the potential step from left. The Schrodinger wave equation in the regions I and II are:

Region I ($x < 0$)

$$\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2}\psi_1 = 0$$

or

$$\frac{d^2\psi_1}{dx^2} + k_1^2\psi_1 = 0 \quad \dots(4.1.2)$$

where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(4.1.3)$$

Region II ($x > 0$)

$$\frac{d^2\psi_2}{dx^2} + \frac{2m(E - V_0)}{\hbar^2}\psi_2 = 0$$

or
$$\frac{d^2\psi_2}{dx^2} + k_2'^2\psi_2 = 0 \quad \dots(4.1.4)$$

where
$$k_2' = \sqrt{\frac{2m(E - V_0)}{\hbar^2}} \quad \dots(4.1.5)$$

Solution of Eqn. (4.1.2) is

$$\psi_1 = A \exp(ik_1x) + B \exp(-ik_1x) \quad \dots(4.1.6)$$

and solution of Eqn. (4.1.4) is

$$\psi_2 = C \exp(ik_2'x) + D \exp(-ik_2'x) \quad \dots(4.1.7)$$

where A, B, C and D are arbitrary constants.

Case I: $E < V_0$: When the energy E of the particle is less than the height V_0 of the potential step, the kinetic energy of the particle is negative in the region II. Classical physics does not allow the particle to enter the region II. In this case k_2' is imaginary and we may write

$$k_2' = ik_2 = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}} \quad \dots(4.1.8)$$

The solution of Eqn.(4.1.4) in the region II can be expressed as

$$\psi_2 = C \exp(-k_2x) + D \exp(k_2x) \quad \dots(4.1.9)$$

The second term on the right hand side of Eqn.(4.1.9) is an increasing function. This leads to the conclusion that the probability density of finding the particle increases as x increases without limit, which is physically not acceptable and therefore we must set $D = 0$. So the solution of Schrodinger equation in region II becomes

$$\psi_2 = C \exp(-k_2x) \quad \dots(4.1.10)$$

Now we use the following boundary conditions to determine the constants B and C in terms of A.

(i)
$$\psi_1(0) = \psi_2(0)$$

(ii)
$$\left(\frac{\partial \psi_1}{\partial x} \right)_{x=0} = \left(\frac{\partial \psi_2}{\partial x} \right)_{x=0}$$

Applying above conditions to the functions $\psi_1(x)$ and $\psi_2(x)$, we obtain following equations:

$$A + B = C \quad \dots(4.1.11)$$

$$ik_1(A - B) = -k_2 \quad \dots(4.1.12)$$

From these equations, we get

$$B = \frac{k_1 - ik_2}{k_1 + ik_2} A \quad \dots(4.1.13)$$

$$C = \frac{2k_1}{k_1 + ik_2} A \quad \dots(4.1.14)$$

We can express the relationship between B and A and between C and A in a more convenient form by making use of following transformations:

$$k_1 + ik_2 = re^{i\delta}$$

$$k_1 - ik_2 = re^{-i\delta}$$

where

$$r = \sqrt{k_1^2 + k_2^2} \quad \text{and} \quad \tan \delta = \frac{k_2}{k_1}$$

Hence

$$B = Ae^{-2i\delta} \quad \dots(4.1.15)$$

The wave function ψ_1 in the region I is

$$\begin{aligned} \psi_1 &= A \exp(ik_1x) + A \exp(-2i\delta) \exp(-ik_1x) \\ &= A \exp(-i\delta) [\exp(ik_1x + i\delta) + \exp(-ik_1x - i\delta)] \\ &= 2A \exp(-i\delta) \cos(k_1x + \delta) \end{aligned} \quad \dots(4.1.16)$$

The wave function in the region II is

$$\psi_2 = C \exp(-k_2x) \quad \dots(4.1.17)$$

The wave function in the region I is superposition of two waves. The first term $A \exp(ik_1x)$ corresponds to a wave traveling to the right and the second term $B \exp(-ik_1x)$ to a wave traveling to the left. Superposition of these two waves give rise to a standing wave represented by Eqn.(4.1.16). The magnitude of the ratio B/A is unity *i.e.*, the incident and the reflected waves have the same amplitude. From this we conclude that the wave function given

by Eqn. (4.1.16) describes the situation in which a particle incident from the left is reflected back by the potential hill. This behavior is analogous to the classical behavior of electromagnetic waves at a metal surface.

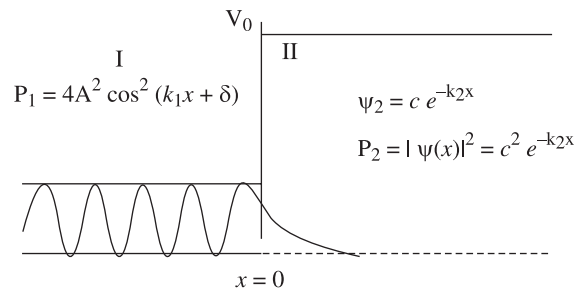


Fig. 4.1.2 Probability density in classically forbidden and in allowed regions

The wave function in the classically forbidden region is exponentially decaying in nature and predicts finite probability (although small) of finding the particle in this region. Notice that the probability density shows oscillatory behavior in the region I ($x < 0$). This is a quantum mechanical interference result having no classical analogue.

The probabilities of finding the particle in the regions I and II are given by

$$P_I = \psi_1^* \psi_1 = 4A^2 \cos^2(k_1 x + \delta)$$

and

$$P_{II} = |\psi_2|^2 = c^2 \exp(-2k_2 x)$$

Case II ($E > V_0$): In this case k'_2 is real. The wave function in the region II is

$$\psi_2 = C \exp(ik'_2 x) + D \exp(-ik'_2 x) \quad \dots(4.1.18)$$

The first term in above equation corresponds to a wave traveling to the right and the second term to a wave traveling to the left. There is nothing to reflect the wave in region II, we must, therefore, set $D = 0$. Appropriate boundary conditions at the junction of regions I and II are:

$$\psi_1(0) = \psi_2(0)$$

$$\left(\frac{d\psi_1}{dx} \right)_{x=0} = \left(\frac{d\psi_2}{dx} \right)_{x=0}$$

Applying these boundary conditions to the wave functions ψ_1 and ψ_2 , we have

$$A + B = C \quad \dots(4.1.19)$$

$$k_1 A - k_1 B = k'_2 C \quad \dots(4.1.20)$$

From Eqns. (4.1.19) and (4.1.20), we get

$$B = \frac{k_1 - k'_2}{k_1 + k'_2} A \quad \dots(4.1.21)$$

$$C = \frac{2k_1}{k_1 + k'_2} A \quad \dots(4.1.22)$$

The current densities associated with incident wave, reflected wave and transmitted waves are

$$J_i = \frac{\hbar k_1}{m} |A|^2 \quad \dots(4.1.23)$$

$$J_r = \frac{\hbar k_1}{m} |B|^2 \quad \dots(4.1.24)$$

$$J_t = \frac{\hbar k'_2}{m} |C|^2 \quad \dots(4.1.25)$$

The coefficients for energy reflection R and transmission (T) are given by

$$R = \frac{J_r}{J_i} = \frac{|B|^2}{|A|^2} = \frac{(k_1 - k_2')^2}{(k_1 + k_2')^2} \quad \dots(4.1.26)$$

$$T = \frac{J_t}{J_i} = \frac{|C|^2}{|A|^2} = \frac{4k_1k_2'}{(k_1 + k_2')^2} \quad \dots(4.1.27)$$

Notice that

$$R + T = 1 \quad \dots(4.1.28)$$

which is in accordance with the principle of conservation of energy.

One of the peculiar results which quantum mechanics predicts is that although the particle has enough energy to cross over the step even then there is a non-zero probability of its being reflected ($R \neq 0$).

4.2 POTENTIAL BARRIER (TUNNEL EFFECT)

A potential barrier is a region in which the potential energy of a particle exceeds the total energy. Let us consider a potential barrier defined by

$$\begin{aligned} V(x) &= 0 && \text{for } x < 0 \\ &= V && \text{for } 0 \leq x \leq L \\ &= 0 && \text{for } x > L \end{aligned} \quad \dots(4.2.1)$$

The potential barrier is sketched in the Fig. (4.2.1). Assume that a particle moving from left to right encounters the potential barrier of height V and width L on its path.

In terms of classical mechanics the behavior may be predicted as follows:

- (i) If the energy of the particle is greater than the height of the barrier ($E > V$), the particle passes over the barrier without any hindrance. Inside the barrier, the velocity of the particle diminishes and beyond it the particle acquires its initial value.
- (ii) If $E < V$, the particle is reflected from the barrier and is unable to penetrate through the barrier.

Quantum mechanical treatment of this problem predicts different results. If $E > V$, there is a finite probability that the particle will be reflected from the barrier. If $E < V$, there is a finite probability that the particle will penetrate through the barrier and will be found on the other side of the barrier. Thus the quantum mechanics allows the particle to leak through the barrier. This phenomenon is called **tunnel effect**. This is a purely quantum mechanical result having no classical analogue. Thus by this mechanism the alpha-particles are emitted by radioactive nuclei, although the potential barrier is such that classically they cannot be able to surmount it.

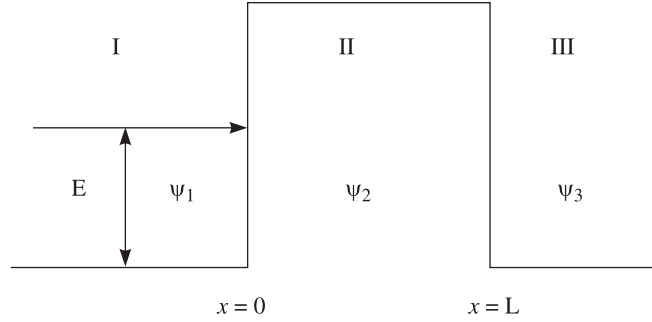


Fig. 4.2.1 One dimensional potential barrier

In the Fig. (4.2.1) the potential barrier divides the space into three regions I, II and III. The Schrödinger wave equations in these regions are:

Region I

$$\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2}\psi_1 = 0$$

or

$$\frac{d^2\psi_1}{dx^2} + k_1^2\psi_1 = 0 \quad \dots(4.2.2)$$

where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(4.2.3)$$

Region II

$$\frac{d^2\psi_2}{dx^2} + \frac{2m(E - V)}{\hbar^2}\psi_2 = 0$$

or

$$\frac{d^2\psi_2}{dx^2} + k_2'^2\psi_2 = 0 \quad \dots(4.2.4)$$

where

$$k_2' = \sqrt{\frac{2m(E - V)}{\hbar^2}} \quad \dots(4.2.5)$$

Here k_2' is imaginary and therefore we can write

$$k_2' = ik_2, \quad k_2 = \sqrt{\frac{2m(V - E)}{\hbar^2}} \quad \dots(4.2.6)$$

Region III

$$\frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2}\psi_3 = 0$$

or

$$\frac{d^2\psi_3}{dx^2} + k_3^2\psi_3 = 0 \quad \dots(4.2.7)$$

where

$$k_3 = \sqrt{\frac{2mE}{\hbar^2}} = k_1 \quad \dots(4.2.8)$$

Solutions of Eqns. (4.2.2), (4.2.4) and (4.2.7) are

$$\psi_1(x) = A \exp(ik_1x) + B \exp(-ik_1x) \quad \dots(4.2.9)$$

$$\begin{aligned} \psi_2(x) &= C \exp(-ik_2'x) + D \exp(ik_2'x) \\ &= C \exp(k_2x) + D \exp(-k_2x) \end{aligned} \quad \dots(4.2.10)$$

$$\psi_3(x) = F \exp(ik_1x) + G \exp(-ik_1x) \quad \dots(4.2.11a)$$

The term $\exp(ik_1x)$ corresponds to a wave propagating in the positive direction of x -axis and $\exp(-ik_1x)$ to a wave propagating in opposite direction. In region III there must be only one wave that has penetrated through the barrier and is propagating from left to right. We must, therefore, assume $G = 0$.

The wave function $\psi_3(x)$ then becomes

$$\psi_3(x) = F \exp(ik_1x) \quad \dots(4.2.11b)$$

To find out other coefficients we use the following boundary conditions that wave functions must satisfy.

At $x = 0$,

$$\psi_1(0) = \psi_2(0) \quad \dots(4.2.12)$$

$$\left(\frac{d\psi_1}{dx} \right)_{x=0} = \left(\frac{d\psi_2}{dx} \right)_{x=0} \quad \dots(4.2.13)$$

At $x = L$,

$$\psi_2(L) = \psi_3(L) \quad \dots(4.2.14)$$

$$\left(\frac{d\psi_2}{dx} \right)_{x=L} = \left(\frac{d\psi_3}{dx} \right)_{x=L} \quad \dots(4.2.15)$$

These boundary conditions lead to following equations:

$$A + B = C + D \quad \dots(4.2.16)$$

$$ik_1A - ik_1B = k_2C - k_2D \quad \dots(4.2.17)$$

$$C \exp(k_2L) + D \exp(-k_2L) = F \exp(ik_1L) \quad \dots(4.2.18)$$

$$k_2C \exp(k_2L) - k_2D \exp(-k_2L) = ik_1F \exp(ik_1L) \quad \dots(4.2.19)$$

Here we are interested in **transmission coefficient or transmission probability T**, and **reflection coefficient or reflection probability R**. T is defined as the ratio of the current density associated with transmitted beam and that associated with incident beam. Similarly, R is defined as the ratio of current density associated with transmitted beam to that associated with incident beam.

$$T = \frac{J_{\text{trans}}}{J_{\text{inci}}} = \frac{(\hbar k_1/m) |F|^2}{(\hbar k_1/m) |A|^2} = \frac{|F|^2}{|A|^2} = \left(\frac{F}{A}\right)^* \left(\frac{F}{A}\right) \quad \dots(4.2.20)$$

$$R = \frac{J_{\text{ref}}}{J_{\text{inc}}} = \frac{(\hbar k_1/m) |B|^2}{(\hbar k_1/m) |A|^2} = \frac{|B|^2}{|A|^2} = \left(\frac{B}{A}\right)^* \left(\frac{B}{A}\right) \quad \dots(4.2.21)$$

The conservation of energy demands that

$$R + T = 1 \quad \dots(4.2.22)$$

From Eqns. (4.2.16) to (4.2.19) the expressions for $\frac{|F|^2}{|A|^2}$ and $\frac{|B|^2}{|A|^2}$ come out to be

$$\frac{|F|^2}{|A|^2} = \frac{16k_1^2 k_2^2 \exp(2k_2 L)}{(k_2^2 - k_1^2)^2 [1 - \exp(2k_2 L)]^2 + 4k_1^2 k_2^2 [1 + \exp(2k_2 L)]^2} \quad \dots(4.2.23)$$

$$\frac{|B|^2}{|A|^2} = \frac{(k_2^2 + k_1^2)^2 [1 - \exp(2k_2 L)]^2}{(k_2^2 - k_1^2)^2 [1 - \exp(2k_2 L)]^2 + 4k_1^2 k_2^2 [1 + \exp(2k_2 L)]^2} \quad \dots(4.2.24)$$

The expression for T after simplification becomes

$$T = \frac{|F|^2}{|A|^2} = \frac{4k_1^2 k_2^2}{(k_2^2 + k_1^2)^2 \sin^2 h^2 k_2 L + 4k_1^2 k_2^2} \quad \dots(4.2.25)$$

Substituting the expressions for k_1 and k_2 , we have

$$T = \frac{1}{1 + \frac{V^2 \sin^2 h^2 k_2 L}{4E(V-E)}} = \left[1 + \frac{V^2 \sin^2 h^2 k_2 L}{4E(V-E)} \right]^{-1} \quad \dots(4.2.26)$$

The expression for coefficient of reflection comes out to be

$$R = \frac{|B|^2}{|A|^2} = \frac{(k_2^2 + k_1^2)^2}{(k_2^2 + k_1^2)^2 + \frac{4k_1^2 k_2^2}{\sin^2 h^2 k_2 L}} \quad \dots(4.2.27)$$

Substituting the expressions for k_1 and k_2 , we obtain

$$R = \frac{V^2}{V^2 + \frac{4E(V-E)}{\sin^2 h^2 k_2 L}} = \left[1 + \frac{4E(V-E)}{V^2 \sin^2 h^2 k_2 L} \right]^{-1} \quad \dots(4.2.28)$$

Classical limit is obtained by setting $h \rightarrow 0$. In this limit $k_2 \rightarrow \infty$ and $k_1 \rightarrow \infty$. This implies that $T \rightarrow 0$ and $R \rightarrow 1$. The probability of transmission becomes zero and that for reflection is unity. This is the classical prediction.

When the barrier height and width both are large, $k_2 L \gg 1$ and $\sin h k_2 L \rightarrow \frac{1}{2} \exp(k_2 L)$. Under this approximation 1 can be neglected in the expression for T. Thus

$$T = \frac{4E(V-E)}{V^2 \left(\frac{1}{2} \exp(k_2 L) \right)^2} = \frac{16E}{V} \left(1 - \frac{E}{V} \right) \exp(-2k_2 L),$$

where
$$k_2 = \sqrt{\frac{2m(V-E)}{\hbar^2}} \quad \dots(4.2.29a)$$

The exponential term in Eqn. (4.2.29a) is more dominant term than the coefficient $\frac{16E}{V} \left(1 - \frac{E}{V} \right)$ and the latter is assumed to be equal to 1 in most of the application. With this approximation the expression for transmission probability becomes

$$T \cong \exp(-2k_2 L) \quad \dots(4.2.29b)$$

The quantum mechanical analysis of potential barrier problem shows that the particle has finite probability of getting transmitted through the barrier even its energy is less than the height of the barrier.

The transmission probability of the particle depends on (i) width L of the barrier and (ii) the difference $(V - E)$. This dependence of T on the width of the barrier and energy of the incident particle is displayed in the table.

E	V	L	$k_2 = \sqrt{\frac{2m(V-E)}{\hbar^2}}$	$2k_2 L$	T
1 eV	4 eV	0.1 nm	$0.886 \times 10^{10} \text{ m}^{-1}$	1.772	0.17
1 eV	4 eV	0.2 nm	$0.886 \times 10^{10} \text{ m}^{-1}$	3.544	0.03
2 eV	4 eV	0.1 nm	$0.724 \times 10^{10} \text{ m}^{-1}$	1.448	0.23

Notice that when the width of the barrier is doubled, the transmission probability decreases by nearly 6 times whereas when the energy of the incident particle is doubled, the transmission probability increases only by a factor of nearly 1.3 times. So the transmission probability strongly depends on the width of the barrier.

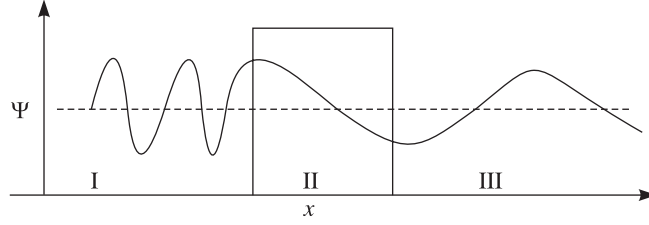


Fig. 4.2.2 Wave functions in the three regions

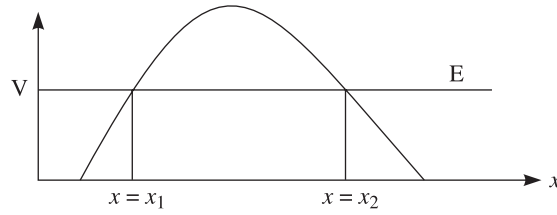


Fig. 4.2.3 A potential barrier of varying width

For potential barrier of variable width, as shown in the Fig. (4.2.3), the transmission probability is given by

$$T \cong \exp \left[-\frac{2}{\hbar} \int_{x_1}^{x_2} \sqrt{2m(V-E)} dx \right] \quad \dots(4.2.30)$$

The emission of alpha-particle from radioactive nuclei, the passage of electron through potential barrier in tunnel diode and the crossing of electron through classically forbidden region between two superconductors are the well-known examples of **tunneling phenomenon**.

Case 2: $E > V$

In this case $k_2 = \sqrt{\frac{2m}{\hbar^2}(V-E)}$ becomes imaginary. Let $k_2 = i\beta$, where $\beta = \sqrt{\frac{2m}{\hbar^2}(E-V)}$.

The expressions for R and T become

$$R = \frac{1}{1 + \frac{4E(E-V)}{V^2 \sin^2 \beta L}} = \left[1 + \frac{4E(E-V)}{V^2 \sin^2 \beta L} \right]^{-1} \quad \dots(4.2.31)$$

$$T = \frac{1}{1 + \frac{V^2 \sin^2 \beta L}{4E(E-V)}} = \left[1 + \frac{V^2 \sin^2 \beta L}{4E(E-V)} \right]^{-1} \quad \dots(4.2.32)$$

(a) When $E \rightarrow V$, $\beta \rightarrow 0$, $\sin \beta L \approx \beta L$ and in this limit

$$T = \frac{1}{1 + \frac{mVL^2}{2\hbar^2}} \quad \dots(4.2.33)$$

(b) Eqn. (4.2.32) shows that when E increases above V , transmission probability T becomes oscillatory due to presence of $\sin \beta L$. The barrier becomes transparent ($T = 1$) when

$$\beta L = n\pi, \quad n = 1, 2, 3, \dots$$

or
$$\frac{2m(E-V)}{\hbar^2} L^2 = n^2 \pi^2$$

or
$$L = \frac{n\lambda}{2} \quad (4.2.34)$$

where
$$\lambda = \frac{h}{\sqrt{2m(E-V)}} = \text{de Broglie wavelength of the particle.}$$

Thus, when the width of the barrier is integral multiple of half the wavelength of the particle, the barrier becomes transparent. This phenomenon is called **resonance scattering**. Resonances are obtained for the values of E given by

$$\beta^2 = \left(\frac{n\pi}{L} \right)^2 = \frac{2m(E-V)}{\hbar^2}$$

or
$$E = V \left[1 + \frac{n^2 \pi^2 \hbar^2}{2mVL^2} \right] \quad \dots(4.2.35)$$

Minimum value of T is obtained when

$$\sin \beta L = 1 \quad \text{or} \quad \beta L = (2n+1)\pi/2, \quad n = 0, 1, 2, 3, \dots$$

or
$$E = V \left[1 + \frac{(2n+1)^2 \pi^2 \hbar^2}{8mVL^2} \right] \quad \dots(4.2.36)$$

For this value of E , T is minimum.

or
$$T_{\min} = \left[1 + \frac{1}{\frac{4E}{V} \left(\frac{E}{V} - 1 \right)} \right]^{-1} \quad \dots(4.2.37)$$

(c) When E decreases below V , T decreases monotonically. When $k_2L \gg 1$, $\sinh k_2L = \frac{1}{2} \exp(k_2L)$. In this case the expression for T becomes

$$T = \left[1 + \frac{V^2 \sinh^2 k_2L}{4E(V-E)} \right]^{-1} \quad (\text{omitting } 1).$$

$$\cong \frac{4E(V-E)}{V^2 \left(\frac{1}{2} \exp k_2L \right)^2} = \frac{16E}{V} \left(1 - \frac{E}{V} \right) \exp(-2k_2L). \quad \dots(4.2.38)$$

The variation of T with E/V and that of T with increasing thickness of barrier L are shown in the Fig. 4.2.4.

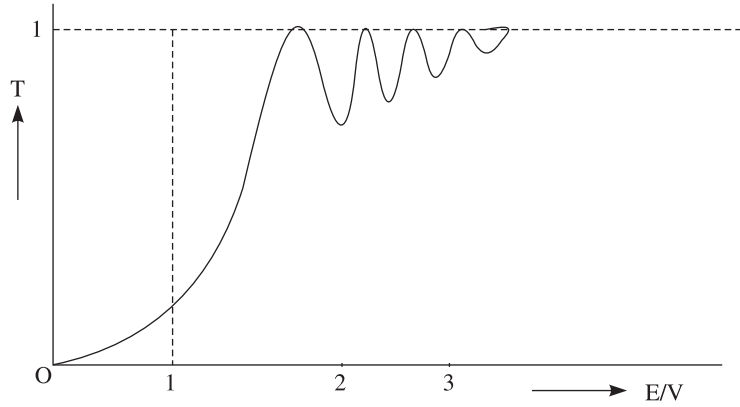


Fig. 4.2.4 Variation of T with E/V

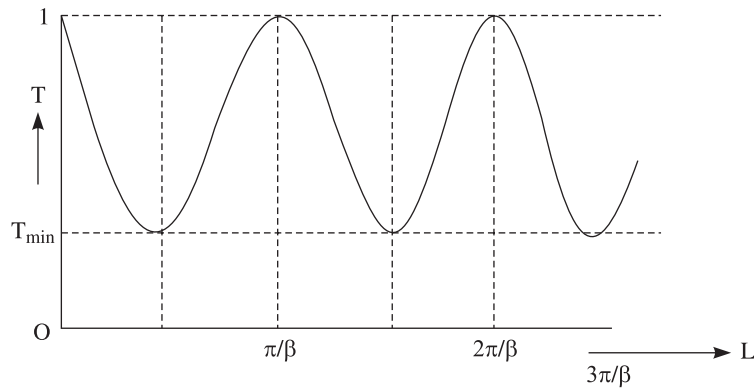


Fig. 4.2.5 Variation of T with thickness L of barrier. Appearance of transmission resonances

4.3 PARTICLE IN A ONE-DIMENSIONAL POTENTIAL WELL OF FINITE DEPTH

Let us consider the motion of a particle in a one-dimensional potential well defined by

$$\begin{aligned} V(x) &= 0 & x < -a \\ &= -V_0 & -a < x < a \\ &= 0 & x > a \end{aligned} \quad \dots(4.3.1)$$

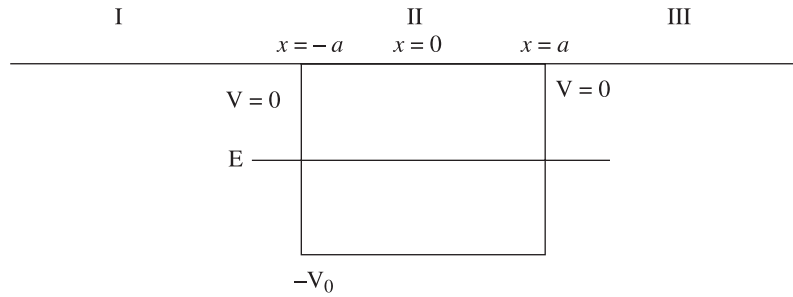


Fig. 4.3.1 One dimensional potential well of depth V_0

We shall first consider the case of the particle which is classically bound to remain within the well, that is, $-V_0 < E < 0$. The entire allowed region for the motion of the particle can be divided into three regions I, II and III. Let ψ_1 , ψ_2 and ψ_3 be the wave functions in the three regions. The Schrodinger equations in the three regions are:

$$x < -a, \quad \frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2}\psi_1 = 0 \quad \dots(4.3.1a)$$

$$\frac{d^2\psi_1}{dx^2} - k^2\psi_1 = 0 \quad \dots(4.3.1b)$$

where $k = \sqrt{-\frac{2mE}{\hbar^2}}$, is a real positive quantity. ...(4.3.2)

$$-a < x < a, \quad \frac{d^2\psi_2}{dx^2} + \frac{2m[E - (-V_0)]}{\hbar^2}\psi_2 = 0 \quad \dots(4.3.3a)$$

$$\frac{d^2\psi_2}{dx^2} + k_2^2\psi_2 = 0 \quad \dots(4.3.3b)$$

where $k_2 = \sqrt{\frac{2m(E + V_0)}{\hbar^2}}$, is a real positive quantity. ...(4.3.4)

$$x > a, \quad \frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2}\psi_3 = 0 \quad \dots(4.3.5)$$

$$\frac{d^2\psi_3}{dx^2} + k^2 \psi_3 = 0 \quad \dots(4.3.6)$$

The general solutions of Schrödinger equations in the three regions are:

$$x < -a, \quad \psi_1 = A_1 \exp(kx) + B_1 \exp(-kx) \quad \dots(4.3.7)$$

$$-a < x < a \quad \psi_2 = A_2 \sin k_2 x + B_2 \cos k_2 x \quad \dots(4.3.8)$$

$$x > a \quad \psi_3 = A_3 \exp(kx) + B_3 \exp(-kx) \quad \dots(4.3.9)$$

When $x \rightarrow -\infty$, $\exp(-kx) \rightarrow \infty$, which is unacceptable. We, therefore, set $B_1 = 0$. Similarly, when $x \rightarrow \infty$, $\exp(kx) \rightarrow \infty$, which is again unacceptable. We again set $A_3 = 0$. So the above solutions become

$$x < -a, \quad \psi_1 = A_1 \exp(kx) \quad \dots(4.3.10)$$

$$-a < x < a \quad \psi_2 = A_2 \sin k_2 x + B_2 \cos k_2 x \quad \dots(4.3.11)$$

$$x > a \quad \psi_3 = B_3 \exp(-kx) \quad \dots(4.3.12)$$

The boundary conditions that the wave functions and their derivatives be continuous at $x = \pm a$. That is,

$$\psi_1(-a) = \psi_2(-a), \quad \psi_2(a) = \psi_3(a)$$

$$\psi_1'(-a) = \psi_2'(-a), \quad \psi_2'(a) = \psi_3'(a)$$

Applying these boundary conditions, we get following equations:

$$A_1 0 + A_2 \sin k_2 a + B_2 \cos k_2 a - B_3 \exp(-ka) = 0$$

$$-A_1 \exp(-ka) - A_2 \sin k_2 a + B_2 \cos k_2 a + B_3 0 = 0$$

$$A_1 0 - A_2 k_2 \cos k_2 a - B_2 k_2 \sin k_2 a + B_3 k \exp(-ka) = 0$$

$$A_1 k \exp(-ka) + A_2 k_2 \cos k_2 a + B_2 k_2 \sin k_2 a + B_3 0 = 0$$

This is a set of four homogeneous equations in four unknown coefficients. Solutions of physical significance exist only if

$$\exp(-2ka) \begin{vmatrix} \sin k_2 a & \cos k_2 a & -1 & 0 \\ -\sin k_2 a & \cos k_2 a & 0 & -1 \\ k_2 \cos k_2 a & -k_2 \sin k_2 a & k & 0 \\ k_2 \cos k_2 a & k_2 \sin k_2 a & & k \end{vmatrix} = 0$$

Since $\exp(-2k_2 a) \neq 0$, we have

$$k_2^2 \sin k_2 a \cos k_2 a + k k_2 \sin^2 k_2 a - k k_2 \cos^2 k_2 a - k^2 \sin k_2 a \cos k_2 a = 0$$

or $k_2 \sin k_2 a (k \sin k_2 a + k_2 \cos k_2 a) - k \cos k_1 a (k_2 \cos k_2 a + k \sin k_2 a) = 0$

or $(k \sin k_2 a + k_2 \cos k_2 a)(k_2 \sin k_2 a - k \cos k_2 a) = 0$

Dividing by $\cos^2 k_2 a$, we obtain

$$(k \tan k_2 a + k_2)(k_2 \tan k_2 a - k) = 0 \quad \dots(4.3.13)$$

This equation is satisfied if

$$k \tan k_2 a = -k_2$$

or $k = -k_2 \cot k_2 a \quad \dots(4.3.14)$

and $k = k_2 \tan k_2 a \quad \dots(4.3.15)$

We know that $k_2^2 = \frac{2m(E + V_0)}{\hbar^2}$ and $-k^2 = \frac{2mE}{\hbar^2}$

$$\Rightarrow k_2^2 = \frac{2mE}{\hbar^2} + \frac{2mV_0}{\hbar^2}$$

$$\Rightarrow k_2^2 = -k^2 + \mu^2 \quad \dots(4.3.16)$$

where $\mu^2 = \frac{2mV_0}{\hbar^2} \quad \dots(4.3.17)$

Notice that μ is a measure of the depth V_0 of the potential well. Eqns. (4.3.14) and (4.3.15) can now be written as

$$k = \sqrt{\mu^2 - k_2^2} = -k_2 \cot k_2 a \quad \dots(4.3.18)$$

$$k = \sqrt{\mu^2 - k_2^2} = k_2 \tan k_2 a \quad \dots(4.3.19)$$

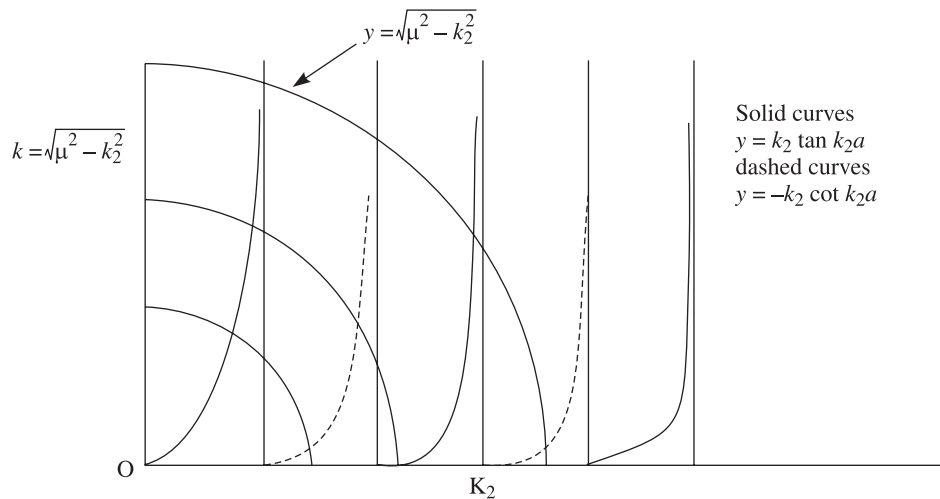


Fig. 4.3.2 The permissible values of k_2 and hence E corresponds to the points of intersection

The solutions (allowed values of k_2) of transcendental Eqns. (4.3.18) and (4.3.19) are given by the points of intersections of curves $y = k_2 \tan k_2 a$ or $y = -k_2 \cot k_2 a$ with $y = \sqrt{\mu^2 - k_2^2}$ which represents a circle of radius μ . It is evident that allowed values of k_2 and hence energy eigen values (which are mutually related through the relation $E = \frac{\hbar^2 k_2^2}{2m} - V_0$) form a discrete spectrum. The number of energy eigen values depend on the depth of potential. For shallow potential, $V_0 \rightarrow 0$, the radius of the circle $\mu \rightarrow 0$ and we get only one point of intersection and hence only one energy eigen value. With increasing strength of potential, the number of energy eigen values increases.

Without going into the details of method of calculating the wave functions corresponding to different energy we simply sketch their forms in Fig. (4.3.3).

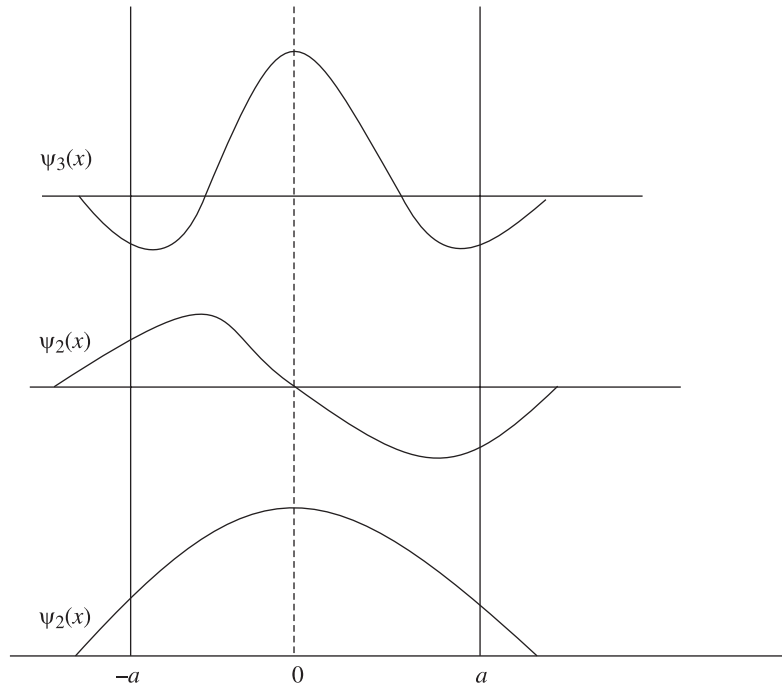


Fig. 4.3.3 Wave functions of a particle in a potential of finite depth ($-V_0 < E < 0$)

It is important to note that the wave function as a whole is either an even function or an odd function of x . Here the lowest energy state is even, the next odd, the next even, and so forth, alternately. This comes about as a result of the fact that the potential $V(x)$ is itself an even function of x .

Another important feature of the wave function is that it extends beyond the limits of the well. Therefore, there is a definite probability that the particle will be found in the classically forbidden region beyond the actual boundaries of the well. This phenomenon is known as *barrier penetration*.

For $E > 0$ (unbound states) the wave functions outside the well become oscillatory in nature like that inside the well and the energy eigen values form a continuous spectrum as shown in the Fig. (4.3.4).

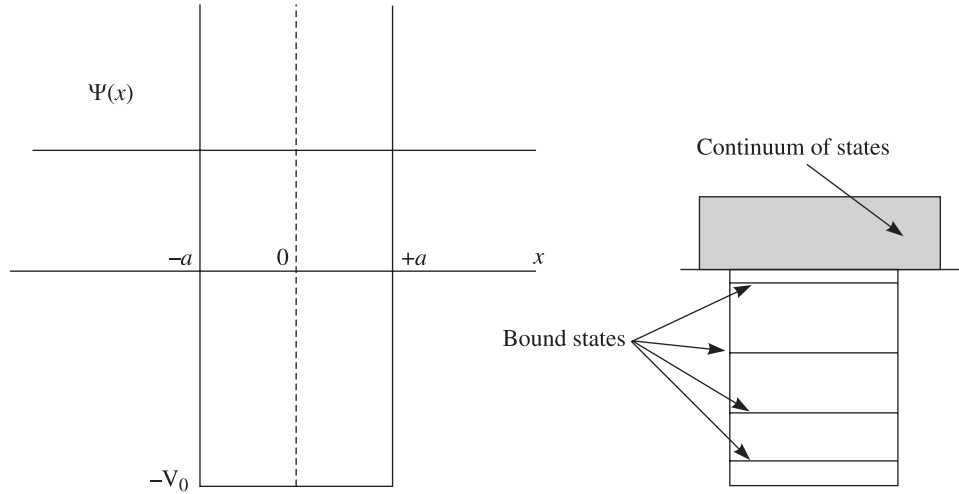


Fig. 4.3.4 Energy states of particle ($E > 0$) in a potential well of finite depth

4.4 THEORY OF ALPHA DECAY

The problem of emission of α -particle from radioactive nuclei is inexplicable in classical physics; quantum mechanics provides a natural explanation. In fact, the theory of α -decay first given by Gamow and independently by Condon and Gurney in 1928, was recognized as a spectacular triumph of newly discovered (1926) quantum mechanics.

Let us try to explain the phenomenon in terms of classical physics. Although nuclei are composed of neutrons and protons, we can think of α -particle as an entity within the nucleus. When the α -particle is outside the nucleus, it experiences a repulsive Coulomb force and the corresponding electrostatic energy is

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r}; \quad r > R \quad \dots(4.4.1)$$

where R is nuclear radius and Z is atomic number of daughter nucleus. The energy $V(r)$ given by Eqn. 4.4.1 is equal to the work that is done against the Coulomb repulsion when an α -particle is brought from infinity towards the nucleus. As the α -particle approaches the nuclear surface, the electrostatic energy increases and becomes maximum at the surface $r = R$ and is given by

$$V(R) = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{R} \approx 29 \text{ MeV for uranium nucleus} \quad \dots(4.4.2)$$

This gives the minimum energy that an α -particle must have to penetrate the nucleus. In other words, an α -particle approaching the nucleus with kinetic energy less than $V(R)$ cannot surmount the repulsive Coulomb forces and will turn back. The magnitude of potential energy $V(R)$ is called *barrier height*. The variation of potential energy $V(r)$ of an α -particle in the force field of daughter nucleus with r is shown in the figure 4.4.1.

Inside the nucleus we do not know the exact shape of the potential energy curve, but we definitely know that the nuclear forces are strong and attractive in nature and hence the corresponding potential energy must be negative and the curve representing the potential energy must have a dip as shown in the Fig. (4.4.1). The strong nuclear forces thus form a *potential well*. Classically an α -particle inside the well cannot escape from the nucleus unless its energy is at least equal to the height of the potential barrier.

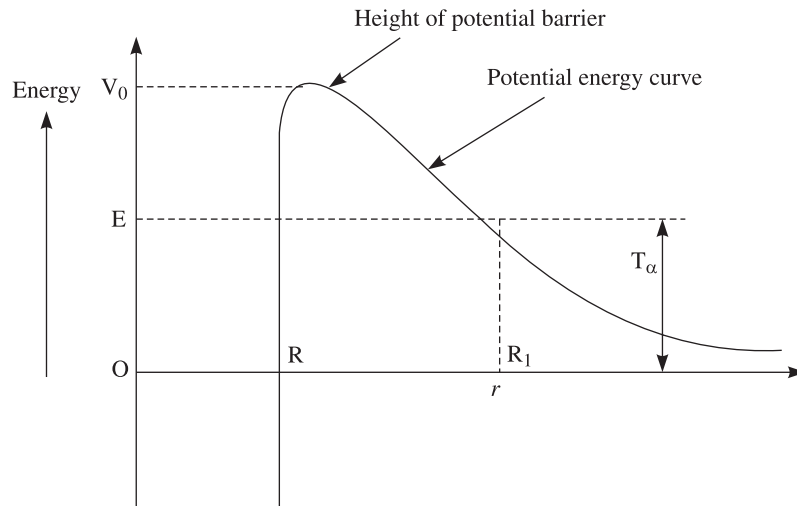


Fig. 4.4.1 Potential energy curve of an alpha-particle inside and outside the nucleus

Let T_α be the kinetic energy of the α -particle such that $T_\alpha < V(R)$. If the α -particle is approaching the nucleus, its whole kinetic energy will be converted into potential energy at point $r = R_1$ and the particle will come momentarily at rest and then it will turn back. The point $r = R_1$ is called the classical turning point. If the α -particle is inside the nucleus, it does not possess sufficient energy to jump over the barrier height. Thus the region from $r = R$ to $r = R_1$ is inaccessible to the α -particle and is called the *thickness of the barrier*. The conclusion drawn from classical view-point that a α -particle with energy less than the barrier height cannot escape from the nucleus is not in accord with observed facts. For instance, the energies of α -particles emitted from uranium nucleus are below 10 MeV, which is much less than the barrier height 29 MeV.

Quantum mechanics, on the other hand, gives straight forward explanation of alpha activity. The central features of the quantum theory are:

- (i) alpha-particle exists as a unit within the nucleus
- (ii) alpha-particle is in constant motion and bounces back and forth from the barrier walls. In each collision with the wall there is a finite probability that the particle will leak through the potential barrier.

Let f be the frequency with which an α -particle collides with the wall in order to escape from the nucleus and T be the *transmission probability* in each collision then the decay probability (λ) is given by

$$\lambda = f T$$

In terms of the velocity v of the α -particle and nuclear radius R the frequency of collision is

$$f = \frac{v}{2R}$$

The transmission probability T of a particle with energy T_α in potential barrier sketched in the Fig. (4.4.2) is given by

$$\ln T = -2 \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2} (V - T_\alpha)} dx$$

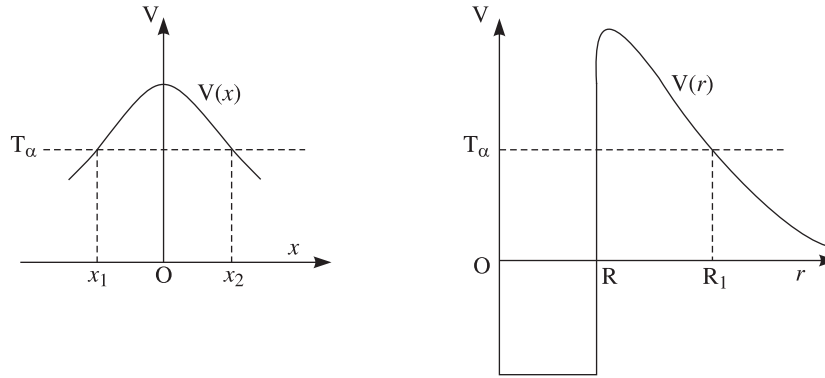


Fig. 4.4.2

Applying this result to the problem of α -decay, we have

$$\begin{aligned} \ln T &= -2 \int_R^{R_1} \sqrt{\frac{2m}{\hbar^2} \left(\frac{2Ze^2}{4\pi\epsilon_0 r} - T_\alpha \right)} dr \\ &= -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} \int_R^{R_1} \sqrt{\left(\frac{2Ze^2}{4\pi\epsilon_0 T_\alpha r} - 1 \right)} dr \end{aligned}$$

Making use of the fact that at $r = R_1$, $V = T_\alpha$, we obtain

$$\frac{2Ze^2}{4\pi\epsilon_0 R_1} = T_\alpha$$

whence

$$R_1 = \frac{2Ze^2}{4\pi\epsilon_0 T_\alpha} \quad \dots(4.4.3)$$

Now

$$\ln T = -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} \int_R^{R_1} \sqrt{\left(\frac{R_1}{r} - 1 \right)} dr \quad \dots(4.4.4)$$

To simplify the integration we make use of the substitution

$$r = R_1 \cos^2 \theta, \quad dr = -2 R_1 \cos \theta \sin \theta d\theta$$

Doing so, we get

$$\ln T = -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} \cdot R_1 \int_0^\beta 2 \sin^2 \theta d\theta$$

where

$$\beta = \cos^{-1} \sqrt{R/R_1}$$

$$\begin{aligned} \ln T &= -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} R_1 \int_0^\beta (1 - \cos 2\theta) d\theta \\ &= -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} R_1 \left[\theta - \frac{1}{2} \sin 2\theta \right]_0^\beta \\ &= -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} R_1 \left[\theta - \cos \theta \sqrt{1 - \cos^2 \theta} \right]_0^\beta \\ &= -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} R_1 \left[\cos^{-1} \sqrt{\frac{R}{R_1}} - \sqrt{\frac{R}{R_1}} \sqrt{1 - \frac{R}{R_1}} \right] \quad \dots(4.4.5) \end{aligned}$$

Now we shall make some approximations, which are valid for thick potential barrier.

$$\cos^{-1} \sqrt{\frac{R}{R_1}} = \frac{\pi}{2} - \sin^{-1} \sqrt{\frac{R}{R_1}} \approx \frac{\pi}{2} - \sqrt{\frac{R}{R_1}} \quad \text{and} \quad \left(1 - \frac{R}{R_1}\right)^{1/2} \approx 1$$

Hence

$$\ln T = -2 \sqrt{\frac{2mT_\alpha}{\hbar^2}} R_1 \left[\frac{\pi}{2} - 2 \sqrt{\frac{R}{R_1}} \right] \quad \dots(4.4.6)$$

Substituting the value of R_1 from Eqn. (4.4.3) in (4.4.6), we have

$$\begin{aligned} \ln T &= \frac{4e}{\hbar} \frac{m}{\pi \epsilon_0} \sqrt{ZR} - \sqrt{\frac{m}{2}} \left(\frac{e^2}{\hbar \epsilon_0} \right) Z T_\alpha^{-1/2} \\ &= a \sqrt{ZR} - b Z T_\alpha^{-1/2} \end{aligned}$$

where a and b are constants defined by

$$a = \frac{4me}{\pi \hbar \epsilon_0}, \quad b = \frac{e^2}{\epsilon_0 \hbar} \sqrt{m/2}$$

The decay probability λ is given by

$$\lambda = fT = \left(\frac{v}{2R} \right) T$$

$$\begin{aligned} \therefore \ln \lambda &= \ln \left(\frac{v}{2R} \right) + \ln T \\ &= \ln \left(\frac{v}{2R} \right) + a\sqrt{ZR} - bZT_{\alpha}^{-1/2} \end{aligned}$$

$$\log_{10} \lambda = \log_{10} \left(\frac{v}{2R} \right) + 0.4343 a\sqrt{ZR} - 0.4343 bZT_{\alpha}^{-1/2} \quad \dots(4.4.7)$$

For a number of α -emitters, a plot of $\log_{10} \lambda$ vs $ZT_{\alpha}^{-1/2}$ is shown in the Fig. (4.4.3). A straight line is obtained whose slope is $-0.4343b$ as required by the theory. The intercept on y-axis gives the value of

$$\log_{10} \left(\frac{v}{2R} \right) + 0.4343 a\sqrt{ZR}$$

and this can be used to determine the value of nuclear radius R . The nuclear radius calculated in this way comes out to be of the same order as obtained from scattering experiments. The correlation between the half-life time (or disintegration constant λ) and energy of the α -particles *viz.*, most energetic α -emitters are short lived and less energetic α -emitters are long lived, is contained in the theory.

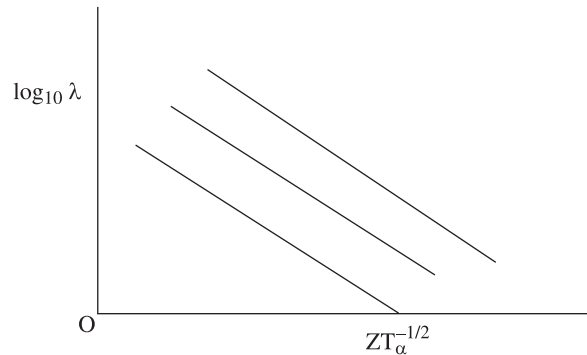


Fig. 4.4.3

QUESTIONS

1. A particle of mass m and total energy E is incident on a one-dimensional rectangular potential barrier of height $V > E$ and of finite thickness a . Show that the particle has finite probability of penetrating the barrier and being seen on the other side. Find the transmission coefficient. (All'd 1995)

2. (a) A particle of mass m and energy E is incident on a one-dimensional step of potential of height V_0 from the left. Discuss the behaviour of the particle for $E < V_0$ and explain how tunneling can be understood without violation of energy conservation principle.
- (b) Discuss the two physical phenomena which can be understood on the basis of tunneling. (All'd 1996)
3. A beam of particles each of mass m and energy E , moving in a region of zero potential energy, approaches a rectangular potential barrier of width a and height V_0 where $V_0 > E$. If $\beta = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$, prove that the

transmission coefficient is given by $T = \frac{16}{V_0} E \left(1 - \frac{E}{V_0}\right) e^{-2\beta a}$. (All'd 2007)

4. (a) A beam of particles of mass m and energy E is incident on a step potential of height V . Obtain expression for reflection and transmission coefficients and discuss the behaviour of the particle in the neighbourhood of $E \sim V$.
- (b) Give three examples of quantum tunneling. (All'd 2006)
5. A beam of particles of mass m and energy E is incident on a step potential of height V_0 from the left. Discuss the solution for $E < V_0$ and explain how tunneling can be understood without violation of energy consideration principle. Give two practical examples of quantum tunnel effect. (All'd 2005)
6. A particle of mass m free to move on a straight line is incident from $x = -\infty$ on a potential barrier

$$V(x) = 0, \text{ for } x < -a, \text{ and } x > a,$$

$$= V_0 \text{ for } -a < x < a$$

If $E < V_0$ then

- (a) Show that there is a non-zero probability of the particle getting transmitted through the barrier and obtain an expression for the transmission coefficient.
- (b) Show that for a high and wide barrier the transmission coefficient reduces to

$$T \approx e^{-2ka} \text{ where } k^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad (\text{All'd 2003})$$

EIGEN VALUES OF $\hat{L}^2$ AND $\hat{L}_z$ AXIOMATIC: FORMULATION OF QUANTUM MECHANICS

5.1 EIGEN VALUES AND EIGEN FUNCTIONS OF $\hat{L}^2$ AND $\hat{L}_z$

The square of angular momentum L^2 and z-component of angular momentum are **compatible observables** and their operators $\hat{L}^2$ and $\hat{L}_z$ commute *i.e.*, $[\hat{L}^2, \hat{L}_z]=0$, therefore they can have common eigen function. When we try to find solution of eigen value equation using the forms for these operators in Cartesian coordinates, the differential equation obtained cannot be separated. For this reason we carry out a transformation to spherical polar coordinates. Let $Y(\theta, \phi)$ be the common eigen function of these operators. Eigen value equations for operators $\hat{L}^2$ and $\hat{L}_z$ are

$$\hat{L}^2 Y(\theta, \phi) = \lambda \hbar^2 Y(\theta, \phi) \quad \dots(5.1.1)$$

$$\hat{L}_z Y(\theta, \phi) = m \hbar Y(\theta, \phi) \quad \dots(5.1.2)$$

where $\lambda \hbar^2$ and $m \hbar$ are the eigen values operators $\hat{L}^2$ and $\hat{L}_z$ respectively. In polar coordinates the operators $\hat{L}^2$ and $\hat{L}_z$ can be expressed as

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(5.1.3)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi} \quad \dots(5.1.4)$$

In view of Eqns. (5.1.3) and (5.1.4) the eigen value Eqns. (5.1.1) and (5.1.2) become

$$\left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \lambda \right] Y(\theta, \phi) = 0 \quad \dots(5.1.5)$$

and
$$\frac{dY(\theta, \phi)}{d\phi} = im\phi$$

Let us try to separate the variables θ and ϕ by assuming

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad \dots(5.1.6)$$

Substituting Eqn. (5.1.6) in (5.1.5), we get

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} \quad \dots(5.1.7)$$

The left hand side of Eqn. (5.1.7) is function of θ only and right hand side is function of φ only, θ and φ are independent variables. This equality can hold if each side is equal to the same constant, say, m^2 .

The Eqn. (5.1.7) thus separates into two equations viz.

$$\frac{d^2 \Phi}{d\varphi^2} + m^2 \Phi = 0 \quad \dots(5.1.8)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(\lambda - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots(5.1.9)$$

The φ -Eqn. (5.1.8) integrates to

$$\Phi(\varphi) = C e^{im\varphi} \quad \dots(5.1.10)$$

where C is a constant. Since $\Phi(\varphi)$ is single valued, we must have

$$\Phi(\varphi) = \Phi(\varphi + 2\pi)$$

$$e^{im\varphi} = e^{im(\varphi + 2\pi)}$$

$$e^{2m\pi i} = 1$$

$$m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(5.1.11)$$

The constant C appearing in Eqn. (5.1.10) is determined by using the normalization condition

$$\int_0^{2\pi} |\Phi(\varphi)|^2 d\varphi = 1$$

$$C^2 \int_0^{2\pi} d\varphi = 1$$

$$C = \frac{1}{\sqrt{2\pi}}$$

So the normalized solution of φ -equation is

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(5.1.12)$$

This determines the eigen function and eigen values of operator of z -component of orbital angular momentum.

To solve the θ -equation, it is convenient to change the independent variable.

Let

$$x = \cos \theta, \quad \sqrt{1-x^2} = \sin \theta. \quad -1 < x < 1$$

$$\frac{d}{d\theta} = \frac{dx}{d\theta} \frac{d}{dx} = -\sin \theta \frac{d}{dx} = -\sqrt{1-x^2} \frac{d}{dx}$$

In terms of new variable x , the θ -equation becomes

$$\frac{d}{dx} \left[(1-x^2) \frac{d\Theta}{dx} \right] + \left[\lambda - \frac{m^2}{1-x^2} \right] \Theta(x) = 0, \quad m = 0, 1, 2, \dots \quad \dots(5.1.13)$$

Equation (5.1.13) is well-known **associated Legendre equation**. Its solution is expressed in terms of polynomials, called **associated Legendre polynomials**.

For $m = 0$, Eqn. (5.1.13) reduces to a relatively simpler equation, called Legendre equation and its solution is expressed in terms of **Legendre polynomials**, denoted by $P_l(x)$. Let us write $\Theta(x) = P(x)$. The Legendre equation is

$$\frac{d}{dx} \left[(1-x^2) \frac{dP}{dx} \right] + \lambda P(x) = 0 \quad \dots(5.1.14a)$$

$$\text{or} \quad (1-x^2) \frac{d^2 P}{dx^2} - 2x \frac{dP}{dx} + \lambda P = 0 \quad \dots(5.1.14b)$$

Let us try power series solution of Eqn. (5.1.14) in the form of

$$P(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \dots = \sum_{l=0}^{\infty} a_l x^l \quad \dots(5.1.15)$$

Substituting Eqn.(5.1.15) in (5.1.14b), we have

$$\begin{aligned} \sum_{l=0}^{\infty} l(l-1) a_l x^{l-2} - \sum_{l=0}^{\infty} l(l-1) a_l x^l - 2 \sum_{l=0}^{\infty} l a_l x^l + \lambda \sum_{l=0}^{\infty} a_l x^l &= 0 \\ \sum_{l=0}^{\infty} l(l-1) a_l x^{l-2} - \sum_{l=0}^{\infty} [l(l+1) - \lambda] a_l x^l &= 0 \\ \sum_{l=0}^{\infty} (l+1)(l+2) a_{l+2} x^l - \sum_{l=0}^{\infty} [l(l+1) - \lambda] a_l x^l &= 0 \quad (\text{Replacing } l \text{ by } l+2) \end{aligned}$$

This equation is valid for all values of x ($-1 < x < 1$). This is possible only if coefficient of each power of x is zero. Hence

$$a_{l+2} = \frac{l(l+1) - \lambda}{(l+1)(l+2)} a_l \quad (\text{Recursion relation}) \quad \dots(5.1.16)$$

For even values of l (0, 2, 4, ...), Eqn. (5.1.16) gives

$$a_2 = -\frac{\lambda}{2!} a_0$$

$$a_4 = -\frac{\lambda(6-\lambda)}{4!} a_0$$

$$a_6 = -\frac{\lambda(6-\lambda)(20-\lambda)}{6!} a_0 \text{ etc.}$$

For odd values of l (1, 3, 5, ...), we have

$$a_3 = \frac{2-\lambda}{3!} a_1$$

$$a_5 = \frac{(2-\lambda)(12-\lambda)}{5!} a_1$$

$$a_7 = \frac{(2-\lambda)(12-\lambda)(30-\lambda)}{7!} a_1 \text{ etc.}$$

In terms of two arbitrary constants a_0 and a_1 , the solution of Legendre equation is written as

$$P(x) = a_0 \left[1 - \frac{\lambda}{2!} x^2 - \frac{\lambda(6-\lambda)}{4!} x^4 - \frac{\lambda(6-\lambda)(20-\lambda)}{6!} x^6 - \dots \right]$$

$$+ a_1 \left[x + \frac{(2-\lambda)}{3!} x^3 + \frac{(2-\lambda)(12-\lambda)}{5!} x^5 + \frac{(2-\lambda)(12-\lambda)(30-\lambda)}{7!} x^7 + \dots \right] \dots (5.1.17)$$

$P(x)$ diverges at $x = \pm 1$, its domain of convergence is $-1 < x < 1$. The solution (5.1.17) consists of two independent infinite series, one consisting of even coefficient a_0 and the other consisting of odd coefficient a_1 . It is readily seen that

$$\lim_{r \rightarrow \infty} \frac{a_{l+2}}{a_l} \rightarrow 1$$

Thus if the infinite series (5.1.17) is not terminated, it will diverge at $x = 1$. This is not acceptable solution. To avoid the singularity of $P(x)$ at $x = 1$, the series (5.1.17) must terminate after finite number of terms.

Let the series terminate for some value of integer l . The recursion relation (5.1.16) gives

$$\lambda = l(l+1), \quad l = 0, 1, 2, 3, 4, 5, \dots \dots (5.1.18)$$

$$\lambda = 0, 2, 6, 12, 20, 30, \dots$$

If this is so, one of the series terminates at $a_l x^l$. From Eqns. (5.1.1) and (5.1.18) we see that the condition of termination of series is the quantization condition for the eigen values of $\hat{L}^2$. So the

eigen values of $\hat{L}^2$ are

$$\lambda \hbar^2 = l(l+1) \hbar^2, \quad l = 0, 1, 2, 3, \dots$$

or

$$\lambda = l(l+1) \quad \dots(5.1.19)$$

This means that allowed values of the observable orbital angular momentum L are

$$L = \sqrt{l(l+1)} \hbar, \quad l = 0, 1, 2, 3, \dots \quad \dots(5.1.20)$$

For even values of l , the even series becomes a polynomial but the odd series remains as an infinite series. So we must set $a_1 = 0$.

Similarly, for odd values of l , the odd series becomes a polynomial and even series remains as an infinite series. So we set $a_0 = 0$.

So the acceptable solutions of Legendre equation are either even polynomials or odd polynomials and may be represented as

$$P_l^{\text{even}}(x) = a_0 \left[1 - \frac{\lambda}{2!} x^2 - \frac{\lambda(6-\lambda)}{4!} x^4 - \frac{\lambda(6-\lambda)(20-\lambda)}{6!} x^6 - \dots \right]$$

$$\text{or} \quad P_l^{\text{odd}}(x) = a_1 \left[x + \frac{(2-\lambda)}{3!} x^3 + \frac{(2-\lambda)(12-\lambda)}{5!} x^5 + \frac{(2-\lambda)(12-\lambda)(30-\lambda)}{7!} x^7 + \dots \right]$$

From these polynomials we have

$$P_0^{\text{even}}(x) = a_0, \quad P_2^{\text{even}}(x) = a_0(1 - 3x^2), \quad P_4^{\text{even}}(x) = a_0(1 - 10x^2 + \frac{35}{3}x^4), \text{ etc.}$$

$$\text{and} \quad P_1^{\text{odd}}(x) = a_1 x, \quad P_3^{\text{odd}}(x) = a_1(x - \frac{5}{3}x^3), \quad P_5^{\text{odd}}(x) = a_1(x - \frac{14}{3}x^3 + \frac{63}{15}x^5) \dots \text{etc.}$$

The constants a_0 and a_1 are determined using the conditions $P_l(1) = 1$.

$$P_0(1) = 1 \Rightarrow a_0 = 1, \quad P_2(1) = 1 \Rightarrow a_0 = -1/2, \quad P_4(1) = 1 \Rightarrow a_0 = 3/8 \text{ etc.}$$

$$P_1(1) = 1 \Rightarrow a_1 = 1, \quad P_3(1) = 1 \Rightarrow a_1 = -3/2, \quad P_5(1) = 1 \Rightarrow a_1 = 15/8 \text{ etc.}$$

Plugging the appropriate values of a_0 and a_1 the Legendre polynomials come out to be

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = (1/2)(3x^2 - 1)$$

$$P_3(x) = (1/2)(5x^3 - 3x)$$

$$P_4(x) = (1/8)(35x^4 - 30x^2 + 3)$$

$$P_5(x) = (1/8)(63x^5 - 70x^3 + 15x) \text{ etc.}$$

The Legendre polynomials $P_l(x)$ are also obtained from general formula called *Rodrigues formula*.

$$P_l(x) = \frac{1}{2^l (l!)} \cdot \frac{d^l}{dx^l} (x^2 - 1)^l \quad \dots(5.1.21)$$

The orthogonality condition for Legendre polynomials is

$$\int_{-1}^1 P_l(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{ll'} \quad \dots(5.1.22)$$

For $m = 0$, the solution of Legendre equation can be written as

$$\Theta_l(x) = N_l P_l(x) \quad \dots(5.1.23)$$

where N_l is a constant which can be determined using the normalization condition

$$\int_{-1}^1 |\Theta(x)|^2 dx = 1$$

$$N_l^2 \int_{-1}^1 |P_l(x)|^2 dx = 1 \quad \Rightarrow \quad N_l = \sqrt{\frac{2l+1}{2}}$$

So the normalized solution of Legendre equation is

$$\Theta_l(\theta) = \sqrt{\frac{2l+1}{2}} P_l(x) \quad (5.1.24)$$

For $m \neq 0$, the solution of associated Legendre Eqn. (5.1.13) for positive values of m are **associated Legendre polynomials**. These are denoted by $P_l^m(x)$ and defined by

$$P_l^m(x) = (1-x^2)^{m/2} \cdot \frac{d^m}{dx^m} P_l(x)$$

$$= \frac{1}{2^l (l!)} \cdot (1-x^2)^{m/2} \frac{d^{l+m}}{dx^{l+m}} (x^2 - 1)^l \quad \dots(5.1.25)$$

From the very definition of $P_l^m(x)$ it is evident that $m \leq l$. For $m \geq l$, $P_l^m(x)$ vanishes. In terms of normalization constant N_{lm} the solution of associated Legendre equation is expressed as

$$\Theta_{lm}(x) = N_{lm} P_l^m(x) \quad \dots(5.1.26)$$

The constant N_{lm} is determined using the normalization condition

$$\int_{-1}^1 |\Theta(x)|^2 dx = 1 \quad \dots(5.1.27)$$

This integral can be evaluated using the result

$$\int_{-1}^1 |P_l^m(x)|^2 dx = \frac{2}{2l+1} \cdot \frac{(l+m)!}{(l-m)!} \quad \dots(5.1.28)$$

From Eqns. (5.1.27) and (5.1.28), we get

$$N_{lm} = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} \quad \dots(5.1.29)$$

The normalized associated Legendre polynomials for any value of l and m (of course $l = 0, 1, 2, 3, \dots$ and $|m| \leq l$ or $-l \leq m \leq l$) are

$$\Theta_{lm}(x) = (-1)^m \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(x), \quad x = \cos \theta \quad \dots(5.1.30)$$

The complete normalized eigen functions of $\hat{L}^2$ are

$$\begin{aligned} Y_{l,m}(\theta, \varphi) &= \Theta_l^m(\theta) \Phi(\varphi) \\ &= (-1)^m \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) \cdot \frac{1}{\sqrt{2\pi}} e^{im\varphi} \\ &= (-1)^m \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) \cdot e^{im\varphi} \end{aligned} \quad \dots(5.1.31)$$

For negative value of m , we have

$$Y_{l,-m} = (-1)^m [Y_{l,m}]^* \quad \dots(5.1.32)$$

The introduction of constant phase factor $(-1)^m$ is a matter of convention, it makes the form of $Y(\theta, \varphi)$ agree with those commonly used in literature. The functions $Y_{lm}(\theta, \varphi)$ are called *spherical harmonics*. The first few of these are:

$$Y_{00} = \sqrt{\frac{1}{4\pi}}, \quad Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin \theta \cdot e^{i\varphi},$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin \theta \cdot e^{-i\varphi}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$$

$$Y_{21} = \sqrt{\frac{15}{8\pi}} (\sin \theta \cdot \cos \theta) \cdot e^{i\varphi}, Y_{2,-1} = -\sqrt{\frac{15}{8\pi}} (\sin \theta \cdot \cos \theta) \cdot e^{-i\varphi}$$

$$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \cdot e^{2i\varphi}, Y_{2,-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta \cdot e^{-2i\varphi}$$

Degeneracy with respect to m

For a general value of l , m can assume integral values from $-l$ to $+l$ in steps of unity *i.e.*, m can take on $(2l + 1)$ values in all. Hence there are $2l + 1$ different eigen functions corresponding to a single eigen value $\sqrt{l(l+1)} \hbar$ of orbital angular momentum L . The eigen values for a given l , are $(2l+1)$ fold degenerate.

5.2 AXIOMATIC FORMULATION OF QUANTUM MECHANICS

This approach of quantum mechanics is based on few postulates. The postulates of thermodynamics are stated in terms macroscopic variables such as pressure, temperature, volume, mass, energy etc. and hence readily understood. The postulates of quantum mechanics are stated in terms of microscopic and abstract concepts and hence it is difficult to form illustrative images of these concepts.

POSTULATE 1

The state of a quantum mechanical system is described by wave function $\psi(r, t)$. The wave function $\psi(r, t)$ contains all information that nature permits about the system. The collection or the totality of wave functions of a system form an infinite-dimensional linear vector space, called *Hilbert space*.

If ϕ_1 and ϕ_2 are two states in which a physical quantity Q has definite values q_1 and q_2 respectively, then the linear combination or the superposition

$$c_1 \phi_1 + c_2 \phi_2,$$

where c_1 and c_2 are arbitrary complex numbers, also represents a possible state of the system but in this state the physical quantity Q has not a definite value; instead the measurement of physical quantity Q yields either a value q_1 or q_2 . Thus the superposition of states produces a new state in which Q has indefinite value. The principle of superposition stated above can be extended to any number of states *i.e.*,

$$c_1 \phi_1 + c_2 \phi_2 + \dots + c_m \phi_m$$

represents a state of the system. The reverse of superposition principle is also true. That is, an arbitrary state wave function ψ can be expanded in terms of the states of the Hilbert space of the system. Thus

$$\psi = c_1 \phi_1 + c_2 \phi_2 + \dots + c_m \phi_m = \sum_{m=1}^m c_m \phi_m \quad \dots(5.2.1)$$

where c_m are arbitrary complex numbers.

POSTULATE 2

To every physical property there corresponds a quantum mechanical operator. The operator corresponding to the property Q is obtained by writing the classical mechanical expression for Q and then making following replacements.

$$q \rightarrow \hat{q} = q, \quad p_q \rightarrow -i\hbar \frac{\partial}{\partial q}, \quad \hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(q)$$

An operator $\hat{Q}$ is said to be Hermitian if its expectation value is real. For each Hermitian operator an eigen value equation is

$$\hat{Q} \varphi_i = q \varphi_i, \quad \dots(5.2.2)$$

where q is eigen value and φ_i is eigen function of the operator, can be set up. The eigen values of Hermitian operator are real and two eigen functions belonging to different eigen values are orthogonal i.e.,

$$\int \varphi_i^* \varphi_j d\tau = \delta_{ij} \quad \dots(5.2.3)$$

The set of eigen functions φ_i constitute an infinite set of linearly independent orthogonal functions. If these functions are normalized, they are said to form a complete orthonormal set. This means that any arbitrary function ψ of the state can be expressed as superposition of this complete set.

$$\psi = \sum_j c_j \varphi_j \quad \dots(5.2.4)$$

If we have a large number of identical systems, all prepared in the same state ψ and measurement of a dynamical variable Q is made on each system, the outcome of each measurement will, in general, be different. The average or expectation value of these results will be given by

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi d\tau \quad \text{or} \quad \langle Q \rangle = (\psi, \hat{Q} \psi) \quad \dots(5.2.5)$$

$$\begin{aligned} \text{i.e.} \quad \langle Q \rangle &= \sum_j \sum_k c_k^* c_j q_j \int \varphi_k^* \varphi_j d\tau \\ &= \sum_j \sum_k c_k^* c_j q_j \delta_{kj} \\ &= \sum_j |c_j|^2 q_j \quad \dots(5.2.6) \end{aligned}$$

Meaning of this equation is that if a measurement of the physical quantity Q represented by the operator $\hat{Q}$ is carried out on the system represented by the state ψ then $|c_j|^2$ gives the probability that the result will be the eigen value q_j . On the other hand if the system is in the state represented by one of the eigen function φ_k then the measurement of Q will give only one eigen value q_k .

POSTULATE 3

The operators of dynamical variables do not, in general, commute with other *i.e.*, $\hat{Q}\hat{R} \neq \hat{R}\hat{Q}$. The difference $\hat{Q}\hat{R} - \hat{R}\hat{Q}$ is called commutator of $\hat{Q}$ and $\hat{R}$ and is denoted by $[\hat{Q}, \hat{R}]$.

$$[\hat{Q}, \hat{R}] = \hat{Q}\hat{R} - \hat{R}\hat{Q} \quad \dots(5.2.7)$$

POSTULATE 4

The time evolution of the state $\psi(x, y, z, t)$ of a system is governed by the Schrodinger equation of motion

$$i\hbar \frac{\partial \psi(r, t)}{\partial t} = \hat{H}\psi(r, t) \quad \dots(5.2.8)$$

where H is the Hamiltonian operator of the system. The Schrodinger equation is a postulate and is to be tested by agreement of its prediction with experiments.

5.3 DIRAC FORMALISM OF QUANTUM MECHANICS

In Dirac formalism the state of a dynamical system is represented by vector, called ket vector and is denoted by symbol $|\alpha\rangle$. The kets of a system form an infinite dimensional abstract linear vector space, called Hilbert space H . To every ket vector in ket space, there exists another vector, called dual vector or bra vector in bra space and is denoted by $\langle\alpha|$. Like ket vectors, the bra vectors form a different Hilbert space H^* . The state of a system is specified by direction of ket vector. Two ket vectors $|\alpha\rangle$ and $c|\alpha\rangle$, where c is a complex number, denote the same state. A dynamical system represented by a ket vector $|\alpha\rangle$ can be equally well represented by corresponding bra vector $\langle\alpha|$.

PROPERTIES OF STATE VECTORS

1. If kets $|\alpha\rangle$ and $|\beta\rangle$ represent two states then their linear combination $c_1|\alpha\rangle + c_2|\beta\rangle$ is also a ket representing another state where c_1 and c_2 are arbitrary complex numbers.
2. We can form a scalar product of a ket vector $|\alpha\rangle$ and a bra vector $\langle\beta|$, which is denoted by $\langle\beta|\alpha\rangle$. If the kets $|\psi\rangle$ and $|\phi\rangle$ represent the states described by wave functions $\psi(r)$ and $\phi(r)$ respectively then

$$\langle\phi|\psi\rangle = \int \phi^*(r)\psi(r)d\tau = \langle\psi|\phi\rangle^*$$

3. A bra vector $\langle\beta|$ is said to be null bra if the scalar product $\langle\beta|\alpha\rangle$ vanishes for any $|\alpha\rangle$.

$$\langle\beta| = 0, \text{ if } \langle\beta|\alpha\rangle = 0 \text{ for any } |\alpha\rangle.$$

4. Two bra vectors $\langle\beta_1|$ and $\langle\beta_2|$ are equal if $\langle\beta_1|\alpha\rangle = \langle\beta_2|\alpha\rangle$ for every $|\alpha\rangle$.

5. If $\langle \alpha | \beta \rangle = 0$, then $|\alpha\rangle$ and $|\beta\rangle$ are said to be orthogonal.

6. If $\langle \alpha | \alpha \rangle = 1$, then $|\alpha\rangle$ is said to be normalized.

7. The scalar product of two vectors obey the rule

$$\langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle^*,$$

$$\langle \alpha | \alpha \rangle = \langle \alpha | \alpha \rangle^* \text{ implies that } \langle \alpha | \alpha \rangle \text{ is real.}$$

8. If $|\gamma\rangle = |\alpha\rangle + |\beta\rangle$ then $\langle \gamma | = \langle \alpha | + \langle \beta |$

$$\text{If } |\delta\rangle = c |\alpha\rangle \text{ then } \langle \delta | = c^* \langle \alpha |$$

9. An operator $\hat{Q}$ converts a ket $|\alpha\rangle$ into another ket $|\beta\rangle$ i.e.,

$$\hat{Q} |\alpha\rangle = |\beta\rangle \quad \text{or} \quad \langle \alpha | \hat{Q} = \langle \beta |$$

10. The operator $\hat{Q}$ is said to be linear if

$$\hat{Q} (c_1 |\alpha_1\rangle + c_2 |\alpha_2\rangle + \dots) = c_1 \hat{Q} |\alpha_1\rangle + c_2 \hat{Q} |\alpha_2\rangle + \dots$$

11. The adjoint of $\hat{Q}$ is denoted by $\hat{Q}^+$ read as $\hat{Q}$ dagger and is defined through the equation

$$\langle \alpha | \hat{Q}^+ | \beta \rangle = \langle \beta | \hat{Q} | \alpha \rangle^* \quad \dots(5.3.1)$$

Expansion Postulate

If $\{|\phi_i\rangle\}$ denotes the complete orthonormal set of eigen vectors of a Hermitian operator, then an arbitrary state $|\psi\rangle$ can be expanded in terms $|\phi_i\rangle$.

$$|\psi\rangle = \sum_i \langle \phi_i | \psi \rangle |\phi_i\rangle = \sum_i |\phi_i\rangle \langle \phi_i | \psi \rangle \quad \dots(5.3.2)$$

This implies that

$$\sum_i |\phi_i\rangle \langle \phi_i| = 1 \quad (\text{completeness rule}) \quad \dots(5.3.3)$$

The expansion coefficients $\langle \phi_i | \psi \rangle$ are the projections of ψ onto ϕ_i .

5.4 GENERAL DEFINITION OF ANGULAR MOMENTUM

Earlier in this chapter we defined orbital angular momentum vector through the relation $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and obtained the corresponding operator $\hat{L}$ by replacing the classical observables with their operators.

It was shown that $\hat{L}$ and its components $\hat{L}_x, \hat{L}_y, \hat{L}_z$ satisfy the commutation relations

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x, [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0 \quad \dots(5.4.1)$$

The eigen values of $\hat{L}^2$ and $\hat{L}_z$ were found to be $l(l+1)\hbar$ and $m\hbar$ respectively where $l = 0, 1, 2, 3, \dots$ and $m = -l, -l+1, \dots, (l-1), l$. It is worth to remember that the eigen values of components of angular momentum are integral multiple of $\hbar$. We know that, spin (angular momentum) has no classical analog and hence no classical expression for its representation. Therefore the way we obtained the operator for $\hat{L}$ will not work for spin. Moreover, the eigen values of operator of component of spin observable are half-integer. Here we shall give general definition of angular momentum and see that the magnitudes of angular momentum equal to $0, 1/2 \hbar, \hbar, 3/2 \hbar, \dots$ come in a natural way.

We define angular momentum J with their components J_x, J_y and J_z as an observable whose operators satisfy the following commutation relations.

$$[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i\hbar \hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i\hbar \hat{J}_y$$

$$[\hat{J}^2, \hat{J}_x] = [\hat{J}^2, \hat{J}_y] = [\hat{J}^2, \hat{J}_z] = 0 \quad \dots(5.4.2)$$

We further define ladder operators $\hat{J}_+$ and $\hat{J}_-$ as

$$\hat{J}_+ = \hat{J}_x + i\hat{J}_y, \quad \hat{J}_- = \hat{J}_x - i\hat{J}_y \quad \dots(5.4.3)$$

The ladder operators are mutually connected through the relations

$$\hat{J}_+^\dagger = \hat{J}_-, \quad \hat{J}_-^\dagger = \hat{J}_+ \quad \dots(5.4.4)$$

The ladder operators satisfy the following commutation relations

$$[\hat{J}_z, \hat{J}_+] = \hbar \hat{J}_+, \quad [\hat{J}_z, \hat{J}_-] = -\hbar \hat{J}_-, \quad [\hat{J}_+, \hat{J}_-] = 2\hbar \hat{J}_z, \quad [\hat{J}^2, \hat{J}_\pm] = 0 \quad \dots(5.4.5)$$

where
$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \quad \dots(5.4.6)$$

The commutation relations can be derived in the same way as the corresponding relations for orbital angular momentum operators were derived. Further it can be shown that

$$\hat{J}_+ \hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z, \quad \hat{J}_- \hat{J}_+ = \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \quad \dots(5.4.7)$$

$$\therefore \hat{J}^2 = \frac{1}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) + \hat{J}_z^2 \quad \dots(5.4.8)$$

Since $[\hat{J}^2, \hat{J}_z] = 0$, it is possible to find a complete set of simultaneous eigenstates of $\hat{J}^2$ and $\hat{J}_z$. Let one of these states belonging to the eigen value $\lambda_j \hbar^2$ of $\hat{J}^2$ and $m\hbar$ of $\hat{J}_z$ be $|\lambda_j m\rangle$. Evidently

$$\hat{J}^2 |\lambda_j m\rangle = \lambda_j \hbar^2 |\lambda_j m\rangle \quad \dots(5.4.9)$$

$$\hat{J}_z |\lambda_j m\rangle = m\hbar |\lambda_j m\rangle \quad \dots(5.4.10)$$

Now we shall first show that there exists a lower and upper limit to the quantum number m . The value of a component of a vector cannot be greater than the value of the vector itself. So

$$(m\hbar)^2 \leq \lambda_j \hbar^2 \Rightarrow m \leq \lambda_j \quad \dots(5.4.11)$$

Thus for a fixed value of λ_j , the value of m is bounded. We can also get the same result as follows. The expectation value of a Hermitian operator cannot be negative. Therefore

$$0 \leq \langle \lambda_j m | \hat{J}_x^2 + \hat{J}_y^2 | \lambda_j m \rangle$$

$$0 \leq \langle \lambda_j m | \hat{J}^2 - \hat{J}_z^2 | \lambda_j m \rangle$$

$$0 \leq \lambda_j \hbar^2 - m^2 \hbar^2$$

$$m^2 \leq \lambda_j$$

Let the upper and lower value of m be m_+ and m_- . Now

$$\begin{aligned} \hat{J}_z \hat{J}_+ | \lambda_j m \rangle &= (\hat{J}_+ \hat{J}_z + \hbar \hat{J}_+) | \lambda_j m \rangle \\ &= \hat{J}_+ (m+1)\hbar | \lambda_j m \rangle \\ &= (m+1)\hbar \hat{J}_+ | \lambda_j m \rangle \end{aligned} \quad \dots(5.4.12)$$

Equation (5.4.12) shows that $\hat{J}_+ | \lambda_j m \rangle$ is an eigenstate of $\hat{J}_z$ belonging to the eigen value $(m+1)\hbar$. The reason why $\hat{J}_+$ is called raising operator is now obvious; it raises the eigen value of $\hat{J}_z$ by one unit ($\hbar$). $\hat{J}_+$ has no effect on the eigen value of $\hat{J}^2$. Similarly we can show that

$$\hat{J}_z \hat{J}_- | \lambda_j m \rangle = (m-1)\hbar \hat{J}_- | \lambda_j m \rangle \quad \dots(5.4.13)$$

By virtue of its property displayed in Eqn. (5.4.13) $\hat{J}_-$ is called lowering operator. On acting on an eigenstate of angular momentum, it lowers the eigen value of $\hat{J}_z$ by $\hbar$ and leaves the eigen value of $\hat{J}^2$ intact. These results can be expressed as

$$\hat{J}_+ | \lambda_j m \rangle = C_+ | \lambda_j, m+1 \rangle \quad \dots(5.4.14)$$

$$\hat{J}_- | \lambda_j m \rangle = C_- | \lambda_j, m-1 \rangle \quad \dots(5.4.15)$$

where C_+ and C_- are constants to be determined. The effect of $\hat{J}_\pm$ is to raise (lower) the eigen value $m\hbar$ in steps of one unit. Since the highest possible value of m is m_+ and the lowest possible value of m is m_- , the states $|\lambda_j, m_++1\rangle$ and $|\lambda_j, m_- - 1\rangle$ do not exist. Hence

$$\hat{J}_+ | \lambda_j m_+ \rangle = 0 \quad \dots(5.4.16)$$

$$\hat{J}_- | \lambda_j m_- \rangle = 0 \quad \dots(5.4.17)$$

Operating both sides of Eqn. (5.4.16) by $\hat{J}_-$, we have

$$\begin{aligned}
 \hat{J}_- \hat{J}_+ |\lambda_j m_+ \rangle &= 0 \\
 (\hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z) |\lambda_j m_+ \rangle &= 0 \\
 \lambda_j \hbar^2 - m_+^2 \hbar^2 - m_+ \hbar^2 &= 0 \\
 \lambda_j - m_+(m_+ + 1) &= 0 \quad \dots(5.4.18)
 \end{aligned}$$

Similarly, operating both sides of Eqn. (5.4.17) by $\hat{J}_+$, we have

$$\begin{aligned}
 \hat{J}_+ \hat{J}_- |\lambda_j m_- \rangle &= 0 \\
 (\hat{J}^2 - \hat{J}_z^2 + \hbar \hat{J}_z) |\lambda_j m_- \rangle &= 0 \\
 \lambda_j \hbar^2 - m_-^2 \hbar^2 + m_- \hbar^2 &= 0 \\
 \lambda_j - m_-(m_- - 1) &= 0 \quad \dots(5.4.19)
 \end{aligned}$$

From Eqns. (5.4.18) and (5.4.19), we have

$$m_+(m_+ + 1) = m_-(m_- - 1)$$

Since $m_+ > m_-$ we must have

$$m_+ = -m_- = j \text{ (say)} \quad \dots(5.4.20)$$

Equation (5.4.20) defines the quantum number j . Substituting $m_+ = j$ in Eqn. (5.4.18), we get

$$\lambda_j = j(j + 1) \quad \dots(5.4.21)$$

From Eqns. (5.4.9) and (5.4.21) we see that eigen value of $\hat{J}^2$ is $j(j + 1)$. The eigenstates belonging to the same eigen value $j(j + 1)$ of $\hat{J}^2$ but different eigen values of $\hat{J}_z$ may be denoted by $|j, j\rangle, |j, j-1\rangle, |j, j-2\rangle, \dots, |j, -j+1\rangle, |j, -j\rangle$

Successive application of lowering operator $\hat{J}_-$ on the state $|j, j\rangle$ will ultimately lead to the state $|j, -j\rangle$. Similarly the successive application of $\hat{J}_+$ on the state $|j, -j\rangle$ will lead to the state $|j, j\rangle$. This means that

$$m_+ - m_- = j - (-j) = 2j$$

is an integer. Therefore the allowed values of j are:

$$j = 0, 1/2, 1, 3/2, \dots$$

Thus the angular momentum can have integral and half-integral values both.

Let us find the eigenstates of $\hat{J}^2$ and $\hat{J}_z$. The expectation value $\hat{J}_- \hat{J}_+$ in the state $|j, m\rangle$ is given by

$$\langle j m | \hat{J}_- \hat{J}_+ | j m \rangle = \langle \hat{J}_+ \rangle_j \langle \hat{J}_+ \rangle_m$$

$$\begin{aligned}
&= |C_+|^2 \langle j, m+1 | j, m+1 \rangle \\
&= |C_+|^2 \quad \dots(5.4.22)
\end{aligned}$$

where we have used the normalization condition $\langle j, m+1 | j, m+1 \rangle = 1$.

Using the result $\hat{J}_- \hat{J}_+ = \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z$ we can write Eqn. (5.4.22) as

$$\begin{aligned}
\langle j, m | \hat{J}_- \hat{J}_+ | j, m \rangle &= \langle j, m | \hat{J}^2 - \hat{J}_z^2 - \hbar \hat{J}_z | j, m \rangle \\
&= j(j+1)\hbar^2 - m^2\hbar^2 - m\hbar^2 \\
&= [j(j+1) - m(m+1)]\hbar^2 \quad \dots(5.4.23)
\end{aligned}$$

From Eqns. (5.4.22) and (5.4.23)

$$C_+ = \hbar \sqrt{j(j+1) - m(m+1)} = \hbar \sqrt{(j-m)(j+m+1)} \quad \dots(5.4.24)$$

Similarly we can find

$$C_- = \hbar \sqrt{j(j+1) - m(m-1)} = \hbar \sqrt{(j+m)(j-m+1)} \quad (5.4.25)$$

So Eqns. (5.4.14) and (5.4.15) become

$$\hat{J}_+ | j, m \rangle = \hbar \sqrt{j(j+1) - m(m+1)} | j, m+1 \rangle \quad \dots(5.4.26)$$

$$\hat{J}_- | j, m \rangle = \hbar \sqrt{j(j+1) - m(m-1)} | j, m-1 \rangle \quad \dots(5.4.27)$$

From Eqns. (5.4.26) and (5.4.27) we see that

$$\hat{J}_+ | j, j \rangle = 0, \quad \hat{J}_- | j, -j \rangle = 0$$

All the relations obtained for angular momentum operator $\hat{\mathbf{J}}$ are also true for orbital angular momentum operator $\hat{\mathbf{L}}$ and spin angular momentum operator $\hat{\mathbf{S}}$. The eigenstates of operator $\hat{L}^2$ and $\hat{L}_z$ are denoted by $|l, m\rangle$ in Dirac notation and by $Y_{lm}(\theta, \phi)$ in coordinate representation. The raising and lowering operators $\hat{L}_+$ and $\hat{L}_-$ in coordinate representation are expressed as

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y = \hbar e^{i\phi} \left[\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right]$$

$$\hat{L}_- = \hat{L}_x - i\hat{L}_y = \hbar e^{-i\phi} \left[-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right]$$

For orbital angular momentum Eqns. (5.4.26) and (5.4.27) assume the form

$$\hat{L}_+ Y_{l,m}(\theta, \phi) = \hbar \sqrt{l(l+1) - m(m+1)} Y_{l,m+1}(\theta, \phi) \quad \dots(5.4.28)$$

$$\hat{L}_- Y_{l,m}(\theta, \phi) = \hbar \sqrt{l(l+1) - m(m-1)} Y_{l,m-1}(\theta, \phi) \quad \dots(5.4.29)$$

These equations may be used to obtain the spherical harmonics for different values of l and m .

Use of Ladder operators to find the eigen functions of $\hat{L}^2$

For a given value of l , m can only take values from $-l$ to $+l$ in steps of unity. From Eqns. (5.4.28) and (5.4.29) we see that

$$\hat{L}_+ Y_{l,l} = 0 \quad \dots(5.4.30)$$

$$\hat{L}_- Y_{l,-l} = 0 \quad \dots(5.4.31)$$

From Eqns. (5.4.28) and (5.4.29) we have

$$Y_{l,m+1} = \frac{1}{\sqrt{l(l+1) - m(m+1)}} e^{i\varphi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{l,m} \quad \dots(5.4.32)$$

$$Y_{l,m-1} = \frac{1}{\sqrt{l(l+1) - m(m-1)}} e^{-i\varphi} \left(-\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{l,m} \quad \dots(5.4.33)$$

For $m = 0$, the solution of Legendre equation was found to be

$$Y_{l,0} = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta) \quad \dots(5.4.34)$$

From, (5.4.34)

$$Y_{00} = \frac{1}{\sqrt{4\pi}} P_0(\cos \theta) = \frac{1}{\sqrt{4\pi}} \quad \dots(5.4.35)$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cdot P_1(\cos \theta) = \sqrt{\frac{3}{4\pi}} \cos \theta \quad \dots(5.4.36)$$

Making use of Eqn. (5.4.32) we can obtain $Y_{l,1}, Y_{l,2}, Y_{l,3}, \dots, Y_{l,l}$ and from Eqn. (5.4.33) we can obtain $Y_{l,-1}, Y_{l,-2}, Y_{l,-3}, \dots, Y_{l,-l}$.

For $l = 1, m = 1, 0, -1$, from Eqn. (5.4.32)

$$\begin{aligned} Y_{1,1} &= \frac{1}{\sqrt{2}} e^{i\varphi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{10} \\ &= \frac{e^{i\varphi}}{\sqrt{2}} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \sqrt{\frac{3}{4\pi}} \cdot (\cos \theta) \\ &= -\sqrt{\frac{3}{8\pi}} \cdot \sin \theta \cdot e^{i\varphi} \quad \dots(5.4.37) \end{aligned}$$

From Eqn. (5.4.33)

$$Y_{1,-1} = \frac{e^{-i\varphi}}{\sqrt{2}} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{10}$$

$$= \sqrt{\frac{3}{8\pi}} \cdot \sin \theta \cdot e^{-i\varphi} \quad \dots(5.4.38)$$

For $l = 2, m = 2, 1, 0, -1, -2$.

$$\begin{aligned} Y_{2,1} &= \frac{e^{i\varphi}}{\sqrt{6}} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \left[\sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1) \right] \\ &= -\sqrt{\frac{15}{8\pi}} (\sin \theta \cdot \cos \theta) e^{i\varphi} \quad \dots(5.4.39) \end{aligned}$$

$$\begin{aligned} Y_{2,2} &= \frac{e^{i\varphi}}{\sqrt{2}} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{21} \\ &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta \cdot e^{2i\varphi} \quad \dots(5.4.40) \end{aligned}$$

$$Y_{2,0} = \sqrt{\frac{2l+1}{4\pi}} \cdot P_2(\cos \theta) = \sqrt{\frac{5}{4\pi}} \cdot \frac{1}{2} \cdot (3 \cos^2 \theta - 1) \quad \dots(5.4.41)$$

$$\begin{aligned} Y_{2,-1} &= \frac{e^{-i\varphi}}{\sqrt{6}} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{20} \\ &= \frac{e^{-i\varphi}}{\sqrt{6}} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \sqrt{\frac{5}{4\pi}} \cdot \frac{1}{2} \cdot (3 \cos^2 \theta - 1) \\ &= \sqrt{\frac{15}{8\pi}} (\sin \theta \cdot \cos \theta) e^{-i\varphi} \quad \dots(5.4.42) \end{aligned}$$

$$\begin{aligned} Y_{2,-2} &= \frac{1}{\sqrt{4}} e^{-i\varphi} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) Y_{2,-1} \\ &= \frac{e^{-i\varphi}}{\sqrt{4}} \left(-\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \varphi} \right) \sqrt{\frac{15}{8\pi}} (\sin \theta \cdot \cos \theta) e^{-i\varphi} \\ &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta \cdot e^{-2i\varphi} \end{aligned}$$

5.5 PARITY

Parity is a purely quantum mechanical quantity having no classical analogue. To arrive at the concept of parity, let us consider the behaviour of the wave function $\psi(x, y, z)$ upon the inversion of coordinate axes. Inversion consists in reversing the direction of all the axes. It is not difficult to see that inversion transforms right handed coordinate system into left handed one. Inversion results change in the signs of all the coordinates and consequently the function $\psi(x, y, z)$ transforms into $\psi(-x, -y, -z)$. This transition can be considered as a result of the action of the inversion operator $\hat{P}$ on $\psi(x, y, z)$ function.

$$\hat{P}\psi(x, y, z) = \psi(-x, -y, -z) \quad \dots(5.5.1)$$

Applying $\hat{P}$ again, we get

$$\begin{aligned} \hat{P}\hat{P}\psi(x, y, z) &= \hat{P}\psi(-x, -y, -z) = \psi(x, y, z) \\ \hat{P}^2\psi(x, y, z) &= \psi(x, y, z) \end{aligned} \quad \dots(5.5.2)$$

It follows that the square of the operator $\hat{P}$ equals unity.

To determine the eigen values of the inversion operator, we must solve the equation

$$\hat{P}\psi(x, y, z) = \lambda\psi(x, y, z) \quad \dots (5.5.3)$$

Now

$$\begin{aligned} \hat{P}\hat{P}\psi(x, y, z) &= \lambda\hat{P}\psi(x, y, z) \\ \hat{P}^2\psi(x, y, z) &= \lambda^2\psi(x, y, z) \\ \psi(x, y, z) &= \lambda^2\psi(x, y, z) \end{aligned} \quad \dots(5.5.4)$$

$$\lambda^2 = 1$$

$$\lambda = \pm 1 \quad \dots(5.5.5)$$

Hence the eigen values of the inversion operator are +1 and -1. With a view to this circumstance, we can write

$$\hat{P}\psi(x, y, z) = \pm\psi(x, y, z) \quad \dots(5.5.6)$$

$$\psi(-x, -y, -z) = \pm\psi(x, y, z) \quad \dots(5.5.7)$$

The quantity depicted by the operator $\hat{P}$ is known as the parity. Thus the wave function $\psi(x, y, z)$ of states with a definite parity value can be divided into two classes: (i) functions ψ_+ that do not change when the inversion operator acts on them and (ii) function ψ_- that change their sign when the inversion operator acts on them. The functions ψ_+ and ψ_- satisfy the relations

$$\hat{P}\psi_+ = \psi_+, \quad \hat{P}\psi_- = -\psi_-$$

States corresponding to the functions ψ_+ are said to be even and those corresponding to the functions ψ_- are said to be odd. The parity of a state described by the function

$$\psi = c_1\psi_+ + c_2\psi_-$$

is indeterminate.

Let us see the effect of parity operator on the spherical harmonics. The inversion transformation ($x \rightarrow -x, y \rightarrow -y, z \rightarrow -z$) in spherical coordinates is equivalent to $r \rightarrow r, \theta \rightarrow \pi - \theta, \varphi \rightarrow \pi + \varphi$. The spherical harmonics are given by

$$Y_{lm}(\theta, \varphi) = \text{const. } P_l^m(\cos \theta) e^{im\varphi}$$

The action of inversion operator on $Y_{lm}(\theta, \varphi)$ is equivalent to replacing $\theta \rightarrow \pi - \theta$, and $\varphi \rightarrow \pi + \varphi$. Thus

$$\begin{aligned} \hat{P}Y_{lm}(\theta, \varphi) &= \text{const. } P_l^m(\cos(\pi - \theta)) \cdot e^{im(\pi + \varphi)} \\ &= \text{const. } [P_l^m(-\cos \theta)] \cdot [(-1)^{|m|} e^{im\varphi}] \\ &= \text{const. } (-1)^{l-|m|} [P_l^m(\cos \theta)] [(-1)^{|m|} e^{im\varphi}] \\ &= \text{const. } (-1)^l [P_l^m(\cos \theta)] [e^{im\varphi}] \\ &= \text{const. } (-1)^l Y_{lm}(\theta, \varphi) \end{aligned}$$

The parity of the state with given value of l is $(-1)^l$. That is all the states with even l are even parity states and all those with odd l are odd.

QUESTIONS AND PROBLEMS

1. Prove the following commutation relations for the operators $L_+ = L_x + iL_y$ and $L_- = L_x - iL_y$.

$$[L_z, L_+] = \hbar L_+, \quad [L_z, L_-] = -\hbar L_-, \quad [L_+, L_-] = 2\hbar L_z$$

Show that the operators L_+ and L_- are in fact angular momentum raising and lowering operators respectively.

(All'd 1995)

2. If L_+ and L_- are the raising and the lowering angular momentum operators show that $\hat{L}_z^2 \psi_{lm}$ is an eigenstate of $\hat{L}_z$ with eigen values $m \pm 2$.

(All'd 1996)

3. Define angular momentum raising and lowering operators. Using these operators and the property $[L^2, L_z] = 0$, obtain eigen values of L^2 .

(All'd 1998)

4. Define angular momentum raising L_+ and lowering L_- operators. In a representation in which L^2 and L_z are diagonal, find the eigen values of the operator $L_- L_+$.

(All'd 1999)

5. (a) What are angular momentum raising and lowering operators?

(b) Find $L \times L$ where L is angular momentum operator.

(c) Show that the eigen values of a Hermitian operator are real.

(All'd 2000)

6. (a) Define angular momentum raising and lowering operators.

(b) Find $L \times L$ and $[L^2, L]$

(c) Find eigen values of the operator $L_+ L_-$

(All'd 2002)

7. (a) Show that L^2 and $[L_+, L_-]$ have simultaneous eigen functions.
 (b) If an operator commutes with L_x and L_y , it will commute with $L_{\pm}$.
 (c) If b is the maximum eigen value of $L_{\pm}$ and a is eigen value of L^2 then show that $a = b(b + \hbar)$
 (All'd 2003)

8. Given $\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$ and $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$

Find the eigen values of L^2 and L_z . (All'd 2003)

9. (a) Define angular momentum raising and lowering operators.

(b) Find $[(\hat{L}_x + \hat{L}_y), \hat{L}_+]$

(c) Show that momentum operator is Hermitian. (All'd 2004)

10. Find the eigen values of square of angular momentum operator

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Use this result to find the energy of a particle of mass m moving freely on a smooth surface at a fixed distance $r = a$ from the origin. (All'd 2006)

PARTICLE IN A BOX

6.1 PARTICLE IN AN INFINITELY DEEP POTENTIAL WELL (BOX)

Consider a particle of mass m , which is restricted to move along x -axis between the region bounded by $x = 0$ and $x = L$. Physically a bead sliding along a perfectly smooth straight wire stretched along x -axis with rigid barriers at $x = 0$ and $x = L$ or an electron confined to move along x -axis in a potential well defined by

$$\begin{aligned} V(x) &= 0 & \text{for } 0 < x < L \\ &= \infty & \text{for } x < 0 \text{ and } x > L \end{aligned} \quad \dots(6.1.1)$$

may represent the problem under investigation. Here V represents the potential energy of the electron. Obviously outside the potential well, kinetic energy of the particle is negative hence this region is inaccessible to the particle. Also at the boundary V is infinite, ensures that the wave function $\psi(x)$ representing the particle must vanish outside the well.

Let E be the energy of the particle. The time-independent Schrodinger equation for the particle is

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

$$\text{or} \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \dots(6.1.2)$$

$$\text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(6.1.3)$$

Solution of Eqn. (6.1.2) is

$$\psi(x) = A \sin kx + B \cos kx \quad \dots(6.1.4)$$

where A and B are arbitrary constants. The boundary conditions for this problem are

$$\psi(0) = 0 \text{ and } \psi(L) = 0$$

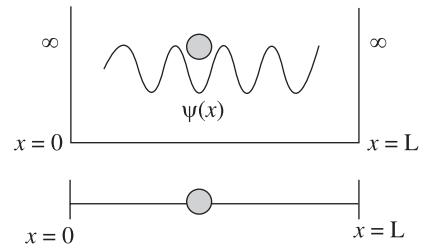


Fig. 6.1.1 Infinitely deep one dimensional potential well

When the first boundary condition is substituted in Eqn. (6.1.4), we get $B = 0$. So the solution (6.1.4) becomes

$$\psi(x) = A \sin kx \quad \dots(6.1.5)$$

Substituting the second boundary condition in Eqn. (6.1.5), we find

$$A \sin kL = 0, \quad A \neq 0$$

$$kL = n\pi, \quad n = 1, 2, 3, \dots$$

$$k = \frac{n\pi}{L} \quad \dots(6.1.6)$$

$$\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad \dots(6.1.7)$$

The value $n = 0$ is inadmissible as it corresponds to $\psi(x) = 0$ everywhere. Since the energy of the particle depends on integer n , this justifies the subscript n to the energy E .

Equation (6.1.7) shows that particle can have only discrete energies *i.e.*, energy of the particle is quantized. The discrete set of energies is called energy levels and the integer n is called the quantum number. The classical mechanics allows the particle to have any energy including zero. Thus the quantization of energy is a quantum mechanical result and has no counterpart in classical physics. The energy levels of the particle are shown in the Fig. (6.1.2). Evidently the energy levels are not equally spaced.

Wave function: The wave function of the particle is

$$\psi(x) = A \sin \frac{n\pi x}{L} \quad \dots(6.1.8)$$

Applying the normalization condition to the wave function we have

$$\int_0^L |\psi(x)|^2 dx = 1$$

$$\int_0^L A^2 \sin^2 \frac{n\pi x}{L} dx = 1$$

whence $A = \sqrt{\frac{2}{L}}$

The normalized wave functions of the particle are

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad \dots(6.1.9)$$

Orthogonality of wave functions: The wave functions of a particle in an infinitely deep potential well are orthogonal. Let us verify it. Let $\psi_m(x)$ and $\psi_n(x)$ be two wave functions corresponding to energies E_m and E_n . Then

$$\begin{aligned}\int_0^L \psi_m(x) \psi_n(x) dx &= \frac{2}{L} \int_0^L \sin \frac{m\pi x}{L} \sin \frac{n\pi x}{L} dx \\ &= \frac{1}{L} \int_0^L \left[\cos \frac{(m-n)\pi x}{L} - \cos \frac{(m+n)\pi x}{L} \right] dx \\ &= \delta_{mn}, \quad \{ \delta_{mn} = 0, \text{ for } m \neq n \text{ and } \delta_{mn} = 1 \text{ for } m = n \}\end{aligned}$$

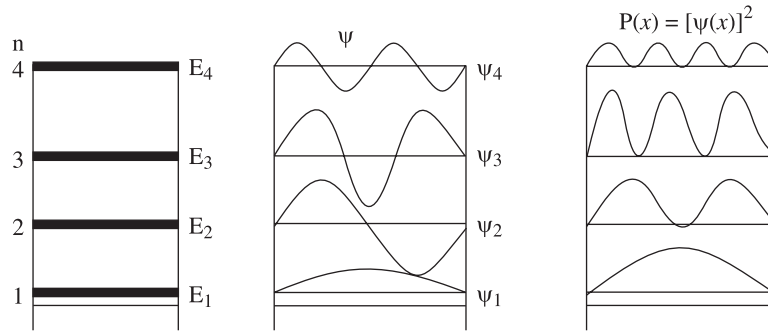


Fig. 6.1.2 Energy levels, wave functions and probability density

Probability density: The probability density $P_n(x)$ of finding the particle anywhere on the x -axis is given by

$$P_n(x) = |\psi(x)|^2 = \frac{2}{L} \sin^2 \frac{n\pi x}{L} \quad \dots(6.1.10)$$

Even if we consider the time dependent wave function to calculate the probability function, it comes out to be independent of time. The energy levels with corresponding wave functions and probability density are shown in the Fig. (6.1.2).

Notice that the wave functions of a particle in a box are similar to the displacement functions of a stretched string. This is to be expected because the boundary conditions are identical in both the cases. The probability density corresponding to the quantum number $n = 1$ is maximum at the center ($x = L/2$) of the potential well whereas the probability density corresponding to the quantum number $n = 2$ is zero at the center of the well. This fact is at variance with the prediction of classical physics according to which the probability of finding the particle is the same everywhere.

As we go higher energy levels with more nodes (the points where wave function vanishes) the maxima and minima of probability come closer together and the variations probability along the length of the box ultimately becomes undetectable. For large quantum numbers we get the classical result of uniform probability density. This is in accord with the **correspondence principle**.

In our daily experience we are concerned with macroscopic objects only. For such objects the spacing of the energy levels is too small to be observed and therefore energy appears to be continuous. But for microscopic objects the spacing of the energy levels are considerable and hence the discrete nature of energy levels becomes perceptible. These facts may be illustrated by examples.

Consider a macroscopic system, say, a bead of mass $m = 10$ gm confined to move along x -axis in a region of dimension $L = 1$ m. The energy of the bead is

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = 5.5 \times 10^{-66} n^2 \text{ J}$$

The first three energy levels are

$$E_1 = 5.5 \times 10^{-66} \text{ J}, E_2 = 22.0 \times 10^{-66} \text{ J}, E_3 = 50.5 \times 10^{-66} \text{ J}$$

Evidently the spacing of the energy levels is too small to be detected. The velocity corresponding to kinetic energy 5.5×10^{-66} J is 3.3×10^{-32} m/s, the bead can hardly be distinguished from its stationary position. Thus, because of the extremely small size of $\hbar$, quantization of energy is unobservable for macroscopic bodies.

Now consider a microscopic system, say, an electron which is confined to in a region of dimension $L = 1$ Å. The energy of electron is

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = 6 \times 10^{-18} n^2 \text{ J} = 38 n^2 \text{ eV}$$

The first three energy levels are

$$E_1 = 38 \text{ eV}, E_2 = 152 \text{ eV}, E_3 = 342 \text{ eV}.$$

These energy levels are sufficiently far apart and therefore the quantization of energy of electron is perceptible. Typical atoms have this dimension and hence quantization of electron energy levels in atoms is conspicuous.

Correspondence principle: The spacing of two successive energy levels is

$$\Delta E = E_{n+1} - E_n = \frac{\pi^2 \hbar^2}{2mL^2} [(n+1)^2 - n^2]$$

For macroscopic bodies $m \rightarrow \infty$, and $L \rightarrow \infty$. $\Delta E \rightarrow 0$. The discrete energy spectrum becomes continuous. This is correspondence principle.

6.2 PARTICLE IN A TWO DIMENSIONAL POTENTIAL WELL

Let the potential well be defined by

$$\begin{aligned} V &= 0 \quad \text{for } 0 < x < L_1, 0 < y < L_2 \\ &= \infty \quad \text{for } x > L_1, y > L_2 \end{aligned} \quad \dots(6.2.1)$$

The Schrodinger equation for the particle confined to move in this two dimensional potential well is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(6.2.2)$$

$$\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2} + k^2 \psi(x, y) = 0$$

where $k = \sqrt{\frac{2mE}{\hbar^2}}$... (6.2.3)

To solve Eqn. (6.2.2) let

$$\psi(x, y) = f_1(x) \cdot f_2(y) \quad \dots (6.2.4)$$

Substituting Eqn(6.2.4) in (6.2.2) we have

$$\frac{1}{f_1(x)} \frac{d^2 f_1(x)}{dx^2} = -\frac{1}{f_2(y)} \frac{d^2 f_2(y)}{dy^2} - k^2 \quad \dots (6.2.5)$$

The left-hand side of above equation is function of x only and the right-hand is function of y only, x and y are independent of each other. This equation is consistent only if each side is equal to the same constant, say $-k_1^2$. (If we choose the separation constant to be positive, the separated equations will have exponential solution, which will not vanish at the boundaries.) Thus

$$\frac{1}{f_1(x)} \frac{d^2 f_1(x)}{dx^2} = -\frac{1}{f_2(y)} \frac{d^2 f_2(y)}{dy^2} - k^2 = -k_1^2 \quad \dots (6.2.6)$$

Equation (6.2.6) separates into two equations

$$\frac{d^2 f_1(x)}{dx^2} + k_1^2 f_1(x) = 0 \quad \dots (6.2.7)$$

$$\frac{d^2 f_2(y)}{dy^2} + k_2^2 f_2(y) = 0 \quad \dots (6.2.8)$$

where $k_2^2 = k^2 - k_1^2$ or $k_1^2 + k_2^2 = k^2$... (6.2.9)

The solution of Eqn. (6.2.7) may written as

$$f_1(x) = A \sin k_1 x + B \cos k_1 x \quad \dots (6.2.10)$$

and that of Eqn. (6.2.8) may be written as

$$f_2(y) = C \sin k_2 y + D \cos k_2 y \quad \dots (6.2.11)$$

Applying the boundary condition: $f_1(x) = 0$ at $x = 0$, we find

$$B = 0.$$

Similarly applying the boundary condition $f_2(y) = 0$ at $y = 0$, we get

$$D = 0.$$

So the solutions (6.2.10) and (6.2.11) become

$$f_1(x) = A \sin k_1 x \quad \dots (6.2.12)$$

$$f_2(y) = C \sin k_2 y \quad \dots (6.2.13)$$

Applying the boundary condition: $f_1(x) = 0$ at $x = L_1$, we have

$$\sin k_1 L_1 = 0 \Rightarrow k_1 L_1 = n_1 \pi \quad n_1 = 1, 2, 3, \dots$$

$$\therefore k_1 = \frac{n_1 \pi}{L_1} \quad \dots(6.2.14)$$

Similarly applying the boundary condition: $f_2(y) = 0$ at $y = L_2$, we have

$$\sin k_2 L_2 = 0 \Rightarrow k_2 L_2 = n_2 \pi, \quad n_2 = 1, 2, 3, \dots$$

$$\therefore k_2 = \frac{n_2 \pi}{L_2} \quad \dots(6.2.15)$$

From Eqn. (6.2.9), we have

$$k^2 = k_1^2 + k_2^2 = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right) \pi^2$$

or
$$\frac{2mE}{\hbar^2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right) \pi^2$$

$$E_{n_1, n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right) \frac{\pi^2 \hbar^2}{2m} \quad \dots(6.2.16)$$

This equation gives the permitted values of energy of a particle trapped in a two dimensional infinitely deep potential well.

The energy levels of a square potential well of width L are given by

$$E_{n_1, n_2} = (n_1^2 + n_2^2) \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(6.2.17)$$

whence
$$E_{1,1} = \frac{\pi^2 \hbar^2}{2mL^2}, E_{1,2} = E_{2,1} = \frac{5\pi^2 \hbar^2}{2mL^2}, E_{2,2} = \frac{8\pi^2 \hbar^2}{2mL^2}$$

$$E_{1,3} = E_{3,1} = \frac{10\pi^2 \hbar^2}{2mL^2}, \text{etc.}$$

The solution of the Schrödinger equation is

$$\psi(x, y) = A \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \quad \dots(6.2.18)$$

6.3 PARTICLE IN A THREE DIMENSIONAL POTENTIAL WELL

Let the three dimensional potential well of infinite depth be defined by

$$\begin{aligned} V(x, y, z) &= 0 \text{ for } 0 < x < L_1, 0 < y < L_2, 0 < z < L_3 \\ &= \infty \text{ outside the well} \end{aligned} \quad \dots(6.3.1)$$

Let a particle of mass m and energy E be confined to move inside the well. The Schrodinger wave equation for the particle is

$$\left. \begin{aligned} \nabla^2 \psi + \frac{2mE}{\hbar^2} \psi &= 0 \\ \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + k^2 \psi &= 0 \end{aligned} \right\} \quad \dots(6.3.2)$$

where $k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(6.3.3)$

We assume the solution of Eqn. (6.3.2) of the form

$$\psi(x, y, z) = f_1(x) \cdot f_2(y) \cdot f_3(z) \quad \dots(6.3.4)$$

Substituting Eqn. (6.3.4) in (6.3.2), we find

$$\frac{1}{f_1(x)} \frac{d^2 f_1(x)}{dx^2} + \frac{1}{f_2(y)} \frac{d^2 f_2(y)}{dy^2} + \frac{1}{f_3(z)} \frac{d^2 f_3(z)}{dz^2} = -k^2 (\text{say}) \quad \dots(6.3.5)$$

The first term is function of x alone, the second term is function of y alone and the third term is function of z alone. Since their sum is independent of x, y, z , this is possible only if each term is separately constant. So we can write

$$\frac{1}{f_1(x)} \frac{d^2 f_1(x)}{dx^2} = -k_1^2 \quad \dots(6.3.6)$$

$$\frac{1}{f_2(y)} \frac{d^2 f_2(y)}{dy^2} = -k_2^2 \quad \dots(6.3.7)$$

$$\frac{1}{f_3(z)} \frac{d^2 f_3(z)}{dz^2} = -k_3^2 \quad \dots(6.3.8)$$

where $k_1^2 + k_2^2 + k_3^2 = k^2 = \frac{2mE}{\hbar^2} \quad \dots(6.3.9)$

The separation constants have been assumed to be negative, otherwise the boundary conditions would not be satisfied. Solutions of Eqns. (6.3.6), (6.3.7) and (6.3.8) may be assumed of the forms

	Degeneracy
$E = 17 \varepsilon_1$ —————	3
223, 132, 322	
$E = 14 \varepsilon_1$ —————	6
123, 132, 213, 231, 321, 312	
$E = 12 \varepsilon_1$ —————	1
222	
$E = 11 \varepsilon_1$ —————	3
113, 131, 311	
$E_3 = 9 \varepsilon_1$ —————	3
122, 212, 221	
$E_2 = 6 \varepsilon_1$ —————	3
112, 121, 211	
1, 1, 1	
$E_1 = E_{111} = 3 \frac{\pi^2 \hbar^2}{2mL^2} = 3 \varepsilon_1$ —————	1

Fig. 6.3.1 Allowed energy states of a particle in a cubical box

$$f_1(x) = A_1 \sin k_1 x + B_1 \cos k_1 x \quad \dots(6.3.10)$$

$$f_2(y) = A_2 \sin k_2 y + B_2 \cos k_2 y \quad \dots(6.3.11)$$

$$f_3(z) = A_3 \sin k_3 z + B_3 \cos k_3 z \quad \dots(6.3.12)$$

The boundary conditions

$$f_1(x) = f_2(y) = f_3(z) = 0 \text{ at } x = y = z = 0 \text{ give } B_1 = B_2 = B_3 = 0.$$

The boundary conditions

$$f_1(x) = 0 \text{ at } x = L_1, f_2(y) = 0 \text{ at } y = L_2, f_3(z) = 0 \text{ at } z = L_3 \text{ give}$$

$$k_1 = \frac{n_1 \pi}{L_1}, k_2 = \frac{n_2 \pi}{L_2}, k_3 = \frac{n_3 \pi}{L_3}, \text{ where } n_1, n_2, n_3 = 1, 2, 3, \dots$$

From Eqn. (6.3.9)

$$\begin{aligned} E_{n_1, n_2, n_3} &= (k_1^2 + k_2^2 + k_3^2) \frac{\hbar^2}{2m} \\ &= \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \frac{\pi^2 \hbar^2}{2m} \end{aligned} \quad \dots(6.3.13)$$

The solution of Schrödinger is

$$\psi(x, y, z) = A \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \sin \frac{n_3 \pi z}{L_3} \quad \dots(6.3.14)$$

If $L_1 = L_2 = L_3 = L$ (*i.e.*, the shape of the well is cubical) then the energy levels are given by

$$E_{n_1, n_2, n_3} = (n_1^2 + n_2^2 + n_3^2) \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(6.3.15)$$

and the corresponding normalized wave functions are

$$\psi(x, y, z) = \left(\frac{8}{L^3} \right)^{1/2} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \sin \frac{n_3 \pi z}{L} \quad (6.3.16)$$

The ground state energy level is

$$E_{1, 1, 1} = 3 \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(6.3.17)$$

Next few energy levels are

$$E_{1, 1, 2} = E_{1, 2, 1} = E_{2, 1, 1} = 6 \frac{\pi^2 \hbar^2}{2mL^2} \quad \dots(6.3.18)$$

Notice that three sets of quantum numbers (1, 1, 2), (1, 2, 1) and (2, 1, 1) *i.e.*, three quantum states corresponds to the same energy state. We say that this energy level is **3-fold degenerate**. The degeneracy of other energy levels is shown in the Fig. (6.3.1).

6.4 DEGENERACY

Consider an eigen value equation

$$\hat{Q}u = qu \quad \dots(6.4.1)$$

If there are n independent eigen functions $u_1, u_2, \dots, u_n$ belonging to the same eigen value q , then this eigen value is said to be n -fold degenerate. The linear combination of the eigen function

$$\psi = c_1 u_1 + c_2 u_2 + \dots + c_n u_n$$

is also an eigen function of the operator $\hat{Q}$ with the same eigen value q . The eigen functions $u_1, u_2, u_3, \dots, u_n$ are said to be linearly independent if the equation

$$c_1 u_1 + c_2 u_2 + \dots + c_n u_n = 0$$

can only be satisfied with all c 's equal to zero. This means that no member of the set of eigen functions can be expressed as a linear combination of the remaining members. For example, the functions $u_1 = 3x$, $u_2 = 5x^2 - x$, $u_3 = x^2$ are not linearly independent since $u_2 = 5u_3 - (1/3)u_1$. On the other hand the functions $u_1 = 1$, $u_2 = x$, $u_3 = x^2$ are linearly independent, since none of them can be written as a linear combination of the other two. The degree of degeneracy of an eigen value is equal to the number of linearly independent eigen functions corresponding to that eigen value.

The stationary state wave functions ψ_{112} , ψ_{121} , ψ_{211} for the particle in a cubic box are degenerate and their linear combination is also an eigen function of the particle with the same energy eigen value.

6.5 DENSITY OF STATES

The allowed energy levels and associated quantum states for a particle confined to move in a cubical enclosure of side L are given by

$$\begin{aligned} E_{n_1 n_2 n_3} &= \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} (k_1^2 + k_2^2 + k_3^2) \\ &= \frac{\hbar^2}{2m} \left[\left(\frac{n_1 \pi}{L} \right)^2 + \left(\frac{n_2 \pi}{L} \right)^2 + \left(\frac{n_3 \pi}{L} \right)^2 \right] \end{aligned} \quad \dots(6.5.1)$$

$$\psi(x, y, z)_{n_1 n_2 n_3} = \text{const.} \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \sin \frac{n_3 \pi z}{L} \quad \dots(6.5.2)$$

where n_1 , n_2 and n_3 are non-zero positive integers. The particle described by wave function ψ has wave vector k whose components are given by

$$k = \left\{ \frac{n_1 \pi}{L}, \frac{n_2 \pi}{L}, \frac{n_3 \pi}{L} \right\}. \quad \dots(6.5.3)$$

We can plot the components of the wave vector k in three dimensional space with k_1 , k_2 , k_3 as Cartesian axes. This space is called k -space. In k -space the allowed values k form a cubical point lattice with spacing between points being π/L . Each lattice point in k -space represents a permissible state of the particle. These lattice points divide the k -space into cells, each of volume $(\pi/L)^3$. The contribution to the unit cell of points lying at the corners of the unit cell is unity. Each lattice point, which corresponds to a quantum states, occupies a volume $(\pi/L)^3$ in k -space.

We wish to find the number of quantum states with wave vectors whose magnitude lie in the interval k and $k + dk$. This number is equal to the number of lattice points in k -space lying between two spherical shells, centered at the origin, of radii k and $k + dk$ in the positive octant. The volume of the region lying between the spherical shell of radii k and $k + dk$ in the positive octant is $\frac{1}{8}(4\pi k^2 dk)$. So the number of states with wave vectors whose magnitudes lie in the range k to $k + dk$ is

$$\left(g(k) dk = \frac{\frac{1}{8}(4\pi k^2 dk)}{(\pi/L)^3} = \frac{V}{2\pi^2} k^2 dk \right) \quad \dots(6.5.4)$$

where $V = L^3$ is the volume of the enclosure. The function $g(k)$, which represents the number of quantum states per unit energy range at energy E , is called the *density of states*.

Making use of the relations

$$p = \hbar k = \sqrt{2mE}$$

the expression for the density of states can be written as

$$g(p) dp = \frac{V}{h^3} 4\pi p^2 dp \quad \dots(6.5.5)$$

$$g(E)dE = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{E} dE \quad \dots(6.5.6)$$

Periodic Boundary Conditions

The formula for the density of states is independent of the detailed form of boundary conditions imposed at the surface of the enclosure. We shall show this by using an alternative boundary condition, the periodic boundary condition, which is most often used. For a cubic enclosure of side L this condition is expressed as

$$\psi(0, y, z) = \psi(L, y, z)$$

$$\psi(x, 0, z) = \psi(x, L, z)$$

$$\psi(x, y, 0) = \psi(x, y, L)$$

The solution of Schrodinger wave equation for a particle in a box is

$$\psi(x, y, z) = \text{const.} \exp i\{k_1 x + k_2 y + k_3 z\}$$

The wave vector k is now restricted to the values

$$k = \left\{ \frac{2\pi}{L} n_1, \frac{2\pi}{L} n_2, \frac{2\pi}{L} n_3 \right\}$$

Notice that the n_i 's now can be positive or negative integers. Now to calculate the density of states, instead of taking positive octant of a sphere in k -space, we take the whole sphere. The spacing of lattice points in k -space is now $2\pi/L$. The number of states whose wave vector k has magnitude in the range k and $k + dk$ is given by

$$g(k)dk = \frac{4\pi k^2 dk}{(2\pi/L)^3} = \frac{V}{2\pi} k^2 dk \quad \dots(6.5.7)$$

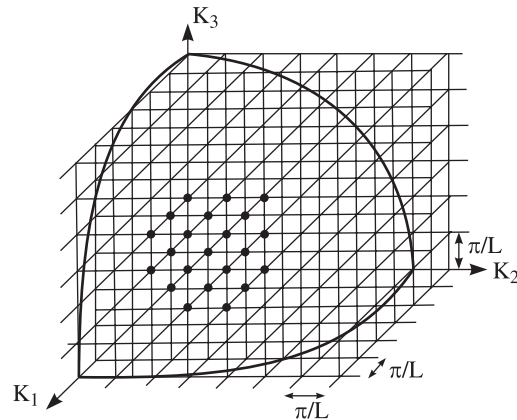


Fig. 6.5.1 Three dimensional k -space. Each lattice point represents a state.

6.6 SPHERICALLY SYMMETRIC POTENTIAL WELL

A spherically symmetric potential well is defined by

$$\begin{aligned} V(r) &= 0 \text{ for } r < r_0 \\ &= \infty \text{ for } r = r_0 \end{aligned} \quad \dots(6.6.1)$$

The Schrodinger equation for the particle inside the potential well is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

We assume that the wave function depends only on radial distance r . The Schrodinger equation simplifies to

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) + \frac{2mE}{\hbar^2} \psi = 0 \quad \dots(6.6.2)$$

$$\text{or} \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) + k^2 \psi = 0 \quad \dots(6.6.3)$$

$$\text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \quad \dots(6.6.4)$$

A great convenience results if we employ the transformation

$$\psi(r) = \frac{u(r)}{r} \quad \dots(6.6.5)$$

In terms of new variable Eqn. (6.6.3) transforms to

$$\frac{d^2 u}{dr^2} + k^2 u = 0 \quad \dots(6.6.6)$$

Its solution is

$$u = A \sin (kr + \alpha)$$

$$\text{or} \quad \psi = \frac{A}{r} \sin(kr + \alpha) \quad \dots(6.6.7)$$

where A and α are constants.

At $r = 0$, ψ is finite. This gives $\alpha = 0$. Whence

$$\psi = \frac{A}{r} \sin kr \quad \dots(6.6.8)$$

At $r = r_0$, $\psi = 0$ whence

$$\sin kr_0 = 0$$

$$k = \frac{n\pi}{r_0}, \quad n = 1, 2, 3, \dots$$

$$\sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{r_0} \quad \dots(6.6.9)$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mr_0^2}$$

The wave function of the particle is

$$\psi(r) = \frac{A}{r} \sin \frac{n\pi r}{r_0} \quad \dots(6.6.10)$$

The wave function can be normalized making use of the condition

$$\begin{aligned} \int_0^{r_0} |\psi(r)|^2 dr &= 1 \\ \int_0^{r_0} \left(\frac{A^2}{r^2} \sin^2 \frac{n\pi r}{r_0} \right) 4\pi r^2 dr &= 1 \\ 2\pi A^2 \int_0^{r_0} \left(1 - \cos \frac{2\pi r}{r_0} \right) dr &= 1 \\ \therefore A &= \frac{1}{\sqrt{2\pi r_0}} \quad \dots(6.6.11) \end{aligned}$$

Hence
$$\psi(r) = \frac{1}{\sqrt{2\pi r_0}} \frac{1}{r} \sin \frac{n\pi r}{r_0} \quad \dots(6.6.12)$$

Most probable distance: The probability of finding the particle at a distance r is

$$P(r)dr = |\psi(r)|^2 4\pi r^2 dr = \left[\frac{1}{2\pi r_0} \frac{1}{r^2} \sin^2 \frac{n\pi r}{r_0} \right] 4\pi r^2 dr$$

The most probable distance is obtained by using the condition

$$\begin{aligned} \frac{dP(r)}{dr} &= 0, \text{ and } \frac{d^2P(r)}{dr^2} = -ive \\ \frac{2}{r_0} \left[\left(2 \sin \frac{n\pi r}{r_0} \right) \left(\cos \frac{n\pi r}{r_0} \right) \right] \left(\frac{n\pi}{r_0} \right) &= 0 \\ r_{mp} &= \frac{r_0}{2} \quad \dots(6.6.13) \end{aligned}$$

The probability of finding the particle in the region $r < r_{mp}$ is given by

$$\begin{aligned}
 P &= \int_0^{r_0/2} P(r) dr \\
 &= \int_0^{r_0/2} \left[\left(\frac{1}{2\pi r_0} \right)^2 \frac{1}{r^2} \sin^2 \left(\frac{n\pi r}{r_0} \right) \right] 4\pi r^2 dr \\
 &= \frac{1}{2}.
 \end{aligned}$$

SOLVED EXAMPLES

Ex. 1. A particle in the ground state is located in a one dimensional potential well of width L with absolutely impenetrable walls $0 < x < L$. Find probability of finding the particle in the region $L/3 < x < 2L/3$ in ground state.

Sol. Ground state normalized wave function of the particle is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

The required probability is given by

$$\begin{aligned}
 P &= \int_{L/3}^{2L/3} |\psi(x)|^2 dx = \frac{2}{L} \int_{L/3}^{2L/3} \sin^2 \frac{\pi x}{L} dx = \frac{2}{L} \int_{L/3}^{2L/3} \left(1 - \cos \frac{2\pi x}{L} \right) dx \\
 &= \frac{1}{3} + \frac{\sqrt{3}}{2\pi} = 0.61.
 \end{aligned}$$

Ex. 2. A particle is located in a two dimensional square potential well with absolutely impenetrable walls ($0 < x < L$, $0 < y < L$). Find the probability of finding the particle within a region $0 < x < L/3$, $0 < y < L/3$ with lowest energy.

Sol. Wave function in the ground state is

$$\psi = \frac{2}{L} \sin \frac{\pi x}{L} \sin \frac{\pi y}{L}$$

Required probability

$$\begin{aligned}
 P &= \int_0^{L/3} \int_0^{L/3} |\psi|^2 dx dy = \frac{4}{L^2} \int_0^{L/3} \int_0^{L/3} \left(\sin^2 \frac{\pi x}{L} \sin^2 \frac{\pi y}{L} \right) dx dy \\
 &= \frac{1}{L^2} \int_0^{L/3} \left(1 - \cos \frac{2\pi x}{L} \right) dx \int_0^{L/3} \left(1 - \cos \frac{2\pi y}{L} \right) dy \\
 &= 0.32.
 \end{aligned}$$

Ex. 3. The wave function of a particle in one dimensional box of length L is given by

$$\phi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}. \quad \text{Find the expectation value of } x \text{ and } x^2.$$

Sol.

$$\begin{aligned} \langle x \rangle &= \int_0^L \psi^* \hat{x} \psi dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{L}{2} \end{aligned}$$

$$\begin{aligned} \langle x^2 \rangle &= \frac{2}{L} \int_0^L x^2 \sin^2 \frac{n\pi x}{L} dx \\ &= \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}. \end{aligned}$$

Ex. 4. Show that the wave function $\psi_n = A \sin \frac{n\pi x}{L}$ of a particle moving in one dimensional potential well of width L is not eigen function of $\hat{p}_x$. What can be said about the function $\psi = A \exp(\pm ikx)$?

$$\begin{aligned} \text{Sol. } \hat{p}_x \psi_n &= -i\hbar \frac{\partial}{\partial x} A \sin \frac{n\pi x}{L} \\ &= -\frac{i\hbar n\pi}{L} A \cos \frac{n\pi x}{L} \end{aligned}$$

So the function $A \sin n\pi x/L$ is not an eigen function of p_x -operator.

$$\hat{p}_x \psi_n = -i\hbar \frac{\partial}{\partial x} A \exp(\pm ikx) = \pm \hbar k [A \exp(\pm ikx)]$$

So the function $A \exp(\pm ikx)$ is an eigen function of p_x -operator with eigen value $\hbar k$.

Ex. 5. Show that the wave functions

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

are orthogonal.

$$\begin{aligned} \text{Sol. } \int_0^L \psi_m \psi_n dx &= \frac{2}{L} \int_0^L \sin \frac{m\pi x}{L} \sin \frac{n\pi x}{L} dx \\ &= \frac{1}{L} \int_0^L \left[\cos \frac{(n-m)\pi x}{L} - \cos \frac{(n+m)\pi x}{L} \right] dx \\ &= 0 \end{aligned}$$

Therefore the functions are orthogonal.

QUESTIONS AND PROBLEMS

1. A one dimensional potential barrier of height V extends from $x = 0$ to $x = \infty$. A particle possessing kinetic energy E is incident from left on the potential barrier (potential step). Analyze the problem quantum mechanically for the cases (i) $E < V$ (ii) $E > V$.
2. What do you mean by tunnel effect? Calculate the transmission probability of a particle incident on the potential barrier for case in which kinetic energy of the particle is less than the height of the barrier. Discuss the effect of height and width of the barrier on the transmission probability.
3. Set up Schrodinger equation for a particle is trapped in an infinitely deep potential well of width L and obtain the wave functions and energy levels of the particle.
 - (a) Discuss the effect of width of the well on energy eigen values of the particle.
 - (b) Compare the classical and quantum mechanical probability of finding the particle in the well at different energy states.
4. A particle is confined to move in one dimensional box with perfectly rigid walls at $x = 0$ and $x = L$. Analyze the problem quantum mechanically. Find the quantum mechanical probability of finding the particle at $x = L/4, L/3, L/2, 2L/3$.
5. Give quantum mechanical treatment of motion of a particle confined to move in a two dimensional potential well. Explain the term degeneracy in this context.
6. A particle of mass m is constrained to in a box of sides L_1, L_2 and L_3 . Set up Schrodinger equation for the particle and solve for eigen values and eigen functions. If the box is cube of side L , find the degree of degeneracy of the second, third, fourth and sixth energy levels.
7. A particle is confined to move in a cubical box of side L . Find the eigen functions and eigen values. Discuss the degeneracy of eigen functions choosing a suitable eigen value. (All'd 1997)
8. Find the eigen values and eigen functions of a particle moving in a one dimensional square well potential with infinite high walls. Can the particle in such a well ever have zero total energy? If not then explain clearly, why not? (All'd 1998)
9. Find the eigen values and eigen functions of a particle moving in a one dimensional square well potential with infinitely high walls. (All'd 2004)
10. What is meant by free and bound states of a quantum mechanical system? (All'd 2001)
11. A particle of mass m is confined to a one dimensional box of length L . Obtain expressions for the wave functions and allowed energies as a function of the quantum number n . Generalize the results to a two dimensional box and find energy of the ground state. What is its degeneracy? (All'd 2000)
12. A particle of mass m is restricted to move in a rectangular potential box given by

$$V = 0 \text{ if } 0 < x < a, 0 < y < b, 0 < z < c \\ = \infty \text{ elsewhere.}$$

Where a, b, c are constants. Solve the Schrodinger equation for the particle and find expression for its wave functions and energies.

13. Show that the expression for density of states for a particle of mass m confined to move in volume V is

$$g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}.$$

HARMONIC OSCILLATOR

7.1 INTRODUCTION

Classical Treatment: A particle attached to a fixed point, say $x = 0$, with a force, which is proportional to its displacement from the mean position and is directed towards the fixed point, constitutes a harmonic oscillator. Its equation of motion is

$$m\ddot{x} + kx = 0$$

$$\ddot{x} + \omega^2 x = 0, \quad \omega = \sqrt{\frac{k}{m}} \quad \dots(7.1.1)$$

where m is mass of the particle, k is force constant and x is displacement, ω is called the classical angular frequency of the oscillator. The solution of Eq. (7.1.1) is

$$x = A \cos (\omega t + \delta) \quad \dots(7.1.2)$$

A is amplitude and δ is initial phase of the particle. The potential energy of the oscillator is

$$V(x) = \frac{1}{2} m \omega^2 x^2 \quad \dots(7.1.3)$$

and the total energy is given by

$$E = \frac{1}{2} m \omega^2 A^2 \quad \dots(7.1.4)$$

The oscillator can be made to oscillate with any desired amplitude A and therefore the energy E may assume any value depending on the amplitude. In other words the energy is a continuous variable. A graph showing the variation of potential energy with displacement is shown in the Fig. (7.1.1). Corresponding to amplitudes A_1 and A_2 , the energies of oscillator are $1/2 k A_1^2$ and $1/2 k A_2^2$ respectively. By adjusting the amplitude between A_1 and A_2 , the oscillator can be made to oscillate with any energy between $E_1 = (1/2) m \omega^2 A_1^2$ and $E_2 = (1/2) m \omega^2 A_2^2$. Thus there are infinite energy levels between E_1 and E_2 . This is what we mean by the statement that energy is a continuous variable.

The velocity of the particle in executing simple harmonic oscillation is zero at the turning points $x = A$ and $x = -A$ and is maximum at the equilibrium point $x = 0$. This means that the particle spends maximum time at the turning points and minimum time at the equilibrium point. The classical

probability of finding the particle is maximum at the turning point and is minimum at the equilibrium point. This fact is displayed in the Fig. (7.1.2). Classical physics does not allow the particle to go beyond the turning points.

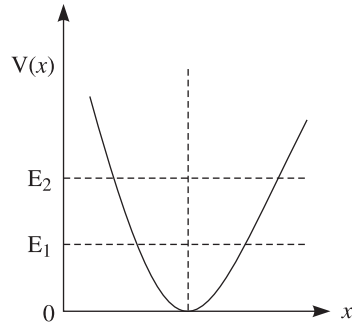
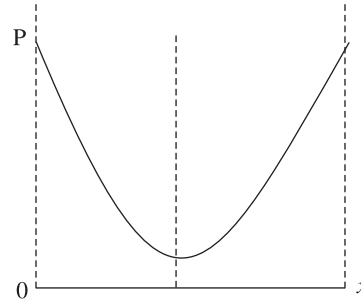
Fig. 7.1.1 $V(x)$ vs x graph.

Fig. 7.1.2 Classical probability

Quantum Mechanical Treatment: The Schrodinger equation for the harmonic oscillator is an eigen value equation

$$\hat{H}\psi = E\psi$$

$$-\frac{\hbar}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad \text{where, } V = \frac{1}{2}m\omega^2 x^2$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}m\omega^2 x^2 \right) \psi = 0 \quad \dots(7.1.5)$$

We shall transform this equation into a convenient form by introducing a new independent variable ξ defined by

$$\xi = \alpha x \quad \dots(7.1.6)$$

The parameter α will be chosen in such a way that the new equation looks simple.

Now
$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi} \frac{d\xi}{dx} = \alpha \frac{d\psi}{d\xi}$$

$$\frac{d^2\psi}{dx^2} = \alpha \frac{d}{dx} \left(\frac{d\psi}{d\xi} \right) = \alpha \frac{d}{d\xi} \left(\frac{d\psi}{d\xi} \right) \frac{d\xi}{dx} = \alpha^2 \frac{d^2\psi}{d\xi^2}$$

In terms of new variable Eqn. (7.1.5) becomes

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{2mE}{\hbar^2 \alpha^2} - \frac{m^2 \omega^2 \xi^2}{\hbar^2 \alpha^4} \right) \psi = 0 \quad \dots(7.1.7)$$

Let us choose

$$\alpha^2 = \frac{m\omega}{\hbar} \quad \dots(7.1.8)$$

Equation (7.1.7) now becomes

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{2E}{\hbar\omega} - \xi^2 \right) \psi = 0 \quad \dots(7.1.9)$$

Introducing the dimensionless parameter β defined by

$$\beta = \frac{2E}{\hbar\omega} \quad \dots(7.1.10)$$

Eqn. (7.1.9) becomes

$$\frac{d^2\psi}{d\xi^2} + (\beta - \xi^2) \psi = 0 \quad \dots(7.1.11)$$

Asymptotic solution ($\xi \rightarrow \pm \infty$) : The wave function $\psi(\xi)$ must satisfy the condition

$$\psi(\pm \infty) = 0$$

In the limit $\xi \rightarrow \infty$, β may be neglected. Eqn. (7.1.11) assumes the form

$$\frac{d^2\psi}{d\xi^2} - \xi^2 \psi = 0 \quad \dots(7.1.12)$$

The solution to this equation is

$$\psi = \exp\left(\pm \frac{1}{2} \xi^2\right)$$

We omit the positive sign because it does not satisfy the condition $\psi(\pm \infty) \rightarrow 0$. Hence the asymptotic solution of Eqn. (7.1.11) has the form

$$\psi = \exp\left(-\frac{1}{2} \xi^2\right) \quad \dots(7.1.13)$$

Let us verify that Eqn. (7.1.13) satisfies (7.1.12). From Eqn. (7.1.13)

$$\frac{d\psi}{d\xi} = -\xi\psi, \quad \frac{d^2\psi}{d\xi^2} = -\left(\psi + \xi \frac{d\psi}{d\xi}\right) = (\xi^2 - 1)\psi = \xi^2\psi \text{ for } \xi \rightarrow \infty.$$

This ensures that Eqn. (7.1.13) is an asymptotic solution of Eqn. (7.1.11). We may now assume that the solution of Eqn. (7.1.11) is of the form

$$\psi(\xi) = H(\xi) \exp\left(-\frac{1}{2} \xi^2\right) \quad \dots(7.1.14)$$

where, $H(\xi)$ is unknown function to be determined. Substituting Eqn. (7.1.14) in (7.1.11) we obtain

$$\frac{d^2H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + (\beta - 1)H(\xi) = 0 \quad \dots(7.1.15)$$

The unknown function $H(\xi)$ obeying the differential Eqn. (7.1.15) is known as *Hermite function*. Solution of Eqn. (7.1.15) is obtained in the form of power series. We assume the solution of the form

$$H(\xi) = \sum_{n=0}^{\infty} a_n \xi^n = a_0 + a_1 \xi + a_2 \xi^2 + \dots + a_n \xi^n + \dots \quad \dots(7.1.16)$$

Now,

$$\frac{dH}{d\xi} = \sum_{n=0}^{\infty} n a_n \xi^{n-1} = 0 + a_1 + 2a_2 \xi + \dots + n a_n \xi^{n-1} + \dots$$

$$2\xi \frac{dH}{d\xi} = \sum_{n=0}^{\infty} 2n a_n \xi^n \quad \dots(7.1.17)$$

$$\begin{aligned} \frac{d^2 H}{d\xi^2} &= \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} = 0 + 0 + 2a_2 + \dots + n(n-1) a_n \xi^{n-2} + \dots \quad \dots(7.1.18) \\ &= \sum_{n=0}^{\infty} (n+2)(n+1) a_{n+2} \xi^n \end{aligned}$$

Substituting Eqns. (7.1.16), (7.1.17), (7.1.18) in (7.1.15), we have

$$\sum_{n=0}^{\infty} [(n+1)(n+2) a_{n+2} + (\beta - 1 - 2n) a_n] \xi^n = 0 \quad \dots(7.1.19)$$

Equation (7.1.19) holds for all values of ξ . Hence the coefficient of each power of ξ must vanish separately. Hence

$$a_{n+2} = \frac{2n+1-\beta}{(n+1)(n+2)} a_n \quad \dots(7.1.20)$$

This equation is called the recurrence formula for the coefficients a_n . Since the recurrence formula determines the coefficients a_{n+2} in terms of a_n , the power series (7.1.16) contains only with even or only odd powers of ξ

For $n = 0, 2, 4, 6, \dots$

$$a_2 = \frac{1-\beta}{2!} a_0, \quad a_4 = \frac{(1-\beta)(5-\beta)}{4!} a_0, \quad a_6 = \frac{(1-\beta)(5-\beta)(9-\beta)}{6!} a_0$$

In this way all the even coefficients are expressed in terms of a_0 .

For $n = 1, 3, 5, \dots$

$$a_3 = \frac{3-\beta}{3!} a_1, \quad a_5 = \frac{(3-\beta)(7-\beta)}{5!} a_1, \quad a_7 = \frac{(3-\beta)(7-\beta)(11-\beta)}{7!} a_1$$

In this way all the odd coefficients are expressed in terms of a_1 . Thus the power series of Eqn. (7.1.16) contains only two arbitrary constants a_0 and a_1 . Since even coefficients ($a_2, a_4, a_6, \dots$) are related to a_0 and odd coefficients ($a_3, a_5, a_7, \dots$) to a_1 , we can split the solution (7.1.16) in even and odd series as follows:

$$H(\xi) = a_0 \left[1 + \frac{1-\beta}{2!} \xi^2 + \frac{(1-\beta)(5-\beta)}{4!} \xi^4 + \frac{(1-\beta)(5-\beta)(9-\beta)}{6!} \xi^6 + \dots \right] + a_1 \left[\xi + \frac{3-\beta}{3!} \xi^3 + \frac{(3-\beta)(7-\beta)}{5!} \xi^5 + \frac{(3-\beta)(7-\beta)(11-\beta)}{7!} \xi^7 + \dots \right] \quad \dots(7.1.21)$$

$$\text{or } H(\xi) = a_0 \text{ (even series)} + a_1 \text{ (odd series)} \quad \dots(7.1.22)$$

Let us see whether the solution $\psi(\xi)$ expressed in the form $\psi(\xi) = H(\xi) \exp(-\frac{1}{2} \xi^2)$ qualifies to be a physically acceptable solution or not. Any acceptable solution must vanish at infinity *i.e.*, $\psi \rightarrow 0$ as $\xi \rightarrow \infty$. Let us examine the asymptotic behavior of $H(\xi)$ and $\exp(\xi^2)$. A suitable way to compare $H(\xi)$ and $\exp(\xi^2)$ is to express them in power series. $H(\xi)$ has already been found in power series. So

$$\begin{aligned} \exp(\xi^2) &= 1 + \frac{\xi^2}{1!} + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + \dots + \frac{\xi^n}{(n/2)!} + \frac{\xi^{n+2}}{\{(n+2)/2\}!} + \dots \infty \\ &= \sum_{n=0,2,4} \frac{1}{\left(\frac{n}{2}\right)!} \xi^n = \sum_{n=0,2,4} b_n \xi^n ; b_n = \frac{2}{(n/2)!} \quad \dots(7.1.23) \end{aligned}$$

The ratio of successive coefficients in this series is

$$\frac{b_{n+2}}{b_n} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n}{2}+1\right)!} = \frac{2}{n+2} \xrightarrow{n \rightarrow \infty} \frac{2}{n} \quad \dots(7.1.24)$$

The ratio of successive coefficients in $H(\xi)$ is

$$\frac{a_{n+2}}{a_n} = \frac{2n+1-\beta}{(n+1)(n+2)} \xrightarrow{n \rightarrow \infty} \frac{2}{n} \quad \dots(7.1.25)$$

Thus for large values of n , $H(\xi)$ behaves like $\exp(\xi^2)$ and the solution $\psi(\xi)$ becomes

$$\psi(\xi) = H(\xi) \exp\left(-\frac{1}{2} \xi^2\right) \approx \exp(\xi^2) \exp\left(-\frac{1}{2} \xi^2\right) = \exp\left(\frac{1}{2} \xi^2\right)$$

Obviously for $\xi \rightarrow \infty$, ψ does not remain finite and hence it cannot be an acceptable solution so long as $H(\xi)$ is of the form expressed by Eqn. (7.1.22). There is a simple way out of this dilemma. If all the coefficients a_n 's beyond the certain value of n vanish in the series representing $H(\xi)$ then $\psi \rightarrow 0$ as $\xi \rightarrow \infty$ because of the term $\exp\left(-\frac{1}{2} \xi^2\right)$. In other words if $H(\xi)$ terminates as polynomial

with finite number of terms instead of infinite series then it is acceptable. From the recursion formula

$$a_{n+2} = \frac{2n+1-\beta}{(n+1)(n+2)} a_n \quad \dots(7.1.26)$$

it is evident that our requirement is met if $\beta = 2n + 1$ for some value of n then $a_{n+2} = a_{n+4} = a_{n+6} = \dots = 0$. This restriction on β implies that

$$\begin{aligned} \beta &= \frac{2E}{\hbar\omega} = 2n + 1 \\ E_n &= \left(n + \frac{1}{2} \right) \hbar\omega \end{aligned} \quad \dots(7.1.27)$$

Thus the harmonic oscillator can have only a discrete set of energies given by Eqn. (7.1.27). It is remarkable to observe that the lowest energy state corresponds to $n = 0$ and has energy $1/2 \hbar\omega$, called *zero-point energy*. The restriction $\beta = 2n + 1$ takes care of only one sequence of coefficients, either the sequence of even n starting with a_0 or the sequence of odd n starting with a_1 . If n is even, only even powers of ξ appear in the polynomial while if n is odd, only odd powers of ξ appear. If the restriction $\beta = 2n + 1$ is satisfied, only one of the series (either even series or odd series) terminates as a polynomial and the other remains as infinite series and $H(\xi)$ can be written as

$$H(\xi) = a_0 (\text{polynomial}) + a_1 (\text{infinite series}) \quad \dots(7.1.28)$$

$$\text{or} \quad H(\xi) = a_0 (\text{infinite series}) + a_1 (\text{polynomial}) \quad \dots(7.1.29)$$

If $H(\xi)$ represented by Eqn. (7.1.28) is to be an acceptable function a_1 must be chosen equal to zero. Similarly $H(\xi)$ expressed by Eqn. (7.1.29) will be acceptable solution if $a_0 = 0$. So the acceptable forms of $H(\xi)$ are

$$H(\xi) = a_0 \left[1 - \frac{\beta-1}{2!} \xi^2 + \frac{(\beta-1)(\beta-5)}{4!} \xi^4 + \dots \right] \quad \dots(7.1.30)$$

$$\text{or} \quad H(\xi) = a_1 \left[\xi - \frac{\beta-3}{3!} \xi^3 + \dots \right] \quad \dots(7.1.31)$$

For example if we put $n = 4$, $\beta = 9$ the even series becomes polynomial

$$H(\xi) = a_0 \left[1 - 4\xi^2 + \frac{4}{3}\xi^4 \right]$$

and for $n = 3$, $\beta = 7$ the odd series becomes a polynomial

$$H(\xi) = a_1 \left[\xi - \frac{2}{3}\xi^3 \right]$$

It is customary to choose the arbitrary constants a_0 or a_1 such that the coefficient of the highest power of ξ in the polynomial is 2^n or $2^{(\beta-1)/2}$. The resulting polynomials are called *Hermite polynomials*. (For example, if $\beta = 9$ or $n = 4$ the highest power of ξ is 4, therefore we choose

$$\frac{(\beta-1)(\beta-5)}{4!} a_0 = 2^4 \quad \text{or} \quad \frac{4}{3} a_0 = 16 \quad \text{or} \quad a_0 = 12. \quad \text{Then the Hermite polynomial becomes}$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

Similarly for $\beta = 7$ or $n = 3$ we choose $a_1(-\frac{2}{3}) = 2^3$ or $a_1 = -12$ then

$$H_3(\xi) = 8\xi^3 - 12\xi$$

Some *Hermite polynomials* are tabulated below.

$$H_0(\xi) = 1$$

$$H_1(\xi) = 2\xi$$

$$H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

$$H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$$

Higher order *Hermite polynomials* can be determined from the recurrence relation

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi), \quad n \geq 1 \quad \dots(7.1.32)$$

The *Hermite polynomials* are defined by Rodrigues formula

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}) \quad \dots(7.1.33)$$

Putting $n = 0, 1, 2, \dots$ We can find $H_0(\xi), H_1(\xi), H_2(\xi), \dots$ etc.

The wave functions $\psi(x)$ of the harmonic oscillator are

$$\psi_n(x) = N_n e^{-\frac{1}{2}\xi^2} H_n(\xi) = N_n e^{-\frac{1}{2}\alpha^2 x^2} H_n(\alpha x) \quad \dots(7.1.34)$$

$$\xi = \alpha x = \sqrt{\frac{m\omega}{\hbar}} x$$

The multiplicative constant N_n can be determined using the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1$$

$$N_n^2 \int_{-\infty}^{\infty} \frac{1}{\alpha} \exp(-\xi^2) H_n^2(\xi) d\xi = 1$$

$$\frac{N_n^2}{\alpha} \cdot 2^n (n!) \sqrt{\pi} = 1 \quad \left\{ \because \int_{-\infty}^{\infty} \exp(-\xi^2) H_m(\xi) H_n(\xi) d\xi = 2^n (n!) \sqrt{\pi} \delta_{mn} \right\}$$

This gives

$$N_n = \sqrt{\frac{\alpha}{2^n n! \sqrt{\pi}}} = \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} \frac{1}{2^{n/2}} \cdot \frac{1}{(n!)^{1/2}} \quad \dots(7.1.35)$$

Some of the normalized wave functions of harmonic oscillator are given below.

$$\psi_0(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}} e^{-\frac{1}{2}\alpha^2 x^2}$$

$$= \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} \exp\left(-\frac{1}{2} \frac{m\omega}{\hbar} x^2 \right) \quad (\text{ground state})$$

$$\psi_1(x) = \sqrt{\frac{\alpha}{2\sqrt{\pi}}} (2\alpha x) e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\psi_2(x) = \sqrt{\frac{\alpha}{8\sqrt{\pi}}} (4\alpha^2 x^2 - 2) e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\psi_3(x) = \sqrt{\frac{\alpha}{48\sqrt{\pi}}} (8\alpha^3 x^3 - 12\alpha x) e^{-\frac{1}{2}\alpha^2 x^2}$$

$$\psi_n(x) = \sqrt{\frac{\alpha}{2^n n! \sqrt{\pi}}} H_n(\xi) e^{-\frac{1}{2}\alpha^2 x^2}$$

where

$$\xi = \alpha x = \sqrt{\frac{m\omega}{\hbar}} x, \quad \alpha^2 = \frac{m\omega}{\hbar}$$

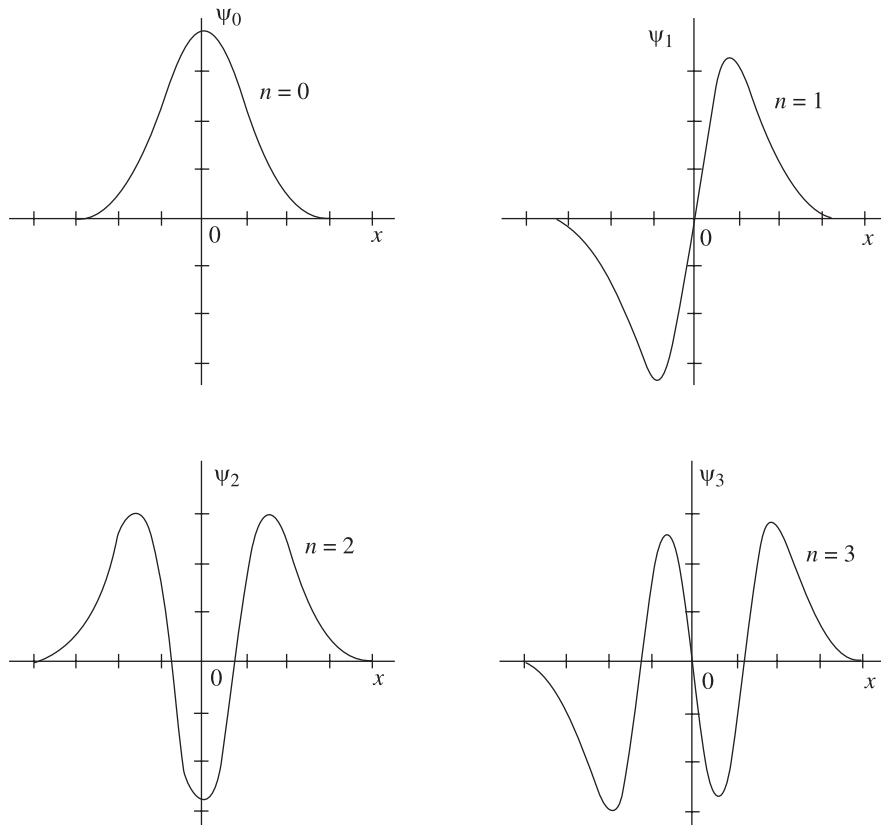


Fig. 7.1.3 Wave functions of harmonic oscillator

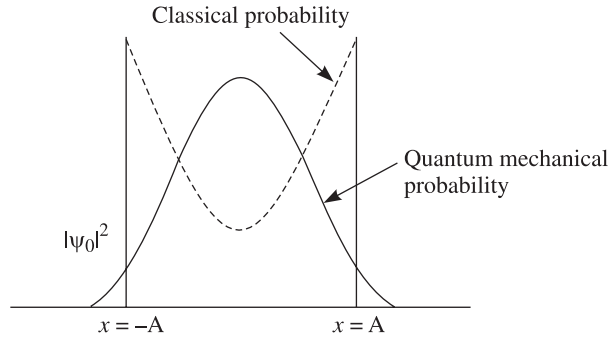


Fig. 7.1.4 Ground state classical and quantum mechanical probability

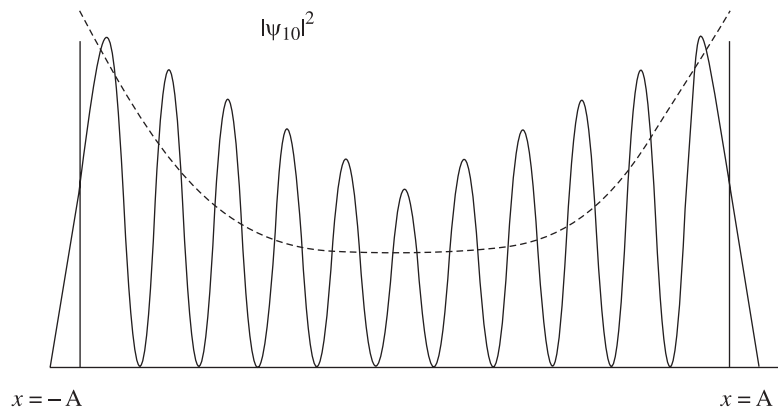


Fig. 7.1.5 Quantum mechanical probability of oscillator in state ψ_{10} . As n becomes very large ($n \rightarrow \infty$) the quantum mechanical probability becomes identical with the classical probability

Probability of finding the harmonic oscillator within classical limits: The ground state wave function of harmonic oscillator is

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{1}{2} \left(\frac{m\omega}{\hbar} \right) x^2}$$

In the ground state the amplitude A of the oscillator is given by

$$\frac{1}{2} m\omega^2 A^2 = \frac{1}{2} \hbar\omega \Rightarrow A = \pm \sqrt{\frac{\hbar}{m\omega}} = \frac{1}{\lambda} \text{ (say)}$$

The probability of finding the oscillator within the classical limits is

$$P_0 = \int_{-A}^A |\psi_0(x)|^2 dx = 2 \int_0^A |\psi_0(x)|^2 dx$$

$$\begin{aligned}
&= 2 \int_0^{1/\lambda} \left(\frac{\lambda}{\sqrt{\pi}} \right) e^{-\lambda^2 x^2} dx \\
&= \frac{2}{\sqrt{\pi}} \int_0^1 e^{-z^2} dz \quad \text{where} \quad \lambda x = z \\
&= \frac{2}{\sqrt{\pi}} \int_0^1 \left(1 - \frac{z^2}{1!} + \frac{z^4}{2!} - \frac{z^6}{3!} + \dots \right) dz \\
&= \frac{2}{\sqrt{\pi}} \left(z - \frac{z^3}{3} + \frac{z^5}{10} - \frac{z^7}{42} + \dots \right)_0^1 \\
&= \frac{2}{\sqrt{\pi}} \left(1 - \frac{1}{3} + \frac{1}{10} - \frac{1}{42} + \dots \right) \\
&= 0.83.
\end{aligned}$$

The ground state probability of finding the oscillator outside the classical limits is 17%.

Correspondence Principle: The position and velocity of oscillator at time t are given by

$$x = A \cos \omega t$$

$$v = -\omega A \sin \omega t = \omega A \left[1 - \frac{x^2}{A^2} \right]^{1/2}$$

Let Δt be the time spent by oscillator in traversing a distance Δx . The classical probability P_c of finding the oscillator within the region Δx is defined as the fraction of time that the oscillator spends within this region. Thus

$$P_c(x) dx = \frac{\Delta t}{T} = \frac{\Delta x / v}{2\pi / \omega} = \frac{1}{2\pi A} \cdot \frac{\Delta x}{\sqrt{1 - \frac{x^2}{A^2}}}$$

At $x = \pm A$, $P_c \rightarrow \infty$. The classical probability P_c is minimum at $x = 0$. Between the classical turning points P_c has non-zero value. For $n = 0$ (ground state) the quantum mechanical probability P of finding the oscillator between classical turning points differs considerably from the classical probability. For $n > 0$, quantum mechanical probability P_{quantum} shows peaks between the points $x = \pm A$. With increasing n , the number of peaks of quantum mechanical probability increases and hence they become crowded. In the limit of large quantum numbers ($n \rightarrow \infty$) the peaks of quantum mechanical probability merge together and P_{quantum} approaches the classical probability. This is the Bohr correspondence principle.

QUESTIONS AND PROBLEMS

1. Give quantum mechanical treatment of one dimensional harmonic oscillator. Obtain the energy levels and wave functions of the oscillator.
2. Set up Schrodinger equation for harmonic oscillator. Write down the expressions for the energy eigen values and wave functions. Sketch first four eigen functions and the corresponding probability of finding the particle. Compare the classical and quantum mechanical probability. What happens when the quantum numbers become very large?
3. Write down Schrodinger equation for harmonic oscillator and the ground state wave function. Find the wave mechanical probability of finding the particle in the ground state within the classical limits.
4. The one dimensional motion of a particle of mass m is described by the following equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi.$$

All symbols have their usual meanings. Find the energy eigen values of the particle. (All'd 1995)

5. (a) The eigen function and the energy of the n th quantum state of a one dimensional harmonic oscillator are given by

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(\alpha x) \exp\left(-\frac{1}{2}\alpha^2 x^2\right), \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

where $\alpha^2 = \frac{m\omega}{\hbar}$ and $H_n(\xi) = (-1)^n \exp(\xi^2) \frac{d^n}{d\xi^n} \exp(-\xi^2).$

Sketch the wave function and the probability density for $n = 2$ state and discuss how the quantum behaviour is different from the classical one.

- (b) Generalize the above results to obtain the wave function and energy eigen values of a two dimensional harmonic oscillator. (All'd 1996)
6. The one dimensional motion of a particle of mass m is described by the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + c_1 x + c_2 x^2$$

where c_1 and c_2 are constants. Find the eigen values of the particle. Do not use perturbation theory to solve the problem. (All'd 1998)

7. A linear harmonic oscillator in its n th quantum state is characterized by a wave function

$$\psi_n = C_n \exp(-\xi^2/2) H_n(\xi), \quad \text{where } H_n(\xi) \text{ is Hermite polynomial and}$$

$$\xi = \sqrt{\frac{m\omega}{\hbar}} x$$

Find $\langle x^2 \rangle$ and the expectation value of the potential energy if the oscillator is in the first energy level.

Given: $\int_{-\infty}^{\infty} \xi^n \exp(-\xi^2) d\xi = \frac{1.3.5.....(2n-1)}{2^n} \sqrt{\pi}.$ (All'd 1999, 2004)

8. Show that the wave functions for a linear harmonic oscillator have definite parity. Explain the origin of zero point energy in a quantum oscillator. (All'd 2000)
9. The wave function for a one dimensional harmonic oscillator is expressed as

$$\Psi_n(x) = \sqrt{\frac{\alpha}{2^n (n!) \sqrt{\pi}}} \exp(-\frac{1}{2} \alpha^2 x^2) H_n(\alpha x), \text{ where } \alpha = \left(\frac{mk}{\hbar^2} \right)^{1/4}$$

- (a) Sketch the wave function and the probability density function for $n = 1$ state as a function of x .
- (b) How is the behaviour of a quantum oscillator different than that of a classical oscillator.
- (c) Write down the energy and wave function for a two dimensional harmonic oscillator by generalizing the results of a one dimensional harmonic oscillator. What is the degeneracy of the first excited state of a two dimensional oscillator. (All'd 2001)
10. What is expectation value? Find expectation value of the potential energy in the ground state of a linear harmonic oscillator. (All'd 2002)
11. For a linear harmonic oscillator, solve the Schrodinger equation showing clearly necessary steps to obtain first three eigen functions and eigen values of the oscillator. Obtain normalization constant for the eigen functions. (All'd 2002)
12. (a) Obtain the wave equation for a linear harmonic oscillator. Solve the equation to find eigen functions and the eigen values.
- (b) The generating function for Hermite polynomial is

$$\exp(2zx - z^2) \text{ or } \exp[x^2 - (z - x)^2] \dots\dots\dots$$

Use this to evaluate the normalization constant. (All'd 2003)

13. Sketch the wave function and the probability density as a function of x for the ground state and first excited state of a linear harmonic oscillator and answer the following:
- (i) What is the parity of the wave function in each case?
- (ii) In what ways is the quantum behaviour different from the classical behaviour of the oscillator?
- (iii) What is the origin of zero point energy in a quantum oscillator? (All'd 2005)
14. (a) The wave function for a one dimensional harmonic oscillator is given by

$$\Psi_n(x) = N_n \exp(-\lambda x^2 / 2) H_n(\sqrt{\lambda} x), \lambda = \frac{m\omega}{\hbar}, \xi = \sqrt{\lambda} x,$$

$$H_n(\xi) = (-1)^n \exp(\xi^2) \frac{d^n}{d\xi^n} \exp(-\xi^2)$$

Sketch the wave functions and the probability densities for the first three states. What is the parity of each state?

- (b) Generalize the result of one dimensional harmonic oscillator to express the energy eigen values and eigen functions of a two dimensional isotropic harmonic oscillator. What is the degeneracy of the first excited state? (All'd 2006)

15. (a) The generating function for a Hermite polynomial is

$$S(\xi, s) = \exp[\xi^2 - (s - \xi)^2] = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} s^n$$

Show that $H_n''(\xi) - 2\xi H_n'(\xi) + 2nH_n(\xi) = 0$.

- (b) Discuss the origin of zero point energy in a harmonic oscillator.

(All'd 2007)

16. The ground state wave function of a linear harmonic oscillator of mass m is

$$\psi_0(x) = A \exp(-\frac{1}{2}\alpha^2 x^2)$$

Where A is normalization constant and $\alpha = \sqrt{\frac{m\omega}{\hbar}}$. Calculate the expectation value of $V = \frac{1}{2}m\omega^2 x^2$ for this state.

RIGID ROTATOR

8.1 INTRODUCTION

A rigid rotator is a system of two particles always remaining at fixed separation and capable of rotating about an axis passing through their center of mass and perpendicular to the line joining them. If the plane, containing the particles, is fixed in space *i.e.*, the orientation of axis of rotation remains fixed then the system is said to be a rigid rotator with fixed axis. If the axis of rotation is free to take any position in space, it is called rigid rotator with free axis. A rigid diatomic molecule can be treated as a rigid rotator with free axis. In this section we shall set up Schrodinger equation for rigid rotator find the eigen values and eigen functions of the equation.

Let m_1 and m_2 be the masses of the particles, r_1 and r_2 be their distances from the center of mass and r their separation. From the definition of center of mass

$$m_1 r_1 = m_2 r_2 \quad \dots(8.1.1)$$

$$r_1 + r_2 = r \quad \dots(8.1.2)$$

From these equations we can find r_1 and r_2 in terms of r . Thus

$$r_1 = \frac{m_2}{m_1 + m_2} r, \quad r_2 = \frac{m_1}{m_1 + m_2} r \quad \dots(8.1.3)$$

The moment of inertia of the rigid rotator about an axis passing through the center of mass and perpendicular to the line joining the particles is

$$I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \quad \dots(8.1.4)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is called reduced mass of the system.

The kinetic energy of particle of mass m moving in space in Cartesian coordinates is given by

$$T = \frac{1}{2} m v^2 = \frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \quad \dots(8.1.5)$$

In spherical polar coordinates (r, θ, ϕ) the expression for kinetic energy is

$$T = \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \dot{\phi}^2 \sin^2 \theta) \quad \dots(8.1.6)$$

If r is fixed (*i.e.*, the particle is moving on the surface of a sphere) then $\dot{r} = 0$ and the expression for kinetic energy simplifies to

$$T = \frac{1}{2} m r^2 (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) \quad \dots(8.1.7)$$

The kinetic energy of rotation of a rigid rotator is equal to the sum of the kinetic energies of the constituent particles.

$$T = T_1 + T_2 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) + \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta) \quad \dots(8.1.8)$$

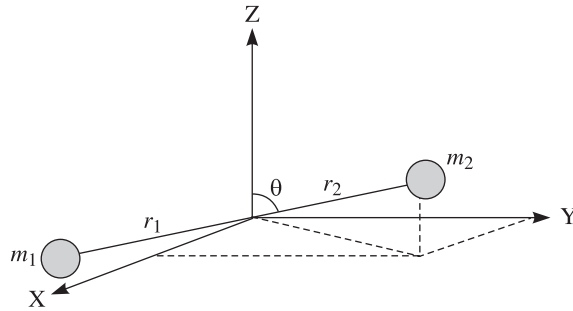


Fig. 8.1.1 Polar coordinates of particles constituting rigid rotator

For a rigid rotator moving in free space, potential energy is zero, hence the total energy of the rotator is

$$E = T = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta)$$

$$E = \frac{1}{2} I (\dot{\theta}^2 + \dot{\phi}^2 \sin^2 \theta), I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(8.1.9)$$

Comparison of Eqns. (8.1.8) and (8.1.9) shows that a rigid rotator behaves like a single particle of mass I moving on the surface of a sphere of fixed radius, equal to unity.

The Schrodinger equation for a particle, in polar coordinates, is expressed as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) = 0$$

To write the equation for rigid rotator, we must replace m by I and put $r = 1$ and $V = 0$ in above equation. Doing so, we obtain

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2IE}{\hbar^2} \psi = 0 \quad \dots(8.1.10)$$

Equation (8.1.10) can also be obtained as follows. The Hamiltonian of a rigid rotator, in absence of potential field, is

$$H = T = \frac{L^2}{2I}, \quad L = \text{angular momentum} \quad \dots(8.1.11)$$

The corresponding operator is

$$\hat{H} = \frac{\hat{L}^2}{2I} = -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad \dots(8.1.12)$$

The energy eigen value equation for rigid rotator is

$$\hat{H}\psi = E\psi$$

$$\text{or} \quad -\frac{\hbar^2}{2I} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi = E\psi \quad \dots(8.1.13)$$

which is the same as Eqn. (8.1.10).

We assume the solution of Eqn. (8.1.13) to be of the form

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi) \quad \dots(8.1.14)$$

Substituting Eqn. (8.1.14) in (8.1.13), we get

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0 \quad \dots(8.1.15)$$

$$\text{where} \quad \beta = \frac{2IE}{\hbar^2} \quad (8.1.16)$$

Transposing the ϕ dependent terms on the right hand side in Eqn. (8.1.15), we get

$$\frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \beta \sin^2 \theta = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad \dots(8.1.17)$$

The left hand side of Eqn. (8.1.17) depends on θ alone whereas right hand side on ϕ alone and both the sides remain equal for all values of independent variables θ and ϕ ; this can happen only when each side is equal to the same constant, say m^2 . So the Eqn. (8.1.17) separates into two equations:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) \Theta = 0 \quad \dots(8.1.18)$$

$$\frac{d^2\Phi}{d\varphi^2} + m^2\Phi = 0 \quad \dots(8.1.19)$$

Solution of Eqn. (8.1.19) is of the form

$$\Phi = C e^{im\varphi} \quad \dots(8.1.20)$$

Since $\Phi(\varphi) = \Phi(\varphi + 2\pi)$, we have $e^{\pm 2\pi im} = 1 \Rightarrow m = 0, \pm 1, \pm 2, \pm 3, \dots$

The constant C in Eqn. (8.1.20) can be obtained making use of normalization condition

$$\int_0^{2\pi} \Phi \Phi^* d\varphi = 1 \quad \dots(8.1.21)$$

$$\text{Thus } \int_0^{2\pi} C e^{2\pi im\varphi} \cdot C e^{-2\pi im\varphi} d\varphi = 0$$

$$C = \frac{1}{\sqrt{2\pi}}$$

So the solution of Φ equation can be written as

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\varphi}, \quad m = 0, \pm 1, \pm 2, \dots \quad \dots(8.1.22)$$

Now let us return to Eqn. (8.1.18). This equation can be transformed into a convenient form by change of independent variable θ to x as follows:

$$x = \cos \theta, \quad \sin \theta = \sqrt{1 - x^2}$$

$$\frac{d\Theta}{d\theta} = \frac{dx}{d\theta} \frac{d\Theta}{dx} = -\sin \theta \frac{d\Theta}{dx} \Rightarrow \frac{d}{d\theta} = -\sin \theta \frac{d}{dx}$$

$$\sin \theta \frac{d\Theta}{d\theta} = -\sin^2 \theta \frac{d\Theta}{dx} = -(1 - x^2) \frac{d\Theta}{dx}$$

Making use of these results, Eqn. (8.1.18) becomes

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{d\Theta}{dx} \right\} + \left(\beta - \frac{m^2}{1 - x^2} \right) \Theta = 0, \quad -1 < x < 1 \quad \dots(8.1.23)$$

Equation (8.1.23) is similar to the famous associated Legendre's equation:

$$\frac{d}{dx} \left\{ (1 - x^2) \frac{dF}{dx} \right\} + \left\{ l(l+1) - \frac{m^2}{1 - x^2} \right\} F = 0 \quad \dots(8.1.24)$$

Writing the constant β appearing in Eqn. (8.1.23) as $\beta = l(l+1)$ where l is another constant, we have

$$\frac{d}{dx} \left\{ (1-x^2) \frac{d\Theta}{dx} \right\} + \left\{ l(l+1) - \frac{m^2}{1-x^2} \right\} \Theta = 0 \quad \dots(8.1.25)$$

$$\beta = l(l+1) = (2IE)/\hbar^2 \quad \dots(8.1.26)$$

Equation (8.1.25) has single-valued and finite solutions only for certain values of parameter β given by

$$\beta = l(l+1) = 0, 2, 6, 12, 20, \dots \quad \dots(8.1.27)$$

$$\text{or} \quad l = 0, 1, 2, 3, 4, \dots \quad \dots(8.1.28)$$

Substituting the value β in Eqn. (8.1.27), we find

$$E = \frac{l(l+1)\hbar^2}{2I}, \quad l = 0, 1, 2, 3, \dots \quad (8.1.29)$$

This gives the possible values of energy that a rigid rotator can have. Thus the energy of rotator forms a discrete spectrum. It is customary to write the energy of a rigid rotator in the form

$$E_l = Bch l(l+1) \quad \dots(8.1.30)$$

where $B = h/8\pi^2 Ic$. The separation of adjacent energy levels increases linearly with l .

$$E_l - E_{l-1} = Bch [l(l+1) - l(l-1)] = 2Bchl$$

Wave functions of rigid rotator: For $m = 0$, the associated Legendre equation assumes the form

$$\frac{d}{dx} \left\{ (1-x^2) \frac{d\Theta}{dx} \right\} + l(l+1)\Theta = 0 \quad \dots(8.1.31)$$

Acceptable solutions of Eqn. (8.1.30) are expressed in the form of polynomials, known as Legendre polynomials, which are represented by $P_l(x)$ and defined by

$$P_l(x) = \frac{1}{2^l l!} \frac{d^l}{dx^l} (x^2 - 1)^l \quad \dots(8.1.32)$$

It is a simple matter to obtain Legendre polynomials from Eqn. (8.1.32). Some of them are given below:

$$l = 0, \quad P_0(x) = 1$$

$$l = 1, \quad P_1(x) = x$$

$$l = 2, \quad P_2(x) = \frac{1}{2}(3x^2 - 1)$$

$$l = 3, \quad P_3(x) = \frac{1}{2}(5x^3 - 3x)$$

$$l = 4, \quad P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

Higher order polynomials can be obtained from the following recurrence formula:

$$P_{l+1}(x) = \frac{2l+1}{l+1} x P_l(x) - \frac{l}{l+1} P_{l-1}(x) \quad \dots(8.1.33)$$

Legendre polynomials form an orthogonal system in the interval $-1 \leq x \leq 1$ i.e.,

$$\int_{-1}^1 P_l^*(x) P_{l'}(x) dx = \frac{2}{2l+1} \delta_{ll'} \quad \dots(8.1.34)$$

The square of the norm of Legendre polynomials has the following value:

$$\int_{-1}^1 P_l^*(x) P_l(x) dx = \frac{2}{2l+1} \quad \dots(8.1.35)$$

The finite solutions of Eqn. (8.1.24) in the interval $[-1, +1]$, for the positive value of m , are the **associated Legendre polynomials**, which are denoted as $P_l^m(x)$ and defined by

$$\begin{aligned} P_l^m(x) &= (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x), \quad m \leq l \\ &= (1-x^2)^{m/2} \cdot \frac{d^m}{dx^m} \left[\frac{1}{2^l (l!)} \cdot \frac{d^l}{dx^l} (x^2-1)^l \right] \end{aligned} \quad \dots(8.1.36)$$

The associated Legendre polynomials satisfy the condition

$$\int_{-1}^1 P_l^m(x) P_k^m(x) dx = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!} \delta_{lk} \quad \dots(8.1.37)$$

The recurrence relation for the associated Legendre polynomials is:

$$x P_k^m(x) = \frac{(l-m)(l-m+1)}{2l+1} P_{l+1}^m(x) + \frac{l+m}{2l+1} P_{l-1}^m(x) \quad \dots(8.1.38)$$

and

$$\sqrt{1-x^2} P_l^{m+1}(x) = \frac{(l-m)(l-m+1)}{2l+1} P_{l+1}^m(x) - \frac{(l+m)(l+m+1)}{2l+1} P_{l-1}^m(x) \quad \dots(8.1.39)$$

The solutions of Eqn. (8.1.25) can be written as

$$\Theta_l^m(x) = N_{lm} P_l^m(x) \quad \dots(8.1.40)$$

where N_{lm} is normalization constant and can found making use of condition in Eqn. (8.1.37). The normalized solution of Eqn. (8.1.25) is

$$\Theta_{lm}(x) = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} P_l^m(x)$$

$$\begin{aligned}
&= \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} (1-x^2)^{m/2} \frac{d^m}{dx^m} P_l(x) \\
&= (-1)^m \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} (1-x^2)^{m/2} \cdot \frac{d^m}{dx^m} \left[\frac{1}{2^l (l!)} \cdot \frac{d^l}{dx^l} (x^2-1)^l \right] \quad \dots(8.1.41)
\end{aligned}$$

The inclusion of phase factor $(-1)^m$ is a matter of convention. Finally, the complete solution of θ -Eqn.(8.1.13) can be written as

$$\begin{aligned}
\psi(\theta, \varphi) &= \Theta(\theta)\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!}} e^{im\varphi} P_l^m(\cos\theta) \\
&= \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} e^{im\varphi} \sin^m \theta \frac{d^m}{d(\cos\theta)^m} P_l(\cos\theta) \quad \dots(8.1.42)
\end{aligned}$$

For negative value of m , the solution of Schrodinger equation for rigid rotator is obtained from the formula

$$\psi_{l,-m}(\theta, \varphi) = (-1)^m [\psi_{l,m}(\theta, \varphi)]^* \quad \dots(8.1.43)$$

The functions $\psi(\theta, \varphi)$ defined by Eqn.(8.1.42) are called **spherical harmonics** and are usually denoted by $Y_{lm}(\theta, \varphi)$. These functions are the solutions of Eqn. (8.1.13). In fact the eigen functions of Hamiltonian operator for a particle moving on a sphere or of rigid rotator always come out to be the spherical harmonics.

The physical interpretation of $\psi(\theta, \varphi)$ is that $|\psi(\theta, \varphi)|^2 d\Omega$, where $d\Omega = \sin \theta d\theta d\varphi$, represents the probability of finding the axis of the rotator pointing in the solid angle element $d\Omega = \sin \theta d\theta d\varphi$ about the direction θ, φ . A rigid rotator is a simple model of rigid diatomic molecule.

QUESTIONS AND PROBLEMS

1. What do you mean by rigid rotator? Set up Schrodinger wave equation for rigid rotator. Obtain its wave function and energy levels.

PARTICLE IN A CENTRAL FORCE FIELD

9.1 REDUCTION OF TWO-BODY PROBLEM IN TWO EQUIVALENT ONE-BODY PROBLEM IN A CENTRAL FORCE

The potential energy of a particle in a centrally symmetric field depends only on the distance from the particle to the center of the force *i.e.*, $V = V(r)$. The Hamiltonian operator of the particle has the form

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad \dots(9.1.1)$$

Consider a system consisting of two particles moving under their mutual interaction, which is described by a spherically symmetric potential. Owing to the central symmetry of the force field, it is expedient to solve the problem in spherical polar coordinates. The well-known two-body problem in central force is hydrogen atom in which electron and nucleus move under their mutual interaction. In classical mechanics, the energy of a system consisting of two interacting particles is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(r) \quad \dots(9.1.2)$$

and the Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r)$$

where m_1 and m_2 are the masses, p_1 and p_2 are the momenta of the particles. The Schrodinger equation of the system is

$$\hat{H}\psi = E\psi$$

$$\left[-\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r) \right] \psi = E\psi \quad \dots(9.1.3)$$

Let $r_1(x_1, y_1, z_1)$ and $r_2(x_2, y_2, z_2)$ be the radius vectors of the particles. The radius vector $r_0(x_0, y_0, z_0)$ of the center of mass is given by

$$x_0 = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \quad y_0 = \frac{m_1 y_1 + m_2 y_2}{m_1 + m_2}, \quad z_0 = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

Let us introduce the relative radius vector $\mathbf{r}(x, y, z)$ defined by

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$$

or $x = x_2 - x_1, \quad y = y_2 - y_1, \quad z = z_2 - z_1 \quad \dots(9.1.4)$

Now

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{\partial}{\partial x} \frac{\partial x}{\partial x_1} + \frac{\partial}{\partial x_0} \frac{\partial x_0}{\partial x_1} = -\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial x_0} \\ \frac{\partial^2}{\partial x_1^2} &= \left(\frac{\partial}{\partial x_1} \right)^2 = \left(-\frac{\partial}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial}{\partial x_0} \right)^2 \\ &= \frac{\partial^2}{\partial x^2} - \frac{2m_1}{m_1 + m_2} \frac{\partial^2}{\partial x \partial x_0} + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial x_0^2} \end{aligned} \quad \dots(9.1.5)$$

Similarly, $\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial x^2} + \frac{2m_2}{m_1 + m_2} \frac{\partial^2}{\partial x \partial x_0} + \left(\frac{m_2}{m_1 + m_2} \right)^2 \frac{\partial^2}{\partial x_0^2} \quad \dots(9.1.6)$

From Eqns. (9.1.5) and (9.1.6), we get

$$\frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial x_2^2} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial x^2} + \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial x_0^2} \quad \dots(9.1.7)$$

Similarly, $\frac{1}{m_1} \frac{\partial^2}{\partial y_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial y_2^2} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial y^2} + \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial y_0^2} \quad \dots(9.1.8)$

$$\frac{1}{m_1} \frac{\partial^2}{\partial z_1^2} + \frac{1}{m_2} \frac{\partial^2}{\partial z_2^2} = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial z^2} + \frac{1}{m_1 + m_2} \frac{\partial^2}{\partial z_0^2} \quad \dots(9.1.9)$$

Adding Eqns. (9.1.7), (9.1.8) and (9.1.9), we have

$$\frac{1}{m_1} \nabla_1^2 + \frac{1}{m_2} \nabla_2^2 = \frac{1}{\mu} \nabla_r^2 + \frac{1}{m_1 + m_2} \nabla_0^2 \quad \dots(9.1.10)$$

where ∇_r^2 is the Laplacian operator with respect to the components of vector $\mathbf{r}(x, y, z)$ and ∇_0^2 is the Laplacian operator with respect to the components of the vector $\mathbf{r}_0(x_0, y_0, z_0)$. μ is the reduced mass of the system. The Hamiltonian operator of the system is

$$\hat{H} = -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_0^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(r) \quad \dots(9.1.11)$$

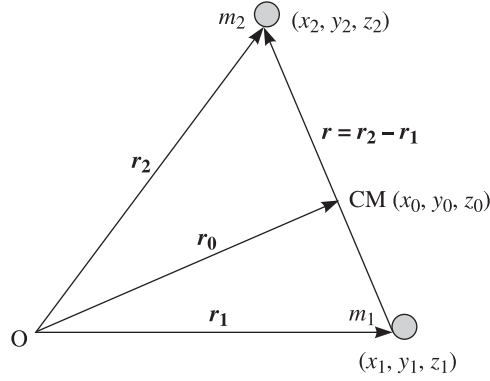


Fig. 9.1.1 Two body problem in central force

The Hamiltonian thus breaks up into the sum of two independent Hamiltonians, one of which contains the total mass of the system and the position vector of the center of mass, and the second contains the reduced mass and the vector of mutual arrangement of the particles. The Schrodinger equation of the system is

$$-\frac{\hbar^2}{2(m_1 + m_2)} \nabla_0^2 \psi - \frac{\hbar^2}{2\mu} \nabla_r^2 \psi + V(r)\psi = E\psi \quad \dots(9.1.12)$$

We shall seek the solution of Eqn. (9.1.12) in the form of the product of two functions

$$\psi = \psi_0(x_0, y_0, z_0) \psi_r(x, y, z) \quad \dots(9.1.13)$$

Substituting Eqn. (9.1.13) in (9.1.12), we obtain

$$\left\{ -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_0^2 \psi_0 \right\} + \left\{ -\frac{\hbar^2}{2\mu} \nabla_r^2 \psi_r + V(r) \right\} = E \quad \dots(9.1.14)$$

The sum of these expressions at any values of r_0 and r must equal to the constant quantity E . This is possible only if each of the expressions equals its own constant and the sum of these constants is E . Consequently we arrive at two differential equations.

$$(i) \quad -\frac{\hbar^2}{2(m_1 + m_2)} \nabla_0^2 \psi_0 = E_0 \psi_0 \quad \dots(9.1.15)$$

$$(ii) \quad -\frac{\hbar^2}{2\mu} \nabla_r^2 \psi_r + V(r) \psi_r = E_r \psi_r \quad \dots(9.1.16)$$

$$\text{with} \quad E_0 + E_r = E \quad \dots(9.1.17)$$

Equation (9.1.15) is the Schrodinger equation for a free particle having the mass $(m_1 + m_2)$

and describes the translational motion of the entire system. It is evident that E_0 is the kinetic energy of motion of the system as a whole.

Equation (9.1.16) describes the motion of a fictitious particle of mass μ moving in a central force characterized by potential energy $V(r)$. It differs from the Schrodinger equation for a particle in a central force field only in containing the reduced mass of the system of particles instead of the mass of the one particle. The energy E_r is the internal energy of the system.

9.2 HYDROGEN ATOM

Hydrogen atom is a system consisting of electron and proton moving under their mutual interaction. The Schrodinger equation for the system is

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} (E - V) \psi = 0 \quad \dots(9.2.1)$$

where E is the internal energy of the system and $V = -\frac{Ze^2}{4\pi\epsilon_0 r}$ is the electrostatic potential energy of the system. Since the potential energy is the function of r only, the task of finding the solution of Schrodinger equation becomes easier in spherical polar coordinates. The Schrodinger equation in polar coordinates is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V) \psi = 0 \quad \dots(9.2.2)$$

where the wave function ψ is function of polar coordinates r, θ, ϕ . Multiplying Eqn. (9.2.2) by $r^2 \sin^2 \theta$, we obtain

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} (E - V) \psi = 0 \quad (9.2.3)$$

Let us assume that the wave function $\psi(r, \theta, \phi)$ can be written as the product of functions $R(r), \Theta(\theta)$ and $\Phi(\phi)$.

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots(9.2.4)$$

From above relation, we have

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{dR}{dr}, \quad \frac{\partial \psi}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta}, \quad \frac{\partial^2 \psi}{\partial \phi^2} = R \Theta \frac{d^2 \Phi}{d\phi^2} \quad \dots(9.2.5)$$

Substituting these values in Eqn. (9.2.3) and dividing the resulting equation by $R \Theta \Phi$, we get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} (E - V) = 0$$

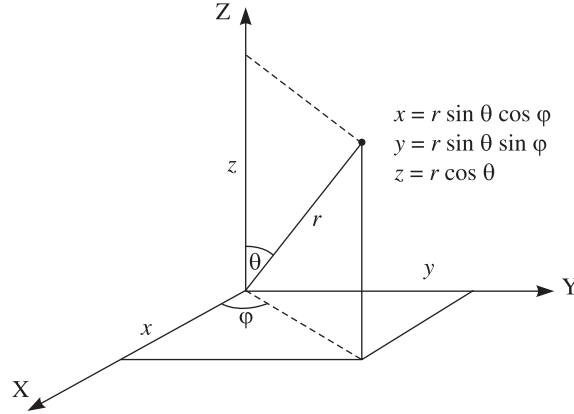


Fig. 9.2.1 Spherical polar coordinates of a point

or

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} (E - V) = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\varphi^2} \quad \dots(9.2.6)$$

Left hand side of this equation is function of r and θ whereas the right hand side is function of φ only. This equality can hold only if each side is equal to the same constant. Usually the separation constant is denoted by m_l^2 . Thus, we have

$$\frac{d^2 \Phi}{d\varphi^2} = -m_l^2 \Phi \quad \dots(9.2.7)$$

and

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2\mu r^2 \sin^2 \theta}{\hbar^2} (E - V) = m_l^2 \quad \dots(9.2.8)$$

Dividing Eqn. (9.2.8) by $\sin^2 \theta$ and transferring the r -dependent terms on left hand side and θ -dependent terms on the right hand side of equality sign, we have

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} (E - V) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right)$$

Again the equality of two functions of independent variables demands that each side be equal to the same constant. The equations obtained by equating both sides to a constant were already solved

in classical physics where the separation constant was chosen of the form $l(l+1)$ and the two equations obtained were

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu r^2}{\hbar^2} (E - V) = l(l+1) \quad \dots(9.2.9)$$

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = l(l+1) \quad \dots(9.2.10)$$

For the sake of convenience we write the three equations together

$$\frac{d^2 \Phi}{d\varphi^2} + m_l^2 \Phi = 0 \quad \dots(9.2.11)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left\{ l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right\} \Theta = 0 \quad \dots(9.2.12)$$

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu}{\hbar^2} \left(E - V - \frac{l(l+1)\hbar^2}{2\mu r^2} \right) \right] R = 0 \quad \dots(9.2.13)$$

Notice that an extra term $\frac{l(l+1)\hbar^2}{2\mu r^2}$ appears as addend in potential energy $V(r)$. It is often called *centrifugal potential energy* since its negative gradient is equal to the centrifugal force experienced by the particle while moving in a circular orbit of radius r . The kinetic energy associated with the rotational motion is $\frac{L^2}{2I} = \frac{l(l+1)\hbar^2}{2\mu r^2}$. So this term may be interpreted as the centrifugal energy of the particle.

The solution of φ Eqn. (9.2.11) is

$$\Phi(\varphi) = A e^{im_l \varphi}$$

where A is constant. In order that the function $\Phi(\varphi)$ be single valued it must satisfy the condition

$$\Phi(\varphi) = \Phi(\varphi + 2\pi) \Rightarrow \exp(i2\pi m_l) = 1$$

$$\cos 2\pi m_l + i \sin 2\pi m_l = 1$$

$$\cos 2\pi m_l = 1$$

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(9.2.14)$$

The separation constant m_l is now called the *magnetic quantum number*. The constant A can be determined making use of the normalizing condition.

$$\int_0^{2\pi} \Phi^*(\varphi) \Phi(\varphi) d\varphi = 1 \Rightarrow A = \frac{1}{\sqrt{2\pi}}$$

The normalized $\Phi(\varphi)$ function then becomes

$$\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} \exp(im_l \varphi) \quad \dots(9.2.15)$$

The method of finding the solution of Eqn. (9.2.12) is quite complicated. The finite and well-behaved solutions are found only if the constant l is an integer and equal to or greater than $|m_l|$ i.e.,

$$l \geq |m_l| \quad \text{or} \quad |m_l| \leq l$$

This condition can be expressed in the form

$$m_l = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l \quad \dots(9.2.16)$$

The constant l is now called *orbital quantum number* or *azimuthal quantum number*.

Before solving the θ Eqn. (9.2.12), it is convenient to change the independent variable θ to x through the transformation $x = \cos \theta$. The resulting equation is known as the associated Legendre equation and its acceptable solutions are expressed in the form of polynomials, called *associated Legendre functions*. Since these polynomials depend on l and m_l , and are written as $\Theta_{l, m_l}(\theta)$. The normalized associated Legendre polynomials, for positive value of m_l are given by

$$\Theta_{l, m_l}(x) = (-1)^{m_l} \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m_l)!}{(l+m_l)!}} \cdot (1-x^2)^{m_l/2} \cdot \frac{d^{m_l}}{dx^{m_l}} \left(\frac{1}{2^l (l!)} \frac{d^l}{dx^l} (x^2-1)^l \right)$$

where $x = \cos \theta$

$$\text{or} \quad \Theta_{lm_l}(\theta) = (-1)^{m_l} \sqrt{\frac{2l+1}{2} \cdot \frac{(l-m_l)!}{(l+m_l)!}} \cdot P_l^{m_l}(\cos \theta) \quad \dots(9.2.17)$$

For negative value m_l , we have

$$\Theta_{l, m_l}(\theta) = (-1)^{m_l} \left[\Theta_{l, -m_l} \right]^* \quad \dots(9.2.18)$$

Some of these polynomials are tabulated below. The product $\Theta(\theta)\Phi(\varphi)$ is called the spherical harmonics $Y_{l, m_l}(\theta, \varphi)$.

Normalized associated Legendre Functions $\Theta_{l, m_l}(\theta)$

l	m_l	$\Theta(\theta)$	$Y(\theta, \phi)$
0	0	$\Theta_{00} = 1/\sqrt{2}$	$Y_{00} = \sqrt{\frac{1}{4\pi}}$
1	0	$\Theta_{10} = \frac{1}{2}\sqrt{6} \cos \theta$	$Y_{10} = \sqrt{\frac{3}{4\pi}} \cdot \cos \theta$
1	± 1	$\Theta_{1\pm 1} = \frac{1}{2}\sqrt{3} \sin \theta$	$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \cdot \sin \theta \cdot e^{\pm i\phi}$
2	0	$\Theta_{20} = \frac{1}{4}\sqrt{10}(3 \cos^2 \theta - 1)$	$Y_{20} = \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)$
2	± 1	$\Theta_{2\pm 1} = \frac{1}{2}\sqrt{15} \sin \theta \cos \theta$	$Y_{2\pm 1} = \mp \sqrt{\frac{15}{8\pi}} \cdot (\cos \theta \cdot \sin \theta) \cdot e^{\pm i\phi}$
2	± 2	$\Theta_{2\pm 2} = \frac{1}{4}\sqrt{15} \sin^2 \theta$	$Y_{2\pm 2} = \sqrt{\frac{15}{32\pi}} \cdot \sin^2 \theta \cdot e^{\pm 2i\phi}$

Solution of Radial Equation: For bound state, the energy E is negative so the radial equation becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2\mu(-E)}{\hbar^2} + \frac{2\mu Z e^2}{4\pi\epsilon_0 \hbar^2 r} - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(9.2.19)$$

Equation (9.2.19) can be written in a convenient form making use of transformation

$$\rho = \alpha r \quad \dots(9.2.20)$$

where α is a constant and is so chosen that resulting equation look simpler. When Eqn. (9.2.20) is substituted in Eqn. (9.2.19), we get

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[\frac{-2\mu E}{\hbar^2 \alpha^2} + \frac{2\mu Z e^2}{4\pi\epsilon_0 \alpha \hbar^2} \frac{1}{\rho} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad \dots(9.2.21)$$

Now α is chosen to make the first term in square bracket equal to $1/4$. So

$$\alpha = \sqrt{\frac{-8\mu E}{\hbar^2}} \quad \dots(9.2.22)$$

In the second term in square bracket the coefficient of $1/\rho$ is put equal to λ .

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0 \hbar} \left(\frac{\mu}{-2E} \right)^{1/2} \quad \dots(9.2.23)$$

Equation (9.2.21) now becomes

$$\frac{1}{\rho^2} \frac{d}{d\rho} \left(\rho^2 \frac{dR}{d\rho} \right) + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] R = 0 \quad \dots(9.2.24)$$

For large ρ , the first term of Eqn. (9.2.24) reduces to $d^2R/d\rho^2$ and Eqn. (9.2.24) becomes

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0 \quad \dots(9.2.25)$$

The solution of Eqn. (9.2.25) is

$$R(\rho) = e^{\pm \rho/2}$$

Positive sign leads to an unacceptable solution. So we choose the negative sign.

$$R(\rho) = e^{-\rho/2} \quad \dots(9.2.26)$$

To determine the nature of solution near origin (for small ρ) we put

$$R(\rho) = \frac{1}{\rho} F(\rho) \quad \dots(9.2.27)$$

where $F(\rho)$ is unknown function. Substituting Eqn. (9.2.27) in (9.2.24), we have

$$\frac{d^2F(\rho)}{d\rho^2} + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right] F(\rho) = 0 \quad \dots(9.2.28)$$

For $l = 1$ ($l \neq 0$) the last term $l(l+1)/\rho^2$ is large near origin ($\rho \rightarrow 0$), Eqn. (9.2.28) reduces to

$$\frac{d^2F(\rho)}{d\rho^2} - \frac{l(l+1)}{\rho^2} F(\rho) = 0 \quad \dots(9.2.29)$$

Solution of Eqn. (9.2.29) can be obtained in form

$$F(\rho) = \text{constant } \rho^s \quad \dots(9.2.30)$$

Substituting Eqn. (9.2.30) in Eqn. (9.2.29), we have

$$s(s-1) - l(l+1) = 0$$

This gives $s = -l$ or $s = l+1$

$$\therefore R(\rho) = \frac{F(\rho)}{\rho} = \frac{\rho^s}{\rho} = \rho^{s-1} = \rho^{-l-1} \text{ or } \rho^l$$

Near origin $\rho \rightarrow 0$, $\frac{1}{\rho^{l+1}} \rightarrow \infty$ this is not acceptable.

However near origin $\rho \rightarrow 0$, $\rho^l \rightarrow 0$, this is acceptable. So we can assume the solution of Eqn. (9.2.24) of the form

$$R(\rho) = e^{-\rho/2} \cdot \rho^l \cdot L(\rho) \quad \dots(9.2.31)$$

where $L(\rho)$ is unknown function to be determined. Substituting Eqn. (9.2.31) in (9.2.24), we get

$$\rho \frac{d^2 L(\rho)}{d\rho^2} + [2(l+1) - \rho] \frac{dL(\rho)}{d\rho} + [\lambda - (l+1)] L(\rho) = 0 \quad \dots(9.2.32)$$

Let us assume the power series solution of Eqn. (9.2.32) of the form

$$L(\rho) = a_0 + a_1 \rho + a_2 \rho^2 + \dots = \sum_{r=0}^{\infty} a_r \rho^r \quad \dots(9.2.33)$$

Substituting Eqn. (9.2.33) in (9.2.32) and equating the coefficient of ρ^r equal to zero, we get

$$a_{r+1} = \frac{r+l+1-\lambda}{(r+1)(r+2l+2)} a_r \quad \dots(9.2.34)$$

For large value of r

$$\frac{a_{r+1}}{a_r} \xrightarrow{r \rightarrow \infty} \frac{1}{r}$$

The ratio of successive coefficients of series

$$e^\rho = 1 + \rho + \frac{\rho^2}{2!} + \dots + \frac{\rho^r}{r!} + \frac{\rho^{r+1}}{(r+1)!} + \dots$$

is
$$\frac{b_{r+1}}{b_r} = \frac{1}{r+1} \xrightarrow{r \rightarrow \infty} \frac{1}{r}$$

So for large value of ρ the function $L(\rho)$ behaves like e^ρ . Hence

$$R(\rho) \xrightarrow{\rho \rightarrow \infty} \rho^l \cdot e^{-\rho/2} \cdot e^\rho \rightarrow \rho^l \cdot e^{\rho/2} \rightarrow \infty$$

This form of $R(\rho)$ is not acceptable. If infinite series $L(\rho)$ terminates after finite number of terms *i.e.*, it becomes a polynomial, then it will be valid solution of Eqn.(9.2.32). From the recursion relation (9.2.34) we see that this requirement is met if r reaches some integer, say $n' (= r)$, given by

$$n' + (l+1) - \lambda = 0$$

or

$$\lambda = n' + l + 1$$

then $a_{r+1} (= a_{n'+1})$ and all higher coefficients become zero and $L(\rho)$ becomes a polynomial of degree n' . Since n' is a non-negative integer, so is λ . The integer λ is denoted by n and is called principal quantum number

$$\therefore n = \lambda = n' + l + 1 \quad (9.2.35)$$

Since

$$\begin{aligned} n' &> 0 \\ n - l - 1 &> 0 \\ l &< n - 1 \end{aligned} \quad \dots(9.2.36)$$

This puts restriction on the values that l can take on for a given value of n . Putting the value of λ in (9.2.23), we have

$$E = -\frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\mu e^4 Z^2}{\hbar^2 n^2}, \quad n = 1, 2, 3, \dots \quad \dots(9.2.37)$$

$$E = -(13.6 \text{ eV}) \frac{Z^2}{n^2}$$

Thus, the energy of electron in hydrogen atom is quantized. The integer n is called principal quantum number.

Radial wave functions: Laguerre polynomials are defined by

$$L_q(\rho) = e^\rho \frac{d^q}{d\rho^q} (e^{-\rho} \rho^q) = \left(e^\rho \cdot \frac{d}{d\rho} e^{-\rho} \right)^q \cdot \rho^q \quad \dots(9.2.38)$$

Laguerre Polynomials

$$L_0(\rho) = 1$$

$$L_1(\rho) = 1 - \rho$$

$$L_2(\rho) = 2 - 4\rho + \rho^2$$

$$L_3(\rho) = 6 - 18\rho + 9\rho^2 - \rho^3$$

$$L_4(\rho) = 24 - 96\rho + 72\rho^2 - 16\rho^3 + \rho^4$$

$$L_5(\rho) = 120 - 600\rho + 600\rho^2 - 200\rho^3 + 25\rho^4 - \rho^5$$

$$L_6(\rho) = 720 - 4320\rho + 5400\rho^2 - 2400\rho^3 + 450\rho^4 - 36\rho^5 + \rho^6$$

Associated Laguerre polynomials are defined by

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} L_q(\rho) = \frac{d^p}{d\rho^p} \left[e^\rho \cdot \frac{d^q}{d\rho^q} (\rho^q \cdot e^{-\rho}) \right] \quad \dots(9.2.39)$$

Polynomials $L_q^p(\rho)$ satisfy the differential equation

$$\rho \frac{d^2}{d\rho^2} L_q^p(\rho) + (p+1-\rho) \frac{d}{d\rho} L_q^p(\rho) + (q-p) L_q^p(\rho) = 0 \quad \dots(9.2.40)$$

Comparison of Eqn.(9.2.32) with $\lambda = n$ and Eqn. (9.2.40), we have

$$p = 2l + 1 \quad \text{and} \quad q = n + l$$

In view of this correspondence we can write the solution of Eqn. (9.2.32) as L_{n+l}^{2l+1} .

The solution of radial equation can be written as

$$R_{nl}(\rho) = N_{nl} \cdot \rho^l \cdot e^{-\rho/2} \cdot L_{n+l}^{2l+1}(\rho) \quad \dots(9.2.41)$$

where

$$L_{n+l}^{2l+1} = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{(n+l)!}{(n-l-1-k)! \cdot (2l+1+k)! \cdot k!} \rho^k$$

The normalization constant N_{nl} can be determined making use of following property of Laguerre polynomial.

$$\int_0^\infty e^{-\rho} \rho^{p+1} \cdot [L_q^p(\rho)]^2 d\rho = \frac{2q-p+1}{(q-p)!} \cdot (q!)^3 \quad \dots(9.2.42)$$

Normalization condition for $R_{nl}(r)$ is

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1, \quad \dots(9.2.43)$$

Remembering that

$$\rho = \alpha r = \left(\frac{2Z}{na_0} \right) r, \text{ where Bohr radius } a_0 = 4\pi\epsilon_0 \cdot \frac{\hbar^2}{\mu e^2} = 0.53 \text{ \AA}.$$

the normalization condition Eqn. (9.2.43) assumes the form

$$N_{nl}^2 \int_0^\infty \frac{1}{\alpha^3} \cdot \rho^{2l} \cdot e^{-\rho} \left| L_{n+l}^{2l+1}(\rho) \right|^2 \cdot \rho^2 d\rho = 1$$

$$\frac{N_{nl}}{\alpha^3} \cdot \left[\frac{2(n+l)-(2l+1)+1}{(n-l-1)!} \cdot \{(n+l)!\}^3 \right] = 1$$

$$N_{nl} = \pm \left(\frac{2Z}{na_0} \right)^{3/2} \cdot \sqrt{\frac{(n-l-1)!}{2n \{(n+l)!\}^3}}$$

In above expression negative sign is chosen to make $R_{10}(r)$ positive. The radial wave function is given by

$$R_{nl}(\rho) = -\left(\frac{2Z}{na_0}\right)^{3/2} \cdot \sqrt{\frac{(n-l-1)!}{2n\{(n+l)!\}^3}} \cdot e^{-\rho/2} \cdot \rho^l \cdot L_{n+l}^{2l+1}(\rho) \quad \dots(9.2.44)$$

Some of the radial wave functions are:

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} \cdot e^{-Zr/a_0}$$

$$R_{20} = \left(\frac{Z}{2a_0}\right)^{3/2} \cdot 2\left(1 - \frac{Zr}{2a_0}\right) \cdot e^{-Zr/2a_0}$$

$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \cdot \frac{1}{\sqrt{3}} \cdot \frac{Zr}{a_0} \cdot e^{-Zr/2a_0}$$

$$R_{30}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot 2\left[1 - \frac{2Zr}{3a_0} - \frac{2}{27} \cdot \left(\frac{Zr}{a_0}\right)^2\right] \cdot e^{-Zr/3a_0}$$

$$R_{31}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{4\sqrt{2}}{3} \cdot \frac{Zr}{a_0} \cdot \left(1 - \frac{Zr}{6a_0}\right) \cdot e^{-Zr/3a_0}$$

$$R_{32}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \cdot \frac{2\sqrt{2}}{27\sqrt{5}} \cdot \left(\frac{Zr}{a_0}\right)^2 \cdot e^{-Zr/3a_0}$$

The complete wave function is given by

$$\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r) \cdot Y_{lm_l}(\theta, \phi)$$

$$\Psi_{nlm_l}(r, \theta, \phi) = \left[\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{(2n)\{(n+l)!\}^3} \right]^{1/2} \cdot e^{-Zr/na_0} \cdot \left(\frac{2Zr}{na_0}\right)^l \cdot L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \cdot Y_{lm_l}(\theta, \phi) \quad \dots(9.2.45)$$

The wave function $\Psi_{n,l,m_l}(r, \theta, \phi)$ represents a quantum state of electron and is characterized by a set of quantum numbers n, l, m_l . For $n=1$ there is only one state Ψ_{100} , for $n=2$ there are four states $\Psi_{200}, \Psi_{210}, \Psi_{211}, \Psi_{21\pm 1}$. In spectroscopy the states corresponding to a given value of l are denoted according to the following scheme.

$l = 0$, s -state; $l = 1$, p -state; $l = 2$, d -state, $l = 3$, f -state etc.

Complete wave functions of hydrogen-like atom

n	l	m_l	state	$\Psi = R(r)\Theta(\theta)\Phi(\varphi)$
1	0	0	1s	$\Psi_{100} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{\sqrt{\pi}} e^{-Zr/a_0}$
2	0	0	2s	$\Psi_{200} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{4\sqrt{2\pi}} \left(2 - \frac{r}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	2p	$\Psi_{210} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{4\sqrt{2\pi}} \left(\frac{r}{a_0}\right) e^{-Zr/2a_0} \cdot \cos\theta.$
2	1	± 1	2p	$\Psi_{21\pm 1} = \left(\frac{Z}{a_0}\right)^{3/2} \frac{1}{8\sqrt{\pi}} a_0^{-3/2} \left(\frac{r}{a_0}\right) e^{-Zr/2a_0} (\sin\theta.) e^{\pm i\varphi}$

Electron Probability Density: The complete wave function describing the behaviour of electron in hydrogen atom is

$$\Psi_{nlm_l}(r, \theta, \varphi) = R_{nl}(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\varphi)$$

The probability density of electron around the point (r, θ, φ) is

$$|\Psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2 \quad \dots(9.2.46)$$

Now

$$|\Phi|^2 = \Phi^* \Phi = \frac{1}{2\pi}$$

$|\Phi|^2$ measures the probability of finding the electron at a particular azimuth angle φ . Here we see that likelihood of finding the electron is independent of angle φ . $|\Theta|^2$ measures the electron probability density in a direction θ . For s -electron $l = 0$, $m_l = 0$, $|\Theta|^2 = \frac{1}{2}$ which is independent of θ . According to quantum mechanics the electron charge density may be thought of as being spread over the space and $|\Theta|^2$ gives the angular dependence of charge density. Evidently, for s -electron the distribution of charge or charge cloud is spherical. For p -electron $l = 1$, $m_l = 1, 0, -1$, the corresponding charge distribution that is given by $|\Theta|^2$ is of dumb-bell shape. For other states, the charge distribution is complicated.

9.3 MOST PROBABLE DISTANCE OF ELECTRON FROM NUCLEUS

The radial function $R(r)$ is plotted against r for 1s, 2s and 2p electron. The function $|R|^2$ is a measure of probability density of finding the electron at a distance r . The probability of finding the electron in a volume $d\tau$ at point (r, θ, φ) is given by

$$P(r, \theta, \varphi) = |\psi_{nlm_l}(r, \theta, \varphi)|^2 d\tau = |\psi_{nlm_l}(r, \theta, \varphi)|^2 r^2 \sin\theta dr d\theta d\varphi \quad \dots(9.3.1)$$

The ground state wave function of electron is

$$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}} \cdot e^{-r/a_0} \quad \dots(9.3.2)$$

The probability of finding the electron between r and $r + dr$, irrespective of coordinates θ and φ is

$$\begin{aligned} P(r)dr &= \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \cdot \left(\frac{1}{\pi a_0^3} \right) e^{-2r/a_0} \cdot r^2 dr \\ &= \frac{4}{a_0^3} \cdot e^{-2r/a_0} \cdot r^2 dr \end{aligned} \quad \dots(9.3.3)$$

The most probable is the value of radial distance r given by condition

$$\frac{d}{dr} P(r) = \frac{d}{dr} \left[\frac{4}{a_0^3} r^2 e^{-2r/a_0} \right] = 0 \quad \dots(9.3.4)$$

$$r = a_0$$

Thus, the maximum probability of finding 1s electron is at a distance $r = a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.53 \text{ \AA}$.

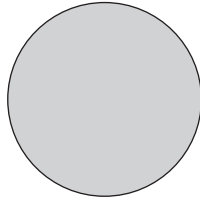


Fig. 9.3.1 Angular probability function in s -state $[|\Theta_{00}|^2]$

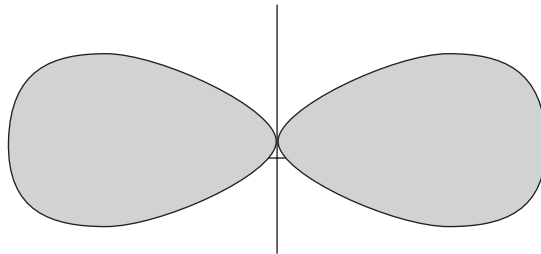


Fig. 9.3.2 Angular probability function in p -state

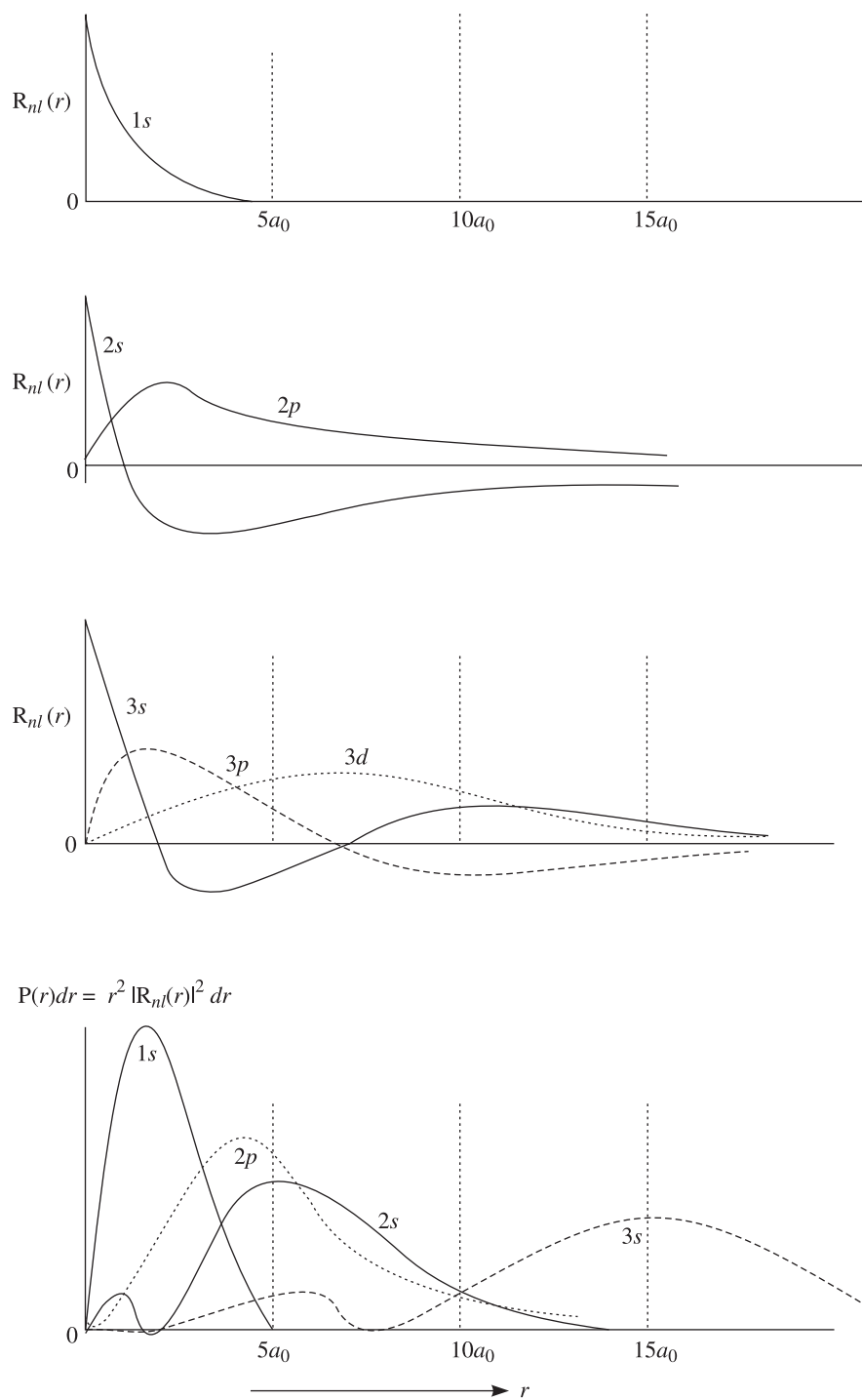


Fig. 9.3.3 Radial wave function and radial probability

9.4 DEGENERACY OF HYDROGEN ENERGY LEVELS

We have seen that each quantum state is characterized by a set of three quantum numbers n, l, m_l . For $n=1, l=0, m_l=0$, the corresponding state is denoted by ψ_{100} . This state is the ground state. For $n=2, l=0, 1$. For $l=0, m_l=0$ and for $l=1, m_l=1, 0, -1$. Thus there are four states namely $\psi_{200}, \psi_{211}, \psi_{210}, \psi_{21\pm 1}$. Since total energy of electron depends only on principal quantum number n , all the four states corresponding to $n=2$, have the same energy. This energy level is said to be four-fold degenerate. Here the degeneracy is due to the symmetry of Coulomb potential. In atoms other than hydrogen, the energy E depends on n and l both because the Coulomb potential is modified due to screening effect. Even in hydrogen atom this degeneracy is removed by applying external magnetic field.

In addition to the above degeneracy there is also another degeneracy, which arises because the states having the same n and l but different m_l have also the same energy. Since there are $2l+1$ different values of m_l for each value of n and l , each level is $2l+1$ fold-degenerate. This degeneracy is common to all central fields *i.e.*, to all potentials that are function of radial distance r only. This degeneracy is removed by applying a non-central field such as magnetic field. Magnetic field causes energy levels of different m_l to have different energies. This splitting of energy levels by an external magnetic field is responsible for the phenomenon of *Zeeman Effect*.

9.5 PROPERTIES OF HYDROGEN ATOM WAVE FUNCTIONS

The operator of the square of angular momentum is

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

and that of the z -component of angular momentum is

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

Now

$$\begin{aligned} \hat{L}^2 \psi &= -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] R \Theta \Phi \\ &= -\hbar^2 R \left[\frac{\Phi}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{\Theta}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \right] \\ &= -\hbar^2 R \left[\frac{\Phi}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \left(\frac{m_l^2}{\sin^2 \theta} \Phi \right) \Theta \right] \\ &= -\hbar^2 R \Phi \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \left(\frac{m_l^2}{\sin^2 \theta} \right) \Theta \right] \end{aligned}$$

$$\begin{aligned}
 &= -\hbar^2 R \Phi [-l(l+1)\Theta] \\
 &= l(l+1)\hbar^2 \psi
 \end{aligned}$$

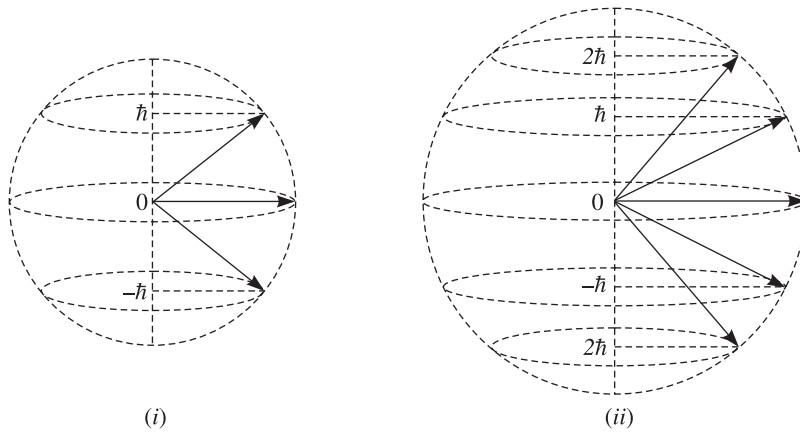
Thus the eigen value of operator $\hat{L}$ is $l(l+1)\hbar^2$. This means that the measurement of the square of angular momentum will yield a value given by

$$|L|^2 = l(l+1)\hbar^2 \quad \text{or} \quad |L| = \sqrt{l(l+1)}\hbar^2$$

Since the magnitude of angular momentum is determined by quantum number l therefore l is called orbital angular momentum quantum number. The quantum number l can assume only definite values, *i.e.*, the magnitude of angular momentum is quantized.

Now,

$$\begin{aligned}
 \hat{L}_z \psi &= -i\hbar \frac{\partial}{\partial \phi} [R \Theta \Phi] \\
 &= -i\hbar R \Theta \frac{\partial \Phi}{\partial \phi} \\
 &= -i\hbar m_l R \Theta \Phi \\
 &= m_l \hbar \psi
 \end{aligned}$$



(i) For $l = 1$, $L = \sqrt{2}\hbar$, $L_z = \hbar, 0, -\hbar$

(ii) For $l = 2$, $L = \sqrt{6}\hbar$, $L_z = 2\hbar, \hbar, 0, -\hbar, -2\hbar$

Fig. 9.5.1 Allowed orientations of angular momentum vector

Thus the z -component of angular momentum can have only discrete values. In other words the angular momentum vector L can have only certain orientations in space. In vector model of atom, the angular momentum vector performs *precessional motion* around the z -direction in such a way

that its projection onto the z -axis has fixed value and the average value of x and y components become zero. The *quantization* of direction angular momentum vector (and any vector associated with it, such as magnetic moment) is known as *space quantization*. For p -electron $l = 1$,

$$|\mathbf{L}| = \sqrt{1(1+1)}\hbar = \sqrt{2}\hbar \text{ and } m_l = 1, 0, -1.$$

The vector $\mathbf{L}$ for this electron has only three orientations. Similarly for d -electron $l = 2$,

$$|\mathbf{L}| = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar \text{ and } m_l = 2, 1, 0, -1, -2.$$

The vector $\mathbf{L}$ of this electron can have only five orientations. The possible directions of angular momentum vector $\mathbf{L}$ are, in general, given by

$$\cos\theta = \frac{m_l}{\sqrt{l(l+1)}}$$

SOLVED EXAMPLES

Ex. 1. Verify that the spherical harmonics $Y_{1,1}$ and $Y_{2,1}$ are orthogonal.

Sol.

$$\begin{aligned} \int Y_{1,1}^* Y_{2,1} d\tau &= \int_0^\pi \int_0^{2\pi} \sqrt{\frac{3}{8\pi}} \sin\theta \cdot e^{-i\varphi} \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta \cdot e^{i\varphi} \cdot \sin\theta d\theta d\varphi \\ &= \frac{3\sqrt{5}}{8\pi} \int_0^\pi \sin^2\theta \cdot \cos\theta \cdot \sin\theta d\theta \int_0^{2\pi} d\varphi \\ &= \frac{3\sqrt{5}}{8\pi} \left[\int_0^\pi (1 - \cos^2\theta) \cos\theta \cdot \sin\theta d\theta \right] [2\pi] \\ &= 0. \text{ (To evaluate the integral put } \cos\theta = x) \end{aligned}$$

Ex. 2. The ground state function of H -atom is $\psi = A \exp(-r/a_0)$, where A is constant. Using the normalization condition find the value of A .

Show that $\langle r \rangle = \frac{3a_0}{2}$

Sol. Normalization condition

$$\begin{aligned} \int |\psi|^2 d\tau &= 1 \\ \int_0^\infty A^2 e^{-2r/a_0} \cdot 4\pi r^2 dr &= 1 \end{aligned}$$

$$4\pi A^2 \int_0^{\infty} r^2 e^{-2r/a_0} dr = 1$$

$$4\pi A^2 \left(\frac{a_0}{2}\right)^3 \int_0^{\infty} x^2 e^{-x} dx = 1 \quad (\text{Put } 2r/a_0 = x)$$

$$A = \frac{1}{\sqrt{\pi a_0^3}} \quad (\text{The value of integral is } \Gamma(3))$$

$$\langle r \rangle = \int_0^{\infty} \psi^*(r) r \psi(r) \cdot 4\pi r^2 dr = \frac{a_0}{4} \int_0^{\infty} x^3 e^{-x} dx = \Gamma(4) = \frac{3a_0}{2}$$

Ex. 3. For hydrogen atom $\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} \exp(-r/a_0)$, find the probability of finding the electron

in a sphere of radius $r = a_0$.

$$\text{Sol. } P = \int_0^{a_0} \psi_{100}^2 \cdot 4\pi r^2 dr = \frac{4}{a_0^3} \int_0^{a_0} r^2 \exp(-2r/a_0) dr = \frac{-5}{e^2} + 1 = 0.32$$

(Evaluate the integral by method 'integration by parts'.)

Ex. 4. For hydrogen atom $\psi_{210} = A[\exp(-r/2a_0)] \cdot r \cdot \cos \theta$, find A .

Sol. Normalization condition

$$1 = \int_0^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} A^2 [\exp(-r/a_0)] r^4 dr \cdot \cos^2 \theta \cdot \sin \theta \cdot d\phi$$

$$1 = 2\pi A^2 \int_0^{\infty} r^4 \exp(-r/a_0) dr \int_0^{\pi} \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi$$

$$1 = 2\pi A^2 \left[\int_0^{\infty} r^4 \exp(-r/a_0) dr \right] \left[\frac{2}{3} \right] [2\pi]$$

$$1 = 2\pi A^2 \cdot 2\pi \cdot \frac{2}{3} \cdot a_0^5 \int_0^{\infty} x^4 \exp(-x) dx \quad [\text{The value of integral is } \Gamma(5)]$$

$$A = \left(\frac{1}{32\pi a_0^5} \right)^{1/2}$$

$$\therefore \Psi_{210} = \left(\frac{1}{32\pi a_0^5} \right)^{1/2} r \cos \theta \cdot \exp(-r/2a_0)$$

$$\text{Now, } \langle r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \Psi^* r \Psi r^2 dr \sin \theta d\theta d\phi = A^2 \int_0^\infty r^5 \exp(-r/a_0) dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi$$

$$= A^2 a_0^6 \frac{2}{3} \cdot 2\pi \int_0^\infty x^5 \exp(-x) dx = A^2 \frac{4\pi}{3} a_0^6 \Gamma(6) = 5a_0$$

QUESTIONS AND PROBLEMS

1. Establish Schrodinger equation for hydrogen atom and obtain its energy levels and wave functions.

Write the ground state wave function for hydrogen atom and calculate the most probable distance of the electron from the nucleus. Sketch radial wave functions and radial probability in $1s$, $2s$, $2p$, $3s$, $3p$ states

2. Spherical harmonics are defined by

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi} \cdot \frac{(l-m)!}{(l+m)!}} \cdot \frac{(1-x^2)^{lm/2}}{l! \cdot 2^l} \frac{d^{lm}}{dx^{lm}} \left[\frac{d^l}{dx^l} (x^2-1) \right]$$

where $x = \cos \theta$.

Find Y_{00} , Y_{10} , Y_{11} , Y_{1-1} , Y_{20} , Y_{21} , Y_{2-1} , Y_{22} , Y_{2-2} .

3. Laguerre polynomials are defined by

$$L_q^p(\rho) = \frac{d^p}{d\rho^p} \left[e^\rho \cdot \frac{d^q}{d\rho^q} (\rho^q \cdot e^{-\rho}) \right]$$

Find L_1^1 , L_2^1 , L_3^3 .

4. The wave functions of hydrogen-like atoms are given by

$$\Psi_{nlm_l}(r, \theta, \phi) = \left[\left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{(2n)\{(n+l)!\}^3} \right]^{1/2} \cdot e^{-Zr/na_0} \cdot \left(\frac{2Zr}{na_0} \right) \cdot L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) \cdot Y_{lm_l}(\theta, \phi)$$

Find Ψ_{100} , Ψ_{210} , $\Psi_{21\pm 1}$.

5. Write the radial equation of the hydrogen atom in dimensionless form and explain all the symbols used. Solve the equation to obtain an expression for energy eigen values. (All'd 1995)
6. Write down the Schrodinger equation for a positronium atom which consists of a positron and an electron. Reduce the equation to two equivalent one body problem and discuss the significance of each one of them. If the ground state wave function for hydrogen atom is given by

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0).$$

What would be the corresponding wave function for positronium atom?

(All'd 1996)

7. The radial part of the wave function for $n = 2, l = 1$ state of hydrogen atom is given by

$$\psi_{21}(r) = \left(\frac{2}{a_0}\right)^{3/2} \left(\frac{r}{\sqrt{3} a_0}\right) \exp(-r/2a_0), \quad a_0 \text{ is Bohr radius.}$$

- (a) What is the parity of the radial wave function and of total wave function for the above state?
- (b) Plot the probability distribution function as a function of r and obtain the most probable distance between the proton and the electron.
- (c) Calculate the size of the hydrogen atom $\langle r^2 \rangle^{1/2}$ for this state. (All'd 1996)
8. (a) The radial equation for the hydrogen atom is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \left[\frac{2m}{\hbar^2} \left(E - V(r) - \frac{l(l+1)}{r^2} \right) \right] R = 0$$

Write it in dimensionless form. Find its solution in the limit $r \rightarrow 0$ and $r \rightarrow \infty$.

- (b) Substitute $R(r) = \chi(r)/r$ in the above equation to get the following equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} + \left[V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right] \chi = E\chi$$

Explain physical significance of the term $\frac{l(l+1)\hbar^2}{2mr^2}$.

(All'd 1998)

9. (a) Show that the probability of finding the electron in the ground state of hydrogen atom is maximum at a distance equal to the Bohr radius.
- (b) Explain briefly the Lamb shift with reference to the first excited state of the hydrogen atom. (All'd 1998)
10. Solve the radial equation for the hydrogen atom

$$\rho L''(\rho) + (2l+2-\rho)L'(\rho) + [\lambda - l(l+1)]L(\rho) = 0$$

where

$$\lambda = \frac{Ze^2}{4\pi\epsilon_0\hbar} \left(\frac{\mu}{-2E} \right)^{1/2} \quad \text{and} \quad \alpha = \sqrt{\frac{-8\mu E}{\hbar^2}}$$

to find the energy levels. What functions are $L(\rho)$.

(All'd 1999)

11. The normalized ground state wave function for the electron in the hydrogen atom is

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} \exp(-r/a_0)$$

- (a) Sketch the wave functions and the probability density versus r .
 (b) Find the radius at which electron is most likely to be found.
 (c) Find the probability of locating the electron between $r = a_0/2$ and $r = 3a_0/2$.

Where a_0 is Bohr radius.

(All'd 2000)

12. The ground state of the hydrogen atom is described by the function

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0)$$

- (a) Calculate the probability of finding the electron in the range $a_0/2 < r < 2a_0$.
 (b) Sketch the radial probability density as a function of r . At what value of r , it is maximum? What would be the corresponding probability for a classical orbit?
 (c) Calculate the average radius of the hydrogen atom?

(All'd 2001)

13. (a) Solve the radial equation of the hydrogen atom in the limit $r \rightarrow 0$ and $r \rightarrow \infty$.
 (b) The normalized ground state wave function of the hydrogen atom is

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0)$$

Find the expectation value of r and most probable radius of the orbit in the ground state.

(All'd 2002)

14. Solve the radial equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \left[\frac{2mE}{\hbar^2} - \frac{2mV(r)}{\hbar^2} - \frac{l(l+1)}{r^2} \right] R = 0$$

of the hydrogen atom, where symbols have their usual meanings and show that the energy values are exactly the same as those obtained by Bohr.

(All'd 2003)

15. Solve the radial equation for the hydrogen atom and compare your result with those obtained by Bohr.

(All'd 2004)

16. In a hydrogen atom the wave function describing the electron in $1s$ state is given as

$$\psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0)$$

- (a) Calculate average distance of the electron from the nucleus.
 (b) Probability $P(r)dr$ as a function of r and compare it with the prediction of Bohr model.

(All'd 2005)

17. Find solution of the radial equation of hydrogen atom and show that the result obtained agrees with that of Bohr.

(All'd 2006)

18. (a) The complete wave function of the hydrogen atom for $2p$ state is

$$\psi_{210} = \frac{1}{4} \sqrt{\frac{1}{2\pi a_0^3}} \left(\frac{r}{a_0} \right) \cos\theta \exp(-r/2a_0)$$

Prove that the wave function is normalized.

- (b) Find the expectation value of the distance of the electron from the nucleus in the hydrogen atom in $2p$ state.

(All'd 2007)

19. Write down the Hamiltonian for hydrogen atom and reduce it to relative and center of mass coordinates.

(All'd 2007)

20. A particle is moving in free space at a fixed distance $r = a$ i.e., on the surface of a smooth sphere. Write the Hamiltonian and Schrodinger equation for such a system and solve it to find the energy eigen values.

(All'd 2004)

21. A positronium atom consists of an electron and a positron interacting via coulomb force. Reduce the Schrodinger equation to two equivalent one body problem.

(All'd 2000)

UNIT

III

STATISTICAL MECHANICS

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PRELIMINARY CONCEPTS

1.1 INTRODUCTION

The main objective of statistical mechanics is to predict the properties of a macroscopic system from the knowledge of the behaviour of particles constituting the system. In a physical system containing a very large number of particles (atoms and molecules or other constituents) it is usually impossible, for practical reasons, to apply the basic physical laws (classical or quantum) directly to each particle. Instead, it is often advantageous to take a statistical approach, in which one describes the distribution of particles in various states in a statistical manner. The existence of a very large number of particles of the system can be used to advantage in the statistical description. The theory of random processes and quantities form the mathematical tools for this approach.

In statistical mechanics the description of a state of a many particle system is given by stating how the particles are distributed in various allowed microstates. Depending on the nature of the particles, three kinds of statistics or distribution laws are used to describe the properties of the system. The three statistics are:

1. Maxwell-Boltzmann or classical statistics.
2. Bose-Einstein statistics.
3. Fermi-Dirac statistics.

Fermi-Dirac statistic and Bose-Einstein statistics are quantum statistics.

1.2 MAXWELL-BOLTZMANN (M-B) STATISTICS

M-B statistics is applicable to the system of *identical, distinguishable* particles. The particles are so far apart that they are *distinguishable* by their position. In the language of quantum mechanics, the application of classical statistics is valid if the average separation between particles is much greater than the average de Broglie wavelength of the particle. In this situation the wave functions of the particles don't overlap. The particle may have any spin. The classical statistics put no restriction on the number of particles that occupy a state of the system. M-B statistics can be safely applied to dilute gases at room and higher temperature.

1.3 BOSE-EINSTEIN (B-E) STATISTICS

B-E statistics is applicable to the system of *identical, indistinguishable* particles, which have *integral spin* (0, 1, 2,...). Particles with integral spin are called *bosons*. Bosons don't obey Pauli's exclusion principle. So any number of bosons can occupy a single quantum state. The particles are close enough so that their wave functions overlap. Examples of bosons are *photons (spin 1)*, *phonons (quantum of acoustical vibration)*, *pions*, *alpha particle*, *helium atom* etc.

1.4 FERMI-DIRAC (F-D) STATISTICS

F-D statistics is applicable to the system of *identical, indistinguishable* particles, which have *odd-half-integral spin* (1/2, 3/2, 5/2,...). Particles with odd-half-integral spin are called *fermions* and they obey Pauli's exclusion principle. Hence, not more than one *fermion* can occupy a quantum state. The F-D statistics is valid if the average separation between fermions is comparable to the average de Broglie wavelength of fermions so that their wave functions overlap. Examples of fermions are electrons, positrons, μ -mesons, protons, neutrons etc.

In the limit of high temperature and low particle density the two quantum statistics (B-E and F-D) yield results identical to those obtained using the classical statistics.

1.5 SPECIFICATION OF THE STATE OF A SYSTEM

A system consisting of micro-particles (such as atoms and molecules) is described by the laws of quantum mechanics. In quantum mechanical description the most precise possible measurement on a system always shows this system to be in someone of a set of discrete quantum states characteristic of the system. The microscopic state of a system is described completely by specifying the particular quantum state in which the system is found. Each quantum state of an isolated system is associated with a definite value of energy and is called an energy level. There may be several quantum states corresponding to the same energy of the system. These quantum states are then said to be degenerate. Every system has a lowest possible energy. There is usually only one possible quantum state of the system corresponding to this lowest energy; this state is said to be the ground state of the system. (Exceptions may be there.)

For illustration we take an example. Consider a particle of mass m restricted to move inside a box of sides L_x , L_y , L_z located at the origin of cartesian axes such that $0 \leq x \leq L_x$, $0 \leq y \leq L_y$, $0 \leq z \leq L_z$. Schrodinger equation for the particle is

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + k^2 \psi = 0, \quad k^2 = \frac{2mE}{\hbar^2} \quad \dots(1.5.1)$$

The solution of the Eqn. (1.5.1) subject to the boundary conditions: $\psi=0$ at $x=0, x=L_x, y=0, y=L_y, z=0, z=L_z$ is found to be

$$\psi(x, y, z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z} \quad \dots(1.5.2)$$

where n_x, n_y, n_z are positive integers and each can take on values 1, 2, 3,..... The allowed energies of the particle comes out to be

$$E = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \quad \dots(1.5.3)$$

If $L_x = L_y = L_z = L$, then the energy of the particle is given by

$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(1.5.4)$$

and the state of the particle is given by the wave function

$$\psi(x, y, z) = A \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L} \quad \dots(1.5.5)$$

The triad n_x, n_y, n_z defines a quantum state of the particle. For ground state, $n_x = n_y = n_z = 1$.

This state is represented as $\psi_{111}(x, y, z)$. The energy in this state is $E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2}$. A single quantum state corresponds to the lowest energy level. When only one quantum state belongs to an energy level, that energy level is said to be non-degenerate. The ground state is thus **non-degenerate**. If many different quantum states belong to a single energy level, that energy level is said to be **degenerate**. The **degeneracy** of an energy level is given by the number of ways that the integer $(n_x^2 + n_y^2 + n_z^2)$ can be written as the sum of squares of the three positive integers. Some of the lower energy levels of a particle in box are given below.

$$E_{111} = \frac{3\pi^2 \hbar^2}{2mL^2}, E_{112} = E_{121} = E_{211} = \frac{6\pi^2 \hbar^2}{2mL^2},$$

$$E_{122} = E_{212} = E_{221} = \frac{9\pi^2 \hbar^2}{2mL^2},$$

$$E_{113} = E_{131} = E_{311} = \frac{11\pi^2 \hbar^2}{2mL^2},$$

$$E_{222} = \frac{12\pi^2 \hbar^2}{2mL^2},$$

$$E_{123} = E_{132} = E_{213} = E_{231} = E_{321} = E_{312} = \frac{14\pi^2\hbar^2}{2mL^2},$$

$$E_{223} = E_{232} = E_{322} = \frac{17\pi^2\hbar^2}{2mL^2}$$

Notice that the second, third and fourth energy levels are **3-fold degenerate**, the fifth energy level is non-degenerate, sixth energy level is 6-fold degenerate and the seventh energy level is 3-fold degenerate and so on.

	Degeneracy
$E_{223}, E_{132}, E_{322}$	3
$E_{123}, E_{132}, E_{213}, E_{231}, E_{321}, E_{312}$	6
E_{222}	1
$E_{113}, E_{131}, E_{311}$	3
$E_{122}, E_{212}, E_{221}$	3
$E_{112}, E_{121}, E_{211}$	3
E_{111}	1

Fig. 1.5.1 Energy levels of a particle in a box

1.6 DENSITY OF STATES

The allowed energy levels and associated quantum states for a particle confined to move in a cubical enclosure of side L are given by

$$E = \frac{p^2}{2m} = \frac{\pi^2\hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(1.6.1)$$

This equation can be written as

$$n_x^2 + n_y^2 + n_z^2 = \frac{2mL^2}{\pi^2\hbar^2} E = R^2 \quad \dots(1.6.2)$$

where

$$R = \sqrt{\frac{2mL^2 E}{\pi^2\hbar^2}} \quad \dots(1.6.3)$$

A quantum state (microstate) of the particle is given by

$$\psi(x, y, z)_{n_x, n_y, n_z} = \text{const.} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L} \quad \dots(1.6.4)$$

When we plot the positive integers n_x, n_y, n_z along the x, y, z axes of the Cartesian coordinate system in three dimensional space, the resulting space is called **number space**. In this space each triad $\{n_x, n_y, n_z\}$ is represented by a point. When all the triplets (n_x, n_y, n_z) , formed by the allowed values of integers n_x, n_y, n_z are plotted in number space, we get a lattice of points. In number space, Eqn. (1.6.2) represents a sphere of radius R given by Eqn. (1.6.3). Each quantum state (microstate) which is described by Eqn. (1.6.4) is represented by a point n in this number space. Now draw a sphere

of radius $R = \sqrt{\frac{2mL^2E}{\pi^2\hbar^2}}$ in number space. The number of lattice points which lie on the surface of this sphere lying in the positive octant is equal to the number of quantum states with energy E . We are interested in the number of quantum states with energy less than E . This number is denoted by $\Phi(E)$ and is equal to the number of lattice points lying within the positive octant of sphere of radius R . Obviously,

$$\Phi(E) = \frac{1}{8} \frac{4\pi}{3} R^3, \quad L^3 = V$$

$$\text{or} \quad \Phi(E) = \frac{4\pi V}{3h^3} (2mE)^{3/2} \quad \dots(1.6.5)$$

The number of quantum states with energy lying in the range dE about E is

$$\Omega(E)dE = \frac{\partial\Phi}{\partial E} dE = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \quad \dots(1.6.6)$$

The density of states $g(E)$ is defined as the number of quantum states in the unit energy range about E and is given by

$$g(E) = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{E} \quad \dots(1.6.7)$$

The number of quantum states in the energy range dE about E is

$$g(E)dE = \frac{2\pi V}{h^3} (2m)^{3/2} \sqrt{E} dE \quad \dots(1.6.8)$$

Assuming that the particle has only translational energy, we have

$$E = \frac{p^2}{2m}, \quad dE = \frac{p}{m} dp$$

With the help of these results we can transform the expression for density of states in terms of momentum. Thus the number of quantum states such that the magnitude of momentum of the particle lies in the range p and $p + dp$ is

$$g(p) dp = \frac{V}{h^3} 4\pi p^2 dp \quad \dots(1.6.9)$$

If we take $E = (3/2) kT$, $T = 300$ K, $m = 10^{-22}$ g, $L = 10$ cm, $dE = 0.01 E$, we find that

$$g(E)dE = 10^{28}$$

So even for a system as simple as a particle in a box, the density of states can be very large at room temperature.

1.7 N-PARTICLE SYSTEM

For an N-particle system, the density of states is tremendously large. To see this, consider a system of N non-interacting particles in a cube of side L. The energy of the system is

$$E = \sum_{i=1}^N E_i = \frac{\pi^2 \hbar^2}{2mL^2} \sum_{i=1}^N [n_{xi}^2 + n_{yi}^2 + n_{zi}^2] \quad \dots(1.7.1)$$

A quantum state of the system is defined by the set of 3N integers

$$\{ n_{1x}, n_{1y}, n_{1z}, n_{2x}, n_{2y}, n_{2z}, \dots, n_{Nx}, n_{Ny}, n_{Nz} \}$$

Using the concept of 3N dimensional number space we can calculate the number $\Phi(E)$ of quantum states with energy less than E. This calculation is somewhat difficult and we state the result.

$$\Phi(E) = \frac{V^N}{h^{3N}} \frac{(2\pi mE)^{3N/2}}{(3N/2)!} \quad \dots(1.7.2)$$

The number of states within the energy interval dE at E is

$$\Omega(E) dE = g(E) dE = \frac{\partial \Phi}{\partial E} dE = \frac{V^N}{h^{3N}} \cdot \frac{3N}{2} \cdot \frac{(2\pi m)^{3N/2}}{(3N/2)!} E^{(\frac{3N}{2}-1)} dE \quad \dots(1.7.3)$$

If $E = (3/2)kT$, $T = 300$ K, $m = 10^{-22}$ g, $L = 10$ cm, $N = 6.02 \times 10^{23}$, $\Delta E = 0.01 E$, we have

$$g(E) dE = 10^N$$

This shows that as the number of particles in the system increases, the density of quantum states becomes so high that they form continuum. For a system consisting of 10^{23} particles the allowed states are so crowded that it is impossible to enumerate and work with individual states. The best we can do is to work with density of states $g(E)$, which is the number of states per unit energy range. For a large system the density of states may be taken to be a smooth rapidly increasing function of energy.

1.8 MACROSCOPIC (MACRO) STATE

Consider a system containing a very large number N of particles in a vessel of fixed volume V at pressure, temperature T. The total energy of the system is E. The state of the system specified by parameters, which can be measured in laboratory such as pressure P, temperature T, volume V called the macroscopic description of state of the system. These parameters refer to the system as a whole. If the system is in equilibrium, the macroscopic characteristics P, V, T, E don't vary with time.

1.9 MICROSCOPIC (MICRO) STATE

The most complete description of many particle system is given by specifying the positions and momenta of its constituent particles. The state of the system characterized by positions and momenta of all its particles is called the microscopic or microstate. The state of a particle moving in space is specified by 3 spatial coordinates (x, y, z) and 3 momentum coordinates (p_x, p_y, p_z) . These 6 numbers x, y, z, p_x, p_y, p_z completely determine the state of the particle. If there are N -particles in the system, the state of the entire system is specified by $6N$ numbers: of which $3N$ are spatial coordinates and $3N$ are momentum coordinates. In equilibrium the macroscopic variables P, V, T characterizing the system are independent of time. However, the particles of the system are in random motion and the microscopic states of the system undergo continuous change in course of time. So there are an enormously large number of microscopic states corresponding to each macrostate. In other words, a macrostate is realized through an enormously large number of microstates. The aim of the statistical mechanics is to establish a relation between macrostate and microstates.

The statistical treatment of a thermodynamic system may be developed using either classical or quantum mechanics. In what follows we shall use quantum mechanics at most points. Objects of real world obey quantum mechanics. Objects described by quantum mechanics don't usually have arbitrary internal energy. Bounded systems exist only in certain well-defined energy well-defined quantum states. In other words, the energy of a system restricted to certain region of space is quantized. The allowed energies of the system are called energy levels. In such systems one also finds that some distinct states have the same energy, such states are said to be **degenerate**. The number of distinct states corresponding to the same energy level is called the degree of degeneracy of the level. For a small system we may identify the various quantum states and their energies without too much difficulty. For a large system the situation is quite different. The energy levels of a large system are very much close together and the mean separation between the energy levels is extremely small and so they may be assumed to form continuum.

The most detailed description of a state of a N -particle system is given by a specification of the state of each of the N -particles. We can make a chart showing *which* particles are in each of the various quantum states having energy ϵ_1 , *which* ones in the states with energy ϵ_2 and so on. This description specifies a state of the system, which we call a microscopic state.

Usually, the microstates themselves are not very useful. If the particles are identical, it is of no concern precisely *which* particles are in *which* energy states. Instead, we want to know *how many* particles are in energy state, without regard to *which* particle they are. Thus a different and more directly useful kind of the state description consists in specifying only the number of particles in each of the possible energy level.

The specification that there are

n_1 particles in energy level ϵ_1 with degeneracy g_1

n_2 particles in energy level ϵ_2 with degeneracy g_2

.....

n_i particles in energy level ϵ_i with degeneracy g_i

is a description of a *macrostate* of the system. A macrostate is a less detailed specification of the system than the microstate. The number of ways Ω in which this macrostate may be achieved is

called microstates of that macrostate. The quantity Ω is also called *statistical weight or thermodynamic probability* of that macrostate. The larger Ω is, the greater the probability of finding the system in that macrostate. If the volume V , the number of particles N and the total energy E of the system is kept constant, the equilibrium state of the system will correspond to that macrostate in which Ω is maximum. The principal objective of statistical mechanics is to determine the possible distribution of particles among the various energy levels and quantum states. If the distribution of particles of a system among its quantum states is known, the macroscopic properties of the system can be determined.

If a system is composed of N identical and *distinguishable* particles, the total number of microstates Ω corresponding to a macrostate specified by the set of occupation numbers $\{n_1, n_2, \dots\}$ is given by

$$\Omega = \frac{N!}{n_1! n_2! \dots} (g_1)^{n_1} (g_2)^{n_2} \dots \quad \dots(1.9.1)$$

In a gas containing N molecules, the molecules are *distinguishable* if the mean separation between the molecules is much larger than their de Broglie wavelength. In deriving the above formula for the number of microstates, it is assumed that there is no restriction on the number of particles that can occupy a quantum state.

If the system is composed of N *indistinguishable bosons*, the total number of microstates corresponding to a macrostate specified by the set of occupation numbers $\{n_1, n_2, \dots\}$ is given by

$$\Omega = \frac{(n_1 + g_1 - 1)!}{n_1! (g_1 - 1)!} \cdot \frac{(n_2 + g_2 - 1)!}{n_2! (g_2 - 1)!} \dots = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(1.9.2)$$

If the system is composed of N *indistinguishable fermions*, the total number of microstates corresponding to a macrostate specified by the set of occupation numbers $\{n_1, n_2, \dots\}$ is given by

$$\Omega = \frac{g_1!}{n_1! (g_1 - n_1)!} \cdot \frac{g_2!}{n_2! (g_2 - n_2)!} \dots = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!} \quad \dots(1.9.3)$$

SOLVED EXAMPLES

Ex. 1. Two particles are to be distributed in an energy level, which is 3 fold-degenerate. Find the possible microstates if the particles are (i) distinguishable (ii) indistinguishable bosons (iii) indistinguishable fermions.

Sol.

(i) If the particles are distinguishable, they can be labeled as A and B. Here $N = 2$, $n_1 = 2$, $g_1 = 3$. The number of possible microstates is:

$$\Omega = \frac{N!}{n_1! n_2! \dots} (g_1)^{n_1} (g_2)^{n_2} \dots$$

$$\Omega = \frac{2!}{2!} (3)^2 = 9$$

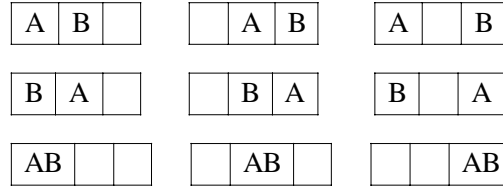


Fig. 1.9.1 Distribution of two distinguishable particles A and B in a triply degenerate energy level

It is worth to note that if there are more than one particle in a given quantum state, an interchange of order in which the labelled objects appear does not produce a new microstate. So the AB and BA are the same.

(ii) If the particles are indistinguishable **bosons**, the number of possible microstates is

$$\Omega = \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!} = \frac{4!}{2!2!} = 6$$

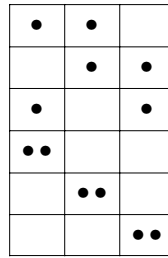


Fig. 1.9.2 Distribution of two indistinguishable particles (bosons) in a triply degenerate level

The number of microstates is 6.

(iii) The particles are indistinguishable **Fermions**.

The number of microstates is $\Omega = \frac{g_1!}{n_1!(g_1 - n_1)!} = \frac{3!}{2!1!} = 3$.

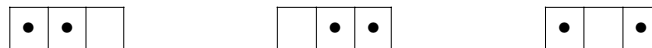


Fig. 1.9.3 Distribution of two indistinguishable particles (fermions) in a triply degenerate level

Ex. 2. Four particles are to be distributed among four energy levels $\epsilon_1 = 1$, $\epsilon_2 = 2$, $\epsilon_3 = 3$, $\epsilon_4 = 4$ units having degeneracies $g_1 = 1$, $g_2 = 2$, $g_3 = 2$, $g_4 = 1$ respectively. The total energy of the system is 10 units. Find the possible distribution (macrostates) and the microstates corresponding to most probable macrostate. Assume that the particles are: (i) distinguishable, (ii) indistinguishable bosons and (iii) indistinguishable fermions.

Sol.

(i) **Particles are distinguishable**

The possible macrostates are:

$\Omega_{2,0,0,2} = \{2, 0, 0, 2\}$, $\Omega_{1,1,1,1} = \{1, 1, 1, 1\}$, $\Omega_{0,3,0,1} = \{0, 3, 0, 1\}$, $\Omega_{1,0,3,0} = \{1, 0, 3, 0\}$, $\Omega_{0,2,2,0} = \{0, 2, 2, 0\}$. Distribution of particles (circles) is shown in the table.

$\epsilon_4 = 4$	o o	o	o	-----	-----
$\epsilon_3 = 3$	-----	o	-----	o o o	o o
$\epsilon_2 = 2$	-----	o	o o o	-----	o o
$\epsilon_1 = 1$	o o	o	-----	o	-----

The number of microstates in above macrostates is given by

$$\Omega_{n_1, n_2, \dots} = \frac{N!}{n_1! n_2! \dots} g_1^{n_1} g_2^{n_2} \dots$$

$$\Omega_{2,0,0,2} = \frac{4!}{2!0!0!2!} 1^2 \cdot 2^0 \cdot 2^0 \cdot 1^2 = 6$$

$$\Omega_{1,1,1,1} = \frac{4!}{1!1!1!1!} 1^1 \cdot 2^1 \cdot 2^1 \cdot 1^1 = 96$$

$$\Omega_{0,3,0,1} = \frac{4!}{0!3!0!1!} 1^0 \cdot 2^3 \cdot 2^0 \cdot 1^0 = 32$$

$$\Omega_{1,0,3,0} = \frac{4!}{1!0!3!0!} 1^1 \cdot 2^0 \cdot 2^3 \cdot 1^0 = 32$$

$$\Omega_{0,2,2,0} = \frac{4!}{0!2!2!0!} 1^0 \cdot 2^2 \cdot 2^2 \cdot 1^0 = 96$$

The most probable macrostates are $\{1, 1, 1, 1\}$ and $\{0, 2, 2, 0\}$.

The possible microstates corresponding to the macrostate $\Omega_{1,1,1,1}$ are shown in the table. Since the particles are distinguishable, they have been labelled A, B, C and D.

Table 1.9.1: Microstates associated with macrostate $\Omega_{1,1,1,1}$ for non-degenerate level

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
ϵ_4	A	A	A	A	A	A	B	B	B	B	B	B	C	C	C	C	C	C	D	D	D	D	D	D
ϵ_3	B	B	C	C	D	D	A	A	C	C	D	D	A	A	B	B	D	D	A	A	B	B	C	C
ϵ_2	C	D	B	D	B	C	C	D	A	D	A	C	B	D	A	D	A	B	B	C	A	C	A	B
ϵ_1	D	C	D	B	C	B	D	C	D	A	C	A	D	B	D	A	B	A	C	B	C	A	B	A

The macrostate $\{1, 1, 1, 1\}$ has 24 microstates as shown in the table. If the degeneracies of the second and third levels are considered, it is found that each of the 24 microstates has 4 microstates. The microstates corresponding to the first microstate are shown below:

ϵ_4	A	
ϵ_3	B	
ϵ_2	C	
ϵ_1	D	

ϵ_4	A	
ϵ_3		B
ϵ_2	C	
ϵ_1	D	

ϵ_4	A	
ϵ_3		B
ϵ_2		C
ϵ_1	D	

ϵ_4	A	
ϵ_3	B	
ϵ_2		C
ϵ_1	D	

Similarly each of the 24 microstates gives 4 microstates. Thus the total number of microstates corresponding to the macrostate $\{1,1,1,1\}$ is 96.

(ii) Particles are **bosons**

The possible microstates are:

$\{2, 0, 0, 2\}$, $\{1, 1, 1, 1\}$, $\{0, 3, 0, 1\}$, $\{1, 0, 3, 0\}$, $\{0, 2, 2, 0\}$

ε_i	g_i	macrostates					
		$\{n_i\}$	$\{n_i\}$	$\{n_i\}$	$\{n_i\}$	$\{n_i\}$	
4	1	2	1	1	0	0	
3	2	0	1	0	3	2	
2	2	0	1	3	0	2	
1	1	2	1	0	1	0	

The number of microstates associated with a macrostate $\{n_1, n_2, \dots\}$ is

$$\Omega = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$\Omega_{2,0,0,2} = \frac{(2+1-1)!}{2!(1-1)!} \frac{(0+2-1)!}{0!(2-1)!} \frac{(0+2-1)!}{0!(2-1)!} \frac{(2+1-1)!}{2!(1-1)!} = 1$$

Similarly

$$\Omega_{1,1,1,1} = 4, \quad \Omega_{0,3,0,1} = 4, \quad \Omega_{1,0,3,0} = 4, \quad \Omega_{0,2,2,0} = 9$$

The most probable macrostate is $\{0, 2, 2, 0\}$. The various microstates associated with this macrostate are shown in the figure.

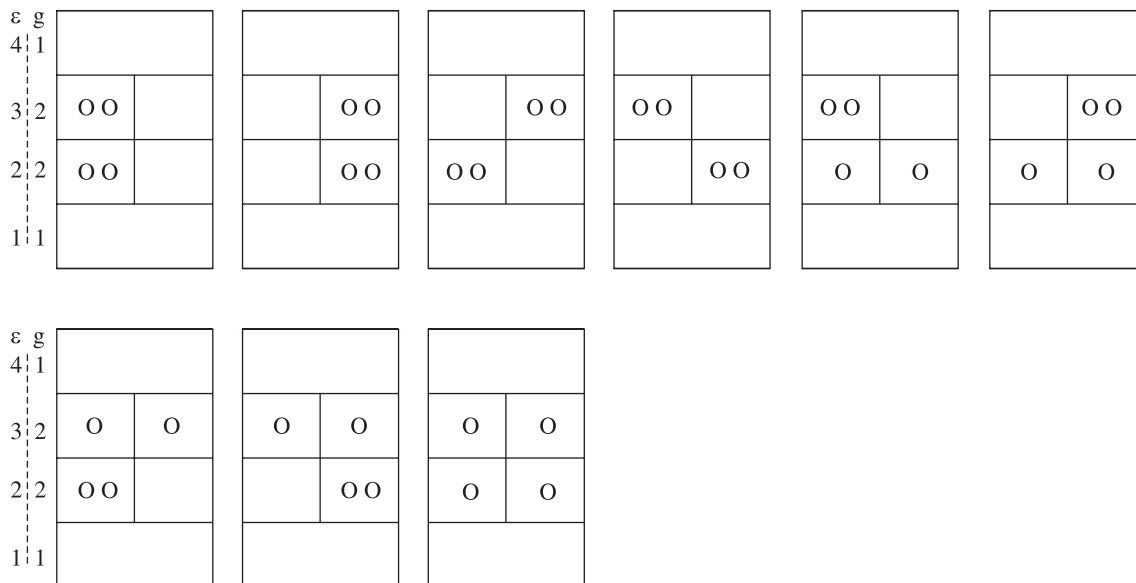


Fig. 1.9.4 Microstates associated with macrostate $\{0,2,2,0\}$

(iii) Particles are **fermions**

There are two possible macrostates. They are $\{1, 1, 1, 1\}$ and $\{0, 2, 2, 0\}$. The number of possible microstates associated with the first macrostate is

$$\Omega_{1,1,1,1} = \prod \frac{g_i!}{n_i!(g_i - n_i)!} = \frac{1!}{1!(1-1)!} \frac{2!}{1!(2-1)!} \frac{2!}{1!(2-1)!} \frac{1!}{1!(1-1)!} = 4$$

Similarly, the number of microstates associated with the second macrostate is

$$\Omega_{0,2,2,0} = 1$$

O		O		O		O			
O		O			O		O	O	O
	O		O	O				O	O
				O			O		

(four microstates corresponding to macrostate $\Omega_{1,1,1,1}$)

(one microstate $\Omega_{0,2,2,0}$)

Fig. 1.9.5 Microstates associated with macrostate $(1, 1, 1, 1)$ and $(0, 2, 2, 0)$

Ex. 3. A system consists of 4 distinguishable particles, labelled 1, 2, 3, and 4. These particles are to be distributed in two non-degenerate energy levels ϵ_1 and ϵ_2 . Find the possible macrostates and corresponding microstates. There is no restriction on the number of particle that can be put in a quantum state.

Sol. For non-degenerate levels $g_1 = g_2 = \dots = 1$, so the number of microstates corresponding to a macrostate is given by

$$\Omega = \frac{N!}{n_1!n_2!\dots}$$

The possible macrostates are $\{4, 0\}$, $\{3, 1\}$, $\{2, 2\}$, $\{1, 3\}$ and $\{0, 4\}$. The number of microstates corresponding to these macrostates is:

$$\Omega_{4,0} = \frac{4!}{4!0!} = 1, \quad \Omega_{3,1} = \frac{4!}{3!1!} = 4, \quad \Omega_{2,2} = \frac{4!}{2!2!} = 6, \quad \Omega_{1,3} = \frac{4!}{1!3!} = 4, \quad \Omega_{0,4} = \frac{4!}{0!4!} = 1$$

So there are five macrostates and 16 microstates in total. The macrostate $\Omega_{2,2}$ has maximum number of microstates (=6) and hence it is the most probable macrostate of the system. These microstates are shown in the table.

Energy Levels ε_1 ε_2		Macrostate $\{n_1, n_2\}$	Microstates
1 2 3 4	×	{4, 0}	1
1 2 3	4	{3, 1}	4
1 2 4	3		
1 3 4	2		
2 3 4	1		
1 2	3 4	{2, 2}	6
1 3	2 4		
1 4	2 3		
2 3	1 4		
2 4	1 3		
3 4	1 2		
1	2 3 4	{1, 3}	4
2	1 3 4		
3	1 2 4		
4	1 2 3		
×	1 2 3 4	{0, 4}	1

Ex. 4. A system consisting of 4 identical distinguishable particles has total energy 12 units. The particles are to be distributed in 4 non-degenerate energy levels with energies $\varepsilon_1 = 1$, $\varepsilon_2 = 2$, $\varepsilon_3 = 3$ and $\varepsilon_4 = 4$ units. Find the possible macrostates and their microstates. Assume that any number of particles can be put in the allowed energy levels.

Sol. The possible macrostates are:

{1, 0, 1, 2}, {0, 2, 0, 2}, {0, 1, 2, 1}, {0, 0, 4, 0}

<u>o o</u>	<u>o o</u>	<u>o</u>	<u>o o o o</u>	$\varepsilon_4 = 4$
<u>o</u>		<u>o o</u>		$\varepsilon_3 = 3$
	<u>o o</u>	<u>o</u>		$\varepsilon_2 = 2$
<u>o</u>				$\varepsilon_1 = 1$

Fig. 1.9.6 Distribution of four particles in four energy levels

The number of microstates Ω belonging to the above macrostates is:

$$\Omega_{1,0,1,2} = \frac{4!}{1!0!1!2!} = 12$$

$$\Omega_{0,2,0,2} = \frac{4!}{0!2!0!2!} = 6$$

$$\Omega_{0,1,2,1} = \frac{4!}{0!1!2!1!} = 12$$

$$\Omega_{0,0,4,0} = \frac{4!}{0!0!4!0!} = 1$$

Ex. 5. A system composed of 6 bosons has total energy 6 units. These particles are to be distributed in energy levels $\epsilon_0 = 0$, $\epsilon_1 = 1$, $\epsilon_2 = 2$, $\epsilon_3 = 3$, $\epsilon_4 = 4$, $\epsilon_5 = 5$, $\epsilon_6 = 6$. Each level is triply degenerate. Calculate the thermodynamic probability (statistical weight) of all the macrostates and of the system.

Sol. The possible macrostates are $\{5,0,0,0,0,0,1\}$, $\{4,1,0,0,0,1,0\}$, $\{4,0,1,0,1,0,0\}$, $\{3,2,0,0,1,0,0\}$, $\{4,0,0,2,0,0,0\}$, $\{3,1,1,1,0,0,0\}$, $\{2,3,0,1,0,0,0\}$, $\{3,0,3,0,0,0,0\}$, $\{2,2,2,0,0,0,0\}$, $\{1,4,1,0,0,0,0\}$, $\{0,6,0,0,0,0,0\}$. There are 11 macrostates.

The thermodynamic probability (statistical weight) of a macrostate is given by

$$\Omega = \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

$$\Omega_I = 63, \quad \Omega_{II} = 135, \quad \Omega_{III} = 135, \quad \Omega_{IV} = 180, \quad \Omega_V = 90, \quad \Omega_{VI} = 270,$$

$$\Omega_{VII} = 180, \quad \Omega_{VIII} = 100, \quad \Omega_{IX} = 216, \quad \Omega_X = 135, \quad \Omega_{XI} = 28$$

The thermodynamic probability of the system is

$$\Omega = \sum_i \Omega_i = 63 + 135 + 135 + 180 + 90 + 270 + 180 + 100 + 216 + 135 + 28 = 1532.$$

Note: For fermions, the macrostates 1, 2, 3, 5, 10 and 11, in which there can be more than one particle in a quantum state, are not allowed.

	1	2	3	4	5	6	7	8	9	10	11
ϵ_6	0										
ϵ_5		0									
ϵ_4			0	0							
ϵ_3					00	0	0				
ϵ_2			0			0		000	00	0	
ϵ_1		0		00		0	000		00	0000	000000
ϵ_0	00000	0000	0000	000	0000	000	00	000	00	0	

Ex. 6. A system consisting of 6 fermions has total energy 6 units. These particles are to be distributed in 5 energy levels $\epsilon_0 = 0$, $\epsilon_1 = 1$, $\epsilon_2 = 2$, $\epsilon_3 = 3$, $\epsilon_4 = 4$ units. Each energy level is triply degenerate. Find the possible microstates.

Sol. The possible macrostates are 5. They are:

$$\{3,2,0,0,1\}, \{3,1,1,1,0\}, \{2,3,0,1,0\}, \{3,0,3,0,0\}, \{2,2,2,0,0\}$$

The thermodynamic probability (the number of microstates) of a macrostate is given by

$$\Omega = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

The number of microstates associated with first macrostate is

$$\Omega_I = \frac{3!}{3!(3-3)!} \cdot \frac{3!}{2!(3-2)!} \cdot \frac{3!}{0!(3-0)!} \cdot \frac{3!}{0!(3-0)!} \cdot \frac{3!}{1!(3-1)!} = 9$$

Similarly, the number of microstates associated with other macrostates can be calculated. They come out to be

$$\Omega_{II} = 27, \quad \Omega_{III} = 9, \quad \Omega_{IV} = 1, \quad \Omega_V = 27.$$

The thermodynamic probability of the system is $\Omega = \Sigma \Omega_I = 9 + 27 + 9 + 1 + 27 = 73$.

PHASE SPACE

2.1 INTRODUCTION

The specification of the state of a particle in classical mechanics involves the concept of phase space. To understand the meaning of phase space, consider a particle moving in one dimension, along the x -axis, say. In classical mechanics the state of motion at any instant is specified by specifying its position coordinate x and momentum coordinate p_x . Now imagine a two dimensional conceptual space with x and p_x as orthogonal axes. We call this space phase space. At any instant t , the state of the particle is represented by a point (x, p_x) in the phase space and this point is called *phase point* or *representative point*. As the particle moves on the straight line, x and p_x take on different values and the corresponding representative point traces a trajectory in phase space. Thus the evolution of successive states of the particle will be represented by a trajectory in phase space. A point on the trajectory in phase space represents a definite state of motion of the particle.

Consider a one dimensional harmonic oscillator of mass m with total energy E . Let q and p denote the instantaneous position and momentum of the particle. The total energy of the oscillator is given by

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = E, \quad \omega = \text{frequency of oscillator}$$

This equation can be put in the form

$$\frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{2mE} = 1$$

The form of this equation shows that if we plot the instantaneous position q and momentum p on q - p plane for one cycle of motion, we get an ellipse with semi-major axis, $a = \sqrt{\frac{2E}{m\omega^2}}$ and semi-minor axis, $b = \sqrt{2mE}$. Each point on the ellipse represents same state of the oscillator. The area of the ellipse is

$$A = \pi ab = \pi \sqrt{\frac{2E}{m\omega^2}} \cdot \sqrt{2mE} = 2\pi \left(\frac{E}{\omega} \right)$$

According to quantum mechanics energy of oscillator is given by $E = \left(n + \frac{1}{2}\right)\hbar\omega$, $n = 0, 1, 2, \dots$. The area of the ellipse then becomes

$$A = \left(n + \frac{1}{2}\right)2\pi\hbar = \left(n + \frac{1}{2}\right)h$$

The area between two successive ellipses (which represent two successive energy levels) is

$$\Delta A = h = \text{Planck's constant.}$$

Usually the spatial coordinate of a particle is denoted by q and the corresponding momentum by p . Then the state of the particle is specified by stating its position and momentum coordinates (q, p) . To specify the state of the particle more precisely, it is convenient to subdivide the ranges of the variables q and p into arbitrarily small discrete interval. One can choose fixed intervals of size δq for the subdivision of q and fixed interval of size δp for the subdivision of p . The phase space is then subdivided into small cells of equal size and of two dimensional volume (*i.e.*, area) $\delta q \delta p = h_0$ where h_0 is a constant having the dimensions of angular momentum. The state of the system can then be specified by stating that its coordinates lies in some interval between q and $q + \delta q$ and its momentum lies in some interval between p and $p + \delta p$ *i.e.*, by stating that the representing point (q, p) lies in a particular cell of phase space. The specification of the state of the system clearly becomes more precise as one decreases the size chosen for the cells into which phase space has been divided *i.e.*, as one decreases the magnitude chosen for h_0 . Of course, h_0 can be chosen arbitrarily small in this classical description.

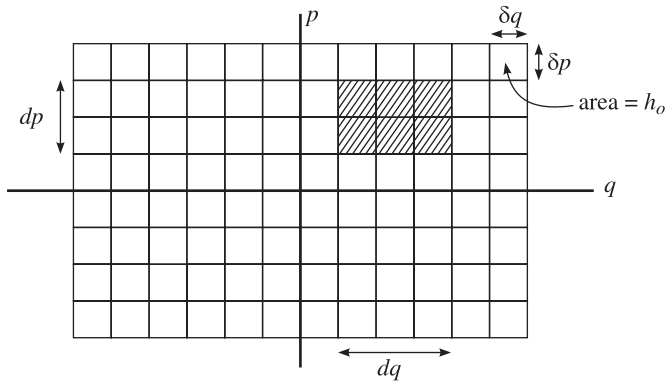


Fig. 2.1.1 Subdivision of phase space in cells of size $\delta q \delta p = h_0$

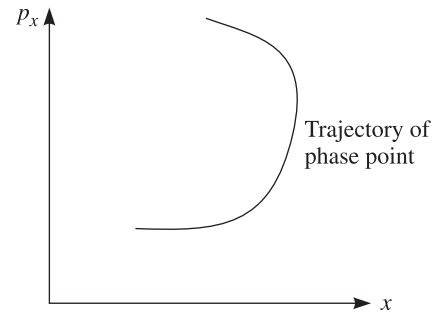


Fig. 2.1.2 Trajectory of a phase point in phase space

A particle moving in three dimensions requires 3 position coordinates (x, y, z) and 3 momentum coordinates (p_x, p_y, p_z) to specify its state of motion. The corresponding phase space has 6 dimensions with spatial coordinates x, y, z , and momentum coordinates p_x, p_y, p_z as orthogonal axes and the state of the particle is specified by a point (x, y, z, p_x, p_y, p_z) . If we denote the position and momentum coordinates by $q_1, q_2, q_3, p_1, p_2, p_3$ respectively then the state of the particle is denoted by point $(q_1, q_2, q_3, p_1, p_2, p_3)$. Each point in this 6-dimensional phase space represents a possible state of

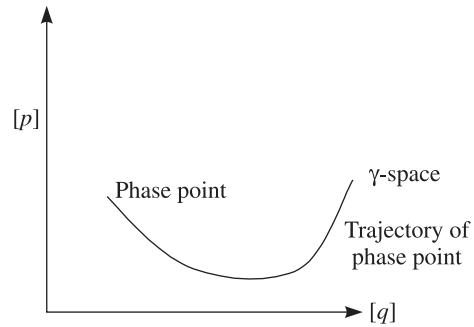
motion of the particle. If the particle under consideration is a molecule of a gas, the corresponding 6-dimensional phase space is called μ -space. (μ stands for molecule). The state of a system consisting of N -particles at any instant will be represented by N phase points in μ -space.

Like-wise the state of a N -particle system is specified by $3N$ position coordinates $x_1, y_1, z_1; x_2, y_2, z_2; \dots, x_N, y_N, z_N$ and $3N$ momentum coordinates $p_{x1}, p_{y1}, p_{z1}; \dots, p_{xN}, p_{yN}, p_{zN}$. Instead of denoting position coordinates by x, y, z and momentum coordinates by p_x, p_y, p_z let us denote them by generalized position coordinates q_1, q_2, q_3 and by generalized momentum coordinates p_1, p_2, p_3 respectively. So the state of the N -particle system is specified by $3N$ generalized position coordinates $q_1, q_2, q_3, \dots, q_{3N-2}, q_{3N-1}, q_{3N}$ and corresponding generalized momentum coordinates $p_1, p_2, p_3, \dots, p_{3N-2}, p_{3N-1}, p_{3N}$. These $6N$ coordinates along with the equations of motion viz

Hamilton's equations $\dot{q}_k = \frac{\partial H}{\partial p_k}, \dot{p}_k = -\frac{\partial H}{\partial q_k}, k=1,2,3, \dots, 3N$, where H is Hamiltonian of the

system, completely determine the behaviour of the system. We now imagine a $6N$ dimensional space with $6N$ rectangular axes, one for each of the spatial coordinates $q_1, q_2, \dots, q_{3N}$ and for each momentum coordinate $p_1, p_2, \dots, p_{3N}$. This $6N$ dimensional phase space of the N -particle system is called γ -space. The state of the entire system (gas) at any time t is completely specified by a phase point in γ -space. In course of time the spatial and momentum coordinates undergo continuous change, the corresponding phase point traces a trajectory in γ -space; the motion of the phase point is governed by Hamilton's equations. Each phase point on the trajectory in γ -space represents a possible microstate of the entire system.

Once again the γ -space can be subdivided into little cells of volume $\delta q_1 \delta q_2 \dots \delta q_{3N} \delta p_1 \delta p_2 \dots \delta p_{3N} = (h_0)^{3N}$. The state of the system can then again be specified by stating in which particular range or cell in phase space, the coordinates $q_1, q_2, \dots, q_{3N}, p_1, p_2, \dots, p_{3N}$ of the system can be found.



$[q]$ stands for $3N$ spatial coordinates and $[p]$ for $3N$ momentum coordinates.

Fig. 2.1.3 Trajectory of phase point in γ -space

2.2 DENSITY OF STATES IN PHASE SPACE

Consider a particle moving in x -direction. Classical physics puts no restriction on the accuracy with which the simultaneous specification of position and momentum can be made. That is the uncertainties δq and δp in specification of position and momentum can be made as small as we like. In other words, the size of the cell $\delta q \delta p = h_0$ into which the phase space is subdivided can be chosen arbitrarily small. But quantum mechanics imposes a limitation on the accuracy with which a simultaneous specification of coordinate q and its corresponding momentum p can be made. According to Heisenberg uncertainty principle, the uncertainties in δq and δp are such that $\delta q \delta p \geq h$, where h is Planck's constant. The subdivision of the phase space into cells of volume less than h is physically meaningless.

For a particle free to move in three dimensions, if Δx and Δp_x denote the uncertainty in position and momentum then

$$\Delta x \cdot \Delta p_x \approx h$$

Similar relations hold for other components also.

$$\Delta y \cdot \Delta p_y \approx h$$

$$\Delta z \cdot \Delta p_z \approx h$$

$$\text{Hence } \Delta x \cdot \Delta y \cdot \Delta z \cdot \Delta p_x \cdot \Delta p_y \cdot \Delta p_z \approx h^3 \quad \dots(2.2.1)$$

The product $\Delta x \cdot \Delta y \cdot \Delta z \cdot \Delta p_x \cdot \Delta p_y \cdot \Delta p_z = h^3$ represents an element of volume in phase space. Two particles whose representative points lie in such an elementary cell cannot be distinguished and hence the representative points in this cell represent a single quantum state. It follows from above that different quantum states shall corresponds to different elements of volume in the phase space only if the size of these elements is no less than h^3 . Therefore a volume equal to h^3 in the phase space may be allotted to each microscopic state of the particle. In other words, each elementary cell of phase space represents a microstate of the particle. The state of a particle is specified by stating in which particular cell the coordinates x, y, z, p_x, p_y, p_z of the particle lie. The process of dividing the phase space into cells finite size is termed **quantization of phase space**. The number of cells $d\Omega$ in an element of phase volume $d\Gamma$ is

$$d\Omega = \frac{d\Gamma}{h^3} = \frac{dx dy dz dp_x dp_y dp_z}{h^3} = \frac{dV dp_x dp_y dp_z}{h^3}.$$

The total number of cells (microstates or quantum states) in the entire phase space of the particle is given by

$$\Omega = \frac{\iiint \iiint dx dy dz dp_x dp_y dp_z}{h^3} = \frac{V}{h^3} \iiint dp_x dp_y dp_z \quad \dots(2.2.2)$$

where $V = \iiint dx dy dz$ is the volume in coordinate available to the particle.

In many applications we are interested in a quantity $g(p)dp$ which represents the number of states (cells) of the particle moving in volume V such that the magnitude of momentum lies in the interval p and $p + dp$ irrespective of its direction. To calculate this number we change the volume element in momentum space $dp_x dp_y dp_z$ in spherical polar coordinates. Thus

$$dp_x dp_y dp_z = p^2 dp \sin \theta d\phi$$

$$\text{Hence } g(p) dp = \frac{V}{h^3} \int_p^{p+dp} p^2 dp \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{V}{h^3} (4\pi p^2 dp)$$

In terms of energy $E = p^2/2m$ the number of states in the energy range dE about E is given by

$$g(E)dE = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \quad \dots(2.2.3)$$

If the particle has internal degree of freedom such as spin, there will be $(2s + 1)$ spin states corresponding to each momentum or energy states. Therefore, the number of states then becomes

$$g(E)dE = (2s + 1) \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \quad \dots(2.2.4)$$

For spin 1/2 particles (such as electrons) $s = 1/2$, the number of states in the energy range dE at E is

$$g(E)dE = \frac{4\pi V}{h^3} (2m)^{3/2} E^{1/2} dE \quad (\text{for spin } 1/2 \text{ particles}) \quad \dots(2.2.5)$$

The function $g(E)$ is called the **density of states** and is defined as the number of quantum states per unit energy range at energy E and is given by

$$g(E) = (2s + 1) \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} \quad \dots(2.2.6)$$

2.3 NUMBER OF QUANTUM STATES OF AN N-PARTICLE SYSTEM

In $6N$ -dimensional γ -space of an N -particle system, a quantum state of the system is assigned an element of *hypervolume* h^{3N} . The number of *cells* (*quantum states or microstates*) in a volume element

$dq_1 \dots dq_{3N}, dp_1 \dots dp_{3N}$ at point (q, p) in γ -space is $d\Omega = \frac{dq_1 \dots dq_{3N} \cdot dp_1 \dots dp_{3N}}{h^{3N}}$. The total number of accessible states in γ -space is

$$\begin{aligned} \Omega &= \frac{1}{h^{3N}} \int dq_1 \dots dq_{3N} \cdot dp_1 \dots dp_{3N} \\ &= \frac{1}{h^{3N}} \int dq_1 \dots dq_{3N} \cdot \int dp_1 \dots dp_{3N} \\ &= \frac{1}{h^{3N}} \cdot V^N \cdot \int dp_1 \dots dp_{3N} \\ &= \frac{V^N}{h^{3N}} \int d^3 p_1 \cdot d^3 p_2 \dots d^3 p_N \\ \Omega &= \frac{V^N}{h^{3N}} \int d^{3N} p \\ \Omega &= \frac{V^N}{h^{3N}} \cdot \frac{(2\pi mE)^{3N/2}}{(3N/2)}, \quad E = \frac{p^2}{2m}, \quad (\text{for large } N) \quad \dots(2.3.1) \end{aligned}$$

ENSEMBLE FORMULATION OF STATISTICAL MECHANICS

3.1 ENSEMBLE

The method of ensemble in statistical physics was introduced in 1902 by the American physicist J.W. Gibbs. Consider a system consisting of N molecules with total energy E enclosed in a vessel of volume V . The macroscopic state of the system is described by pressure P , volume V and energy E . With passage of time the coordinates and momenta of molecules and hence the microscopic states of the system undergo continuous change. Meaning thereby, a macrostate is realized through an enormously large number of microstates. Now imagine a large number (possibly infinite) of systems, which are exactly identical in structure to the system of interest, but suitably randomized in microscopic states such that they represent at one time the possible states of the actual system attained in the course of time. This mental collection of similar non-interacting, independent systems is called an *ensemble*. All the members of an ensemble, which are identical in feature like N , V and E are called the elements or systems. These elements, although identical in structure are randomized in the sense that they differ from one another in the coordinates and momenta of the individual molecules *i.e.*, the elements differ in their unobservable microscopic states.

The state of an N -particle system (element, or component) of an ensemble can be specified by the $3N$ canonical coordinates $q_1, q_2, \dots, q_{3N}$, and $3N$ canonical momenta $p_1, p_2, \dots, p_{3N}$ of the N molecules. The $6N$ dimensional space spanned by the $3N$ spatial and $3N$ momentum coordinates is called γ -**space** of the system. An element of the ensemble is represented by a point and the ensemble is represented by a distribution of points in γ -space usually a continuous distribution.

Instead of denoting the spatial and momentum coordinates of an N -particle system by $q_1, \dots, q_{3N}$, and $p_1, \dots, p_{3N}$, it is convenient to denote them by $q_1, \dots, q_f, p_1, \dots, p_f$ respectively. Of course, $f = 3N$. The system is said to have f degrees of freedom. In $2f (= 6N)$ dimensional γ -space having $2f$ rectangular axes, one for each of spatial coordinates $q_1, \dots, q_f$ and one for each of corresponding momentum coordinates $p_1, \dots, p_f$, the state of the system is represented by a point. In this space the ensemble of system looks like cloud of points. The ensemble may be conveniently described by a **density function** $\rho(p, q, t)$ where (p, q) is an abbreviation for $p_1, p_2, \dots, p_f, q_1, q_2, \dots, q_f$ so defined that $\rho(p, q, t) d^f p d^f q$ is the number of representative points which at time t are contained in the infinitesimal volume element $d^f p d^f q$ of γ -space centered about the point (p, q) . An ensemble is

completely specified by $\rho(p, q, t)$. It is to be emphasized that the members of an ensemble are the mental copies of a system and do not interact with one another.

Each element of the ensemble is a quantum mechanical system of N interacting molecules in a container of volume V . The value of N and V along with the force law between the molecules, are sufficient to determine the eigen values and the quantum states of the Schrodinger equation along with their associated degeneracy. These energies are the only energies available to the system.

3.2 DENSITY OF DISTRIBUTION (PHASE POINTS) IN γ -SPACE

The state of an ensemble can be described in terms of the density $\rho(q, p, t)$ with which the representative points are distributed in γ -space. For an ensemble consisting of very large number of systems, the distribution of representative points is continuous and the density of phase points in γ -space can be treated as a continuous function. With passage of time, the microstates of the systems undergo change and their representative points move in γ -space from one region to another. So the density ρ of phase points is function of $q_1, \dots, q_f, p_1, \dots, p_f$ and time t and may be written as

$$\rho = \rho(q_1, \dots, q_f, p_1, \dots, p_f, t) = \rho(q, p, t) \quad \dots(3.2.1)$$

The meaning of ρ is such that

$$\rho dq_1, \dots, dq_f dp_1, \dots, dp_f \quad \text{or} \quad \rho d\Gamma \quad \dots(3.2.2)$$

represents the number of systems in infinitesimal hypervolume $d\Gamma = dq dp = dq_1, \dots, dq_f . dp_1, \dots, dp_f$ located at point (q, p) . The number of systems dM in hypervolume $d\Gamma$ is

$$dM = \rho d\Gamma \quad \dots(3.2.3)$$

and the total number of systems in the ensemble is

$$M = \int \rho d\Gamma \quad \dots(3.2.4)$$

Where the integration is over the accessible phase space of the ensemble. The average value of a physical quantity $Q(q, p)$ is given by

$$\langle Q \rangle = \frac{\int Q(q, p) \rho(q, p, t) d\Gamma}{\int \rho(q, p, t) d\Gamma} \quad \dots(3.2.5)$$

The concept of ensemble is introduced to facilitate the calculation of average value, a physical system.

3.3 PRINCIPLE OF EQUAL A PRIORI PROBABILITY

To specify the microscopic state of a system, the phase space of the system is subdivided into small cells of equal size. Each cell represents a microscopic state of the system. According to the postulate of equal a priori probability, *an isolated system in equilibrium is equally likely to be in any of its accessible microscopic states satisfying the macroscopic conditions of the system.*

A many particle isolated system, according to quantum mechanics, possesses discrete energy levels and discrete quantum states. It is found that many distinct quantum states correspond to the same energy levels. The number of different quantum states having the same energy is called the degeneracy of that energy level. The particles constituting the system are distributed among the various energy states. The specification of the macroscopic parameters, such as total energy E , volume V , the total number N of particles of the system, defines a particular macroscopic state of the system. Let the allowed energy levels be denoted by $\epsilon_1, \epsilon_2, \dots, \epsilon_i$ and the occupation number of these energy levels by $n_1, n_2, \dots, n_i$. Let the system obey the constraints

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \epsilon_i = E \quad \dots(3.3.1)$$

There can be a large number of different ways in which the total energy E of the system can be distributed among N -particles constituting the system. Each of these different ways specifies a particular microscopic state of the given system. To a given macroscopic state there may be a large number of microscopic states. According to the principle of *equal a priori probability*, when a system is in statistical equilibrium, all the microstates are equally probable.

There is no direct proof of this postulate. It does not contradict any known laws of mechanics. All calculations based on this postulate have yielded results that are in very good agreement with observations. The validity of this postulate can therefore be accepted with great confidence as the basis of our theory.

3.4 ERGODIC HYPOTHESIS

In statistical mechanics we often deal with average or the mean of a quantity. The average of a physical quantity can be determined in two ways:

- (i) One could consider an ensemble of a large number of identical systems and average the physical quantity over all these systems at one instant of time to determine its ensemble average.
- (ii) A system could be followed over a very long period of time, during which the physical quantity of the system takes different values. The average of the physical quantity over the long period gives the time averaged value of the quantity.

According to ergodic hypothesis the mean over the ensemble is equal to the mean over time. So far, there is no proof of the validity of this statement in the general case and is taken as one of the basic assumptions of statistical physics. The *ergodic hypothesis* and the *principle of equal a priori probability* are the main postulates that are employed for studying the properties of an ensemble.

3.5 LIOUVILLE'S THEOREM

Consider an isolated system specified by spatial and momentum coordinates $q_1, \dots, q_f, p_1, \dots, p_f$. In $2f$ dimensional γ -space the ensemble of systems appears as a cloud of points. In course of time the phase points move in γ -space because of change in position and momentum coordinates. This will

result in change in the distribution density $\rho(q, p, t)$ of phase points. Let us define $\rho(q, p, t)$ such that $\rho(q, p, t) = dq_1, \dots, dq_f dp_1, \dots, dp_f$ represents the number of phase points (systems) in hypervolume $d\Gamma = dq dp$ located at point (q, p) . The Liouville's theorem gives the rate of change of density $\rho(q, p, t)$ at a fixed point in γ -space.

Consider an element of hypervolume of phase space located between q_1 and $q_1 + dq_1$, q_2 and $q_2 + dq_2$, ..., q_f and $q_f + dq_f$ and p_1 and $p_1 + dp_1$, p_2 and $p_2 + dp_2$, ..., p_f and $p_f + dp_f$. The volume of this element is $d\Gamma = dq_1, \dots, dq_f \cdot dp_1, \dots, dp_f$. The coordinates and momenta of the phase points vary according to the Hamilton's equations of motion

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dots(3.5.1)$$

where $H = H(q_1, \dots, q_f, p_1, \dots, p_f)$ is Hamiltonian of the system. The change in q 's and p 's results a change in the number of phase points in the element of hypervolume. In time dt , the change in the number of phase points within this hypervolume of phase space is

$$\left(\frac{\partial \rho}{\partial t} dt \right) d\Gamma$$

This change is equal to the difference in the number of phase points entering and leaving this volume in time dt . The number of phase points entering this volume in time dt through the face located at $q_1 = \text{constant}$ is

$$\rho(q, p, t)(\dot{q}_1 dt) dq_2 \dots dq_f dp_1 \dots dp_f$$

The number of phase points leaving through the opposite face located at $q_1 + dq_1 = \text{constant}$ is

$$\left\{ \rho \dot{q}_1 + \frac{\partial}{\partial q_1} (\rho \dot{q}_1) dq_1 \right\} dt dq_2 \dots dq_f dp_1 \dots dp_f$$

The net number of phase points entering the hypervolume element in time dt

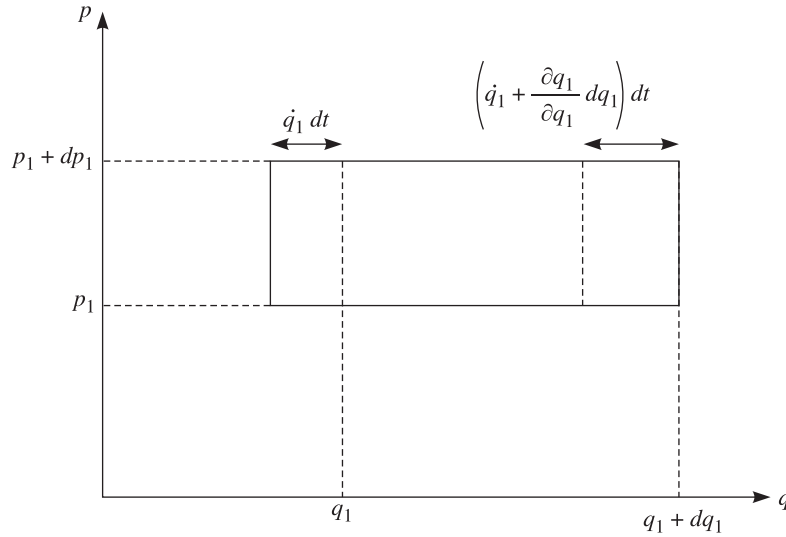
$$\begin{aligned} &= \rho \dot{q}_1 dt dq_2 \dots dq_f dp_1 \dots dp_f - \left\{ \rho \dot{q}_1 + \frac{\partial (\rho \dot{q}_1)}{\partial q_1} dq_1 \right\} dt dq_2 \dots dq_f dp_1 \dots dp_f \\ &= -\frac{\partial}{\partial q_1} (\rho \dot{q}_1) dt dq_1 \dots dq_f dp_1 \dots dp_f \\ &= -\frac{\partial (\rho \dot{q}_1)}{\partial q_1} dt d\Gamma \end{aligned}$$

The total net increase in time dt of the number of phase points in the hypervolume of phase space is obtained by summing the net number of phase points entering the hypervolume through all the faces labeled by $q_1, \dots, q_f, p_1, \dots, p_f$. Thus one obtains

$$\frac{\partial \rho}{\partial t} dt d\Gamma = - \left[\sum_{i=1}^f \frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \sum_{i=1}^f \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right] dt d\Gamma$$

or

$$\frac{\partial \rho}{\partial t} = - \sum_{i=1}^f \left[\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right] \quad \dots(3.5.2)$$

**Fig. 3.5.1** A volume element in phase space

Equation (3.5.2) can be written as

$$\frac{\partial \rho}{\partial t} = - \sum_{i=1}^f \left[\left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \rho \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) \right] \quad \dots(3.5.3)$$

Making use of Hamilton's equations, we have

$$\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0 \quad \dots(3.5.4)$$

In view of Eqn. (3.5.4), Eqn.(3.5.3) reduces to

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_{i=1}^f \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \quad \dots(3.5.5)$$

Making use of Hamilton's equations of motion we can write Eqn. (3.5.5) as

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_{i=1}^f \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \quad \dots(3.5.6)$$

Equation (3.5.5) or (3.5.6) is known as the Liouville theorem. It gives the rate of change of density at a fixed point in γ -space. In view of the following results:

$$\sum_i^f \frac{\partial \rho}{\partial q_i} \dot{q}_i = \sum_i^f \frac{\partial \rho}{\partial q_i} \frac{\partial q_i}{\partial t} = \left(\frac{\partial \rho}{\partial t} \right)_{p,t}$$

and

$$\sum_i^f \frac{\partial \rho}{\partial p_i} \dot{p}_i = \sum_i^f \frac{\partial \rho}{\partial p_i} \frac{\partial p_i}{\partial t} = \left(\frac{\partial \rho}{\partial t} \right)_{q,t}$$

we can write Eqn. (3.5.5) as follows:

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} + \sum_{i=1}^f \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0$$

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} + \left(\frac{\partial \rho}{\partial t} \right)_{p,t} + \left(\frac{\partial \rho}{\partial t} \right)_{q,t} = 0$$

$$\frac{d\rho}{dt} = 0 \quad \dots(3.5.7)$$

Thus, the total derivative of density $\rho(q, p, t)$, which is a measure of the rate of change of ρ in the immediate vicinity of a *moving* phase point (q and p changing) in γ -space, is zero. In other words, the density of a group of phase points remains constant along their trajectories in the γ -space. The distribution of phase points moves in γ -space like an incompressible fluid. Gibbs called this conclusion the *principle of the conservation of density in phase*.

From Eqn. (3.5.7) we can obtain another fundamental principle of statistical mechanics. Consider a region in γ -space which, although finite, is small enough for the density ρ to be treated as uniform throughout; if the hypervolume of the region is $\delta\Gamma$, the number δM of the phase points in this region will be given by

$$\delta M = \rho \delta\Gamma \quad \dots(3.5.8)$$

On differentiating this expression with respect to time t , it is seen that

$$\frac{d}{dt}(\delta M) = \frac{d\rho}{dt} \delta\Gamma + \rho \frac{d(\delta\Gamma)}{dt} \quad \dots(3.5.9)$$

If it is supposed that the boundaries of the region under consideration are permanently determined by the phase points that were originally on the surface, then no phase points can enter or leave this region. In other words, the points on the outer surface act like a continuous thin skin by which all the points in the region are enclosed. The *hypersurface* enclosing the region changes its shape and moves about in gamma space due to the flow of phase points. Further, since each phase point represents a definite system, these points can neither be created nor destroyed. So $\frac{d}{dt}(\delta M) = 0$.

Eqn. (3.5.9) then becomes

$$\frac{d\rho}{dt} \delta\Gamma + \rho \frac{d(\delta\Gamma)}{dt} = 0 \quad \dots(3.5.10)$$

Since $\frac{d\rho}{dt} = 0$, we have

$$\frac{d(\delta\Gamma)}{dt} = 0 \quad \dots(3.5.11)$$

This means that the volume or *extension-in-phase* in γ -space of the particular region, occupied by a definite number of phase points, does not change with time. Since every finite arbitrary extension-in-phase may be regarded as composed of infinitesimal parts, the result may be generalized. This theorem, mathematically expressed by Eqn. (3.5.11) is called the *principle of conservation of extension in phase*.

3.6 STATISTICAL EQUILIBRIUM

An ensemble is said to be in statistical equilibrium if the density of phase points is independent of time at all points in γ -space *i.e.*

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = 0 \text{ for all } q\text{'s and } p\text{'s.}$$

Consider an ensemble of conservative systems for which energy E is constant in time and is function of q 's and p 's. Thus

$$\rho = \rho(E), \quad E = E(q, p) \quad \text{and} \quad \frac{dE}{dt} = 0 \quad \dots(3.6.1)$$

Therefore
$$\frac{\partial \rho}{\partial q_i} = \frac{d\rho}{dE} \cdot \frac{\partial E}{\partial q_i}, \quad \frac{\partial \rho}{\partial p_i} = \frac{d\rho}{dE} \cdot \frac{\partial E}{\partial p_i} \quad \dots(3.6.2)$$

According to Liouville's theorem

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_i^f \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \quad \dots(3.6.3)$$

Making use of Eqn. (3.6.2) in (3.6.3), we have

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \frac{d\rho}{dE} \sum_i^f \left(\frac{\partial E}{\partial q_i} \dot{q}_i + \frac{\partial E}{\partial p_i} \dot{p}_i \right) \quad \dots(3.6.4)$$

Since $E = E(q, p)$ and $dE/dt = 0$, we have

$$\frac{dE}{dt} = \sum_i^f \left(\frac{\partial E}{\partial q_i} \dot{q}_i + \frac{\partial E}{\partial p_i} \dot{p}_i \right) = 0 \quad \dots(3.6.5)$$

From Eqns. (3.6.4) and (3.6.5)

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = 0 \text{ for all } q\text{'s and } p\text{'s.} \quad \dots(3.6.6)$$

Thus, an ensemble is in statistical equilibrium if density of phase points (or the probability of finding the phase points) in the various regions of γ -space is independent of time. This means that every portion of the phase space continues to contain the same number of phase points at all times. Under these conditions, the average values of the properties of the systems in the ensemble also do not change with time.

THERMODYNAMIC FUNCTIONS

3.7 ENTROPY

Entropy is a very important thermodynamic function, which connects thermodynamics to statistical mechanics. It is known from thermodynamics that when a system, with constant volume and energy, is in equilibrium the entropy is maximum. On the other hand, according to statistical mechanics, such a system is in equilibrium when the total thermodynamic probability is a maximum. It appears, therefore, as suggested by Boltzmann, that there should be a relationship between entropy and thermodynamic probability. The thermodynamic probability Ω is defined as the number of microstates corresponding to the given macrostate. Let the entropy S and Ω be related through the expression

$$S = f(\Omega) \quad \dots(3.7.1)$$

Consider two systems having entropies S_1 and S_2 and thermodynamic probabilities Ω_1 and Ω_2 respectively. In view of Eqn. (3.7.1), we have

$$S_1 = f(\Omega_1) \text{ and } S_2 = f(\Omega_2).$$

Since the entropy is an additive quantity, the entropy of the combined system is equal to $S_{12} = S_1 + S_2$. The thermodynamic probability is a multiplicative quantity, therefore, the joint thermodynamic probability of the combined system is $\Omega_{12} = \Omega_1 \Omega_2$ and $S_{12} = f(\Omega_1 \Omega_2)$.

$$\begin{aligned} S_1 + S_2 &= S_{12} \\ f(\Omega_1) + f(\Omega_2) &= f(\Omega_1 \Omega_2) \end{aligned} \quad \dots(3.7.2)$$

Differentiating Eqn. (3.7.2) with respect to Ω_1 , we have

$$f'(\Omega_1) = [f'(\Omega_1 \Omega_2)] \Omega_2 \quad \dots(3.7.3)$$

Similarly, differentiating Eqn. (3.7.2) with respect to Ω_2 , we have

$$f'(\Omega_2) = [f'(\Omega_1 \Omega_2)] \Omega_1 \quad \dots(3.7.4)$$

From Eqns. (3.7.3) and (3.7.4)

$$\frac{f'(\Omega_1)}{f'(\Omega_2)} = \frac{\Omega_2}{\Omega_1}$$

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) = k, (= \text{a constant, say})$$

$$df(\Omega_1) = k \frac{d\Omega_1}{\Omega_1}$$

$$f(\Omega_1) = k \ln \Omega_1 + C_1$$

Similarly, we can have

$$f(\Omega_2) = k \ln \Omega_2 + C_2$$

C_1 and C_2 are constants. General form of these relations is

$$f(\Omega) = k \ln \Omega + C$$

$$\text{or} \quad S = k \ln \Omega + C \quad \dots(3.7.5)$$

At absolute zero, any system is in most ordered state and this state has only one microstate *i.e.*, $\Omega = 1$ and this state is assigned zero entropy $S = 0$. The constant C in Eqn. (3.7.5) comes out to be zero. So, we have

$$S = k \ln \Omega \quad \dots(3.7.6)$$

where k is Boltzmann constant. Equation (3.7.6) is taken as the statistical definition of entropy.

3.8 FREE ENERGY

In a mechanical system, such as a spring, the work done the system is stored in the system as potential energy and this energy may be recovered as work. In the similar way one can store energy in thermodynamic system, which can be recovered in the form of work. The energy, which can be stored and recovered, is called free energy. The four kinds of free energy that can be stored in thermodynamics system are: (i) **Internal Energy** E , (ii) **Enthalpy** $H = E + PV$, (iii) **Helmholtz Free Energy** $F = E - TS$ and (iv) **Gibb's Free Energy** $G = E - TS + PV$.

The energy of a system also depends on the number of its constituent particles. When a particle leaves a system, it takes away a definite amount of energy with it. When it enters a system, it adds energy to it. To take into account the change in energy contributed by a particle we introduce a quantity, *chemical potential* μ , which is defined as the change in energy of the system associated with unit change in number of particles.

$$\mu = \left(\frac{\partial E}{\partial N} \right) \quad \dots(3.8.1)$$

If a system is to be in equilibrium state, the temperature T , pressure P and chemical potential μ must be the same throughout the system.

The law of conservation of energy for a system with variable number of particles can be written as

$$dE = TdS - PdV + \mu dN \quad \dots(3.8.2)$$

where dN is the change in number of particles. The first term on the right hand side represents the change in energy due to transfer of heat energy to the system, second term represents change in energy due to work done by the system and the third term represents the change in energy due to

change in number of particles in the system

For an *isolated system at constant volume*, $\delta Q = TdS = 0$ and $dV = 0$. For such a system

$$dE = \mu dN$$

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} \quad \dots(3.8.3)$$

Hence the *chemical potential represents the variation of the energy of an isolated system of constant volume brought about by a unit change in number of particles.*

If $U = \text{constant}$ and $N = \text{constant}$ then Eqn.(3.8.2) becomes

$$T dS = P dV$$

$$\therefore \left(\frac{\partial S}{\partial V} \right)_{N,E} = \frac{P}{T} \quad \dots(3.8.4)$$

If $V = \text{constant}$, and $E = \text{constant}$, then Eqn. (3.8.2) becomes

$$T dS = -\mu dN$$

$$\therefore \left(\frac{\partial S}{\partial N} \right)_{V,E} = -\frac{\mu}{T} \quad \dots(3.8.5)$$

3. Helmholtz Free Energy

Helmholtz free energy is defined by

$$F = E - TS \quad \dots(3.8.6)$$

Therefore,

$$dF = dE - T dS - S dT \quad \dots(3.8.7)$$

Substituting dE from Eqn. (3.8.2) in (3.8.7), we have

$$dF = -PdV - SdT + \mu dN$$

$$\text{Whence} \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}, \quad -P = \left(\frac{\partial F}{\partial V} \right)_{T,N}, \quad -S = \left(\frac{\partial F}{\partial T} \right)_{N,N} \quad \dots(3.8.8)$$

Thus Helmholtz function F plays a very important role in calculation of thermodynamic quantities of a system.

3.9 ENSEMBLE FORMULATION OF STATISTICAL MECHANICS

There are three kinds of formulations of statistical physics. They are:

- (i) Microcanonical Ensemble.
- (ii) Canonical Ensemble.
- (iii) Grand Canonical Ensemble.

3.10 MICROCANONICAL ENSEMBLE

Consider a system containing N -particles in a volume V with total energy of particles E . The walls of the container are perfectly insulating. Thus, the system is completely isolated from outside world. There can be no exchange of energy and matter from the surroundings. Therefore E , V and N have fixed values. The macroscopic state of the system is specified by E , V , and N . **A collection of a very large number of such identical isolated systems is called a microcanonical ensemble.** The systems of the ensemble are also called *elements* or components. Truly isolated systems can never be realized in the laboratory.

In $6N$ dimensional γ -space the microstate of the N -particle system is represented by a point. The locus of all points in γ -space satisfying the condition $E = \text{constant}$, defines a surface called the **ergodic surface** of energy E . As the state of the system evolves in time according to Hamilton's equations of motion, the representative point traces out a path in γ -space. This path always stays on the same energy surface because by definition energy is conserved for an isolated system.

We cannot specify exactly the energy of a system. However, we can certainly specify the energy within a narrow range, say E and $E + dE$. We can then select two neighboring ergodic surfaces, one at E and the other at $E + \Delta E$. In $6N$ dimensional γ -space the microcanonical ensemble, whose each member has energy between E and $E + \Delta E$, is represented by points that lie between two ergodic surfaces of energies E and $E + \Delta E$. A microcanonical ensemble may be represented by distribution of points in γ -space characterized by a density function $\rho(p, q, t)$ defined in such a way that $\rho(p, q, t) d^{3N}p d^{3N}q$ gives the number of representative points contained in the volume element $d^{3N}p d^{3N}q$ located at point (p, q) in γ -space at the instant t . For microcanonical ensemble the density function satisfies the condition

$$\begin{aligned} \rho(p, q) &= 1 & \text{if } E < H(p, q) < E + \Delta E \\ &= 0 & \text{otherwise} \end{aligned} \quad \dots(3.10.1)$$

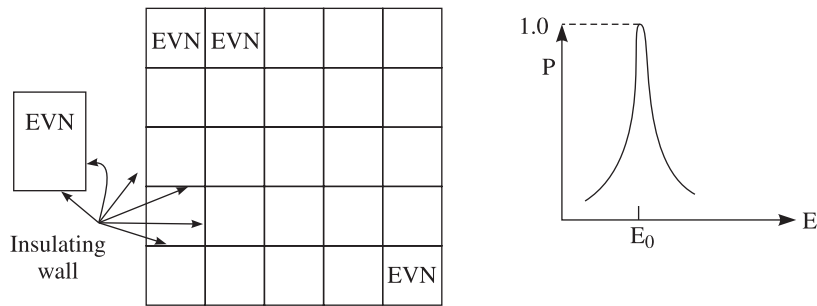


Fig. 3.10.1 Microcanonical ensemble (E V N fixed)

The average of a physical quantity $Q(p, q)$ is defined by

$$\langle R \rangle = \frac{\int d^{3N}p d^{3N}q Q(p, q) \rho(p, q)}{\int d^{3N}p d^{3N}q \rho(p, q)} \quad \dots(3.10.2)$$

3.11 CLASSICAL IDEAL GAS IN MICROCANONICAL ENSEMBLE FORMULATION

The statistical description of a system in this approach is given in terms of statistical weight $\Omega(EVN)$ which leads to the thermodynamic description in terms of entropy S through Boltzmann equation

$$S = k \ln \Omega(EVN). \quad \dots(3.11.1)$$

All other thermodynamic properties of the system can be derived from these relations. We shall consider ideal gas as an example in this formulation.

The number of accessible microstates of an isolated N -particle system occupying a volume V with total energy lying in the range E and $E + dE$ is

$$\Omega(E, V, N) = \left(\frac{V}{h^3} \right)^N \cdot \frac{(3N/2)}{(3N/2)!} (2\pi m)^{3N/2} \cdot E^{[(3N/2)-1]} \quad \dots(3.11.2)$$

For large N this results simplifies to

$$\Omega(E, V, N) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{(3N/2)!} \quad \dots(3.11.3)$$

The entropy of the gas is

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln \left[\left(\frac{V}{h^3} \right)^N \cdot \frac{(2\pi m E)^{3N/2}}{(3N/2)!} \right] \end{aligned}$$

Using Stirling's approximation $\ln n! = n \ln n - n$, we can simplify the expression for entropy as follows.

$$\begin{aligned} S &= k \ln \left[\left(\frac{V}{h^3} \right)^N \left\{ (2\pi m E)^{3/2} \right\}^N \right] - k \left[\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right] \\ S &= k \ln \left[\left(\frac{V}{h^3} \right)^N \left\{ (2\pi m E)^{3/2} \right\}^N \left\{ \left(\frac{2}{3N} \right)^{3/2} \right\}^N \right] + \frac{3}{2} N k \\ S &= N k \ln \left[\frac{V}{h^3} \cdot \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N k \quad \dots(3.11.4) \end{aligned}$$

This expression for the entropy S does not satisfy the additive property. For example, if we increase E , V , N by a factor η , the entropy of the new system does not become ηS . The above expression for entropy gives the entropy of new system S' , where

$$S' = \eta N k \ln \left[\frac{\eta V}{h^3} \cdot \left(\frac{4\pi m \eta E}{3\eta N} \right)^{3/2} \right] + \frac{3}{2} \eta N k = \eta N k \ln \eta + \eta S \neq \eta S$$

This result is known as **Gibbs paradox**. The origin of Gibbs paradox lies in the classical assumption that identical particles are distinguishable. The expression for the number of quantum states Ω was derived making use of this assumption. In fact, when two identical particles are permuted, the resulting $2!$ states produce no observable effects. Similarly, the permutation of N -particles gives $N!$ states which are not distinct states. So the expression for Ω is larger by a factor $N!$. In quantum mechanics, identical particles are inherently *indistinguishable*. The correct expression for the number of quantum states Ω , taking the *indistinguishability* of identical particles into consideration, should be

$$\Omega = \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!} \quad (\text{indistinguishable particles}) \quad \dots(3.11.5)$$

The expression for entropy now modifies to

$$S = k \ln \Omega = N k \ln \left[\frac{1}{h^3} \left(\frac{V}{N} \right) \left(\frac{E}{N} \right)^{3/2} \left(\frac{4\pi m}{3} \right)^{3/2} \right] + \frac{5}{2} N k \quad \dots(3.11.6)$$

For an ideal gas $E = \frac{3}{2} N k T$... (3.11.7)

Therefore $S = N k \ln \frac{V}{N} + \frac{3}{2} N k \ln \frac{2\pi m k T}{h^2} + \frac{5}{2} N k$... (3.11.8)

Equation (3.11.8) is known as **Sackur-Tetrode** equation.

The thermal de Broglie wavelength λ of particle is

$$\lambda = \frac{h}{\sqrt{2\pi m k T}} \quad \dots(3.11.9)$$

The expression for entropy in terms of λ is

$$S = N k \ln \left[\frac{V}{N \lambda^3} \right] + \frac{5}{2} N k T \quad \dots(3.11.10)$$

The other thermodynamic quantities can be calculated from the expression of entropy.

Helmholts free energy

$$\begin{aligned} F &= E - TS \\ &= -N k T \ln \left[\frac{N e}{V} \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \right] \end{aligned} \quad \dots(3.11.11)$$

The pressure of the gas

$$\begin{aligned} P &= T \left(\frac{\partial S}{\partial V} \right)_{E, N} = - \left(\frac{\partial F}{\partial V} \right)_{T, N} \\ &= \frac{N k T}{V} \end{aligned} \quad \dots(3.11.12)$$

Chemical potential

$$\mu = -kT \left(\frac{\partial S}{\partial N} \right)_{E, V} = kT \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right] \quad \dots(3.11.13)$$

3.12 CANONICAL ENSEMBLE AND CANONICAL DISTRIBUTION

Consider a system, with fixed number of particles N and volume V , immersed in a large heat reservoir at temperature T . The wall of the container in which the system is enclosed are heat conducting. When the equilibrium is reached, the temperature of the system attains the value T . The macroscopic state of the system is specified by temperature T , volume V and number of particles N , all of which have fixed values. The energy of the system assumes different values due to exchange of heat with the heat reservoir. Now imagine a large number of such systems, say $M \rightarrow \infty$, which are in thermal contact with each other and immersed in a large heat reservoir kept at temperature T . The aggregate of all these systems is called **canonical ensemble**. Thus, the entire ensemble is at the same temperature T . Each system of the ensemble has the same values of N , V , and T . Now, the entire canonical ensemble is isolated from the surrounding. All the systems (called elements or components) of the canonical ensemble are at the same temperature but the different systems have different energies.

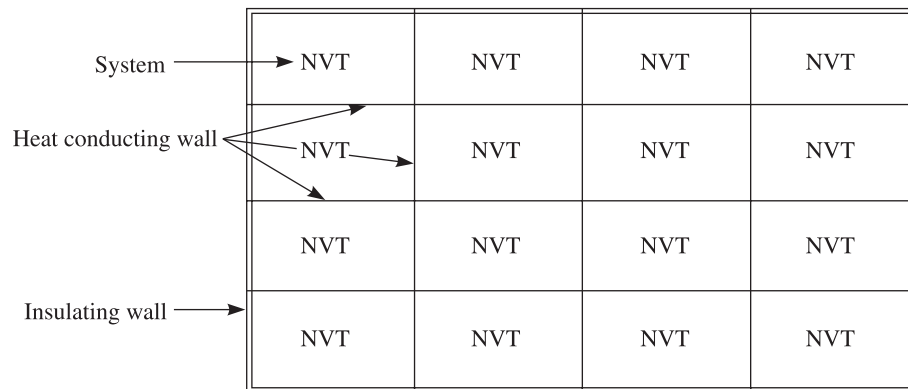


Fig. 3.12.1 Canonical ensemble

In a system consisting of a gas of identical molecules, the individual molecules may be treated as a system and the rest of the molecules as a heat bath. Energy of different molecules (systems) have different values.

Gibbs Canonical Probability Distribution

The Gibbs canonical distribution gives the probabilities of occurrence of different energy states of systems (components) constituting the canonical ensemble. To obtain an expression for this probability consider a system A placed in a heat reservoir, which we denote by A' . Our system of interest A and

the heat reservoir A' constitute a composite system A^* . The composite system is totally isolated and hence it is a microcanonical system. The system A and A' are free to exchange energy but the temperature of the heat reservoir remains constant because of its large size. In thermal equilibrium the temperature of A is the same as that of the heat reservoir. The energy of A is not fixed. The macroscopic state of the system is specified by T, V, N .

We assume that the system A of the ensemble possesses a discrete set of microstates labeled by $1, 2, 3, \dots, r, \dots$ and in these states the system has energy $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_r, \dots$. It is possible that many distinct microstates (quantum states) have the same energy. First we shall consider the non-degenerate system. We also assume that all energy levels are discrete. Let ϵ, ϵ' and ϵ^* denote the energies of the systems A, A' and A^* . The system A has energy ϵ means that its energy lies anywhere between ϵ and $\epsilon + \delta\epsilon$. Similar statements apply to energies of A' and A^* . Since A^* is enclosed within a heat insulating walls, we have

$$\epsilon + \epsilon' = \epsilon^* = \text{constant}$$

$$\text{or} \quad \epsilon' = \epsilon^* - \epsilon \quad \dots(3.12.1)$$

$\Omega_A(\epsilon), \Omega_R(\epsilon')$ and $\Omega_{A^*}(\epsilon^*)$ represent the number of microstates of system A , reservoir R and composite system A^* . The total number of microstates of the composite system A^* is

$$\Omega_{A^*}(\epsilon^*) = \Omega_A(\epsilon)\Omega_R(\epsilon') = \Omega_A(\epsilon)\Omega_R(\epsilon^* - \epsilon)$$

When the system A is in **one** of the accessible state with energy ϵ_r , $\Omega_A(\epsilon_r) = 1$, from above relation it follows that the number of microstates of A^* is equal to the number of microstates of reservoir with energy $\epsilon^* - \epsilon_r$. Thus

$$\Omega_{A^*}(\epsilon^*) = \Omega_R(\epsilon^* - \epsilon_r)$$

According to the fundamental postulate of statistical mechanics, all the accessible states of an **isolated system** are equally probable. Therefore, the probability that the system A is in the state r with energy ϵ_r is proportional to the corresponding number of micro-states accessible to the system A^* .

$$p_r \propto \Omega_R(\epsilon^* - \epsilon_r) \quad \dots(3.12.2)$$

The number $\Omega_R(\epsilon^* - \epsilon_r)$ is a rapidly varying function of energy. It is more convenient to work with more slowly varying function $\ln \Omega_R(\epsilon^* - \epsilon_r)$. Expanding $\ln \Omega_R(\epsilon^* - \epsilon_r)$ about the value ϵ^* , we have

$$\ln \Omega_R(\epsilon^* - \epsilon_r) = \ln \Omega_R(\epsilon^*) - \left(\frac{\partial \ln \Omega_R}{\partial \epsilon'} \right)_{\epsilon'=\epsilon^*} \epsilon_r - \text{higher order terms}$$

Now we assume that our system is a very small in comparison to the reservoir, so that $\epsilon_r \ll \epsilon'$. The higher order terms in the above expansion may be omitted. Therefore,

$$\ln \Omega_R(\epsilon^* - \epsilon_r) = \ln \Omega_R(\epsilon^*) - \beta \epsilon_r \quad \dots(3.12.3)$$

$$\text{where} \quad \beta = \frac{\partial \ln \Omega_R}{\partial \epsilon'} \quad \dots(3.12.4)$$

The derivative is evaluated at fixed energy $\epsilon' = \epsilon^*$. Equation (3.12.3) can be written as

$$\ln \Omega_R(\epsilon^* - \epsilon_r) - \ln \Omega_R(\epsilon^*) = -\beta \epsilon_r$$

or
$$\Omega_R(\epsilon^* - \epsilon_r) = \Omega_R(\epsilon^*) \exp(-\beta \epsilon_r) \quad \dots(3.12.5)$$

$\Omega_R(\epsilon^*)$ is constant (= C say) and is independent of r . Making use of Eqn. (3.12.5) in (3.12.2), we get

$$p_r = C \exp(-\beta \epsilon_r) \quad \dots(3.12.6)$$

The constant C can be determined by the normalization condition that the system must have probability unity of being in some one of its states *i.e.*,

$$\sum_r p_r = 1$$

where the summation is over all states of A irrespective of energy. That is

$$C \sum_r \exp(-\beta \epsilon_r) = 1$$

This gives
$$C = \frac{1}{\sum_r \exp(-\beta \epsilon_r)}$$

Equation (3.12.6) then becomes

$$p_r = \frac{1}{\sum_r \exp(-\beta \epsilon_r)} \exp(-\beta \epsilon_r) = \frac{1}{Z_1} \exp(-\beta \epsilon_r) \quad \dots(3.12.7)$$

where
$$Z_1 = \sum_r \exp(-\beta \epsilon_r) \quad \dots(3.12.8)$$

The summation is performed over the accessible quantum states of the **single system** of the ensemble. Eqn. (3.10.7) is a very general result of fundamental importance in statistical mechanics. It says that ***if a system is in equilibrium at temperature T, the probability that a system selected at random will be found in the state with energy ϵ_r is $p_r = C \exp(-\beta \epsilon_r)$*** . The exponential factor $\exp(-\beta \epsilon_r)$ is called *Boltzmann factor* and the corresponding probability distribution is known as the *canonical distribution*.

The quantity Z_1 defined by $Z_1 = \sum_r \exp(-\beta \epsilon_r)$ is called the *partition function of a single system (component)*.

The quantity β can be shown equal to $1/kT$, k is Boltzmann constant and T is absolute temperature of the system.

It is possible that many different states may have the same energy. Let $g(\epsilon_r)$, called *degeneracy*, be the number of distinct quantum states having the same energy ϵ_r . Then the expression for the partition function becomes

$$Z_1 = \sum_{\text{diff. energy levels}} g(\epsilon_r) e^{-\beta \epsilon_r} \quad \dots(3.12.9)$$

The probability $p(\epsilon_r)$ that a system of canonical ensemble be in a state with energy ϵ_r is then given by

$$p(\epsilon_r) = \frac{1}{Z_1} g(\epsilon_r) \exp(-\beta \epsilon_r) \quad \dots(3.12.10)$$

$$p(\epsilon_r) = \frac{g(\epsilon_r) e^{-\beta \epsilon_r}}{\sum_r g(\epsilon_r) e^{-\beta \epsilon_r}} \quad \dots(3.12.11)$$

So far we have not disclosed the identity of the system of canonical ensemble. The only assumption about A we made was that the system was distinguishable and has size much smaller than the size of the reservoir. In a solid the atoms (microscopic system) are distinguishable by virtue of fixed position. In a dilute gas the molecules are distinguishable because of large inter-molecular separation.

The expression in Eqn.(3.12.10) may be extended to a system composed of molecules, which are distinguishable. Suppose that the gas is in equilibrium at temperature T. If the gas is dilute enough so that the molecules are distinguishable, we can focus attention on a particular molecule of the gas and regard it as a small system (component) in thermal contact with a heat reservoir consisting of all the remaining molecules of the gas. The probability of finding the molecule in any one of its quantum state r where its energy is ϵ_r is then given by the canonical distribution. This result may also be applied to atoms in a solid which are distinguishable by virtue of their fixed (localized) positions at lattice sites.

Another interpretation of probability $p(\epsilon_r)$ is that if $\langle n_r \rangle$ is the mean number of molecules occupying the state with energy level ϵ_r then

$$p(\epsilon_r) = \frac{\langle n_r \rangle}{N}, \quad N = \text{total number of molecules in the gas}$$

Therefore
$$p(\epsilon_r) = \frac{\langle n_r \rangle}{N} = \frac{1}{Z} g(\epsilon_r) e^{-\beta \epsilon_r} \quad \dots(3.12.12)$$

whence
$$\langle n_r \rangle = \frac{N}{Z} g(\epsilon_r) e^{-\beta \epsilon_r} \quad \dots(3.12.13)$$

A system in canonical ensemble in equilibrium with a reservoir has access to all its possible states, and the probability varies exponentially with the energy of the state. The Boltzmann probability

is a probability per quantum state. To get probability per unit range of energy, $f(\epsilon)$ we must multiply p_r by the density of states.

$$f(\epsilon)d\epsilon = p(\epsilon).g(\epsilon)d\epsilon \quad \dots(3.12.14)$$

It is true that $p(\epsilon)$ falls rapidly as energy rises but initially, $g(\epsilon)$ rises even more rapidly, so that the energy distribution has a peak far above the ground state energy, even though the individual states near the peak have extremely low probabilities.

If the energy spectrum of the system (component) is continuous the classical partition function of a distinguishable single system is given by

$$Z_{\text{single system}} = \int \exp(-\epsilon/kT) dq dp \quad \dots(3.12.15)$$

Later we shall see that the partition function of *indistinguishable* N-particle system is given by

$$Z_N = \frac{(Z_{\text{single}})^N}{N!} \quad \dots(3.12.16)$$

Average Energy of particle

If a molecule is found with probability $p(\epsilon_r)$ in a state r of energy ϵ_r , then its mean energy is given by

$$\langle \epsilon \rangle = \sum_r p_r \epsilon_r = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}} \quad (\text{single particle}) \quad \dots(3.12.17)$$

Now,
$$\sum_r \epsilon_r e^{-\beta \epsilon_r} = - \sum_r \frac{\partial}{\partial \beta} e^{-\beta \epsilon_r} = - \frac{\partial}{\partial \beta} \left(\sum_r e^{-\beta \epsilon_r} \right) = - \frac{\partial Z_1}{\partial \beta}$$

Therefore
$$\langle \epsilon \rangle = - \frac{1}{Z_1} \frac{\partial Z_1}{\partial \beta} = - \frac{\partial \ln Z_1}{\partial \beta} \quad \dots(3.12.18)$$

Hence total energy of the **N-particle system** is

$$E = N \langle \epsilon \rangle = -N \frac{\partial \ln Z_1}{\partial \beta} = NkT^2 \frac{\partial \ln Z_1}{\partial T} \quad \dots(3.12.19)$$

3.13 THE EQUIPARTITION THEOREM

Consider a system whose state is described classically in terms of f coordinates $q_1, \dots, q_f$ and f corresponding momenta $p_1, \dots, p_f$. Let the energy of the system be function of these coordinates. For most of the systems, which we shall be dealing with, the energy can be written as

$$E(q, p) = \epsilon_i(p_i) + \epsilon'(q_1, \dots, q_f, p_1, \dots, p_f) \quad \dots(3.13.1)$$

Where the first term is function of the particular momentum p_i only and the second term may depend on all coordinates and momenta except p_i . For example, the energy of a harmonic oscillator can be written as

$$E = \epsilon_{\text{kinetic}} + \epsilon_{\text{potential}} = \frac{p^2}{2m} + \frac{1}{2} \alpha q^2$$

The first term depends on momentum p only and the second term on coordinate q , α is force constant. Suppose that the system under consideration is in thermal equilibrium with a heat reservoir at temperature T . The probability of finding the system with its coordinates lying in the range q and $q + dq$ and momenta in the range p and $p + dp$ is given by canonical distribution

$$P(q, p) = \frac{e^{-\beta E(q, p)}}{\int e^{-\beta E(q, p)} dq dp} \quad \dots(3.13.2)$$

The mean value of energy $\epsilon_i(p_i)$ is given by

$$\langle \epsilon_i \rangle = \frac{\int e^{-\beta E(q, p)} \epsilon_i(p_i) dq dp}{\int e^{-\beta E(q, p)} dq dp} \quad \dots(3.13.3)$$

where the integrals extend over all possible values of all coordinates $[q]$ and momenta $[p]$. Substituting the expression for E from Eqn. (3.13.1) in (3.13.3), we have

$$\begin{aligned} \langle \epsilon_i \rangle &= \frac{\int e^{-\beta(\epsilon_i + \epsilon')} \epsilon_i dq dp}{\int e^{-\beta(\epsilon_i + \epsilon')} dq dp} \\ &= \frac{\int \epsilon_i e^{-\beta \epsilon_i} dp_i \int e^{-\beta \epsilon'} dq dp}{\int e^{-\beta \epsilon_i} dp_i \int e^{-\beta \epsilon'} dq dp} \end{aligned}$$

The primes on the last integrals indicate that these integrals extend over all the coordinates $[q]$ and momenta $[p]$ except p_i . The primed integrals in the numerator and denominator are equal and cancel out. Therefore

$$\begin{aligned} \langle \epsilon_i \rangle &= \frac{\int \epsilon_i e^{-\beta \epsilon_i} dp_i}{\int e^{-\beta \epsilon_i} dp_i} \\ &= \frac{-\frac{\partial}{\partial \beta} \left[\int e^{-\beta \epsilon_i} dp_i \right]}{\int e^{-\beta \epsilon_i} dp_i} \end{aligned}$$

$$= -\frac{\partial}{\partial \beta} \left[\ln \int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right] \quad \dots(3.13.4)$$

If ϵ_i is a quadratic function of p_i then

$$\epsilon_i = a p_i^2 \quad \text{where } a \text{ is a constant.}$$

[For example the kinetic energy of a particle is quadratic function of momentum $\epsilon = p^2/2m$.]

Then the integral in Eqn. (3.13.4) becomes

$$\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i = \int_{-\infty}^{\infty} e^{-a\beta p_i^2} dp_i = \frac{1}{\sqrt{\beta}} \int_{-\infty}^{\infty} e^{-ax^2} dx, \quad \text{where } x = \sqrt{\beta} p_i$$

$$\text{Hence} \quad \ln \left[\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right] = -\frac{1}{2} \ln \beta + \ln \left(\int_{-\infty}^{\infty} e^{-ax^2} dx \right)$$

The last integral does not involve β at all and its derivative with respect to β is zero. So we are left with

$$\langle \epsilon_i \rangle = -\frac{\partial}{\partial \beta} \left\{ -\frac{1}{2} \ln \beta \right\} = \frac{1}{2\beta} = \frac{1}{2} kT \quad \dots(3.13.5)$$

Thus, we arrive at the conclusion that if a system is in thermal equilibrium at temperature T , then each independent quadratic term in its energy contributes a mean value of energy equal to $1/2 kT$ to the total energy of the system. This statement is known as the *theorem of equipartition of energy*.

3.14 ENTROPY IN TERMS OF PROBABILITY

The entropy is connected with the fact that in most thermodynamic states the system is not in a definite quantum state, but is spread over a large number of states according to some probability distribution.

To define entropy in terms of probability distribution consider an ensemble of very large number M ($M \rightarrow \infty$) of systems. Let m_1 systems be in energy state ϵ_1 , m_2 systems in energy state ϵ_2 , and so on. The statistical weight Ω_M of the ensemble or the number of ways in which the systems are distributed among the various energy states is given by

$$\Omega_M \{m_i\} = \frac{M!}{m_1! m_2! \dots} = \frac{M!}{\prod_r m_r!} \quad \dots(3.14.1)$$

The probability p_r that a system chosen at random will be in the state r with energy ϵ_r is

$$p_r = \frac{m_r}{M} \quad \dots(3.14.2)$$

whence $m_r = M p_r$. The entropy of the ensemble is

$$\begin{aligned}
 S_M = k \ln \Omega_M &= k \left[\ln M! - \sum_r \ln m_r! \right] = k \left[M \ln M - M - \sum_r m_r \ln m_r - m_r \right] \\
 &= k \left[M \ln M - \sum_r m_r \ln m_r \right] = k \left[M \ln M - \sum_r M p_r \ln M p_r \right] \\
 &= k \left[M \ln M - M \left(\sum_r p_r \right) (\ln M + M p_r \ln p_r) \right] \\
 &= -kM \left(\sum_r p_r \ln p_r \right) \quad \dots(3.14.3)
 \end{aligned}$$

The entropy is an extensive quantity and therefore entropy of a single system is

$$\begin{aligned}
 S &= \frac{S_M}{M} \\
 &= -k \sum_r p_r \ln p_r \quad \dots(3.14.4)
 \end{aligned}$$

3.15 ENTROPY IN TERMS OF SINGLE PARTICLE PARTITION FUNCTION Z_1

By definition, the entropy of a *single system* is given by

$$\begin{aligned}
 S &= -k \sum_r p_r \ln p_r \\
 &= -k \sum_r p_r (-\beta \epsilon_r - \ln Z_1) \quad \because \quad p_r = \frac{e^{-\beta \epsilon_r}}{Z_1} \\
 &= k \beta \left(\sum_r p_r \epsilon_r \right) + k \ln Z_1 \left(\sum_r p_r \right) \quad \because \sum_r p_r = 1 \\
 &= \frac{\bar{\epsilon}}{T} + k \ln Z_1 \quad \dots(3.15.1)
 \end{aligned}$$

$$\text{or} \quad -kT \ln Z_1 = \bar{E} - TS \quad \dots(3.15.2)$$

DISTRIBUTION FUNCTIONS

4.1 MAXWELL-BOLTZMANN DISTRIBUTION

Consider a system of N identical *distinguishable* non-interacting particles confined to move freely in a vessel of volume V . The system is in equilibrium at temperature T . The total energy of the system is E . A monatomic ideal gas containing N molecules in a container of volume V is an example of our system. A macrostate of the system is specified by specifying how the total energy E of the system is distributed among N particles.

Let $\epsilon_1, \epsilon_2, \dots, \epsilon_i, \dots$ be the allowed single-particle energy levels and $g_1, g_2, \dots, g_i, \dots$ the degeneracies of these energy levels respectively. The description of a macrostate is given by specifying the number of particles in each energy level ϵ_i . Let

n_1 be the number of particles in energy level ϵ_1 with degeneracy g_1

n_2 be the number of particles in energy level ϵ_2 with degeneracy g_2

.....

.....

.....

.....

n_i be the number of particles in energy level ϵ_i with degeneracy g_i and so on.

The set of numbers $\{n_1, n_2, \dots, n_i\}$ defines a macrostate. Our objective is to determine $n_1, n_2, \dots, n_i$. In classical (Maxwell-Boltzmann) statistics all the particles are assumed to be identical and *distinguishable* from one another. We wish to find the number of different arrangements or microstates corresponding to a macrostate. The required number of accessible microstates is equal to the number of ways a given macrostate is realized by arranging the particles in different states. Now consider the i th energy level, which is g_i fold degenerate. Each of the n_i particles can be placed in the g_i states in g_i different ways. The number of different ways of arranging n_i particles in g_i states is equal to the product

$$g_i \cdot g_i \cdot g_i \cdot g_i \cdot \dots \dots \dots (n_i \text{ factors}) = g_i^{n_i}.$$

This number $g_i^{n_i}$ gives number of microstates available to n_i particles, each having energy ϵ_i . The number of microstates available to the system such that n_i particles are in energy level ϵ_1 , n_2 are in energy level ϵ_2 ...and so on, is given by the product

$$g_1^{n_1} \cdot g_2^{n_2} \dots g_i^{n_i} = \prod_i g_i^{n_i}$$

Now we must take into account the possible permutations of the particles among the different energy levels. The number of permutations possible for N particles is $N!$. In other words, N particles can be arranged in $N!$ different sequences. Of these permutations some are irrelevant. When more than one particle is in an energy level, permuting them among themselves has no significance in this situation. Thus the n_i particles in the i th level contribute $n_i!$ irrelevant permutations. If there are n_1 particles in level 1, n_2 particles in level 2 and so on, there are $n_1! n_2! n_3! \dots$ irrelevant permutations. The number of ways N particles can be divided into groups of $n_1, n_2, n_3, \dots$ or the thermodynamic probability of a macrostate $\{n_1, n_2, \dots, n_i\}$ is

$$\frac{N!}{n_1! n_2! n_3! \dots} \quad \text{or} \quad \frac{N!}{\prod_i n_i!}$$

The total number of distinct ways (accessible microstates) in which N particles can be distributed among possible energy levels such that n_1 particles are in level ϵ_1 with degeneracy g_1 , n_2 are in level ϵ_2 with degeneracy $g_2 \dots$ and so on, is

$$\Omega_{\text{MB}} = \frac{N!}{n_1! n_2! n_3! \dots} (g_1)^{n_1} (g_2)^{n_2} \dots = N! \prod_i \left(\frac{g_i^{n_i}}{n_i!} \right) \quad \dots(4.1.1)$$

According to the principle of equal a priori probabilities, all the microstates are equally probable. The most probable macro state specified by $n_1, n_2, \dots$ is one which corresponds to the maximum number of micro states. So to obtain most probable distribution we must maximize Ω_{MB} taking care of the conditions that the total number of particles and the total energy of the system is constant. These two restrictions are expressed as

$$n_1 + n_2 + n_3 + \dots = \sum_i n_i = N \quad \dots(4.1.2)$$

$$n_1 \epsilon_1 + n_2 \epsilon_2 + \dots = \sum_i n_i \epsilon_i = E \quad \dots(4.1.3)$$

Mathematically it is more convenient to maximize $\ln \Omega_{\text{MB}}$ than Ω . So we first simplify $\ln \Omega_{\text{MB}}$.

Now,
$$\ln \Omega_{\text{MB}} = \ln N! + \sum_i (n_i \ln g_i - \ln n_i!)$$

Making use of Stirling formula $\ln n! = n \ln n - n$, we have

$$\ln \Omega_{\text{MB}} = N \ln N - N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i + \sum_i n_i$$

$$= N \ln N + \sum_i n_i \ln g_i - \sum_i n_i \ln n_i \quad \dots(4.1.4)$$

Since $\sum n_i = N$.

The most probable distribution is one for which Ω_{MB} or $\ln \Omega_{\text{MB}}$ is maximum. In other words, a small change δn_i in any of the n_i 's has no effect on the value of Ω_{MB} . We assume that n_i are continuous, so the condition of maximum $\ln \Omega'_{\text{MB}}$ becomes

$$\frac{\partial \ln \Omega_{\text{MB}}}{\partial n_i} = 0 \quad \text{for each } n_i$$

If the change in $\ln \Omega_{\text{MB}}$ corresponding to change δn_i in n_i is $\delta \ln \Omega_{\text{MB}}$ then

$$\delta \ln \Omega_{\text{MB}} = \sum_i \ln g_i \delta n_i - \sum_i n_i \delta \ln n_i - \sum_i \ln n_i \delta n_i = 0$$

since N is constant. Now $\delta \ln n_i = \frac{1}{n_i} \delta n_i$. So

$$\delta \ln \Omega_{\text{MB}} = \sum_i \ln g_i \delta n_i - \sum_i \delta n_i - \sum_i \ln n_i \delta n_i = 0 \quad \dots(4.1.5)$$

Since the total number of particles is constant, $\sum_i \delta n_i = 0$.

$$\text{Therefore,} \quad \delta \ln \Omega_{\text{MB}} = \sum_i \ln g_i \delta n_i - \sum_i \ln n_i \delta n_i = 0 \quad \dots(4.1.6)$$

In order to incorporate the conditions of conservation of number of particles and of energy in above equation we use Lagrange's method of undetermined multipliers. From Eqns. (4.1.2) and (4.1.3) we have

$$\sum_i \delta n_i = \delta n_1 + \delta n_2 + \dots = 0 \quad \dots(4.1.7)$$

$$\sum_i \epsilon_i \delta n_i = \epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \dots = 0 \quad \dots(4.1.8)$$

Multiplying Eqn. (4.1.7) by $-\alpha$ and Eqn. (4.1.8) by $-\beta$, where α and β are quantities independent of n_i , and adding them to Eqn. (4.1.6) we have

$$\sum_i (-\ln n_i + \ln g_i - \alpha - \beta \epsilon_i) \delta n_i = 0 \quad \dots(4.1.9)$$

Equation (4.1.9) will hold if the quantity in parentheses vanishes for each value of i . Hence

$$\begin{aligned} -\ln n_i + \ln g_i - \alpha - \beta \epsilon_i &= 0 \\ n_i &= g_i e^{-\alpha} e^{-\beta \epsilon_i} \end{aligned} \quad \dots(4.1.10)$$

The ratio n_i/g_i represents the average number of particles per state of the system and is called energy distribution function $f_{\text{MB}}(\epsilon)$. *The distribution function represents the average number of particles in each of state of energy ϵ or the probability of occupancy of each of state of energy ϵ .*

$$f_{\text{MB}}(\epsilon) = \frac{n_i}{g_i} = e^{-\alpha} e^{-\beta\epsilon} \quad \dots(4.1.11)$$

In other words $f_{\text{MB}}(\epsilon)$ gives the probability that a particle, selected randomly from the system, will have its energy ϵ .

This is the classical (MB) distribution function. It is applicable to system whose constituent particles are *distinguishable* and *don't obey Pauli's exclusion principle*. It is the most probable distribution of particles among the accessible energy levels at equilibrium for a system of constant total energy. For a system comprising of large number of particles the most probable distribution describes the actual behaviour of the system. In deriving MB distribution function no assumption regarding the nature of energy was made so it is valid for translational, rotational, vibrational and electronic.

Later we shall prove that the quantity β appearing in the distribution function is related to the temperature T of the system through the relation

$$\beta = \frac{1}{kT} \quad \dots(4.1.12)$$

where k is Boltamann constant. So the MB distribution can be written as

$$f_{\text{MB}}(\epsilon) = e^{-\alpha} e^{-\epsilon/kT} \quad \dots(4.1.13)$$

The constant α may be expressed in terms of total number of particles N .

Since
$$N = \sum n_i = e^{-\alpha} \sum_i g_i e^{-\epsilon_i/kT}$$

Therefore
$$e^{-\alpha} = \frac{N}{\sum_i g_i e^{-\epsilon_i/kT}} \quad \dots(4.1.14)$$

The quantity $\sum_i g_i e^{-\epsilon_i/kT}$ plays a fundamental role in statistical mechanics. It was first introduced by Boltzmann who called it “Zustandsumme” or sum over states. It is called single particle *partition function* Z_1 .

$$Z_1 = \sum_i g_i e^{-\epsilon_i/kT} \quad \dots(4.1.15)$$

In terms of single particle partition function Z_1 the MB distribution function is given by

$$n_i = \frac{N}{Z} g_i e^{-\epsilon_i/kT}, \quad e^{-\alpha} = \frac{N}{Z_1} \quad \dots(4.1.16)$$

If the energy levels of the system are very close together, such as those of molecules in a gas, the $g(\epsilon)$ is replaced by $g(\epsilon) d\epsilon$, which represents the number of states with energies between ϵ and $\epsilon + d\epsilon$. The number of particles occupying the states in the energy range $d\epsilon$ about ϵ is

$$n(\epsilon)d\epsilon = f_{\text{MB}}(\epsilon)g(\epsilon)d\epsilon \quad \dots(4.1.17)$$

For a system of free particles each of mass m , enclosed in a vessel of volume V , the number of states in the energy range $d\epsilon$ about ϵ is

$$g(\epsilon)d\epsilon = g_s \cdot \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \quad \dots(4.1.18)$$

where $g_s = (2s + 1)$ is spin degeneracy, s = spin of the particle. For electron $s = 1/2$, $g_s = 2$. For spin 0 particle $g_s = 1$. The function $g(\epsilon)$ is called *density of states*.

The expression for partition for a gas, with continuous energy levels, is obtained by replacing the summation sign by integral sign.

$$Z_1 = \int g(\epsilon) e^{-\beta\epsilon} d\epsilon \quad \dots(4.1.19)$$

The value of parameter $e^{-\alpha}$ can be determined as follows:

$$\begin{aligned} e^{-\alpha} &= \frac{N}{Z_1} = \frac{N}{\int g(\epsilon) e^{-\beta\epsilon} d\epsilon} = \frac{N}{g_s \left(\frac{2\pi V}{h^3} (2m)^{3/2} \right) \int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon} \\ &= \frac{N(\beta)^{3/2}}{g_s \left(\frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty x^{1/2} e^{-x} dx \right)}, \quad x = \beta\epsilon, dx = \beta d\epsilon \\ &= \frac{N}{g_s \left(\frac{V}{h^3} \right) \left(\frac{\beta}{2\pi m} \right)^{3/2}} \quad \text{where} \quad \int_0^\infty x^{1/2} e^{-x} dx = \Gamma 3/2 = \frac{1}{2} \sqrt{\pi} \\ &= \frac{N}{g_s V} \left(\frac{\beta h^2}{2\pi m} \right)^{3/2} \quad \dots(4.1.20) \end{aligned}$$

So $e^{-\alpha}$ is temperature dependent ($\beta = 1/kT$).

Substituting the value of $e^{-\alpha}$ in the expression for MB distribution we have

$$f_{\text{MB}}(\epsilon) = \frac{N}{g_s V} \left(\frac{\beta h^2}{2\pi m} \right)^{3/2} e^{-\beta\epsilon}, \quad \beta = \frac{1}{kT} \quad \dots(4.1.21)$$

The number of particles occupying the energy states in the interval $d\epsilon$ at ϵ in a N-particle system in equilibrium at temperature T is

$$n(\epsilon)d\epsilon = f_{\text{MB}}(\epsilon)g(\epsilon)d\epsilon = \frac{2\pi N}{(\pi/\beta)^{3/2}} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon, \quad \beta = \frac{1}{kT} \quad \dots(4.1.22a)$$

$$= 2\pi N \left(\frac{1}{\pi kT} \right)^{3/2} \epsilon^{1/2} \exp(-\beta\epsilon) d\epsilon \quad \dots(4.1.22b)$$

Evaluation of β

The total energy of the N-particle system is

$$\begin{aligned} E &= \int_0^\infty \epsilon n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi/\beta)^{3/2}} \int_0^\infty \epsilon^{3/2} e^{-\beta\epsilon} d\epsilon \\ &= \frac{2\pi N}{(\pi/\beta)^{3/2}} \cdot \frac{1}{\beta^{5/2}} \int_0^\infty x^{3/2} e^{-x} dx, \quad x = \beta\epsilon, \quad dx = \beta d\epsilon \\ &= \frac{2N}{\sqrt{\pi}} \left(\frac{1}{\beta} \right) \Gamma(5/2) \\ &= \frac{2N}{\sqrt{\pi}} \left(\frac{1}{\beta} \right) \left(\frac{3}{4} \sqrt{\pi} \right) \\ &= \frac{3N}{2\beta} \quad \dots(4.1.23) \end{aligned}$$

From kinetic theory we know that, the total translational energy of an ideal gas containing N molecules is

$$E = \frac{3}{2} NkT \quad \dots(4.1.24)$$

Comparison of these two expressions gives

$$\beta = \frac{1}{kT} \quad \dots(4.1.25)$$

4.2 HEAT CAPACITY OF AN IDEAL GAS

The total energy of one mole of an ideal gas is

$$E = \frac{3}{2} N_A kT = \frac{3}{2} RT, \quad R = N_A k = \text{universal gas constant} \quad \dots(4.2.1)$$

The molar heat capacity at constant volume is

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{3}{2} R. \quad \dots(4.2.2)$$

4.3 MAXWELL'S SPEED DISTRIBUTION FUNCTION

Now we shall derive Maxwell speed distribution for a perfect classical gas. To obtain the required distribution function we must convert the energy distribution into appropriate speed distribution. In a perfect gas of free molecules possessing no internal degree of freedom (such as monatomic molecule) all the energy resides in the form of translational kinetic energy of molecules. So

$$\epsilon = \frac{1}{2} m v^2, \quad d\epsilon = m v dv$$

In terms of velocity, the Maxwell distribution function becomes

$$\begin{aligned} n(v) dv &= \frac{2\pi N}{(\pi kT)^{3/2}} \left(\frac{1}{2} m v^2 \right)^{1/2} e^{-mv^2/2kT} m v dv \\ &= 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \end{aligned} \quad \dots(4.3.1)$$

$$\text{or} \quad f(v) dv = \frac{n(v)}{N} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \quad \dots(4.3.2)$$

The function $f(v)$ gives the fraction of all molecules having speeds in the interval dv about v . In other words, $f(v)$ represents the probability that a molecule selected at random from the gas will have its speed in the interval dv about v .

Now suppose that we wish to know how many molecules of the gas have velocities such that the x -component of velocity is in a range dv_x about v_x , the y -component is in a range dv_y about v_y , and z -component is in a range dv_z about v_z . This number of molecules is in a rectangular volume element $dv_x dv_y dv_z$ in velocity space centered on the value (v_x, v_y, v_z) . We shall call this number $n(v_x, v_y, v_z) dv_x dv_y dv_z$.

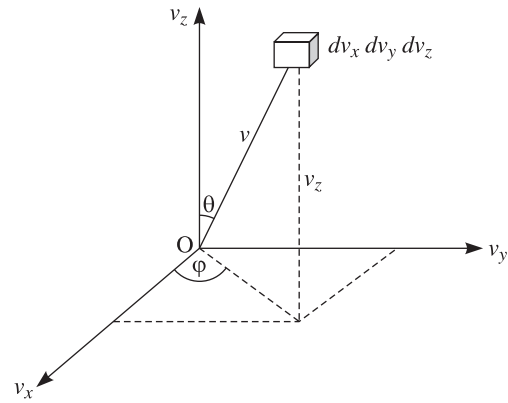


Fig. 4.3.1 Velocity space for molecules

The Maxwell-Boltzmann energy distribution function is

$$f(\epsilon) = \frac{N}{g_s V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} e^{-\epsilon / k T} \quad \dots(4.3.3)$$

For monatomic spin less molecule $g_s = 1$.

Therefore

$$f(v_x, v_y, v_z) = \frac{N}{g_s V} \left(\frac{h^2}{2\pi m k T} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2) / 2 k T} \quad \dots(4.3.4)$$

Let us find the expression for the density of states $g(v_x, v_y, v_z)$. We know that

$$g(p_x, p_y, p_z) dp_x dp_y dp_z = \frac{V}{g_s h^3} dp_x dp_y dp_z$$

$$g(v_x, v_y, v_z) dv_x dv_y dv_z = \frac{V m^3}{g_s h^3} dv_x dv_y dv_z \quad \dots(4.3.5)$$

Now $n(v_x, v_y, v_z) dv_x dv_y dv_z = f(v_x, v_y, v_z) g(v_x, v_y, v_z) dv_x dv_y dv_z$

$$= N \left(\frac{m}{2\pi k T} \right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2) / 2 k T} dv_x dv_y dv_z \quad \dots(4.3.6)$$

Expression for $n(v_x)$

The number of molecules whose x -component of velocity lies in a range dv_x about v_x regardless of what values the y -component and z -component of velocity may have, is given by

$$\begin{aligned} n(v_x) dv_x &= \int_{v_y = -\infty}^{\infty} \int_{v_z = -\infty}^{\infty} n(v_x, v_y, v_z) dv_x dv_y dv_z \\ &= N \left(\frac{m}{2\pi k T} \right)^{3/2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-m(v_x^2 + v_y^2 + v_z^2) / 2 k T} dv_x dv_y dv_z \\ &= N \left(\frac{m}{2\pi k T} \right)^{3/2} \left(\int_{-\infty}^{\infty} e^{-\frac{1}{2} m v_y^2 / k T} dv_y \int_{-\infty}^{\infty} e^{-\frac{1}{2} m v_z^2 / k T} dv_z \right) \left(e^{-\frac{1}{2} m v_x^2 / k T} dv_x \right) \\ &= N \left(\frac{m}{2\pi k T} \right)^{3/2} \left(\frac{2\pi k T}{m} \right)^{1/2} \left(\frac{2\pi k T}{m} \right)^{1/2} e^{-\frac{1}{2} m v_x^2 / k T} dv_x \end{aligned}$$

$$= N \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-mv_x^2/2kT} dv_x \quad \dots(4.3.7)$$

Table of some useful definite integrals.

$$f(n) = \int_0^{\infty} x^n \exp(-\alpha x^2) dx$$

odd n	$f(n)$	even n	$f(n)$
1	$\frac{1}{2\alpha}$	0	$\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$
3	$\frac{1}{2\alpha^2}$	2	$\frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}}$
5	$\frac{1}{\alpha^3}$	4	$\frac{3}{8} \sqrt{\frac{\pi}{\alpha^5}}$
7	$\frac{3}{\alpha^4}$	6	$\frac{15}{16} \sqrt{\frac{\pi}{\alpha^7}}$

A plot of the distribution functions $n(v)$ and $n(v_x)$ as functions of velocity coordinates is shown in the Fig. (4.3.2).

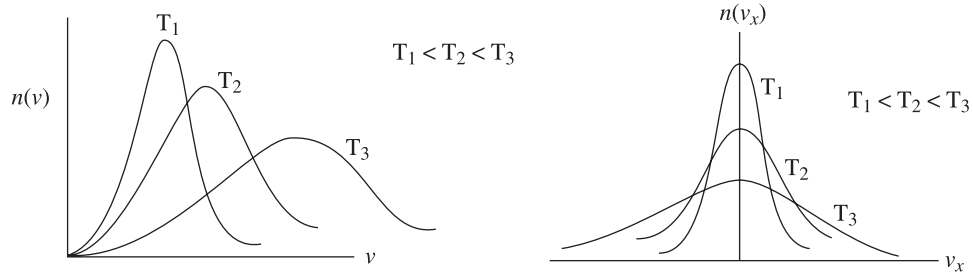


Fig. 4.3.2 Velocity distribution functions at different temperatures

Average velocity $\langle v \rangle$

The average velocity $\langle v \rangle$ of a particle in M-B distribution is given by

$$\langle v \rangle = \frac{\int_0^{\infty} v n(v) dv}{\int_0^{\infty} n(v) dv} = \frac{4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2kT} dv}{N}$$

$$= \sqrt{\frac{8kT}{m\pi}} \quad \dots(4.3.8)$$

Where we have used the standard result: $\int_0^{\infty} x^3 e^{-\alpha x^2} dx = \frac{1}{2\alpha^2}$, where $\alpha = \frac{m}{2kT}$.

Root mean square speed v_{rms}

The root mean square speed is defined by

$$\begin{aligned} v_{rms}^2 &= \frac{1}{N} \int_0^{\infty} v^2 n(v) dv = \frac{1}{N} \left[4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^4 e^{-mv^2/2kT} dv \right] \\ &= \sqrt{\frac{3kT}{m}} \quad \dots(4.3.9) \end{aligned}$$

Where we have used the standard result: $\int_0^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{8\alpha^2} \sqrt{\frac{\pi}{\alpha}}$, $\alpha = \frac{m}{2kT}$.

Most probable speed v_{mp}

The most probable speed corresponds to the maximum value of $n(v)$. Now

$$n(v) = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$

The maximum value of $n(v)$ corresponds to the speed that satisfies the equation

$$\begin{aligned} \frac{dn(v)}{dv} &= 0 \\ \frac{d}{dv} \left(v^2 e^{-mv^2/2kT} \right) &= 0 \\ v = v_{mp} &= \sqrt{\frac{2kT}{m}} \quad \dots(4.3.10) \end{aligned}$$

Therefore

$$\begin{aligned} v_{mp} : \langle v \rangle : v_{rms} &= \sqrt{\frac{2kT}{m}} : \sqrt{\frac{8kT}{m\pi}} : \sqrt{\frac{3kT}{m}} \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ &= 1 : 1.13 : 1.22 \end{aligned}$$

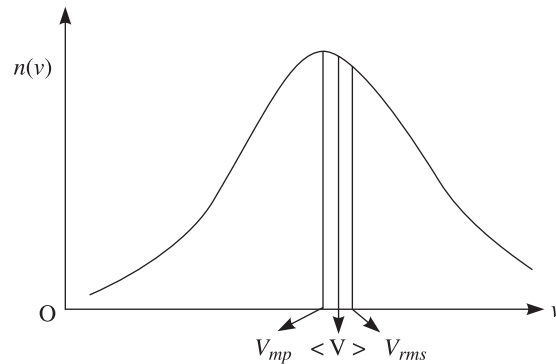


Fig. 4.3.3 Three kinds of velocities associated with Maxwell distribution

4.4 FERMI-DIRAC STATISTICS

Many properties of solid materials such as thermal and electrical conductivity, magnetic properties, specific heats etc. are related to the electron energy states. The understanding of these properties requires the distribution of electrons, which are fermions, in various states. The distribution function for electrons must satisfy two requirements: (1) electrons are indistinguishable particles *i.e.*, it is not possible to label them as electron number 1, number 2 and so on (2) electrons obey Pauli's exclusion principle, which states that no quantum state may be occupied by more than one electron. The distribution function that results from these two considerations was first developed by Fermi and Dirac in 1927. In fact all the particles, which have half odd integral spin ($1/2, 3/2, 5/2, \dots$), obey exclusion principle, are described by F-D statistics. These particles are called fermions.

Consider a system composed of N fermions with total energy E . An assembly of non-interacting fermions is called fermi gas or electron gas if the fermions are electrons. The assembly of free electrons in a metal is a well-known example of fermi gas.

Let the allowed energy levels and the associated degeneracies of the system be $\epsilon_1, \epsilon_2, \dots, \epsilon_i$ and $g_1, g_2, \dots, g_i$ respectively. The occupation numbers of these energy levels are $n_1, n_2, \dots, n_i$ respectively. The most detailed description that is possible in principle is to specify the number of electrons (always 0 or 1) in each of the g_i states of energy ϵ_i . (Because of indistinguishability of electrons, it is meaningless to specify which electrons are in these states.) A macro state is specified by set of numbers $\{n_1, n_2, \dots, n_i\}$. A microstate is specified by specifying which of the g_i states corresponding to each ϵ_i are occupied by electrons.

First suppose that the electrons are distinguishable. Consider a macro state $\{n_1, n_2, \dots, n_i\}$. Here n_i represents the number of electrons in the energy level ϵ_i . We want to calculate the number of ways in which n_i electrons can be placed in g_i states associated with the energy level ϵ_i . The first electron can be placed in any one of the g_i states. This can be done in g_i ways. For each of these choices, the second electron can be placed in $(g_i - 1)$ ways, for each of these, there are $(g_i - 2)$ ways for the third electron and so on. For the last electron there would be $g_i - (n_i - 1)$ ways. The total number of possible ways of placing n_i electrons in the g_i states would be the product of all these

factors. This is equal to

$$g_i(g_i - 1)(g_i - 2) \dots (g_i - n_i + 1)$$

or

$$= \frac{g_i!}{(g_i - n_i)!}$$

Since the electrons are indistinguishable, permuting the n_i electrons among the various states does not produce a physically different state of the system. There are $n_i!$ ways of permuting the particles among themselves in any given arrangement of electrons. These $n_i!$ ways don't count as separate arrangements. So, we over counted the number of possible arrangement by a factor $n_i!$. The number of physically different ways of putting n_i electrons into g_i states of energy ε_i is

$$\Omega_i = \frac{g_i!}{n_i!(g_i - n_i)!} \quad \dots(4.4.1)$$

The number of microstates corresponding to a given macrostate is obtained by multiplying the factors given in above expression. Thus, the number Ω of microstates corresponding to the macrostate specified by the set of occupation numbers $\{n_1, n_2, \dots, n_i\}$ is

$$\Omega = \frac{g_1!}{n_1!(g_1 - n_1)!} \cdot \frac{g_2!}{n_2!(g_2 - n_2)!} \dots = \Omega_1 \Omega_2 \dots = \prod_i \Omega_i \quad \dots(4.4.2)$$

$$\Omega = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \quad \dots(4.4.3)$$

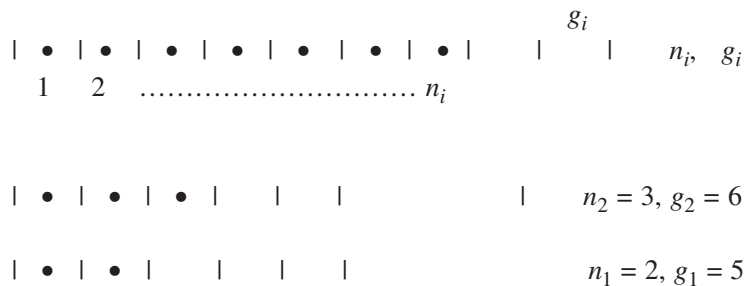


Fig. 4.4.1

According to the fundamental principle of statistical mechanics, for a system of given total energy all the microstates are equally probable. The most probable state of the system is the most probable macrostate, which corresponds to the maximum number of microstates Ω . Maximizing Ω is equivalent to maximizing $\ln \Omega$. In calculation it is more convenient to use $\ln \Omega$ than Ω . So we first calculate $\ln \Omega$.

$$\ln \Omega = \sum_i [\ln g_i! - \ln(g_i - n_i)! - n_i!]$$

Using Stirling's approximation $\ln n! = n \ln n - n$ we have

$$\begin{aligned}\ln \Omega &= \sum_i [g_i \ln g_i - g_i - (g_i - n_i) \ln (g_i - n_i) + (g_i - n_i) - n_i \ln n_i + n_i] \\ \ln \Omega &= \sum_i [g_i \ln g_i - (g_i - n_i) \ln (g_i - n_i) - n_i \ln n_i] \quad \dots(4.4.4)\end{aligned}$$

The most probable distribution is one for which a small change δn_i in any of n_i has no effect on the value of Ω . We assume that n_i are continuous, so the condition of maximum $\ln \Omega$ becomes

$$\frac{\partial \ln \Omega}{\partial n_i} = 0 \quad \text{for each } n_i.$$

If the change in $\ln \Omega$ corresponding to change δn_i in n_i is $\delta \ln \Omega$ then

$$\delta \ln \Omega = \sum_i [\ln (g_i - n_i) - \ln n_i] \delta n_i = 0 \quad \dots(4.4.5)$$

Note that n_i are not independent, but they are related through the conditions that the total number of particle is constant.

$$\sum n_i = N = \text{constant} \quad \dots(4.4.6)$$

And the total energy of the system is constant.

$$\sum n_i \epsilon_i = E = \text{constant} \quad \dots(4.4.7)$$

From these two equations, we have

$$\sum \delta n_i = 0 \quad \dots(4.4.8)$$

and

$$\sum \epsilon_i \delta n_i = 0 \quad \dots(4.4.9)$$

In order to incorporate the conditions of conservation of number of particles and of energy in Eqn. (4.4.5) we use Lagrange method of undetermined multipliers. To do so, we multiply Eqn. (4.4.8) by $-\alpha$ and Eqn. (4.4.9) by $-\beta$ and add them to Eqn. (4.4.5). Here α and β are independent of n_i .

$$\sum_i [\ln (g_i - n_i) - \ln n_i - \alpha - \beta \epsilon_i] \delta n_i = 0$$

$$\ln (g_i - n_i) - \ln n_i - \alpha - \beta \epsilon_i = 0$$

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} + 1} \quad \dots(4.4.10)$$

The ration n_i/g_i is called F-D distribution function and is denoted by f_{FD} .

$$f_{\text{FD}}(\epsilon) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha} e^{\beta \epsilon} + 1} \quad \dots(4.4.11)$$

The function $f_{\text{FD}}(\epsilon)$ is the average number of electrons per quantum state of energy ϵ . It also represents the probability that a state of energy ϵ is occupied. The quantity β is $1/kT$, where T is temperature of the system. The value of α is determined by the normalization condition

$$\sum_i n_i = N = \sum_i \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1}$$

It is customary to express α in terms of another constant μ , called chemical potential. (In solid state physics μ is called Fermi level ϵ_F).

$$\alpha = -\beta\mu = -\beta\epsilon_F \quad \text{or} \quad \alpha = -\frac{\mu}{kT} = -\frac{\epsilon_F}{kT} \quad \dots(4.4.12)$$

In terms of chemical potential μ and Fermi energy ϵ_F the FD distribution becomes

$$f_{\text{FD}}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad \dots(4.4.13)$$

For systems with continuous energy levels, the number of fermions occupying the states in the energy range $d\epsilon$ at ϵ is given by

$$n(\epsilon) d\epsilon = g(\epsilon) f_{\text{FD}}(\epsilon) d\epsilon \quad \dots(4.4.14)$$

The total number of fermion in the system is given by

$$N = \int n(\epsilon) d\epsilon = \int g(\epsilon) f_{\text{FD}}(\epsilon) d\epsilon \quad \dots(4.4.15)$$

For electron gas, the density of states is given by

$$g(\epsilon) d\epsilon = (2s+1) \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon, \quad \dots(4.4.16)$$

$s = 1/2$ for electron.

4.5 BOSE-EINSTEIN STATISTICS

There are many systems, which are composed of weakly interacting identical and indistinguishable particles with integral spin. These particles don't obey Pauli's exclusion principle. Thus any number of particles can occupy the same quantum state. The statistical behaviour of such particles is governed by a different kind of statistics, called Bose-Einstein statistics, named in honor of S.N. Bose and A. Einstein who independently derived it. Particles obeying Bose-Einstein statistics are called *bosons*. Examples of *bosons* are photons (spin 1), H_2 molecule, helium ^4He , meson etc.

Consider a system composed of N bosons. The macrostate state of the system is specified by specifying the occupation numbers $n_1, n_2, \dots$ in energy levels $\epsilon_1, \epsilon_2, \dots$ having degeneracies $g_1, g_2, \dots$. The i th level with energy ϵ_i and degeneracy g_i contains n_i particles. There is no restriction on the number of bosons that a quantum state can accommodate. This level can be pictured as n_i particles in a row divided arbitrarily into g_i states by $g_i - 1$ partitions.

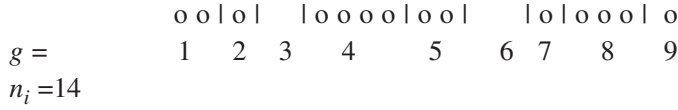


Fig. 4.5.1 Distribution of 14 particles in 9 states separated by 8 partitions

The number of different ways Ω_i , the n_i bosons can be placed in the g_i quantum states without any limit to the number of particles in a state is equal to the number of independent permutations of particles and partitions. There are a total of $(n_i + g_i - 1)$ particles plus partitions, which can be arranged in $(n_i + g_i - 1)!$ ways. Since the permutation of particles among themselves and permutations of partitions among themselves don't produce a different arrangement, we must, therefore, divide $(n_i + g_i - 1)!$ by $n_i! \cdot (g_i - 1)!$. Thus

$$\Omega_i = \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(4.5.1)$$

The total number Ω of different ways to arrange $n_1, n_2, \dots$ bosons in the energy levels $\epsilon_1, \epsilon_2, \dots$, if there are $g_1, g_2, \dots$ states in each level, is

$$\begin{aligned} \Omega &= \frac{(n_1 + g_1 - 1)!}{n_1! (g_1 - 1)!} \cdot \frac{(n_2 + g_2 - 1)!}{n_2! (g_2 - 1)!} \dots \dots \dots \\ &= \prod_i \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \quad \dots(4.5.2) \end{aligned}$$

Since $n_i \gg 1, g_i \gg 1, 1$ may be omitted in the above expression. Thus

$$\Omega = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!} \quad \dots(4.5.3)$$

If the number N of the particles and the total energy E of the system is constant then we have

$$n_1 + n_2 + \dots = \sum_i n_i = N \quad \dots(4.5.4)$$

$$n_1 \epsilon_1 + n_2 \epsilon_2 + \dots = \sum_i n_i \epsilon_i = E \quad \dots(4.5.5)$$

Since N and E are constants, the sum of changes in occupation numbers and the sum of changes in energies of the energy levels must be zero.

$$\sum_i \delta n_i = 0 \quad \dots(4.5.6)$$

$$\sum_i n_i \delta \epsilon_i = 0 \quad \dots(4.5.7)$$

The most probable distribution corresponds to the maximum value of Ω subject to the restrictions expressed by Eqns. (4.5.6) and (4.5.7). It is more convenient to maximize $\ln \Omega$ than Ω . So we first simplify $\ln \Omega$.

$$\ln \Omega = \sum \ln(n_i + g_i)! - \ln n_i! - \ln g_i!$$

Using Stirling approximation we have

$$\begin{aligned} \ln \Omega &= \sum [(n_i + g_i) \ln(n_i + g_i) - (n_i + g_i) - n_i \ln n_i + n_i - g_i \ln g_i + g_i] \\ &= \sum [(n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i] \end{aligned} \quad \dots(4.5.8)$$

The condition of maximum $\ln \Omega$ is

$$\delta \ln \Omega = 0$$

$$\therefore \sum \left[\ln(n_i + g_i) + (n_i + g_i) \cdot \frac{1}{(n_i + g_i)} - \ln n_i - n_i \cdot \frac{1}{n_i} \right] \delta n_i = 0$$

$$\text{or} \quad \sum [\ln(n_i + g_i) - \ln n_i] \delta n_i = 0 \quad \dots(4.5.9)$$

To incorporate the conditions expressed by Eqns. (4.5.6) and (4.5.7), we use Lagrange method of undetermined multipliers. Multiplying Eqn. (4.5.6) by $-\alpha$ and Eqn. (4.5.7) by $-\beta$ and adding them to Eqn. (4.5.9) we have

$$\sum [\ln(n_i + g_i) - \ln n_i - \alpha - \beta \epsilon_i] \delta n_i = 0$$

Since the change δn_i 's are arbitrary, we must have

$$\ln(n_i + g_i) - \ln n_i - \alpha - \beta \epsilon_i = 0$$

This simplifies to

$$n_i = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1} \quad \dots(4.5.10)$$

$$f_{\text{BE}}(\epsilon) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i} - 1} = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}, \quad \beta = 1/kT \quad \dots(4.5.11)$$

Equation (4.5.10) represents the BE distribution function. Eqn. (4.5.11) represents number of bosons per quantum state at energy ϵ_i or the occupation probability of state with energy ϵ of a system in thermal equilibrium at temperature T .

In a system in which the number of bosons is not conserved, the condition $\sum n_i = N = \text{constant}$ does not apply. For example, the number of photons in a cavity increases with increasing temperature. This in contrast to an ideal gas contained in a vessel. Removal of this condition is equivalent to setting $\alpha = 0$ ($\mu = 0$). For such system the B-E distribution becomes

$$\begin{aligned} n_i &= \frac{g_i}{e^{\beta \epsilon_i} - 1} \\ f_{\text{BE}}(\epsilon) &= \frac{1}{e^{\beta \epsilon} - 1} \quad (\text{for photons } \epsilon = \hbar\omega) \end{aligned} \quad \dots(4.5.12)$$

The parameter α may be determined from the condition $\sum n_i = N$. It increases monotonically with temperature for FD and BE statistics both. This can be seen as follows. The number of bosons occupying the states with energy between ϵ and $\epsilon + d\epsilon$ is given by

$$n(\epsilon)d\epsilon = f_{\text{BE}}(\epsilon) g(\epsilon) d\epsilon \quad \dots(4.5.13)$$

The total number of bosons in the system is

$$\begin{aligned} N &= \int_0^{\infty} f_{\text{BE}}(\epsilon) g(\epsilon) d\epsilon \\ &= \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^{\infty} \frac{\epsilon^{1/2} d\epsilon}{e^{\alpha} \cdot e^{\epsilon/kT} - 1} \end{aligned} \quad \dots(4.5.14)$$

Putting $\epsilon/kT = q$, in the above integral, we have

$$N = \frac{2\pi V(2mkT)^{3/2}}{h^3} \int_0^{\infty} \frac{q^{1/2} dq}{e^{\alpha} e^q - 1} \quad \dots(4.5.15)$$

With increasing T , the factor multiplying the integral in the above expression (4.5.15) increases. Since N is constant, the integral must decrease. This implies that α increases with rise in temperature. Thus α is an increasing function of T . Since N is finite, the integral must always converge and so α must always be non-negative.

APPLICATIONS OF QUANTUM STATISTICS

FERMI-DIRAC STATISTICS

5.1 SOMMERFELD'S FREE ELECTRON THEORY OF METALS

According to free electron model, the valence electrons of atoms constituting the metal are free to move within the limits of the metal. The positive ion cores produce a constant average potential in which free electrons move. The potential energy of interaction of electrons with the ion cores is constant throughout the solid and may be assumed to be zero for convenience. The free electrons don't leave the boundaries of the metal because of the electrostatic force. The potential energy of electrons may be assumed to be infinitely great at the boundaries. *Thus the electrons in a metal may be treated as a gas which is composed of non-interacting spin 1/2 fermions confined in box. Because of this analogy the assembly of free electrons in a metal is called Fermi gas.* Quantum mechanical treatment of motion of electron in a box shows that energy of electron is quantized. The energy of electron, which is free to move in a cubical box of side L is given by

$$\epsilon = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(5.1.1)$$

where n_x, n_y, n_z are integers, each can take on values 1, 2, ...The set of integers n_x, n_y, n_z and spin quantum number 1/2 define a state of electron. It is found that more than one quantum state correspond to a single energy level. The different quantum states belonging to a energy level are called *degenerate states* and the number of such states is called the *degeneracy* of that energy level.

The density of states (the number of quantum states per unit energy interval) at energy ϵ is given by

$$g(\epsilon) = (2s + 1) \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}. \quad \dots(5.1.2)$$

For electron spin $s = 1/2$, and $(2s + 1) = 2$. The free electrons in a metal are distributed among various available quantum states according to Pauli's exclusion principle. The Fermi-Dirac distribution function gives the probability that a state with energy ϵ is occupied at temperature T.

Fermi-Dirac Distribution for Electron Gas and Fermi Energy

F-D distribution is

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/kT} + 1} \quad \dots(5.1.3)$$

At $T = 0$ K, for the energy states $\epsilon < \mu$ where μ is chemical potential, the exponential term $\exp(\epsilon - \mu)/kT \rightarrow \exp(-\infty) \rightarrow 0$ and therefore,

$$f_{FD} = 1$$

At $T = 0$ K, for energy states $\epsilon > \mu$, the exponential term $\exp(\epsilon - \mu)/kT \rightarrow \exp(\infty) \rightarrow \infty$. So

$$f_{FD} = 0.$$

The value of chemical potential at $T = 0$ K is denoted by μ_0 . Thus at $T = 0$ K, all the energy states below the $\epsilon = \mu_0$ are occupied and those above it are empty. The energy $\epsilon = \mu_0$ is called Fermi energy $\epsilon_F(0)$. Thus, the Fermi energy is the maximum value of energy that a fermion can acquire at 0 K. In other words, the energy of the top most filled level in a Fermi gas at absolute zero is the Fermi energy.

At $T \neq 0$ K, the probability the energy level $\epsilon = \mu_0 = \epsilon_F$ is occupied is

$$f_{FD}(\epsilon = \mu = \epsilon_F) = \frac{1}{e^0 + 1} = \frac{1}{2}$$

That is, at Fermi energy one half the energy states will be occupied. The variation of F-D distribution with energy at different temperatures is shown in the Fig. (5.1.1).

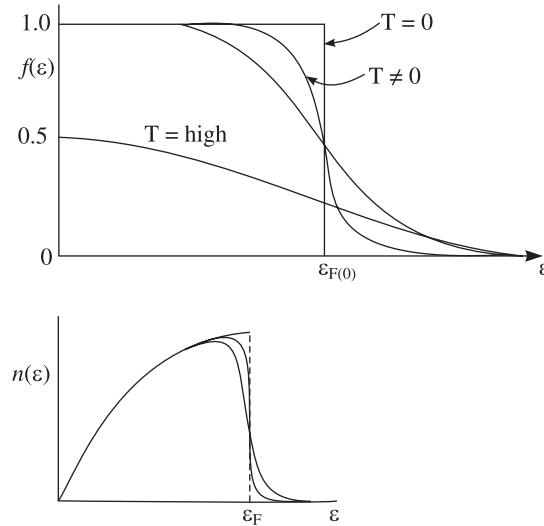


Fig. 5.1.1 Dependence of Fermi distribution function f_{FD} and number of electrons with temperature

From the figure, it is evident that at temperature T above 0 K, some of the states just below ϵ_F that were occupied at $T = 0$ K are now empty and some of those states just above the ϵ_F are now

occupied. The explanation for this is that as the temperature of the Fermi gas is raised, a small fraction of the electrons occupying the states just below the Fermi level gain thermal energy and get excited to the states just above the **Fermi level**.

For a free electron gas the number of states in the energy interval $d\varepsilon$ at ε is

$$g(\varepsilon) d\varepsilon = \frac{4\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} d\varepsilon \quad \dots(5.1.4)$$

The number of electrons occupying the energy states between the energy interval $d\varepsilon$ at ε is

$$\begin{aligned} n(\varepsilon)d\varepsilon &= f_{\text{FD}}(\varepsilon) g(\varepsilon)d\varepsilon \\ &= \frac{g(\varepsilon)}{1 + \exp(\varepsilon - \mu)/kT} d\varepsilon \end{aligned} \quad \dots(5.1.5)$$

The Fermi energy is in general a function of temperature. Its value is determined by the condition

$$N = \int n(\varepsilon) d\varepsilon = \int f_{\text{FD}}(\varepsilon) g(\varepsilon) d\varepsilon = \int \frac{g(\varepsilon)}{1 + \exp(\varepsilon - \mu)/kT} d\varepsilon$$

where the integral is taken over all the energy states available to the electrons of the system. Substituting the value of $g(\varepsilon)$ in above expression we have

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{1 + \exp(\varepsilon - \mu)/kT} d\varepsilon \quad \dots(5.1.6)$$

At

$$T = 0 \text{ K,}$$

$$f_{\text{FD}} = 1 \quad \text{for } \varepsilon < \mu_0 = \varepsilon_{\text{F}_0}$$

$$= 0 \quad \text{for } \varepsilon > \mu_0 = \varepsilon_{\text{F}_0}$$

So the limits of integration can be taken from 0 to ε_{F_0} . Then

$$N = \frac{4\pi V(2m)^{3/2}}{h^3} \int_0^{\varepsilon_{\text{F}_0}} \varepsilon^{1/2} d\varepsilon \quad (\text{since } f_{\text{FD}} = 1)$$

$$= \frac{4\pi V(2m)^{3/2}}{h^3} \left(\frac{2}{3} \varepsilon_{\text{F}_0}^{3/2} \right)$$

$$\varepsilon_{\text{F}_0} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \quad \dots(5.1.7)$$

$$= \left(3.646 \times 10^{-19} \text{ eV} \cdot \text{m}^2 \right) \left(\frac{N}{V} \right)^{2/3} \quad \dots(5.1.8)$$

For copper $N/V = 8.5 \times 10^{28} \text{ m}^{-3}$, the Fermi energy is

$$\epsilon_{F_0} = (3.646 \times 10^{-19} \text{ eV} \cdot \text{m}^2)(8.5 \times 10^{28} \text{ m}^{-3})^{2/3} = 7.0 \text{ eV}$$

The energy of an electron confined to move in a cubical box of side L is

$$\epsilon = \frac{n^2 h^2}{8mL^2}$$

The quantum number of electron occupying the highest energy state $\epsilon = \epsilon_{F_0}$ is

$$n_{\max} = \frac{\sqrt{8m\epsilon_{F_0}}}{h} L$$

For a box of size $L = 1 \text{ cm}$, $n_{\max} = 43 \times 10^6$. Thus, we see that the quantum numbers of the occupied states may from 1 to 43 million. The existence of such a huge number of states allows us to treat the energy levels as continuous.

In order to express density of states $g(\epsilon)$ in terms of Fermi energy ϵ_{F_0} we multiply the expressions for $g(\epsilon)$ and ϵ_{F_0} . Doing so we get

$$g(\epsilon) = \frac{3N}{2\epsilon_{F_0}^{3/2}} \epsilon^{1/2} \quad \dots(5.1.9)$$

For 1 mol of copper, $N = N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$, $\epsilon_{F_0} = 7 \text{ eV}$, we have

$$g(\epsilon_{F_0}) = \frac{3 \times 6.02 \times 10^{23}}{2(7 \text{ eV})^{3/2}} (7 \text{ eV})^{1/2} = 1.3 \times 10^{23} \text{ states/eV}$$

With this huge number of states per unit energy range, it is clear that we may consider the energy to be virtually continuous.

Fermi temperature T_F

The Fermi temperature T_F of a Fermi gas is defined as

$$T_F = \frac{\epsilon_{F_0}}{k} \quad \dots(5.1.10)$$

where k is Boltzmann constant. Fermi temperatures for typical metals are of the order of 10^5 K , which is quite high. No metal remains in solid state at this temperature.

For $T \ll T_F$ or $kT \ll \epsilon_{F_0}$ the F-D distribution is called **degenerate** and for $T \gg T_F$ the distribution is **non-degenerate**. The parameter $\alpha = -\mu/kT$ is negative for degenerate systems and positive for non-degenerate systems. This means that $\mu > 0$ at low temperature and $\mu < 0$ at high temperature.

At $T = 0 \text{ K}$ the system is **completely degenerate**, at $T \ll T_F$ the system is **degenerate** and at intermediate temperature it is **slightly (weakly) degenerate**.

Table 5.1.1 Fermi energy, Fermi temperature and Fermi velocity of some metals

Element	$N/V \text{ cm}^{-3}$ (10^{22})	$\epsilon_F \text{ eV}$	$T_F \text{ K}$ (10^4)	$v_F \text{ cm/s}$ (10^8)
Li	4.6	4.7	5.5	1.3
K	1.34	2.1	2.4	0.85
Cu	8.5	7.0	8.2	1.56
Au	5.9	5.5	6.4	1.39

Degeneration of Fermi Gas

A many particle system is said to degenerate if its behaviour shows deviations from the expected classical behaviour. At $T = 0 \text{ K}$, a Fermi gas is **completely (strongly) degenerate**. In the temperature range $0 < T \ll T_F$ the gas is **degenerate**. At $T < T_F$ it is weakly (slightly) degenerate. At $T > T_F$ it is **non-degenerate**.

(i) Completely Degenerate Fermi Gas ($T = 0 \text{ K}$)

Let us calculate the energy, entropy and pressure of completely degenerate Fermi gas. The average energy of electrons at 0 K is

$$\begin{aligned}
 \langle \epsilon \rangle &= \frac{1}{N} \int \epsilon n(\epsilon) d\epsilon = \frac{1}{N} \int \epsilon f_{FD}(\epsilon) g(\epsilon) d\epsilon \\
 &= \frac{4\pi V}{Nh^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{1 + \exp(\epsilon - \epsilon_F)/kT} \\
 &= \frac{4\pi V}{Nh^3} (2m)^{3/2} \int_0^{\epsilon_{F0}} \epsilon^{3/2} d\epsilon \quad (\text{At } T = 0 \text{ K, } f_{FD} = 1 \text{ for } \epsilon < \epsilon_{F0}) \\
 &= \frac{4\pi V}{Nh^3} (2m)^{3/2} \left(\frac{2}{5} \epsilon_{F0}^{5/2} \right) \quad \dots(5.1.11)
 \end{aligned}$$

Making use of the result

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \left(\frac{2}{3} \epsilon_{F0}^{3/2} \right) \quad \dots(5.1.12)$$

We can express $\langle \epsilon \rangle$ as

$$\langle \epsilon_0 \rangle = \frac{3}{5} \epsilon_{F0} \quad \dots(5.1.13)$$

The total energy of the system is

$$E(0) = \frac{3}{5} N \epsilon_{F_0} \quad \dots(5.1.14)$$

Entropy of Fermi gas at absolute zero is zero.

$$S_0 = 0$$

Pressure of the gas is given by the relation

$$PV = \frac{2}{3} \langle E \rangle$$

At

$$T = 0$$

$$P = \frac{2}{3} \frac{\langle E \rangle}{V} = \frac{2}{5} \frac{N}{V} \epsilon_{F_0} \quad \dots(5.1.15)$$

Thus a Fermi gas exerts very high pressure ($\approx 10^6$ Atm.) even at $T = 0$.

(ii) Degenerate Fermi Gas ($T \ll T_F$)

At $T \ll T_F$ the chemical potential $\mu > 0$ ($\alpha < 0$) and at $T > T_F$, $\mu < 0$ ($\alpha > 0$). The variation of chemical potential with temperature is shown in the Fig. (5.1.2)

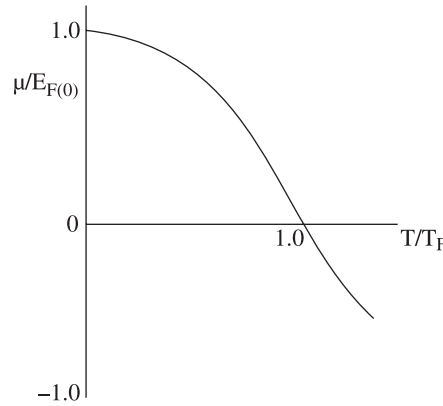


Fig. 5.1.2 Variation of chemical potential with temperature

The total number of electrons in a Fermi gas is

$$N = \int_0^\infty f_{FD}(\epsilon) g(\epsilon) d\epsilon = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{1 + \exp(\epsilon - \epsilon_F)/kT} d\epsilon \quad \dots(5.1.16)$$

The result of integral of this type can be obtained making use of the following standard result:

$$\int_0^\infty \frac{\epsilon^p d\epsilon}{1 + \exp[(\epsilon - \epsilon_F)/kT]} = \frac{1}{p+1} \left[\epsilon_F^{p+1} + \sum_{n=1}^\infty 2(kT)^{2n} \left(1 - \frac{1}{2^{2n-1}} \right) \zeta(2n) \frac{d^{2n}}{d\epsilon_F^{2n}} (\epsilon_F^{p+1}) \right] \quad \dots(5.1.17)$$

In present case, $p = 1/2$, $n = 1, 2, 3, \dots$ $\zeta(2) = \frac{\pi^2}{6} = 1.645$.

The function $\zeta(n)$ is called Riemann zeta function, see appendix.

Making use of this result in Eqn. (5.1.16), we have

$$\begin{aligned} N &= C \cdot \frac{2}{3} \left[\epsilon_F^{3/2} + 2(kT)^2 \left(1 - \frac{1}{2} \right) \zeta(2) \left(\frac{3}{4} \epsilon_F^{-1/2} \right) \right] \\ &= \frac{2}{3} C \epsilon_F^{3/2} \left[1 + \frac{\pi^2}{8 \epsilon_F^2} (kT)^2 \right] \end{aligned} \quad \dots(5.1.18)$$

where $C = \frac{4\pi V}{h^3} (2m)^{3/2} \quad \dots(5.1.19)$

In the limit $T \rightarrow 0$

$$N = \frac{2}{3} C \epsilon_{F_0}^{3/2} \quad \text{or} \quad C = \frac{3}{2} N \epsilon_{F_0}^{-3/2} \quad \dots(5.1.20)$$

Therefore $\epsilon_{F_0} = \left(\frac{3N}{2C} \right)^{2/3} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \quad \dots(5.1.21)$

Since kT/ϵ_F is small, we see that ϵ_F does not change rapidly with temperature. Therefore, we can set $\epsilon_F = \epsilon_{F_0}$ in the second term on the right hand side of Eqn. (5.1.18). After putting $N = \frac{2}{3} C \epsilon_{F_0}^{3/2}$, in Eqn. (5.1.18) we get

$$\frac{2}{3} C \epsilon_{F_0}^{3/2} = \frac{2}{3} C \epsilon_F^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right]$$

From this we get

$$\epsilon_F = \epsilon_{F_0} \left[1 + \frac{\pi^2}{8} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right]^{-2/3} \quad \dots(5.1.22)$$

Using the result $(1+x)^{-2/3} = 1 - 2x/3$ we can write

$$\epsilon_F = \epsilon_{F_0} \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right] \quad \dots(5.1.23)$$

Thus, the Fermi energy (chemical potential) of a Fermi gas decreases with increasing temperature.

Total energy of electron gas at low temperature

The total energy of electron gas is given by

$$\begin{aligned}
 E &= \int_0^{\infty} \epsilon f_{FD}(\epsilon) g(\epsilon) d\epsilon = C \int_0^{\infty} \frac{\epsilon^{3/2}}{1 + \exp(\epsilon - \epsilon_F)/kT} d\epsilon \quad \text{where } g(\epsilon) = C \epsilon^{1/2} \\
 &= \frac{2C}{5} \left[\epsilon_F^{5/2} + 2(kT)^2 (1/2)(\pi^2/6) \left(\frac{15}{4} \epsilon_F^{1/2} \right) \right] \\
 &= \frac{2C}{5} \epsilon_F^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{kT}{\epsilon_F} \right)^2 \right] \quad \dots(5.1.24)
 \end{aligned}$$

Substituting $C = \frac{3}{2} N \epsilon_{F_0}^{-3/2}$ and ϵ_F and recalling that ϵ_F does not change rapidly with temperature we can express the total energy of electron gas as

$$\begin{aligned}
 E &= \frac{2}{5} \left[\frac{3}{2} N \epsilon_{F_0}^{-3/2} \right] \left[\epsilon_{F_0}^{5/2} \left\{ 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right\} \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right] \\
 E &\approx \frac{3}{5} N \epsilon_{F_0} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 - \frac{\pi^2}{16} \left(\frac{kT}{\epsilon_F} \right)^4 + \dots \right] \quad \dots(5.1.25)
 \end{aligned}$$

The pressure of the electron gas is given by

$$P = \frac{2}{3} \frac{E}{V} = \frac{2}{5} \frac{N}{V} \epsilon_{F(0)} \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 - \dots \right] \quad \dots(5.1.26)$$

The total energy E and pressure P of a degenerate Fermi gas increase with temperature in the same manner. The pressure of degenerate Fermi gas is greater than that of an ideal classical gas. This is because fermions obey Pauli's exclusion principle. A quantum state can accommodate at most only one fermion and they are prevented to occupy already occupied low lying energy levels. Fermions tend to remain as far apart as possible and hence exert larger pressure. This behaviour of fermions is contrary to that of bosons, which do not obey Pauli's exclusion principle. Many bosons can occupy a single energy level *i.e.*, they can assemble in low energy states. This is why a Bose gas exerts less pressure than a classical gas.

$$E_{Fermi \text{ gas}} > E_{Classical \text{ gas}} > E_{Bose \text{ gas}}$$

$$P_{Fermi \text{ gas}} > P_{Classical \text{ gas}} > P_{Bose \text{ gas}}$$

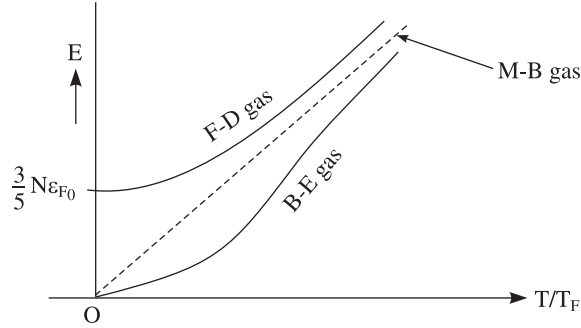


Fig. 5.1.3 Variation of E of FD and BE gas with temperature

5.2 ELECTRONIC HEAT CAPACITY

According to classical theory, when a system of particles is heated, all the particles absorb heat and contribute to the heat capacity. Thus the classical theory applied to electron gas in a monovalent metal predicts electronic contribution to heat capacity equal to $3R/2$. But experimental results are found to be less than 1% of the classical value. This anomaly is removed if one uses Fermi-Dirac distribution function to the electron gas. When a metal is heated only a small fraction of electrons, which are within an energy kT below the Fermi level are excited thermally to vacant states above the Fermi level. Electrons, which are deeply situated below the Fermi level don't participate in thermal excitation because the energy kT is not enough to take them to the vacant levels above the Fermi level. This explains why electronic contribution to heat capacity is very small.

The total energy of electron gas is

$$E \approx \frac{3}{5} N \epsilon_{F_0} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\epsilon_{F_0}} \right)^2 \right] \quad \dots(5.2.1)$$

The heat capacity of electron gas is

$$C_{ve} = \frac{\partial E}{\partial T} = \left(\frac{N\pi^2 k^2}{2\epsilon_{F_0}} \right) T \quad \dots(5.2.2)$$

Let us calculate the value of C_{ve} for copper. For copper $\epsilon_{F_0} = 7 \text{ eV}$. Substituting $N_A = 6.02 \times 10^{26} (\text{kmol})^{-1}$, $k = 1.38 \times 10^{-23} \text{ J/K}$, Room temperature $T = 300 \text{ K}$, $kT = 0.026 \text{ eV}$.

$$\begin{aligned} C_{ve} &= \frac{\pi^2}{2} \cdot \frac{kT}{\epsilon_{F_0}} \cdot kN_A = \frac{(3.14)^2}{2} \cdot \frac{0.026 \text{ eV}}{7.0 \text{ eV}} \cdot (1.38 \times 10^{-23} \text{ J/K})(6.02 \times 10^{26} \text{ kmol}^{-1}) \\ &= 1460 \text{ J (kmol)}^{-1} \text{ K}^{-1}. \end{aligned}$$

We know that at very low temperature, the lattice heat capacity varies as T^3 (Debye T^3 law) while the electronic heat capacity varies linearly with temperature T . At very low temperature the lattice heat capacity decreases very rapidly and the electronic heat capacity dominates. At high

temperature the lattice heat capacity dominates over the electronic contribution. The total heat capacity is given by

$$C_v = A T + B T^3 \text{ where } A \text{ and } B \text{ are constants.}$$

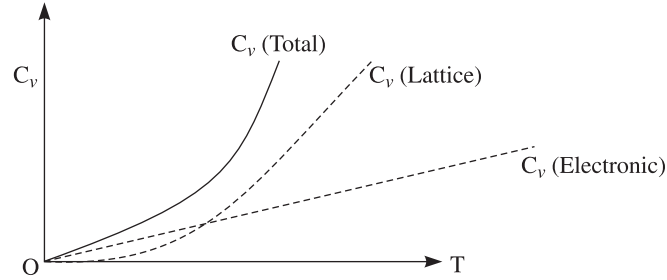


Fig. 5.2.1 Variation of heat capacity with temperature

5.3 THERMIONIC EMISSION (RICHARDSON-DUSHMANN EQUATION)

The emission of electrons from a substance when it is heated to a high temperature is called *thermionic emission*. The thermionic current density depends on the temperature T , work function and the nature of the emitting surface. The expression, which represents the dependence of thermionic current on temperature and work function of emitting material, was first derived by Richardson making use thermodynamic principle and later by Dushman using quantum statistics developed by Fermi and Dirac.

According free electron model, the electron are distributed among various available quantum states according to Pauli's exclusion principle. At $T = 0$ K, all the states up to fermi level ϵ_F are filled and those above it are empty. The work function ϕ denotes the energy required to liberate the electron at Fermi level from the metal. In order to liberate electron from a metal, the energy ϵ imparted to it must exceed $(\epsilon_F + \phi)$. For an electron to escape, it must arrive at the emitting surface with momentum p suitably directed. We take the emitting material in the shape of a rectangular box with emitting surface perpendicular to x -axis. For electron emission to take place, the x -component of momentum p_x must be greater than the critical value p_{xc} given by

$$p_x \geq p_{xc} = \sqrt{2m(\epsilon_F + \phi)} \quad \dots(5.3.1)$$

Let $n(p_x)dp_x$ represent the number of electrons per unit volume having x -component of momentum in the range dp_x at p_x . The thermionic current density J is given by

$$J = \int_{p_{xc}}^{\infty} n(p_x) dp_x \cdot e \cdot v_x = \frac{e}{m} \int_{p_{xc}}^{\infty} p_x \cdot n(p_x) dp_x \quad \dots(5.3.2)$$

where v_x is x -component of velocity of electron.

The number of quantum states in volume element $dx dy dz dp_x dp_y dp_z$ of phase space is $\frac{2}{h^3} dx dy dz dp_x dp_y dp_z$. The presence of factor 2 accounts for the fact that for a given momentum

state p_x, p_y, p_z , there can be two spin states: spin up and spin down. The number of quantum states in unit volume of coordinate space and in volume element $dp_x dp_y dp_z$ of momentum space is denoted by $g(p_x, p_y, p_z) dp_x dp_y dp_z$ and will be given by

$$g(p_x, p_y, p_z) dp_x dp_y dp_z = 2 \frac{dp_x dp_y dp_z}{h^3}.$$

The number of electrons per unit volume with momentum between p_x and $p_x + dp_x$, p_y and $p_y + dp_y$, p_z and $p_z + dp_z$ is

$$\begin{aligned} n(p_x, p_y, p_z) dp_x dp_y dp_z &= 2 \frac{dp_x dp_y dp_z}{h^3} \cdot f_{FD}(\epsilon) \\ &= 2 \frac{1}{1 + \exp[(\epsilon - \epsilon_F)/kT]} \cdot \frac{dp_x dp_y dp_z}{h^3} \end{aligned} \quad \dots(5.3.3)$$

where $\epsilon = (p_x^2 + p_y^2 + p_z^2)/2m$ is the energy of electron.

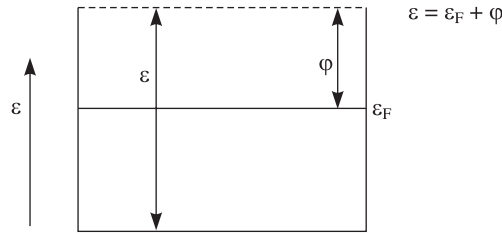


Fig. 5.3.1 Energy of electron ϵ in terms of Fermi energy ϵ_F and work function ϕ

The number of electrons with x-component of momentum between p_x and $p_x + dp_x$, irrespective of the values that p_y and p_z can assume, is given by

$$n(p_x) dp_x = \frac{2}{h^3} dp_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{1}{1 + \exp(\epsilon - \epsilon_F)/kT} dp_y dp_z \quad \dots(5.3.4)$$

At any temperature $(\epsilon - \epsilon_F)/kT \gg 1$ so 1 may be neglected in the denominator of the FD distribution. Under this approximation we have

$$\begin{aligned} n(p_x) dp_x &= \frac{2}{h^3} dp_x \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\exp \left(-\frac{p_x^2 + p_y^2 + p_z^2}{2m} + \epsilon_F \right) / kT \right] dp_y dp_z \\ &= \frac{2}{h^3} \exp \left(\frac{\epsilon_F}{kT} \right) \cdot \exp \left(-\frac{p_x^2}{2mkT} \right) dp_x \cdot \int_{-\infty}^{\infty} \exp \left(-\frac{p_y^2}{2mkT} \right) dp_y \cdot \int_{-\infty}^{\infty} \exp \left(-\frac{p_z^2}{2mkT} \right) dp_z \end{aligned}$$

$$= \frac{2}{h^3} \exp\left(\frac{\epsilon_F}{kT}\right) \cdot \exp\left(-\frac{p_x^2}{2mkT}\right) \cdot (\sqrt{2\pi mkT})(\sqrt{2\pi mkT}) dp_x \dots (5.3.5)$$

where we have used the standard result: $\int_0^\infty \exp(-\alpha x^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$. In view of this result we have

$$n(p_x) dp_x = \frac{4\pi mkT}{h^3} \cdot \exp\left(\frac{\epsilon_F}{kT}\right) \cdot \exp\left(-\frac{p_x^2}{2mkT}\right) dp_x \dots (5.3.6)$$

The thermionic current now becomes

$$\begin{aligned} J &= \frac{e}{m} \cdot \frac{4\pi mkT}{h^3} \cdot \exp\left(\frac{\epsilon_F}{kT}\right) \cdot \int_{p_{xc}}^\infty p_x \cdot \exp\left(-\frac{p_x^2}{2mkT}\right) dp_x \\ &= \left(\frac{4\pi me k^2}{h^3}\right) T^2 \exp\left(\frac{\epsilon_F - \frac{p_{xc}^2}{2m}}{kT}\right) \\ &= \left(\frac{4\pi me k^2}{h^3}\right) T^2 e^{-\phi/kT} \\ &= AT^2 \exp(-\phi/kT) \dots (5.3.7) \end{aligned}$$

where

$$A = \frac{4\pi me k^2}{h^3} = 1.20 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2} \dots (5.3.8)$$

From above relation

$$\begin{aligned} \ln \frac{J}{T^2} &= \ln A - \frac{\phi}{kT} \\ \log_{10} \frac{J}{T^2} &= \log_{10} A - 0.434 \frac{\phi}{kT} \end{aligned}$$

A plot of $\log_{10} J/T^2$ against $1/T$ is a straight line. The intercept on y-axis gives $\log_{10} A$ and the slope of the line gives the work function of the emitting material.

The value of A determined from experiment does not agree with the theoretical value obtained by putting the values of constants in the expression for A . A correction needs in the expression for the thermionic current density. When an electron leaves the emitting surface, the latter becomes positive and pulls the outgoing electron back to the material. If r denotes the fraction of electrons reflected

back to the material, the thermionic current density will be given by

$$J = (1 - r)A T^2 \exp\left(-\frac{\Phi}{kT}\right) \quad \dots(5.3.9)$$

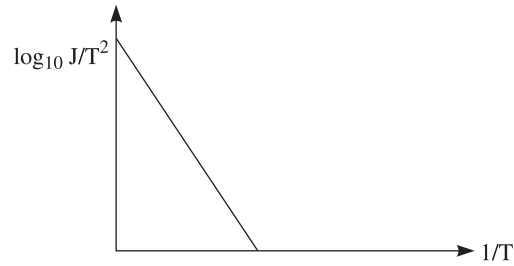


Fig. 5.3.2 Variation of $\log_{10} J/T^2$ with $1/T$

5.4 AN IDEAL BOSE GAS

A Bose gas is a many particle system consisting of non-interacting bosons which are indistinguishable particles having integral spin (0, 1, 2). The appropriate distribution function which describes the behaviour of bosons is Bose-Einstein distribution function.

For an ideal BE gas of N bosons in an enclosure of volume V , the mean occupation number n_r in r th single particle state (the most probable number of particles with energy ϵ_r) is

$$n_r(\epsilon_r) = \frac{g_r}{\exp[\alpha + \beta\epsilon_r] - 1} = \frac{g_r}{\exp[\beta(\epsilon_r - \mu)] - 1}, \quad \beta = 1/kT \quad \dots(5.4.1)$$

where
$$\alpha = -\beta\mu = -\frac{\mu}{kT} \quad \dots(5.4.2)$$

The parameter μ is called chemical potential and can be determined as a function of N and temperature T by the condition

$$\begin{aligned} N = \sum_{r=0}^{\infty} n_r &= \frac{g_1}{\exp[\beta(\epsilon_1 - \mu)] - 1} + \frac{g_2}{\exp[\beta(\epsilon_2 - \mu)] - 1} + \dots \\ &= n_1 + n_2 + \dots \end{aligned} \quad \dots(5.4.3)$$

where the sum is over the discrete energy levels.

The total number of particle in the system is

$$N = g_s \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1} \quad \dots(5.4.4)$$

Where $g_s = 2s + 1$ is spin degeneracy, s = spin of the boson. For spinless boson $s = 0$ and $g_s = 1$

The mean occupation number is always positive or zero *i.e.*, $n_r \geq 0$ for all values of ϵ . We take the energy scale such that the ground state energy ϵ_1 is zero. The occupation number of the ground state is

$$n_1 = \frac{g_1}{e^{-\beta\mu} - 1}, \quad g_1 = 1, \epsilon_1 = 0 \quad (\text{ground state is non-degenerate}) \quad \dots(5.4.5)$$

The condition $n_1 \geq 0$ implies that $\mu \leq 0$. Thus μ of an ideal B-E gas is always negative. From Eqn. (5.4.3) we see that left hand side *i.e.*, N is constant, so must be the right hand side. This implies that as T is lowered (or β is increased), μ which is negative, must increase. Thus, the maximum value of μ is zero, $\mu_{\max} = 0$.

Let us define a function η by equation

$$\eta = \exp(\mu\beta)$$

η is called **fugacity (absolute activity)** of system. The values chemical potential μ and fugacity η satisfy the inequality

$$-\infty \leq \mu \leq 0, \quad 0 \leq \eta = \exp\mu\beta \leq 1 \quad \dots(5.4.6)$$

We define a temperature T_C , called **critical temperature**, which corresponds to the maximum value of chemical potential *i.e.*, $\mu = 0$. This temperature is given by

$$N = g_s \frac{2\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\epsilon/kT_C} - 1} \quad \dots(5.4.7)$$

To find the value of integral, we change the variable from ϵ to x by substitution $x = \epsilon/kT_C$. Doing so, we get

$$N = g_s V \left(\frac{2\pi mkT_C}{h^2} \right)^{3/2} \left[\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1} \right]$$

The value of the quantity in square bracket is represented by function $F_{3/2}(1)$ whose value is equal to 2.61. (See appendix). Therefore,

$$N = g_s V \left(\frac{2\pi mkT_C}{h^2} \right)^{3/2} F_{3/2}(1) = g_s \frac{V}{\lambda_0^3} F_{3/2}(1) \quad \dots(5.4.8)$$

$$N = g_s \frac{V}{\lambda_0^3} = 2.61 \quad \therefore F_{3/2}(1) = 2.61 \quad \dots(5.4.9)$$

where

$$\lambda_0 = \frac{h}{\sqrt{2\pi mkT_C}}$$

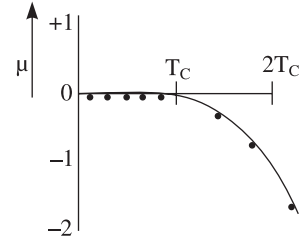


Fig. 5.4.1 Variation chemical potential μ with temperature T

is the thermal de Broglie wavelength of the particle at $T = T_C$. The critical temperature T_C is given by

$$T_C = \frac{h^2}{2\pi mk} \left(\frac{\rho}{2.61} \right)^{2/3}, \quad \rho = \frac{N}{V} \cdot (\text{for spinless particle } s = 0, g_s = 1) \quad \dots(5.4.10)$$

For 1 kmol of Helium gas $N = N_A = 6.023 \times 10^{26} \text{ kmol}^{-1}$. $m = 6.65 \times 10^{-27} \text{ kg}$, $N/V = 2.2 \times 10^{28} \text{ m}^{-3}$,

$$T_C = 3.13 \text{ K}.$$

The Eqn. (5.4.4) which gives the total number of particles in the system is not valid when $T < T_C$.

Let us see why? The expression for density of states viz. $g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}$ contains a factor $\epsilon^{1/2}$. For ground state $\epsilon_1 = 0$, $g(0) = 0$ and hence $n_1 = 0$. The occupation number corresponding to ground state energy ($\epsilon = 0$) does not contribute to the total number of particles. In fact $g(\epsilon)$ for ground state is not zero but 1. At high temperature this replacement of Σ by $\int$ does not introduce any significant error because the ground state is thinly populated and the contribution of this term may be omitted. At very low temperature $T < T_C$ we cannot overlook the first term in the sum given by Eqn. (5.4.3). Instead we must explicitly retain the first term as such and write the remaining terms as integral as given below.

$$N = \frac{1}{e^{-\beta\mu} - 1} + \sum_{i=2}^{\infty} n_i = \frac{1}{e^{-\beta\mu} - 1} + g_s \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} - 1} d\epsilon \quad \dots(5.4.11)$$

$$N = N_0 + N_{exc} \quad \dots(5.4.12)$$

The first term in Eqns. (5.4.11 and 5.4.12) represents the number of particles in the ground state ($\epsilon_1 = 0$). These particles do not contribute to the energy and momentum of the system. The second term represents aggregate of particles occupying the higher energy state $\epsilon > 0$. Only these particles contribute to the energy and momentum of the system.

At higher temperature ($T > T_C$) the number of particles in the ground state ($\epsilon = 0$) is negligibly small and hence may be omitted.

Below T_C , the chemical potential is very close to zero ($\mu \rightarrow 0$) and the number of particles in the excited states ($\epsilon > 0$) is given by

$$N_{exc} = g_s V \frac{2\pi}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{\epsilon^{1/2} d\epsilon}{\eta^{-1} e^{\beta\epsilon} - 1}, \quad \mu \rightarrow 0, \quad \eta = e^{\mu\beta} \rightarrow 1 \quad \dots(5.4.13)$$

$$= g_s V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left[\frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{1/2} dx}{\eta^{-1} e^x - 1} \right], \quad x = \beta\epsilon \quad \dots(5.4.14)$$

$$N_{exc} = g_s \frac{V}{\lambda^3} \left(\frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{(3/2)-1}}{\eta^{-1}e^x - 1} dx \right) = g_s \frac{V}{\lambda^3} F_{3/2}(\eta) = g_s \frac{V}{\lambda^3} F_{3/2}(1) \quad \dots(5.4.15)$$

From Eqns. (5.4.8) and (5.4.15), we have

$$\frac{N_{exc}}{N} = \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.4.16)$$

Equation (5.4.16) gives the fraction of particles occupying the states with energy $\epsilon > 0$. The fraction of particles occupying the ground state is given by

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.4.17)$$

A plot of $N_{\epsilon=0}/N$ as a function T/T_C is shown in the Fig. 5.4.2. From the figure, it is evident that for $T > T_C$, the number of particles in the ground state is negligible. As T falls below T_C , the number of particles in the ground state suddenly increases rapidly. **The process of dropping particles rapidly into the ground state with zero energy is known as *Bose-Einstein condensation*.** The particles in this state possess zero energy and zero momentum. They contribute neither pressure nor do they possess viscosity. (Viscosity is related to transport of momentum.) B-E condensation is second order phase transition. A B-E gas at temperature below T_C is called *degenerate* and T_C is known as *degeneracy temperature* or *condensation temperature*. The ordinary condensation of vapour into liquid takes place in conventional coordinate space whereas Bose-Einstein condensation occurs in momentum space.

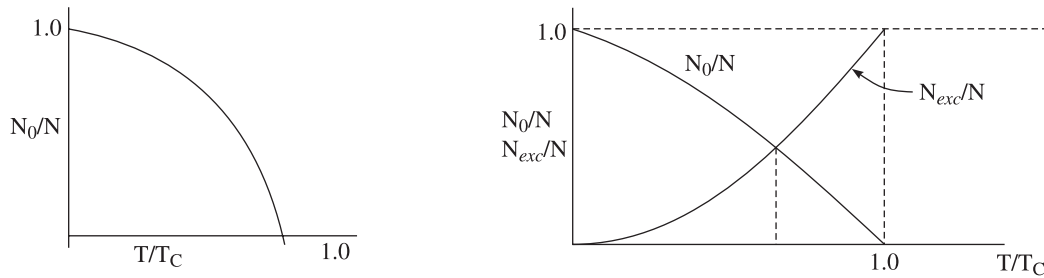


Fig. 5.4.2 Fraction of particles in the ground state and excited state as function of temperature

5.5 DEGENERATION OF IDEAL BOSE GAS

Degeneration of a system refers to the state in which it shows significant deviation from the properties ideal Boltzmann gas. This can be illustrated by calculating energy, pressure, entropy, specific heat etc., of the Bose gas. We shall calculate these quantities for $T < T_C$ and $T > T_C$. Below T_C , Bose gas is strongly degenerate.

Strongly Degenerate Bose Gas ($T < T_C$)

Total Energy E: In the degenerate state the thermodynamic properties of the system, such as total energy, pressure, entropy are less than those of classical Boltzmann gas.

The total number of particles in the system is

$$N = g_s \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{\eta^{-1} e^{\beta\epsilon} - 1} d\epsilon, \quad \eta = e^{\beta\mu}. \quad \dots(5.5.1)$$

Total energy of the system is

$$E = \int_0^\infty \epsilon n(\epsilon) d\epsilon$$

$$E = g_s \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{\eta^{-1} e^{\beta\epsilon} - 1} d\epsilon \quad \dots(5.5.2)$$

Putting $\beta\epsilon = x$ in Eqns. (5.5.1) and (5.5.2), we have

$$N = g_s 2\pi V \left(\frac{2mkT}{h^2} \right)^{3/2} \int_0^\infty \frac{x^{1/2} dx}{\eta^{-1} e^x - 1} \quad \dots(5.5.3)$$

and

$$E = g_s (2\pi V) kT \left(\frac{2mkT}{h^2} \right)^{3/2} \int_0^\infty \frac{x^{3/2} dx}{\eta^{-1} e^x - 1} \quad \dots(5.5.4)$$

In terms of thermal de Broglie wavelength

$$\lambda = \frac{h}{\sqrt{2\pi mkT}}$$

we can express N and E as follows.

$$N = g_s \frac{V}{\lambda^3} \cdot \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{\eta^{-1} e^x - 1} dx = g_s \frac{V}{\lambda} F_{3/2}(\eta) \quad \dots(5.5.5)$$

where

$$F_{3/2}(\eta) = \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{(3/2)-1}}{\eta^{-1} e^x - 1} dx \quad \dots(5.5.6)$$

Now,

$$E = g_s (2\pi V) (kT) \left(\frac{2mkT}{h^2} \right)^{3/2} \int_0^\infty \frac{x^{3/2}}{\eta^{-1} e^x - 1} dx$$

$$= g_s \frac{V}{\lambda^3} \cdot \frac{3}{2} kT \cdot \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{x^{3/2}}{\eta^{-1} e^x - 1} dx$$

$$= g_s \cdot \frac{V}{\lambda^3} \cdot \frac{3}{2} kT \cdot F_{5/2}(\eta) \quad \dots(5.5.7)$$

where

$$F_{5/2}(\eta) = \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{x^{(5/2)-1}}{\eta^{-1} e^x - 1} dx \quad \dots(5.5.8)$$

Below condensation temperature T_C , $\eta \rightarrow 1$, the total energy of the system is

$$E = \frac{3}{2} NkT \cdot \left(\frac{\lambda_0}{\lambda} \right)^3 \cdot \frac{F_{5/2}(1)}{F_{3/2}(1)} = \frac{3}{2} NkT \cdot \left(\frac{T}{T_C} \right)^{3/2} \cdot \frac{1.342}{2.612}$$

$$E = 0.77 NkT \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.5.9)$$

At $T = T_C$,

$$E_0 = 0.514 \left(\frac{3}{2} NkT \right) = 0.514 E_{\text{classical}} \quad \dots(5.5.10)$$

Thus, at $T = T_C$, the total energy of a Bose gas is one-half of the ideal Boltzmann gas.

Pressure P : The pressure of Bose gas is given by

$$P = \frac{2}{3} \cdot \frac{E}{V} = \frac{2}{3V} \left[\frac{3}{2} NkT (0.514) \left(\frac{T}{T_C} \right)^{3/2} \right] = 0.5234 \frac{NkT}{V} \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.5.11)$$

At $T = T_C$,

$$P_0 = 0.5134 \frac{NkT_0}{V} \quad \dots(5.5.12)$$

Thus, at $T = T_C$, the pressure of Bose gas is nearly one-half of the ideal gas. This is because the particles in the ground state have zero momentum and contribute nothing to the pressure.

Specific Heat : The specific heat is given by

$$C_v = \left(\frac{\partial E}{\partial T} \right)_N = \frac{\partial}{\partial T} \left[(0.77 NkT) \left(\frac{T}{T_C} \right)^{3/2} \right] = 1.926 Nk \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.5.13)$$

Entropy : It is given by

$$S = \int_0^T \frac{C_v}{T} dT = \int_0^T \frac{1.926 Nk}{T} \left(\frac{T}{T_C} \right)^{3/2} dT = 1.28 Nk \left(\frac{T}{T_C} \right)^{3/2} \quad \dots(5.5.14)$$

At $T = 0$, $S = 0$.

Non-degenerate Bose Gas $T > T_C$

Energy

For $T > T_C$, $\eta \ll 1$. In this condition

$$N = N_{\text{exc}} = g_s \frac{V}{\lambda^3} \cdot F_{3/2}(\eta) \quad \dots(5.5.15)$$

Total energy from Eqn. 5.5.7

$$E = g_s \frac{3}{2} kT \cdot \frac{V}{\lambda^3} \cdot F_{5/2}(\eta)$$

From Eqns. (5.5.15) and (5.5.7)

$$E = \frac{3}{2} N kT \cdot \frac{V}{\lambda^3} \cdot \frac{F_{5/2}(\eta)}{F_{3/2}(\eta)} = \frac{3}{2} N kT \left[1 - 0.462 \left(\frac{T_C}{T} \right)^{3/2} - \dots \right] \quad \dots(5.5.16)$$

Pressure P

$$P = \frac{2}{3} \cdot \frac{E}{V} = \frac{N kT}{V} \left[1 - 0.462 \left(\frac{T_C}{T} \right)^{3/2} - \dots \right] \quad \dots(5.5.17)$$

Specific Heat C_v

$$\begin{aligned} C_v &= \left(\frac{\partial E}{\partial T} \right)_V = \frac{\partial}{\partial T} \left[\frac{3}{2} N kT \left\{ 1 - 0.462 \left(\frac{T_C}{T} \right)^{3/2} - \dots \right\} \right] \\ &= \frac{3}{2} N k \left[1 + 0.231 \left(\frac{T_C}{T} \right)^{3/2} + \dots \right] \end{aligned} \quad \dots(5.5.18)$$

Entropy S

$$S = S(T_C) + \int_{T_C}^T \frac{C_v dT}{T} = S(T_C) + \frac{3}{2} N k \left[\ln \frac{T}{T_C} + 0.154 \left(1 - \frac{T_C}{T} \right)^{3/2} + \dots \right] \quad \dots(5.5.19)$$

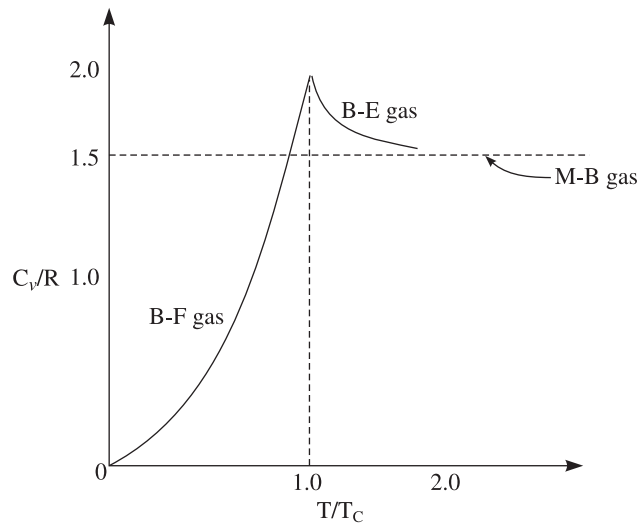


Fig. 5.5.1 Variation of C_v with temperature

5.6 BLACK BODY RADIATION: PLANCK'S RADIATION LAW

The thermal radiation in a cavity maintained at temperature T is a well-known example of B-E system. In quantum picture the radiation is regarded as an assembly of particles, called photons, each of which has spin 1. The energy ϵ and momentum p of photon are given by $\epsilon = \hbar\omega$ and $p = (\hbar\omega/c) = \epsilon/c$.

To obtain the energy of photon gas we need to know the number of quantum states $g(p) dp$ available to photons with momentum in the range dp at p . Since photon has zero rest mass, the expression for density of states

$$g(\epsilon) d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \quad \dots(5.6.1)$$

as such cannot be applied. To apply it to photons we must convert it in terms of momentum p through substitutions $\epsilon = p^2/2m$ and $d\epsilon = (2p dp/2m)$. Making use of this substitution we get

$$g(p) dp = \frac{4\pi V}{h^3} p^2 dp \quad \dots(5.6.2)$$

This expression for the number of quantum states accessible to photons needs correction. Electromagnetic waves are purely transverse and there can be two sets of waves polarized in mutually perpendicular planes or right and left circular polarizations. Thus, a photon of definite momentum can be in two possible states. The net effect is to multiply the above expression for the density of states by two. Thus, the number of photon states in which the photon has momentum in the range p and $p + dp$ is

$$g(p) dp = \frac{8\pi V}{h^3} p^2 dp \quad \dots(5.6.3)$$

In terms of frequency ω , the number of states in the frequency range $d\omega$ at ω is

$$\begin{aligned} g(\omega) d\omega &= \frac{8\pi V}{h^3} \left(\frac{\hbar\omega}{c} \right)^2 d \left(\frac{\hbar\omega}{c} \right) \\ &= \frac{V}{\pi^2 c^3} \omega^2 d\omega \end{aligned} \quad \dots(5.6.4)$$

According to B-E distribution the mean number of photons per quantum state at energy ϵ is

$$f(\epsilon) = \frac{1}{e^{\beta\epsilon} - 1} = \frac{1}{e^{\beta\hbar\omega} - 1}, \quad \beta = \frac{1}{kT} \quad \dots(5.6.5)$$

The number of photons in the frequency range ω and $\omega + d\omega$ is

$$n(\omega) d\omega = f(\omega) g(\omega) d\omega = \frac{V}{\pi^2 c^3} \cdot \frac{\omega^2 d\omega}{e^{\beta\hbar\omega} - 1} \quad \dots(5.6.6)$$

The energy of photon gas in the frequency range ω and $\omega + d\omega$ is

$$\varepsilon(\omega) d\omega = \hbar\omega \cdot n(\omega) d\omega = \left(\frac{V\hbar}{\pi^2 c^3} \right) \left(\frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1} \right) \quad \dots(5.6.7)$$

The energy density in the frequency range ω and $\omega + d\omega$ is

$$u(\omega, T) d\omega = \frac{\hbar}{\pi^2 c^3} \cdot \frac{\omega^3}{e^{\beta\hbar\omega} - 1} d\omega \quad \dots(5.6.8)$$

or

$$u(\lambda, T) d\lambda = \frac{16\pi^2 \hbar c}{\lambda^5} \frac{1}{[\exp(2\pi\hbar c / \lambda kT)] - 1} d\lambda \quad \dots(5.6.9)$$

This is the *Planck's radiation law*. Stefan's law and Wien's law both have been derived from this law.

5.7 VALIDITY CRITERION FOR CLASSICAL REGIME

The mean occupation number $n(\varepsilon)$ of energy state ε , according to classical (M-B) statistics, is

$$n(\varepsilon) = \frac{g_i}{e^\alpha e^{\varepsilon/kT}} = g_i e^{-\alpha} e^{-\varepsilon/kT} \quad \dots(5.7.1)$$

and that according to quantum statistics is

$$n(\varepsilon) = \frac{g_i}{e^\alpha e^{\varepsilon/kT} \pm 1} \quad \dots(5.7.2)$$

+ sign for F-D and – sign for B-E statistics

The quantum statistics become identical with the M-B statistics in the limit

$$e^\alpha e^{\varepsilon/kT} \gg 1 \quad \dots(5.7.3)$$

for all values of ε . For $\varepsilon = 0$ the Eqn. (5.7.3) reduces to

$$e^\alpha \gg 1 \quad \dots(5.7.4)$$

Equation (5.7.4) will certainly hold for $\varepsilon > 0$. So the equation represents the criterion for the validity of classical statistics. Now the parameter α is determined from the condition

$$\begin{aligned} N &= \sum_i n_i = \sum_i g_i(\varepsilon_i) e^{-\alpha} e^{-\beta\varepsilon_i} \\ N e^\alpha &= \sum_i g_i(\varepsilon_i) e^{-\beta\varepsilon_i} \longrightarrow \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} e^{-\beta\varepsilon} d\varepsilon \\ &= \frac{2\pi V}{h^3} (2m)^{3/2} \frac{1}{2} \sqrt{\pi} \end{aligned}$$

$$\therefore e^{\alpha} = \left(\frac{V}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \quad \dots(5.7.5)$$

So, in view of Eqn. (5.7.5) the criterion (5.7.4) becomes

$$\left(\frac{V}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \gg 1 \quad \dots(5.7.6)$$

If a is the average separation between the particles of the system then each particle may be allotted a cubical volume a^3 . This must be equal to V/N . So $(V/N)^{1/3}$ gives the mean distance between the molecules. Now the thermal de Broglie wavelength of particles is given by

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m\varepsilon}} = \frac{h}{\sqrt{3mkT}}, \quad \varepsilon = \frac{3}{2}kT$$

$$\text{So} \quad \frac{1}{\lambda^3} = \left(\frac{3mkT}{h^2} \right)^{3/2} \approx \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \quad \dots(5.7.7)$$

In view of Eqn.(5.7.7), the condition (5.7.6) becomes

$$\left(\frac{a}{\lambda} \right)^3 \gg 1$$

$$a \gg \lambda \quad \dots(5.7.8)$$

Thus, the classical statistics is valid if the average separation between particles is much greater than the mean de Broglie wavelength of the particles. This condition will be satisfied when (i) the temperature is large, (ii) number density is very small (*i.e.*, the gas is dilute), and (iii) mass of particle is not too small. When these conditions are not met, the particles are close together and their wave function overlap and they are no longer distinguishable.

Let us illustrate this by example. Consider helium gas at N.T.P., the average separation between molecules is

$$a = \left(\frac{V}{N} \right)^{1/3} = \left(\frac{22.4 \times 10^3}{6.6 \times 10^{23}} \right)^{1/3} = 32 \times 10^{-8} \text{ cm} = 32 \text{ \AA}$$

The de Broglie wavelength of molecule is

$$\lambda = \frac{h}{\sqrt{3mkT}} = \frac{6.6 \times 10^{-34} \text{ Js}}{\sqrt{3 \times 6.8 \times 10^{-27} \text{ kg} \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}}} = 0.8 \times 10^{-10} \text{ m} = 0.8 \text{ \AA}$$

Since $a \gg \lambda$, classical (M-B) statistics can be applied to helium gas at room temperature.

Now consider liquid helium gas at 10 K. The average separation between molecules is

$$a = \left(\frac{V}{N} \right)^{1/3} = (5 \times 10^{-23} \text{ cm}^3)^{1/3} \approx 4 \times 10^{-8} \text{ cm} = 4 \text{ \AA}$$

de Broglie wavelength of molecule is

$$\lambda = \frac{h}{\sqrt{3mkT}} = \frac{6.6 \times 10^{-34} \text{ Js}}{\sqrt{3 \times 6.8 \times 10^{-27} \text{ kg} \times 1.38 \times 10^{-23} \text{ J/K} \times 10 \text{ K}}} = 4 \times 10^{-10} \text{ m} = 4 \text{ \AA}$$

Since $a \approx \lambda$, quantum (B-E) statistics must be applied to liquid helium.

For conduction electrons in metals the average separation between electrons is

$$a = \left(\frac{V}{N} \right)^{1/3} = (10^{-23} \text{ cm}^3)^{1/3} \approx 2 \times 10^{-8} \text{ cm} = 2 \text{ \AA}$$

The de Broglie wavelength of electron is

$$\lambda = \frac{h}{\sqrt{3mkT}} = \frac{6.6 \times 10^{-34} \text{ Js}}{\sqrt{3 \times 9.1 \times 10^{-31} \text{ kg} \times 1.38 \times 10^{-23} \text{ J/K} \times 300 \text{ K}}} = 62 \times 10^{-10} \text{ m} = 62 \text{ \AA}$$

Since the condition $\lambda \gg a$ is satisfied, quantum (F-D) statistics is most appropriate for the treatment of conduction electrons in metals.

5.8 COMPARISON OF M-B, B-E AND F-D STATISTICS

1. The distribution functions for the three statistics giving the mean number $\bar{n}_i$ of particles occupying a state with energy ϵ_i are given by

$$\bar{n}_i = g_i e^{-\alpha} e^{-\beta \epsilon_i} \quad (\text{M-B})$$

$$\bar{n}_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} - 1} \quad (\text{B-E})$$

$$\bar{n}_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1} \quad (\text{F-D})$$

In the classical limit $g_i \gg n_i$, B-E and F-D both distribution functions approach the M-B distribution function. M-B statistics is a classical statistics, B-E and F-D statistics are quantum statistics.

2. M-B statistics applies to systems comprising of *distinguishable* particles, whereas B-E and F-D statistics apply to *indistinguishable* particles.
3. Spin of particles constituting the system is not a criterion for the applicability of M-B statistics. B-E statistics is applicable to particles having integral spins 0, 1, 2, ... Such

particles are called *bosons*. Examples of *bosons* are: photons, phonons, hydrogen molecule, liquid helium, mesons, etc. F-D statistics applies to particles having half-integral spins $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. Such particles are called *fermions*. Examples of fermions are: electrons, protons, neutrons, ...etc.

4. M-B and B-E statistics put no restriction on the number of particles that can occupy a quantum state. F-D statistics permits at the most one particle that a quantum state can accommodate.
5. To specify a microstate of a system, the classical phase space is divided into cells whose volume may be taken as small as we please. A cell in this phase space represents a microstate of the system. In quantum mechanical description the phase space is divided into cells whose volume is not less than h^3 , h being Planck's constant. A cell of volume h^3 represents a quantum state (microstate) of the system.
6. At high temperature both quantum statistics (B-E and F-D) approach the M-B statistics.
7. The variation of three distribution functions $f(\epsilon) = n_i / g_i$, with energy at different temperatures is shown in the figures. According to M-B and B-E distribution functions, at a given temperature, particles like to occupy the lower energy states. At lower energy the occupation number is larger for B-E than for M-B distribution function. As the energy of the system increases, the occupation number decreases. According to F-D distribution function, at $T = 0$ K, all the quantum states with energy less than Fermi energy are occupied by electrons in an electron gas and those above the Fermi level are empty. As temperature increases, the electrons in the energy states a little below the Fermi level are excited to empty energy states a little above the Fermi level. At very high temperature the F-D distribution becomes more and more like M-B distribution.

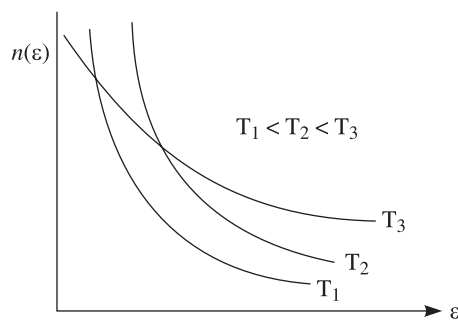


Fig. 5.8.1 M-B statistics

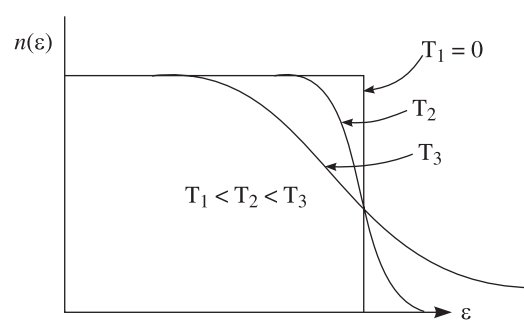


Fig. 5.8.2 F-D statistics

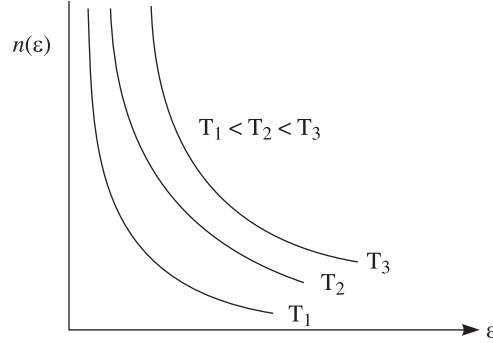


Fig. 5.8.3 B-E statistics

8. The values of g_i/n_i for the three distribution functions are:

$$\text{M-B} \quad \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i}$$

$$\text{B-E} \quad \frac{g_i}{n_i} + 1 = e^{\alpha + \beta \epsilon_i}$$

$$\text{F-D} \quad \frac{g_i}{n_i} - 1 = e^{\alpha + \beta \epsilon_i}$$

When the number of quantum states in an energy level is much larger than the number of indistinguishable particles (bosons or fermions) *i.e.*, $g_i \gg n_i$, the term 1 may be omitted. In this situation, both the quantum statistics reduce to M-B statistics and hence M-B statistics can safely be used to the system. Thus, the classical limit is reached when $g_i \gg n_i$. This condition may be put in other forms as

$$e^{\alpha} \gg 1$$

$$\text{or} \quad \left(\frac{V}{N} \right) \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \gg 1$$

$$\text{or} \quad a \gg \lambda$$

where V = volume of the system, N = total number of particles in the system, T = temperature of the system, a = average separation of particles and λ = de Broglie wavelength of the particles.

This condition is satisfied in a gaseous system when the pressure is not too large and the temperature is not too low under normal conditions.

PARTITION FUNCTION

6.1 CANONICAL PARTITION FUNCTION

The canonical partition function of a single molecule of an N-particles system occupying a volume V at temperature T is defined by

$$z(V,T) = \sum_r e^{-\epsilon_r / kT} \quad \dots(6.1.1)$$

Henceforth, we shall denote single particle partition function by lower case letter z and that of N-particle system by upper case letter Z . The summation in Eqn. (6.1.1) is performed over all discrete quantum states of the particle. If the degeneracy of the energy level ϵ_r is $g(\epsilon_r)$, Eqn. (6.1.1) takes the form

$$z(V,T) = \sum_{\text{energy levels}} g(\epsilon_r) e^{-\epsilon_r / kT} \quad \dots(6.1.2)$$

where summation is only over all different energies ϵ_r . The quantity z is very useful quantity for calculating the macroscopic properties of any thermodynamic system in equilibrium. The evaluation of the sum in Eqn. (6.1.1) requires the knowledge of single particle quantum states of the constituent particles of the system.

There are many problems in which the Hamiltonian can be written as a sum of simpler Hamiltonians. The most obvious example is the case of a dilute monatomic gas where the molecules are on the average far apart and hence their intermolecular interaction can be neglected. The molecules of the gas have kinetic energies only. The total Hamiltonian in this case is expressed as

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} \quad \dots(6.1.3)$$

N is the number of particles (molecules) in the gas.

Another example is the decomposition of Hamiltonian of a polyatomic molecule into its various degrees of freedom viz translational, rotational, vibrational, electronic etc.

$$H = H_{trans} + H_{rot} + H_{vib} + H_{ele} \quad \dots(6.1.4)$$

There are many other problems in physics in which the Hamiltonian by a proper and clever choice of variables can be written as a sum of individual terms as shown above. In all such cases the partition function of a molecule comes out to be a product of partition functions corresponding to each degree of freedom. For example, consider a system comprising of *distinguishable* particles $a, b, c, \dots$. Let the energy states of these particles be $\{\epsilon_j^a\}, \{\epsilon_k^b\}, \{\epsilon_l^c\} \dots$. The superscripts denote the particles and the subscript the energy states. In this case the partition function of the system becomes

$$\begin{aligned} Z(N, V, T) &= \sum_{j, k, l, \dots} e^{-[\epsilon_j^a + \epsilon_k^b + \epsilon_l^c + \dots]/kT} \\ &= \sum_j e^{-\epsilon_j^a/kT} \sum_k e^{-\epsilon_k^b/kT} \sum_l e^{-\epsilon_l^c/kT} \\ &= z_a \cdot z_b \cdot z_c \dots \dots \dots \end{aligned} \quad \dots(6.1.5)$$

This is a very important result. It shows that if we write the N-particle Hamiltonian as a sum of independent terms, then the calculation of Z of the system reduces to a calculation of partition function z of a single particle. Since z requires knowledge only of energy levels of a single particle, its evaluation is quite simple. If the constituent particles are identical (*i.e.*, of the same kind), $z_a = z_b = z_c \dots = z$, the partition function of the system is

$$Z = z^N \quad (\text{distinguishable particles}) \quad \dots(6.1.6)$$

6.2 CLASSICAL PARTITION FUNCTION OF A SYSTEM CONTAINING N DISTINGUISHABLE PARTICLES

In classical approximation, the energy of a N-particle system depends on $3N$ generalized coordinates $q_1, \dots, q_{3N}$, and $3N$ momentum coordinates $p_1, \dots, p_{3N}$. The phase space is divided into cells of volume h^{3N} . To evaluate the partition function from Eqn. (6.1.1) we first take the sum over the

number $\frac{dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}}{h^{3N}}$ of cells of phase space at point $(q_1, \dots, q_{3N}, p_1, \dots, p_{3N})$ and then take the sum (or integral) over all such volume elements. Thus in classical approximation the partition function of a N-particle system is given by

$$Z = \int \dots \int e^{-\epsilon(q, p)/kT} \cdot \frac{dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}}{h^{3N}} \quad \dots(6.2.1)$$

Notice that the transition from quantum partition function to classical partition function can be accomplished by following replacement :

$$\sum_r \rightarrow \int \frac{dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}}{h^{3N}} \quad \dots(6.2.2)$$

For a system of particles possessing only translational kinetic energy, the evaluation of integral in Eqn. (6.2.1) is simple.

$$Z = \frac{1}{h^{3N}} \int d^3q_1 \dots d^3q_N \int \exp\left(-\frac{\beta(p_1^2 + p_2^2 + \dots + p_N^2)}{2m}\right) d^3p_1 \dots d^3p_N$$

where $d^3q_1 = dx dy dz$ and $d^3p_1 = dp_x dp_y dp_z$ etc.

$$\begin{aligned} Z_N &= \frac{V^N}{h^{3N}} \int_{-\infty}^{\infty} \exp\left(-\frac{\beta p_1^2}{2m}\right) d^3p_1 \dots \int_{-\infty}^{\infty} \exp\left(-\frac{\beta p_N^2}{2m}\right) d^3p_N \\ &= \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3/2} \dots \dots \dots N \text{ factors} \\ &= \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \\ Z_N &= V^N \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \quad \dots(6.2.3) \end{aligned}$$

We have already mentioned that the evaluation of partition function for many-particle system reduces to the evaluation of partition function for a single particle. Consider a N-particle system whose constituent particles have translational kinetic energy $\epsilon_r = p^2/2m$ only. Let us illustrate this. In the phase space of a single particle, in the volume element $dx dy dz dp_x dp_y dp_z (= d^3q d^3p)$ there are $\frac{dx dy dz dp_x dp_y dp_z}{h^3}$ or $\frac{d^3q d^3p}{h^3}$ possible quantum states. Therefore, the partition function for a single particle is

$$z = \frac{1}{h^3} \int \dots \int \left\{ \exp\left(-\frac{\beta p^2}{2m}\right) \right\} d^3q d^3p$$

The integration over the ordinary space coordinates gives the volume V occupied by the system of particles. So

$$\begin{aligned} z &= \frac{V}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{ \exp\left(-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}\right) \right\} dp_x dp_y dp_z \\ &= \frac{V}{h^3} \int_{-\infty}^{\infty} \left\{ \exp\left(-\frac{\beta p_x^2}{2m}\right) \right\} dp_x \int_{-\infty}^{\infty} \left\{ \exp\left(-\frac{\beta p_y^2}{2m}\right) \right\} dp_y \int_{-\infty}^{\infty} \left\{ \exp\left(-\frac{\beta p_z^2}{2m}\right) \right\} dp_z \end{aligned}$$

$$= \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{1/2} \left(\frac{2\pi m}{\beta} \right)^{1/2} \left(\frac{2\pi m}{\beta} \right)^{1/2}$$

$$\therefore z = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \frac{V}{\lambda^3}, \lambda = \frac{h}{\sqrt{2\pi mkT}} = \text{de Broglie wavelength of the particle.}$$

The partition function for the *indistinguishable* N-particle system is

$$Z = z^N = V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad \dots(6.2.4)$$

$$\ln Z = N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) - \frac{3}{2} \ln \beta \right], \quad \beta = 1/kT \quad \dots(6.2.5)$$

6.3 THERMODYNAMIC FUNCTIONS OF MONOATOMIC GAS

Mean energy $\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2\beta} = \frac{3}{2} NkT \quad \dots(6.3.1)$

Helmholtz free energy

$$F = -kT \ln Z = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right] \quad \dots(6.3.2)$$

The entropy of the system

$$S = k \left[\ln Z + \beta \bar{E} \right]$$

$$= Nk \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi mk}{h^2} \right) + \frac{3}{2} \right] \quad \dots(6.3.3)$$

$$= Nk \left[\ln V + \frac{3}{2} \ln T + \sigma \right] \quad \dots(6.3.4)$$

where $\sigma = \frac{3}{2} \left[\ln \left(\frac{2\pi mk}{h^2} \right) + 1 \right] \quad \dots(6.3.5)$

The application of Eqn. (6.3.4) in calculating the change in entropy when two samples of the same gases of equal volume and at the same pressure and temperature are mixed leads to the famous

paradox known as **Gibbs paradox**. This equation is valid for a gas of *distinguishable* molecules and needs correction when it is to be applied to a system of *indistinguishable* molecules.

6.4 GIBBS PARADOX

Consider a vessel divided into two compartments by a removable partition. The two compartments are then filled with two different gases. The number of molecules and volumes of the two gases are N_1, V_1 and N_2, V_2 as shown in the Fig. (6.4.1). The gases are at the same temperature and pressure. Now the partition is removed. On removing the partition, the gases are mixed owing to diffusion of

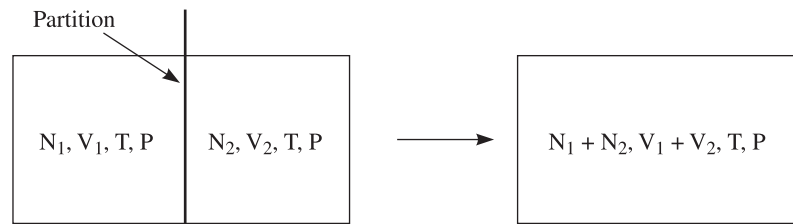


Fig. 6.4.1 Mixing of two different gases initially separated by a partition wall

molecules. The diffusion is an irreversible process. (By putting the partition back in its original position, the gases don't separate and the original state of gases is not achieved.) In irreversible process of mixing of the two different gases the entropy increases. Let us calculate the increase in entropy. The entropy of a gas composed of N identical distinguishable molecules is given by

$$S = Nk \left[\ln V + \frac{3}{2} \ln T + \frac{3}{2} \left(\ln \frac{2\pi mk}{h^2} \right) + \frac{3}{2} \right] \quad \dots(6.4.1)$$

Before mixing the entropy of the combined system is

$$S_{12} = S_1 + S_2 = N_1 k \left[\ln V_1 + \frac{3}{2} \ln T + \frac{3}{2} \left(\ln \frac{2\pi m_1 k}{h^2} \right) + \frac{3}{2} \right] +$$

$$N_2 k \left[\ln V_2 + \frac{3}{2} \ln T + \frac{3}{2} \left(\ln \frac{2\pi m_2 k}{h^2} \right) + \frac{3}{2} \right] \quad \dots(6.4.2)$$

After mixing the entropy of the combined system is

$$S'_{12} = S'_1 + S'_2 = N_1 k \left[\ln (V_1 + V_2) + \frac{3}{2} \ln T + \frac{3}{2} \left(\ln \frac{2\pi m_1 k}{h^2} \right) + \frac{3}{2} \right] +$$

$$N_2 k \left[\ln (V_1 + V_2) + \frac{3}{2} \ln T + \frac{3}{2} \left(\ln \frac{2\pi m_2 k}{h^2} \right) + \frac{3}{2} \right] \quad \dots(6.4.3)$$

The change in entropy is

$$\Delta S = k \left[N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right] \quad \dots(6.4.4)$$

If we take $N_1 = N_2 = N$ and $V_1 = V_2 = V$ then

$$\Delta S = 2 k N \ln 2 = \text{positive number.} \quad \dots(6.4.5)$$

The entropy in the process increases and this result is in agreement with the experiments.

Now suppose that the two compartments of the vessel are filled with the same gases such that $N_1 = N_2 = N$, $V_1 + V_2 = V$. The two samples of the gases are at the same temperature and pressure. If the partition is removed, the increase in entropy of the combined system calculated as before comes out to be equal to

$$\Delta S = 2 N k \ln 2$$

That is, the entropy increases in the process of mixing of two identical samples of the same gases. This conclusion is not correct. Further if we put a large number of partitions in the vessel and remove them one by one, then by increasing the entropy in each act of removing the partition, we



Fig. 6.4.2 Mixing of two identical samples of the same gases

can increase the entropy of the combined system by any amount. The mixing of two identical samples of the same gases is a reversible process because by inserting the partition to its initial position, we get the state of the gases, which are in no way different from that we had before mixing. The total entropy of the system should not change on removal of the partition. This is known as Gibbs paradox. The origin of this paradox lies in the use of expression for entropy derived from the formula of partition function

$$Z = z^N = V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad (\text{distinguishable particles}) \quad \dots(6.4.6)$$

In the derivation of this expression it was assumed that the particles of the system are *distinguishable* and the interchange of positions of two molecules would lead to a physically distinct state of the system. But this is not so. In quantum mechanical treatment of a gas, the molecules are completely *indistinguishable*. A calculation of partition function and entropy, assuming the indistinguishability of molecules, would not give rise to Gibbs paradox. A way out to the Gibbs paradox is to apply a correction to the expression of partition function (6.4.6). We know that N -molecules can be arranged in $N!$ ways by permuting among themselves. If the molecules are considered indistinguishable, then these $N!$ possible permutations of such molecules would not lead

to physically distinct states. So the number of distinct states over which the summation is made in calculation of classical partition function is large by a factor $N!$. The correct partition function will be that which takes into account the indistinguishability of molecules. This is obtained by dividing the expression (6.4.6) of partition function by $N!$.

$$Z = \frac{z^N}{N!} = \frac{1}{N!} \left[V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \right]^N \quad (\text{indistinguishable particles}) \quad \dots(6.4.7)$$

$$\ln Z = N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) \right] - \ln N!$$

Using Stirling's approximation $\ln N! = N \ln N - N$, we obtain

$$\begin{aligned} \ln Z &= N \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) \right] - N \ln N + N \\ &= N \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) + 1 \right] \end{aligned} \quad \dots(6.4.8)$$

Entropy

$$S = k [\ln Z + \beta E], \quad E = (3/2) N k T$$

Therefore

$$\begin{aligned} S &= k \ln Z + \frac{3}{2} N k \\ &= N k \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k}{h^2} \right) + \frac{5}{2} \right] \end{aligned} \quad \dots(6.4.9)$$

Using this formula for calculating the increase in entropy in mixing of two samples of the same gases, we obtain

$$S_{\text{initial}} = S_1 + S_2 = 2Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k}{h^2} \right) + \frac{5}{2} \right] \quad \dots(6.4.10)$$

$$S_{\text{final}} = S'_1 + S'_2 = 2Nk \left[\ln \frac{2V}{2N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{2\pi m k}{h^2} \right) + \frac{5}{2} \right] \quad \dots(6.4.11)$$

Change in entropy on mixing the gases

$$\Delta S = 0$$

6.5 INDISTINGUISHABILITY OF PARTICLES AND SYMMETRY OF WAVE FUNCTIONS

Let us consider a system consisting of two identical particles labelled 1 and 2. If the particle is restricted to move in a certain region, the quantum mechanical treatment of the particle allows it to have discrete quantum states and discrete energy levels. Let $\phi_r(1)$ and $E_r(1)$ denote the r th quantum state (wave function) and energy of particle 1. Similarly $\phi_s(2)$ and $E_s(2)$ denote the s th state and energy of particle 2. Now suppose that both the particles 1 and 2 are present simultaneously in the same region.

If the average separation between the particles is much greater than their de Broglie wavelength *i.e.*, the wave functions of the particles do not overlap, the particles are said to be distinguishable and the wave function of the two particles is simple product of individual particles. Thus

$$\psi(1, 2) = \phi_r(1) \phi_s(2) \quad \dots(6.5.1)$$

$\phi_r(1)$ means that the particle 1 is in the state ϕ_r . This may be generalized to a system of N -particles, where N is very large. The wave function of an N -particle system is

$$\psi(1, 2, 3, \dots) = \phi_r(1) \phi_s(2) \phi_t(3) \dots \phi_z(N) \quad \dots(6.5.2)$$

By distinguishable particles we mean that any interchange of particles among the occupied states *viz.*, $\phi_r(2) \phi_s(1)$ leads to a new state for the system without any change in the total energy of the system. A distribution function, which gives the distribution of particles among the various energy levels, derived on the assumption that the particles are distinguishable, is called classical or Maxwell-Boltzmann distribution.

If the average separation between the particles is less than the de Broglie wavelengths of the particles, then their wave functions overlap. The particles are said to be indistinguishable and quantum statistics is appropriate for their description. The wave function of the whole system must satisfy certain symmetry requirements.

If the system is composed of particles having integral spin (0, 1, 2, ...), it must be described by a wave function that must be symmetric with respect to interchange of two particles. That is, the wave function should not change its sign on interchanging two particles.

$$\psi^s(1, 2) = \psi^s(2, 1)$$

The superscript s stands for symmetry. For a system of two particles, the wave function of the system is obtained from the linear combination of single particle wave functions $\phi_r(1)$ and $\phi_s(2)$. Thus

$$\psi^s(1, 2) = \frac{1}{\sqrt{2}} [\phi_r(1) \phi_s(2) + \phi_r(2) \phi_s(1)] \quad \dots(6.5.3)$$

where $\sqrt{2}$ is normalization factor. We can verify that the wave function Eqn. (6.5.3) of the system remains unchanged on interchanging the particles.

$$\psi^s(2, 1) = \frac{1}{\sqrt{2}} [\phi_r(2) \phi_s(1) + \phi_r(1) \phi_s(2)] = \psi^s(1, 2)$$

Thus, the wave function $\psi^s(1, 2)$ given by Eqn. (6.5.3) satisfies the symmetry requirement. A system consisting of particles of integral spins are described by symmetric wave function and the statistical behaviour of the system is described by quantum statistics called Bose-Einstein statistics. The particles with integral spin are called *bosons*. If n_r represents number of bosons in any quantum state then $n_r = 0, 1, 2, 3, \dots$. There is no restriction on the number of bosons that can be in a quantum state.

A system consisting of particles having half-integral spins ($\frac{1}{2}, \frac{3}{2}, \dots$) must be described by wave function that must be anti-symmetric with respect to interchange of two particles. That is, the wave function must change sign without a change in its magnitude. For a two-particle wave function this requirement can be expressed as

$$\psi^A(1, 2) = -\psi^A(2, 1) \quad \dots(6.5.4)$$

For a two-particle system, the wave function $\psi^A(1, 2)$, which is antisymmetric is obtained from the linear combination of single particle wave functions as follows.

$$\psi^A(1, 2) = \frac{1}{\sqrt{2}} [\phi_r(1)\phi_s(2) - \phi_r(2)\phi_s(1)] \quad \dots(6.5.5)$$

$$= \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_r(1) & \phi_r(2) \\ \phi_s(1) & \phi_s(2) \end{vmatrix}$$

$$= -\psi^A(2, 1)$$

For an N-particle system, the wave function of the system is given by Slater determinant

$$\psi^A(1, 2, 3, \dots, N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_r(1) & \phi_r(2) & \dots & \phi_r(N) \\ \phi_s(1) & \phi_s(2) & \dots & \phi_s(N) \\ \phi_z(1) & \phi_z(2) & \dots & \phi_z(N) \end{vmatrix} \quad \dots(6.5.6)$$

where $\sqrt{N}$ is normalization factor. The particles with half-integral spin are called *fermions*.

Putting $r = s$ in $\psi^A(1, 2)$ given by Eqn.(6.5.5) we have $\psi^A(1, 2) = 0$. That is if we put the two *fermions* in the same state then the wave function vanishes. In other words, *no two fermions can be in the same quantum state*. This statement is called Pauli exclusion principle. If n_r is the number of fermions in any quantum state then $n_r = 0, 1$ for all r .

6.6 PARTITION FUNCTION FOR INDISTINGUISHABLE PARTICLES

Let the wave functions and energies of two non-interacting distinguishable particles 1 and 2 be $\phi_r(1)$, $\epsilon_r(1)$ and $\phi_s(2)$, $\epsilon_s(2)$ respectively. If both the particles are present simultaneously in a region, the combined wave function and energy of the system are given by

$$\psi(1, 2) = \varphi_r(1) \varphi_s(2)$$

$$\varepsilon_{12} = \varepsilon_r(1) + \varepsilon_s(2)$$

The canonical partition function of the system is

$$\begin{aligned} Z &= \sum_{r,s} e^{-\beta \varepsilon_{12}} = \sum_{r,s} e^{-\beta(\varepsilon_r(1) + \varepsilon_s(2))} \\ &= \sum_r e^{-\beta \varepsilon_r(1)} \sum_s e^{-\beta \varepsilon_s(2)} = z_1 \cdot z_2 \end{aligned}$$

where summation extends over all quantum states of the individual particles 1 and 2. If the particles are identical $\varepsilon_r(1) = \varepsilon_s(2)$ and $z_1 = z_2 = z$ (say). The partition function of the system becomes

$$Z = Z^2 \quad (\text{two particle system})$$

Generalization of this result to N-particle system gives

$$Z = z^N \quad (\text{identical distinguishable N-particle system})$$

If the particles 1 and 2 are indistinguishable the wave function $\psi(1, 2)$ of the system must be either symmetric or anti-symmetric. The total energy ε_{12} of the system can be expressed in $2! = 2$ ways as

$$\varepsilon_{12} = \varepsilon_r(1) + \varepsilon_s(2) \quad \text{or} \quad \varepsilon_{12} = \varepsilon_r(2) + \varepsilon_s(1)$$

These two ways of writing the total energy corresponds to a single wave function $\psi^s(1, 2)$ or $\psi^A(1, 2)$. The expression for partition function $Z = \sum_{r,s} e^{-\beta \varepsilon_{12}}$ for the system, contains two terms

$$\varepsilon_{12} = \varepsilon_r(1) + \varepsilon_s(2) \quad \text{and} \quad \varepsilon_{12} = \varepsilon_r(2) + \varepsilon_s(1)$$

corresponding to the same energy. Actually Z should contain only one term. To obtain the correct expression for partition function for a system containing indistinguishable particles Z should be divided by $2!$.

$$Z = \frac{z^2}{2!} \quad (\text{two particle system})$$

This result may be generalized to a system of N indistinguishable particles. Thus

$$Z = \frac{(z_{\text{single}})^N}{N!} \quad (\text{N identical indistinguishable particle system}) \quad (6.6.1)$$

In the classical limit, when the number of quantum states is much greater than the number of particle available i.e., $g_i \gg n_i$, the difference between bosons and fermions may be neglected and Maxwell-Boltzmann statistics along with the expression for partition function

$$Z = \frac{z^N}{N!}$$

may be used without any appreciable error.

If the energy levels of all the particles are the same, then the partition function of a system of N identical, indistinguishable particles, satisfying the condition that the number of available quantum states is much greater than the number of particles, is

$$Z(N, V, T) = \frac{1}{N!} \left[\sum_r e^{-\epsilon_r / kT} \right]^N = \frac{z^N}{N!} \quad \dots(6.6.2)$$

The presence of factor $1/N!$ is in accordance with the rule of correct *Boltzmann counting*. Eqn. (6.6.1) is an extremely important result since it reduces a many body problem to a one-body problem.

The partition function for the indistinguishable N -particle system whose constituent particles have only translational kinetic energy is

$$Z(T, V, N) = \frac{z_{\text{single}}^N}{N!} = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad \dots(6.6.3)$$

6.7 MOLECULAR PARTITION FUNCTION

To a first approximation, the internal degrees of freedom (vibrational, rotational, electronic, nuclear) may be assumed to be independent of each other and the total energy E may be expressed as the sum of translational, rotational, vibrational, electronic and nuclear energies.

$$E = E_t + E_r + E_v + E_e + E_n$$

The partition function of a molecule is

$$\begin{aligned} z &= \sum_i e^{-\beta E_i} = \sum_i e^{-\beta(E_t + E_r + E_v + E_e + E_n)} \\ &= \left(\sum_i e^{-\beta E_t} \right) \left(\sum_i e^{-\beta E_r} \right) \left(\sum_i e^{-\beta E_v} \right) \left(\sum_i e^{-\beta E_e} \right) \left(\sum_i e^{-\beta E_n} \right) \\ &= z_t \cdot z_r \cdot z_v \cdot z_e \cdot z_n \end{aligned} \quad \dots(6.7.1)$$

Thus, the partition function of molecule is the product of the translational, rotational, vibrational, electronic and nuclear partition functions.

The partition function of a gas of N molecules is

$$Z = \frac{1}{N!} \left[z_t^N \cdot z_r^N \cdot z_v^N \cdot z_e^N \cdot z_n^N \right] \quad \dots(6.7.2)$$

6.8 PARTITION FUNCTION AND THERMODYNAMIC PROPERTIES OF MONOATOMIC IDEAL GAS

Consider a monoatomic gas dilute enough so that intermolecular interactions can be neglected. This condition is achieved at pressure below 1 atmosphere and at temperature greater than room temperature. The number of available quantum states far exceeds the number of particles of the gas. Under this condition the molecules of the gas have only translational kinetic energy viz., $\epsilon = p^2/2m$.

The partition function for a single molecule is

$$z = \int_0^{\infty} g(\epsilon) e^{-\beta\epsilon} d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon$$

Making the substitution $x = \beta\epsilon$ we have

$$\begin{aligned} z &= \frac{2\pi V}{h^3} \left(\frac{2m}{\beta} \right)^{3/2} \int_0^{\infty} x^{1/2} e^{-x} dx \\ &= \frac{2\pi V}{h^3} \left(\frac{2m}{\beta} \right)^{3/2} \Gamma(3/2), \quad \Gamma(3/2) = \frac{1}{2} \sqrt{\pi}. \\ &= \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} = V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \\ z &= V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \end{aligned}$$

The partition function for the entire gas is

$$Z = \frac{z^N}{N! h^{3N}} = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad \dots(6.8.1)$$

The same result can also be obtained as follows.

The translational energy states of a molecule confined to move in a cube of length L are given by

$$E_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad \dots(6.8.2)$$

The translational partition function of a single molecule is

$$\begin{aligned} z &= \sum_{n_x, n_y, n_z=1}^{\infty} \exp(-\beta\epsilon_{n_x, n_y, n_z}) \\ &= \sum_{n_x=1}^{\infty} \exp\left(-\frac{\beta h^2}{8mL^2} n_x^2\right) \sum_{n_y=1}^{\infty} \exp\left(-\frac{\beta h^2}{8mL^2} n_y^2\right) \sum_{n_z=1}^{\infty} \exp\left(-\frac{\beta h^2}{8mL^2} n_z^2\right) \\ &= \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2}{8mL^2} n^2\right) \right]^3 \quad \dots(6.8.3) \end{aligned}$$

The expression on the right hand side of Eqn. (6.8.3) can not be expressed in terms of any simple analytic function. So we shall evaluate it in classical approximation. For a microscopic particle the successive terms in the expression for energy differ very little and therefore the summation Σ in Eqn.(6.8.3) can be replaced by integral. So

$$z = \left[\int_0^\infty \exp\left(-\frac{\beta h^2}{8mL^2} dn\right) \right]^3 \quad \dots(6.8.4)$$

Making use of the standard results

$$\begin{aligned} \int_0^\infty x^n \cdot \exp(-\alpha x^2) dx &= \frac{1.3.....(n-1)}{(2\alpha)^{n/2}} \cdot \frac{1}{2} \left(\frac{\pi}{\alpha} \right)^{1/2}, n = 2, 4, 6... \\ &= \frac{2.4.....(n-1)}{(2\alpha)^{(n+1)/2}}, n = 3, 5, 7.... \end{aligned}$$

$$I_0(\alpha) = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}, \quad I_1(\alpha) = \frac{1}{2\alpha}, \quad I_2(\alpha) = \frac{1}{4\alpha} \sqrt{\frac{\pi}{\alpha}}, \quad I_3(\alpha) = \frac{1}{2\alpha^2}$$

we get

$$z = \left[\frac{2\pi mkT}{h^2} \right]^{3/2} \cdot V \quad \dots(6.8.5)$$

6.9 THERMODYNAMIC FUNCTIONS IN TERMS OF PARTITION FUNCTION

Helmholtz Free Energy F

Translational contribution to Helmholtz free energy of an N-particle system is given by

$$F = -kT \ln Z \quad \dots(6.9.1)$$

Making use of Stirling approximation $N! = (N/e)^N$ in Eqn.(6.8.1) we have

$$\ln Z = N \ln \left[\frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad \dots(6.9.2)$$

Therefore

$$F = -NkT \ln \left[\frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad \dots(6.9.3)$$

Translational energy of the system is

$$E = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \left[N \ln \left\{ \frac{eV}{N} \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \right\} \right] = \frac{3N}{2\beta} = \frac{3}{2} NkT \quad \dots(6.9.4)$$

The pressure of the gas is

$$P = -\left(\frac{\partial F}{\partial V} \right)_{T,N} = NkT \frac{\partial}{\partial V} \left[\ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right\} \right]_{T,N} = \frac{NkT}{V} \quad \dots(6.9.5)$$

This gives the equation of state

$$PV = NkT$$

Entropy of the gas is given by

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T} \right)_{V,N} = Nk \frac{\partial}{\partial T} \left[T \ln \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right\} \right]_{V,N} \\ &= Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \frac{2\pi mk}{h^2} + \frac{5}{2} \right] \quad \dots(6.9.6) \end{aligned}$$

Equation (6.9.6) is known as Sackur-Tetrode equation. This equation shows that the entropy S tends to infinity as T tends to zero. This clearly violates the third law of thermodynamics. Had we used the original definition of partition function viz $Z = \sum \exp(-\beta \epsilon_r)$ this difficulty would not have crop up. The problem stems from the replacement of the sum by integral. In fact this replacement is not justified near $T = 0$ where the contribution to energy from the ground state is significant. Whereas in the evaluation of integral for partition function we take $\epsilon = 0$ or $p = 0$ in the ground state. At higher temperature the contribution from ground state is insignificant and so the replacement of sum by integral causes no appreciable error.

6.10 ROTATIONAL PARTITION FUNCTION

A rigid diatomic molecule in which two atoms of masses m_1 and m_2 are separated by a fixed distance r_0 is an example of rigid rotator. The moment of inertia of molecule is

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

The rotational energy levels of the molecule are

$$E_r = \frac{\hbar^2}{2I} J(J+1) \quad \dots(6.10.1)$$

where $J = 0, 1, 2, \dots$ are rotational quantum numbers. The J th energy level is $(2J + 1)$ fold degenerate. Hence the partition function of the molecule is

$$z = \sum_{J=0}^{\infty} (2J+1) e^{-\left[\frac{\beta \hbar^2}{2I} J(J+1) \right]} \quad \dots(6.10.2)$$

$$= \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\Theta}{T} J(J+1)} \quad \dots(6.10.3)$$

where $\Theta = \frac{\hbar^2}{2kI}$ is rotational characteristic temperature.

(i) When I or T is very small, we can express the partition function as

$$z = 1 + 3e^{-2\Theta/T} + 5e^{-6\Theta/T} + \dots \text{smaller terms} \quad \dots(6.10.4)$$

At low temperature the thermal energy kT is not enough to take the molecules to higher energy levels. The lower rotational energy levels will be heavily populated.

(ii) At higher temperature, the rotational energy levels form continuum and hence E_r may be assumed to be continuous. The summation sign in Eqn. (6.10.2) or Eqn. (6.10.3) may be replaced by integral sign. Putting $J(J+1) = x$, we can write Eqn. (6.10.2) as

$$\begin{aligned} z &= \int_0^{\infty} (2J+1) e^{-\frac{\beta \hbar^2}{2I} J(J+1)} dJ = \int_0^{\infty} e^{-\frac{\beta \hbar^2}{2I} x} dx \\ &= \frac{2I}{\beta \hbar^2} = \frac{2IkT}{\hbar^2} = \frac{T}{\Theta} \end{aligned} \quad \dots(6.10.5)$$

The general expression for z taking symmetry into consideration comes out to be

$$z = \frac{2IkT}{\sigma \hbar^2} \quad \dots(6.10.6)$$

where $\sigma = 1$ for heteronuclear (asymmetric) molecule and $\sigma = 2$ for symmetric linear molecule.

At higher temperature $T > \Theta$, for an ideal diatomic gas

$$Z = [z^N] = \left[\frac{T}{\sigma \Theta} \right]^N \quad \dots(6.10.7)$$

Helmholtz free energy

$$F = -NkT \ln \frac{T}{\sigma \Theta} \quad \dots(6.10.8)$$

Mean energy

$$\bar{E} = kT^2 \frac{\partial \ln Z}{\partial T} = NkT \quad \dots(6.10.9)$$

Heat capacity

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = Nk \quad \dots(6.10.10)$$

Entropy

$$\begin{aligned} S &= k \ln Z + \frac{E}{T} \\ &= Nk \left[\ln \frac{IT}{\sigma} + \ln \frac{2k}{h^2} + 1 \right] \end{aligned} \quad \dots(6.10.11)$$

6.11 VIBRATIONAL PARTITION FUNCTION

A diatomic molecule made up of two atoms of masses m_1 and m_2 joined by ‘spring’ of force constant k , acts like a harmonic oscillator. The classical frequency ω of the oscillator is $\omega = \sqrt{\frac{k}{\mu}}$, where μ is the reduced mass of the molecule. The vibrational energy levels of the molecule are given by

$$\epsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega, \quad n = 0, 1, 2, \dots \quad \dots(6.11.1)$$

The energy $\epsilon_0 = 1/2 \hbar \omega$ is called the zero-point energy. The vibrational partition function of the molecule is

$$z = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \left(n + \frac{1}{2} \right)} = e^{-\frac{1}{2} \beta \hbar \omega} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} \quad \dots(6.11.2)$$

The expression $\sum_{n=0}^{\infty} e^{-\beta \hbar \omega n}$ can be in an alternative form as

$$\sum_{n=0}^{\infty} e^{-\beta \hbar \omega n} = 1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \dots = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

Therefore

$$z = e^{-\frac{1}{2} \beta \hbar \omega} \cdot \frac{1}{1 - e^{-\beta \hbar \omega}} \quad \dots(6.11.3)$$

$$= e^{-\Theta/2T} \frac{1}{1 - e^{-\Theta/T}} \quad \dots(6.11.4)$$

where $\Theta = \frac{\hbar\omega}{k}$ is vibrational characteristic temperature. For a system consisting of N distinguishable particles the partition function is

$$\begin{aligned} Z = z^N &= e^{-\frac{1}{2}N\beta\hbar\omega} \left(\frac{1}{1 - e^{-\beta\hbar\omega}} \right)^N \\ &= e^{-N\Theta/2T} \left(\frac{1}{1 - e^{-\Theta/T}} \right)^N \end{aligned} \quad \dots(6.11.5)$$

and

$$\ln Z = -\frac{1}{2}N\beta\hbar\omega - N \ln(1 - e^{-\beta\hbar\omega}) \quad \dots(6.11.6)$$

Helmholtz function

$$F = -kT \ln Z = \frac{1}{2}N\beta\hbar\omega + NkT \ln(1 - e^{-\beta\hbar\omega}) \quad \dots(6.11.7)$$

Mean energy of the system

$$\begin{aligned} E &= -\frac{\partial \ln Z}{\partial \beta} \\ &= N\hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right] \end{aligned} \quad \dots(6.11.8)$$

Heat capacity

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} \quad \dots(6.11.9)$$

$$= Nk \left(\frac{\Theta}{T} \right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2} \quad \dots(6.11.10)$$

Entropy

$$S = k \ln Z + \frac{E}{T}$$

$$= Nk \ln \left(\frac{1}{1 - e^{-\beta \hbar \omega}} \right) + Nk \left(\frac{\hbar \omega}{kT} \right) \left(\frac{1}{1 - e^{-\beta \hbar \omega}} \right) + \frac{N\hbar \omega}{T} \quad \dots(6.11.11)$$

- (i) At high temperature $\beta \hbar \omega = \frac{\hbar \omega}{kT} \ll 1$, thermal energy kT is much greater than the spacing of energy levels. In this case the energy of the system is

$$\begin{aligned} E &= N\hbar \omega \left[\frac{1}{2} + \frac{1}{(1 + \beta \hbar \omega + \dots) - 1} \right] \\ &= N\hbar \omega \left[\frac{1}{2} + \frac{1}{\beta \hbar \omega} \right] \\ &= \frac{N}{\beta} = NkT \end{aligned}$$

Therefore $C_v = Nk$.

- (ii) At low temperature $\beta \hbar \omega = \frac{\hbar \omega}{kT} \gg 1$. The energy of the system is

$$E = N\hbar \omega \left[\frac{1}{2} + e^{-\beta \hbar \omega} \right] \Rightarrow \frac{1}{2} N\hbar \omega$$

Almost all the molecules will be in the ground state and the energy is temperature independent. Therefore C_v will tend to zero.

6.12 GRAND CANONICAL ENSEMBLE AND GRAND PARTITION FUNCTION

In a grand canonical ensemble, each system is enclosed in a container whose walls are both heat conducting and permeable to the passage of particles (molecules). The number of molecules in a system, therefore, can range over all possible values *i.e.*, each system is open with respect to the transport of matter. We construct a grand canonical ensemble by placing a collection of such systems in a large heat bath at temperature T and a large reservoir of molecules. After equilibrium is reached, the entire ensemble is isolated from its surroundings. Since the entire ensemble is at equilibrium with respect to the transport of heat and matter, each system is specified by volume V , temperature T and chemical potential μ .

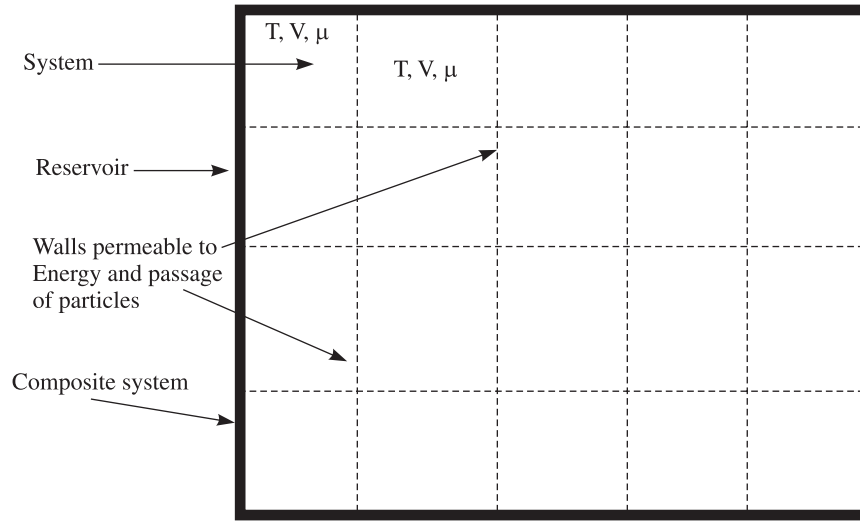


Fig. 6.12.1 Grand canonical ensemble. Each system has fixed volume V and temperature T but is open with respect to molecular transport

Let the system A under study be in contact with a heat reservoir A' . The system A and A' constitute a composite system A^* . Let the system A be in its energy level E_r and has number of particles N_r . The corresponding values for heat reservoir are E' and N' and that of composite system are E^* and N^* . Since the composite system is insulated with respect to energy and passage of particles we must have

$$N_r + N' = N^* \quad \dots(6.12.1)$$

$$E_r + E' = E^* \quad \dots(6.12.2)$$

The probability $P_{N,r}$ that the system A in the ensemble is in the state r and contains N particles is proportional to the number Ω^* of states accessible to the composite system A^* , which is just equal to the number $\Omega'(E', N')$ or $\Omega'(E^* - E_r, N^* - N_r)$ of states accessible to the reservoir. Thus

$$P_{N,r}(E_r, N_r) \propto \Omega'(E', N')$$

$$\text{or} \quad P_{N,r}(E_r, N_r) \propto \Omega'(E^* - E_r, N^* - N_r) \quad \dots(6.12.3)$$

Since A is very small compared to A' , $E_r \ll E^*$ and $N_r \ll N^*$, we can expand $\ln \Omega'$ in Taylor series as follows.

$$\ln \Omega'(E^* - E_r, N^* - N_r) = \ln \Omega'(E^*, N^*) - \left(\frac{\partial \ln \Omega'}{\partial E'} \right)_{E'=E^*} E_r - \left(\frac{\partial \ln \Omega'}{\partial N'} \right)_{N'=N^*} N_r$$

Denoting

$$\beta = \left(\frac{\partial \ln \Omega'}{\partial E'} \right)_{E'=E^*} \quad \text{and} \quad -\beta\mu = \left(\frac{\partial \ln \Omega'}{\partial N'} \right)_{N'=N^*} \quad \dots(6.12.4)$$

we can write

$$\begin{aligned}\ln \Omega'(E^* - E_r, N^* - N_r) &= \ln \Omega'(E^*, N^*) - \beta E_r + \beta \mu N_r \\ \Omega'(E^* - E_r, N^* - N_r) &= \Omega'(E^*, N^*) e^{\beta(\mu N_r - E_r)}\end{aligned}\quad \dots(6.12.5)$$

The probability that any randomly chosen system contains N particles and be in r th energy level with energy E_r is

$$P_{N,r} = C e^{\beta(\mu N_r - E_r)} \quad \dots(6.12.6)$$

where C is a constant. Using the condition for normalization of probability viz., $\sum P_{N,r} = 1$ we have

$$C = \frac{1}{\sum_{N,r} e^{\beta(\mu N_r - E_r)}} \quad \dots(6.12.7)$$

Therefore,

$$P_{N,r} = \frac{e^{\beta(\mu N_r - E_r)}}{\sum_{N,r} e^{\beta(\mu N_r - E_r)}} \quad \dots(6.12.8)$$

The quantity in the denominator of right hand side of Eqn. (6.12.7) is called *Grand Partition Function* and denoted by Z_G . Thus, the grand partition function is

$$Z_G = \sum_{N=0}^{\infty} \sum_{r=0}^{\infty} e^{\beta(\mu N_r - E_r)} \quad \dots(6.12.9)$$

$$\begin{aligned}&= \left(\sum_{r=0}^{\infty} e^{-\beta E_r} \right) \sum_{N=0}^{\infty} e^{\beta \mu N_r} \\ &= Z \sum_{N=0}^{\infty} e^{\beta \mu N_r}\end{aligned}\quad \dots(6.12.10)$$

where Z is canonical partition function.

Let $\langle n_{N,r} \rangle$ denote the number of systems in the ensemble that contains N_r (variable) particles and are in the state r . Then

$$P_{N,r} = \frac{\langle n_{N,r} \rangle}{M} = \frac{e^{\beta(\mu N_r - E_r)}}{Z_G} \quad \dots(6.12.11)$$

where M is total number of systems in the ensemble. The most probable distribution is then given by

$$n_{N,r} = \frac{M}{Z_G} e^{\beta(\mu N_r - E_r)} \quad \dots(6.12.12)$$

6.13 STATISTICAL PROPERTIES OF A THERMODYNAMIC SYSTEM IN TERMS OF GRAND PARTITION FUNCTION

The grand partition function plays a central role in statistical thermodynamics because all the properties of system with a variable number of particles can be expressed in terms of it. In order to express our results in terms of Z_G we shall first derive the entropy S , which is defined as

$$\begin{aligned}
 S &= -k \sum_{N,r} p_{N,r} \ln p_{N,r} \\
 &= -k \sum_{N,r} p_{N,r} [\beta \mu N_r - \beta E_{N,r} - \ln Z_G] \\
 &= -k \left[\mu \beta \sum_{N,r} p_{N,r} N_r - \beta \sum_{N,r} p_{N,r} E_{N,r} - \ln Z_G \right] \\
 &= -k \left[\mu \beta \bar{N} - \beta \bar{E} - \ln Z_G \right] \\
 &= \frac{\bar{E}}{T} - \frac{\mu \bar{N}}{T} + k \ln Z_G \quad \dots(6.13.1a)
 \end{aligned}$$

$$\text{or} \quad -kT \ln Z_G = E - TS - \mu N \quad \dots(6.13.1b)$$

where $\bar{E}$ and $\bar{N}$ are the mean energy and mean number of particles of the system. In a macroscopic system the fluctuations are usually negligibly small, so the mean values are just the actual values of these quantities. Accordingly we frequently omit bars from such quantities.

Other thermodynamic functions are expressed in terms of grand partition function are as follows.

$$\text{Total energy} \quad E \text{ or } U = - \left(\frac{\partial \ln Z_G}{\partial \beta} \right)_{V, \mu} \quad \dots(6.13.2)$$

$$\text{Mean number of particles} \quad \bar{N} = \eta \left(\frac{\partial \ln Z_G}{\partial \eta} \right), \text{ where } \eta = e^{\beta \mu} \quad \dots(6.13.3)$$

$$\text{Mean pressure of the system} \quad \Pi = \frac{1}{\beta} \left(\frac{\partial \ln Z_G}{\partial V} \right)_{\beta, \mu} \quad \dots(6.13.4)$$

6.14 GRAND POTENTIAL Φ

We define *grand potential* Φ as

$$\Phi = \Phi(T, V, \mu) = -kT \ln Z_G(T, V, \mu) = E - TS - \mu N \quad \dots(6.14.1)$$

[This quantity is similar to the Helmholtz function F , which is related to canonical partition function $Z(T, V, N)$ as $F = -kT \ln Z(T, V, N) = E - TS$.]

The other thermodynamic functions are related to grand potential as given below.

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V, \mu}; \quad \bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V, T} \quad \dots(6.14.2)$$

6.15 IDEAL GAS FROM GRAND PARTITION FUNCTION

The canonical partition function $Z(T, V, N)$ for a gas of N particles contained in a volume V and at temperature T is given by

$$Z(T, V, N) = \frac{1}{N!} [z(T, V)]^N = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad \dots(6.15.1)$$

where Z is single particle canonical partition function.

The grand partition function for the gas is

$$Z_G = Z_G(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(T, V, N) = \sum_{N=0}^{\infty} \frac{[ze^{\beta \mu}]^N}{N!} \quad \dots(6.15.2)$$

Eqn. (6.15.2) may be simplified using the property of exponential function.

$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots = \sum_{n=0}^{\infty} \frac{x^n}{n!} \quad \dots(6.15.3)$$

In view of Eqn.(6.15.3) we can write Eqn. (6.15.2) as

$$Z_G = \exp[ze^{\beta \mu}] \quad \dots(6.15.4)$$

Let $\eta = e^{\beta \mu}$. Therefore

$$Z_G = \exp[z\eta] \quad \dots(6.15.5)$$

Now grand potential for the gas is

$$\begin{aligned} \Phi &= -kT \ln Z_G \\ &= -kT z\eta \\ &= -kT \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V e^{\beta \mu} \end{aligned} \quad \dots(6.15.6)$$

The entropy of the gas is

$$S = -\left(\frac{\partial \Phi}{\partial (kT)}\right)_{V, \mu} = V \left(\frac{(2\pi mkT)^{3/2}}{h^3} \right) e^{\beta \mu} \left(\frac{5}{2} - \beta \mu \right) \quad \dots(6.15.7)$$

This is Sakur-Tetrode equation.

The mean number of particles in the system is

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V, T} = V \frac{(2\pi mkT)^{3/2}}{h^3} e^{\beta \mu} = -\frac{\Phi}{kT}$$

From this equation we can get chemical potential

$$\mu = -kT \ln \left[\frac{V}{\bar{N}} \frac{(2\pi mkT)^{3/2}}{h^3} \right] = -kT \ln \frac{z_G}{\bar{N}} \quad \dots(6.15.8)$$

Thus, the chemical potential increases with increase in concentration of particles.

The pressure of the gas is given by

$$\Pi = - \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu} = kT \left(\frac{\bar{N}}{V} \right) \quad \dots(6.15.9)$$

This gives

$$\Pi V = \bar{N} kT$$

which is the perfect gas law.

6.16 OCCUPATION NUMBER OF AN ENERGY STATE FROM GRAND PARTITION FUNCTION: FERMI-DIRAC AND BOSE-EINSTEIN DISTRIBUTION

The state of a system is specified by a set of occupation number $n_1, n_2, \dots, n_r, \dots$ of single particle states with energies $\epsilon_1 \leq \epsilon_2 \leq \dots, \epsilon_r \leq \dots$. Consider a state of the system in which it contains N -particles and total energy $E_{N,r}$, which are given by

$$N = \sum_r n_r \quad \text{and} \quad E_{N,r} = \sum_r n_r \epsilon_r$$

Of course, in grand canonical ensemble, N is variable and free to take on values $N = 0, 1, 2, \dots$

The grand canonical partition function of the system is

$$\begin{aligned} Z_G &= \sum_{N=0}^{\infty} \sum_{n_1, n_2, \dots}^{(N)} e^{\beta \mu N} e^{-\beta E_{N,r}} \\ &= \sum_{N=0}^{\infty} \sum_{n_1, n_2, \dots}^{(N)} e^{\beta \mu (n_1 + n_2 + \dots)} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \end{aligned} \quad \dots(6.16.1)$$

The superscript N over the summation sign means that the occupation numbers obeys the condition $n_1 + n_2 + \dots = N$. In the above summation first sum over all the values of $n_1, n_2, \dots$ for a fixed value of N and then sum over all the values of N from $N = 0$ to ∞ . This way of summation is equivalent to summation over all values of $n_1, n_2, \dots$ independently of each other. So the above expression can be expressed as

$$Z_G = \sum_{n_1} \sum_{n_2} e^{\beta \mu (n_1 + n_2 + \dots)} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

$$\begin{aligned}
&= \left(\sum_{n_1=0}^{\infty} e^{\beta(\mu-\epsilon_1)n_1} \right) \left(\sum_{n_2=0}^{\infty} e^{\beta(\mu-\epsilon_2)n_2} \right) (\dots)(\dots\dots) \\
&= \prod_r \left(\sum_{n_r=0}^{\infty} e^{\beta(\mu-\epsilon_r)n_r} \right) \quad \dots(6.16.2)
\end{aligned}$$

$$= \prod_r (Z_G)_r \quad \dots(6.16.3)$$

where $(Z_G)_r$ is given by

$$(Z_G)_r = \sum_{n_r} e^{\beta(\mu-\epsilon_r)n_r} \quad \dots(6.16.4)$$

If the system consists of *fermions*, then $n_r = 0$ or 1 and therefore

$$(Z_G)_r = \sum_{n_r=0, \text{ or } 1} e^{\beta(\mu-\epsilon_r)n_r} = (1 + e^{\beta(\mu-\epsilon_r)}) \quad \dots(6.16.5)$$

Hence the grand partition function for *fermions* is

$$Z_G = \prod_r (1 + e^{\beta(\mu-\epsilon_r)}) \quad (\text{fermions}) \quad \dots(6.16.6)$$

The *grand potential* for a system of *fermions* is

$$\begin{aligned}
\Phi_{\text{fermions}} &= -kT \ln Z_G \\
&= -kT \sum_r \ln(1 + e^{\beta(\mu-\epsilon_r)}) \\
&= \sum_r -kT \ln(1 + e^{\beta(\mu-\epsilon_r)}) \quad \dots(6.16.7)
\end{aligned}$$

$$= \sum_r \phi_r \quad \dots(6.16.8)$$

The mean occupation number of r th energy state is

$$\bar{n}_r = -\frac{\partial \phi_r}{\partial \mu} \quad (6.16.9)$$

$$\begin{aligned}
&= -\frac{\partial}{\partial \mu} \left[-kT \ln(1 + e^{\beta(\mu-\epsilon_r)}) \right] \\
&= \frac{e^{\beta(\mu-\epsilon_r)}}{1 + e^{\beta(\mu-\epsilon_r)}} \\
&= \frac{1}{e^{\beta(\epsilon_r-\mu)} + 1} \quad \dots(6.16.10)
\end{aligned}$$

This expression for the mean occupation number for state of energy ϵ_r is called *Fermi-Dirac distribution* for particles with half-integral spin (*fermions*).

If the system consists of *bosons*, then $n_r = 0, 1, 2, 3, \dots$ and therefore the grand partition function for particles with integral spin (*bosons*) is

$$\begin{aligned} Z_G &= \prod_r \left(\sum_{n_r=0,1,2,3,\dots} e^{\beta(\mu-\epsilon_r)n_r} \right) \\ &= \prod_r \left(1 + e^{\beta(\mu-\epsilon_r)} + e^{2\beta(\mu-\epsilon_r)} + \dots \right) \\ &= \left(\frac{1}{1 - e^{\beta(\mu-\epsilon_r)}} \right) \quad \mu < \epsilon_r \end{aligned} \quad \dots(6.16.11)$$

The *grand potential* $\Phi = E - TS - \mu N$ for a system of bosons is

$$\begin{aligned} \Phi_{bosons} &= -kT \ln Z_G \\ &= -kT \sum_r \ln \left(1 - e^{\beta(\mu-\epsilon_r)} \right)^{-1} \\ &= kT \sum_r \ln \left(1 - e^{\beta(\mu-\epsilon_r)} \right) \\ &= \sum_r kT \ln \left(1 - e^{\beta(\mu-\epsilon_r)} \right) \end{aligned} \quad \dots(6.16.12)$$

$$= \sum_r \phi_r \quad \dots(6.16.13)$$

The mean occupation number of state of energy ϵ_r is

$$\begin{aligned} \bar{n}_r &= -\frac{\partial \phi_r}{\partial \mu} = -\frac{\partial}{\partial \mu} \left[kT \ln \left(1 - e^{\beta(\mu-\epsilon_r)} \right) \right] \\ &= \frac{e^{\beta(\mu-\epsilon_r)}}{1 - e^{\beta(\mu-\epsilon_r)}} \end{aligned}$$

or
$$\bar{n}_r = \frac{1}{e^{\beta(\epsilon_r-\mu)} - 1} \quad \dots(6.16.14)$$

This is the Bose-Einstein distribution function for a system of particles with integral spin (*bosons*).

For a system of bosons (such as photons, phonons, etc.) whose number is not conserved, the chemical potential μ is zero. The Bose-Einstein distribution for such particles is

$$\bar{n}_r = \frac{1}{e^{\beta\epsilon_r} - 1}, \quad \epsilon_r = \hbar\omega_r \quad (\text{for photons and phonons}) \quad \dots(6.16.15)$$

APPLICATION OF PARTITION FUNCTION

7.1 SPECIFIC HEAT OF SOLIDS

7.1.1 Einstein Model

In 1907 Einstein made an attempt to explain the temperature-dependence of the heat capacity of solids on the basis of quantum theory, and made the following assumptions.

1. The atoms in a solid vibrate about their fixed lattice sites. Their vibrations are independent of each other and the frequency ω of vibration, called Einstein frequency, is the same for all atoms, and is a characteristic constant of the solid. The vibration of an atom can be resolved into three mutually independent equations say along the three Cartesian coordinate axes x , y and z . Thus, a solid containing N_0 atoms is equivalent to $3 N_0$ harmonic oscillators.
2. An oscillator of frequency ω can have only discrete values of energy ϵ given by

$$\epsilon = \left(n + \frac{1}{2} \right) \hbar \omega \quad \text{where } n = 0, 1, 2, 3, \dots \quad \dots(7.1.1)$$

The energy $\frac{1}{2} \hbar \omega$ is called the zero-point energy.

The partition function of one oscillator is

$$z = \sum_{r=0}^{\infty} e^{-\beta \epsilon_r} = \sum_{r=0}^{\infty} e^{-\beta \hbar \omega \left(r + \frac{1}{2} \right)} = e^{-\frac{1}{2} \beta \hbar \omega} \sum_{r=0}^{\infty} e^{-\beta \hbar \omega r} \quad \dots(7.1.2)$$

Let $x = \beta \hbar \omega = \frac{\hbar \omega}{kT}$. The expression for partition function becomes

$$z = e^{-x/2} \sum_{r=0}^{\infty} e^{-x r}$$

$$\begin{aligned}
&= e^{-x/2} [1 + e^{-x} + e^{-2x} + \dots] \\
&= e^{-x/2} \left[\frac{1}{1 - e^{-x}} \right] \quad \dots(7.1.3)
\end{aligned}$$

The Helmholtz free energy for an oscillator is

$$\begin{aligned}
F_1 &= -kT \ln z \\
&= -kT \left[-\frac{x}{2} - \ln(1 - e^{-x}) \right] \\
&= \left[\frac{1}{2} \hbar\omega + \frac{1}{\beta} \ln(1 - e^{-\beta \hbar\omega}) \right] \quad \dots(7.1.4)
\end{aligned}$$

The average energy of an oscillator is

$$\begin{aligned}
\bar{\epsilon} &= -\frac{\partial \ln z}{\partial \beta} = -\frac{\partial}{\partial \beta} \left(-\frac{F_1}{kT} \right) = \frac{\partial}{\partial \beta} (\beta F_1) \\
&= \frac{\partial}{\partial \beta} \left[\frac{1}{2} \beta \hbar\omega + \ln(1 - e^{-\beta \hbar\omega}) \right] \\
&= \frac{1}{2} \hbar\omega + \frac{\hbar\omega}{e^{\beta \hbar\omega} - 1} \quad \dots(7.1.5)
\end{aligned}$$

The energy of crystal containing N atoms is

$$E = 3N\bar{\epsilon} = 3N \left[\frac{1}{2} \hbar\omega + \frac{\hbar\omega}{e^{\beta \hbar\omega} - 1} \right] \quad \dots(7.1.6)$$

The specific heat at constant volume is

$$\begin{aligned}
C_v &= \left(\frac{\partial E}{\partial T} \right)_v = \left(\frac{\partial E}{\partial \beta} \right) \left(\frac{\partial \beta}{\partial T} \right) \\
&= \frac{3N}{kT^2} (\hbar\omega)^2 \frac{e^{\beta \hbar\omega}}{(e^{\beta \hbar\omega} - 1)^2} \\
&= 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 \frac{e^{\beta \hbar\omega}}{(e^{\beta \hbar\omega} - 1)^2} \quad \dots(7.1.7)
\end{aligned}$$

Let us express this result in terms of Einstein temperature Θ_E defined by $\hbar\omega = k\Theta_E$.

$$C_v = 3Nk \left(\frac{\Theta_E}{T} \right) \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \quad \dots(7.1.8)$$

(i) At high temperature $T \gg \Theta_E$,

$$e^{\Theta_E/T} = 1 + \frac{\Theta_E}{T} + \dots$$

The expression for C_v simplifies to

$$C_v = 3Nk \left(\frac{\Theta_E}{T} \right)^2 \frac{1 + \Theta_E/T}{(\Theta_E/T)^2} = 3Nk \left(1 + \frac{\Theta_E}{T} \right) \quad \dots(7.1.9)$$

As $T \rightarrow \infty$, $C_v = 3Nk = 3R$

Thus, at high temperature the heat capacity of solid is independent of temperature and is equal to $3R$ which is the Dulong-Petits law.

(ii) At low temperature Θ_E/T is large and so is $\exp(\Theta_E/T)$. The expression for heat capacity may be simplified as follows.

$$\begin{aligned} C_v &= 3Nk \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T})^2} = 3Nk \left(\frac{\Theta_E}{T} \right)^2 \frac{1}{e^{\Theta_E/T}} \\ &= 3Nk \frac{1}{\left(\frac{T}{\Theta_E} \right)^2 \left[1 + \frac{\Theta_E}{T} + \frac{1}{2!} \left(\frac{\Theta_E}{T} \right)^2 + \frac{1}{3!} \left(\frac{\Theta_E}{T} \right)^3 + \dots \right]} \\ &= 3Nk \frac{1}{\left(\frac{T}{\Theta_E} \right)^2 + \frac{T}{\Theta_E} + \frac{1}{2!} + \frac{1}{3!} \frac{\Theta_E}{T} + \dots} \quad \dots(7.1.10) \end{aligned}$$

As $T \rightarrow 0$, $C_v \rightarrow 0$. The heat capacities computed on the basis of Einstein's model at different temperatures are, in general, in good agreement with the experimental results. However, careful and detailed comparison of the predictions from Einstein's theory with experimental results shows that the agreement is only approximate. It has also been shown by the experiments that at low temperature, the heat capacity varies as T^3 whereas Einstein's theory predicts exponential variation of specific heat with temperature. This difference between theory and the experiment is not very surprising because the model assumed by Einstein is over simplified.

For example, Einstein has assumed that the atoms in the solid are vibrating independent of each other, which cannot be realistic, as atoms are strongly coupled with each other and therefore if an atom is disturbed it must effect the other atoms. Consequently one must consider the vibrations of the groups of atom rather than the vibration of each atom independently. Moreover, Einstein has also assumed that all the atoms vibrate with a single frequency ω , which is again not correct. In order to develop a more appropriate theory, which can provide a realistic explanation of the observed experimental facts, Debye assumed a more realistic model of solid and provided a better theory of specific heat of solid.

7.1.2 Debye Model

The atoms in a solid cannot be assumed to be independent. We must take into account their cooperative interactions. Taking this interaction into consideration, we arrive at a theory of heat capacity that is in agreement with experimental results. At 0 K, the system of atoms comprising a solid is in the ground state having the minimum energy. After receiving energy from outside, an atom moves in a certain direction from its equilibrium position. A force striving to return it to the equilibrium position develops. Therefore while leaving the equilibrium position, the atom acts a certain force on neighbouring atoms, which in turn are to leave their equilibrium positions, as a result of which the motion becomes cooperative. This cooperative motion, in which the displacement of one atom is transferred to the neighbouring atom and then to the next neighbour and so on, is an acoustic wave in the solid.

Taking into account the interaction between atoms, a system of atoms must be considered as a set of coupled oscillators. In this case, any motion of the system of atoms can be represented as a superposition of normal oscillations or normal modes of the system. Each normal mode is characterized by its frequency ω and the energy ϵ of this mode is given by $\epsilon = \hbar\omega$.

A solid can support longitudinal and transverse waves both with different velocities. Transverse mode may have two different directions of polarization. There is a standard method of calculating the number of modes for each polarization in an isotropic solid. The number of modes of acoustic oscillations in the frequency range $d\omega$ at frequency ω , in a solid of volume V is given by

$$g(\omega)d\omega = \frac{V}{2\pi^2 v^3} \omega^2 d\omega \quad \dots(7.1.11)$$

where v is velocity of the wave. In a isotropic solid the velocities of the two transverse waves are equal. Taking the longitudinal and transverse mode both, the number of modes in the frequency interval $d\omega$ about ω is given by

$$g(\omega)d\omega = \frac{V}{2\pi^2} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \omega^2 d\omega \quad \dots(7.1.12)$$

The factor 2 multiplying in $1/v_t^3$ is due to the fact that there are two independent transverse directions of polarization. We define a mean velocity v by

$$\frac{3}{v^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3} \quad \dots(7.1.13)$$

According to Debye, a crystal with N atoms possesses $3N$ modes in all. The maximum frequency ω_D is such that there are $3N$ modes altogether *i.e.*,

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \quad \dots(7.1.14)$$

The cut-off frequency ω_D occurs because at sufficiently high frequency *i.e.*, short wavelength, we cannot ignore the atomic nature of the solid. That is at short wavelengths, the solid is no longer acts as a continuum. A crystal with inter-atomic spacing a cannot propagate waves with wavelengths less than $\lambda_{\min} = 2a$. In this case neighbouring atoms vibrate in anti-phase.

Let us introduce a characteristic temperature Θ_D related to Debye cut-off frequency ω_D defined by

$$\hbar\omega_D = k\Theta_D \quad \text{or} \quad \Theta_D = \frac{\hbar\omega}{k} \quad \dots(7.1.15)$$

So Debye condition (7.1.14) in terms of energy $\epsilon = \hbar\omega$ becomes

$$\begin{aligned} \int_0^{k\Theta_D} g(\epsilon) d\epsilon &= 3N \\ \frac{3V}{2\pi^2 v^3 \hbar^3} \int_0^{k\Theta_D} \epsilon^2 d\epsilon &= 3N \\ \frac{3V}{2\pi^2 v^3 \hbar^3} &= \frac{9N}{(k\Theta_D)^3} \end{aligned} \quad \dots(7.1.16)$$

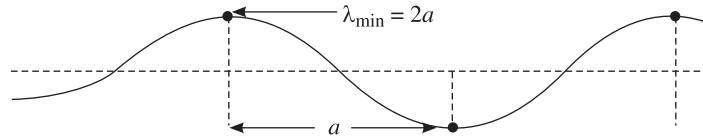


Fig. 7.1.2 Wave of shortest wavelength that can propagate in a one-dimensional crystal

With the help of Eqns. (7.1.12), (7.1.13) and (7.1.14) we can write

$$g(\epsilon) d\epsilon = \frac{9N}{(k\Theta_D)^3} \epsilon^2 d\epsilon \quad \dots(7.1.17)$$

The average number of normal modes (oscillators) with energy ϵ , are given by

$$\bar{n}(\epsilon) = \frac{1}{e^{\epsilon/kT} - 1} \quad \dots(7.1.18)$$

The energy of the crystal is

$$\begin{aligned}
 E &= \int_0^{k\Theta_D} \epsilon g(\epsilon) \bar{n}(\epsilon) d\epsilon \\
 &= \frac{9N}{(k\Theta_D)^3} \int_0^{k\Theta_D} \frac{\epsilon^3 d\epsilon}{e^{\epsilon/kT} - 1} \\
 &= 9NkT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1},
 \end{aligned}$$

where

$$x = \frac{\hbar\omega}{kT} = \frac{\epsilon}{kT}, \quad x_D = \frac{\hbar\omega_D}{kT} = \frac{\Theta_D}{T} \quad \dots(7.1.19)$$

(i) At high temperature ($T \gg \Theta_D$)

$$\frac{x^3}{e^x - 1} = \frac{x^3}{\left(1 + \frac{x}{1} + \dots\right) - 1} \approx x^2 \text{ as } x \text{ is small.}$$

Therefore, Eqn. (7.1.19) simplifies to

$$E = \frac{9NkT^4}{\Theta_D^3} \left(\frac{x^3}{3} \right)_0^{\Theta_D/T} = 3NkT \quad \dots(7.1.20)$$

The molar heat capacity at constant volume is

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = 3Nk = 3R \quad \dots(7.1.21)$$

(ii) At low temperature, $T \ll \Theta_D$, $x \rightarrow \infty$ and the integral

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx = \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \quad (\text{see Appendix A-3})$$

The energy of the system is

$$E = \frac{9NkT^4}{\Theta_D^3} \left(\frac{\pi^4}{15} \right) \quad \dots(7.1.22)$$

The heat capacity

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{9Nk}{\Theta_D^3} \left(\frac{\pi^4}{15} \right) T^3 \quad \dots(7.1.23)$$

Thus, the heat capacity of solid at low temperature varies as T^3 . This law is known as Debye T^3 law.

7.2 PHONON CONCEPT

The energy $\epsilon = \hbar\omega$ corresponding to a mode of acoustic vibration with frequency ω in a solid suggests that a mode should be treated as a *quasiparticle*. Such a *quasiparticle* associated with the modes of acoustic oscillations is called a *phonon*. The introduction of the phonon concept is a fruitful approach, which considerably simplifies the reasoning. The thermal vibrations of a lattice are equivalent to an aggregate of phonons and the latter may be treated as an ideal Bose Gas. The phonon is a *quanta* of acoustic wave with energy $\epsilon = \hbar\omega$ and momentum $p = \frac{\epsilon}{v}$, where v is mean velocity of acoustic wave in solid and is given by $\frac{3}{v^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3}$, v_l and v_t are the velocities of the longitudinal and transverse waves.

The density of states for a gas of phonons is given by

$$g(p)dp = \frac{3V}{h^3} 4\pi p^2 dp \quad \dots(7.2.1)$$

The factor 3 takes into account of three possible polarizations of phonon. V is volume of the solid. Making use of the relation $\epsilon = vp$, the expression for the density of states can be transformed in terms of energy.

$$g(\epsilon)d\epsilon = \frac{3V}{2\pi^2 v^3 \hbar^3} \epsilon^2 d\epsilon \quad \dots(7.2.2)$$

Let the maximum frequency of the acoustic oscillations be ω_D and the energy of the corresponding phonon be $\hbar\omega_D$. We define a characteristic temperature Θ_D such that $\hbar\omega_D = k\Theta_D$ i.e., $\Theta_D = \frac{\hbar\omega}{k}$. The total number of modes of oscillation in the solid containing N atoms is $3N$. Thus

$$\begin{aligned} \int_0^{k\Theta_D} g(\epsilon)d\epsilon &= 3N \\ \frac{3V}{2\pi^2 v^3 \hbar^3} \int_0^{k\Theta_D} \epsilon^2 d\epsilon &= 3N \\ g(\epsilon) &= \frac{9N}{(k\Theta_D)^3} \epsilon^2 \quad \dots(7.2.3) \end{aligned}$$

The phonons are bosons and their number is not conserved so the occupation number of phonons in the state with energy ϵ is given by

$$\bar{n}(\epsilon) = \frac{1}{e^{\epsilon/kT} - 1} \quad \dots(7.2.4)$$

The energy of phonons in the solid is

$$\begin{aligned} E &= \int_0^{k\Theta_D} \epsilon \cdot g(\epsilon) \cdot \bar{n}(\epsilon) \cdot d\epsilon \\ &= \frac{9N}{(k\Theta_D)^3} \int_0^{k\Theta_D} \frac{\epsilon^3}{e^{\epsilon/kT} - 1} d\epsilon \\ &= 9NkT \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx, \quad \dots(7.2.5) \end{aligned}$$

where $x = \frac{\hbar\omega}{kT} = \frac{\epsilon}{kT}$.

At high temperature x is small and $\frac{x^3}{e^x - 1} \cong x^2$. So Eqn. (7.2.5) simplifies to

$$E = 3NkT$$

and hence

$$C_v = 3Nk = 3R \quad (\text{Dulong-Petits Law})$$

At low temperature, x is very large, and the integral in Eqn. (7.2.5) is given by

$$\int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx = \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

Therefore
$$E = \frac{9NkT^4}{\Theta_D^3} \left(\frac{\pi^4}{15} \right) \quad \dots(7.2.6)$$

Heat capacity
$$C_v = \left(\frac{3Nk\pi^4}{5\Theta_D^3} \right) T^3 \quad \dots(7.2.7)$$

Thus, the heat capacity of a solid varies as T^3 at low temperature. This is Debye T^3 law.

7.3 PLANCK'S RADIATION LAW: PARTITION FUNCTION METHOD

Let us denote the single particle states of photon gas by 1, 2, 3, ..., r ,... with energies $\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_r, \dots$ and occupation numbers $n_1, n_2, n_3, \dots, n_r, \dots$. For photons $n_r = 0, 1, 2, \dots$ for all r . *i.e.*, each of the occupation number assumes all possible values 0, 1, 2, ... independent of the values of the other occupation numbers. The partition function of the photon gas is

$$Z = \sum_{n_1, n_2, \dots} e^{-\beta \sum_{r=1}^{\infty} n_r \epsilon_r} \quad \dots(7.3.1)$$

where $\sum_{n_1, n_2, \dots}$ stands for summation over all sets of occupation numbers. Eqn. (7.3.1) can be written as

$$Z = \sum_{n_1} \sum_{n_2} \dots e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad \dots(7.3.2)$$

$$\begin{aligned} &= \left(\sum_{n_1} e^{-\beta n_1 \epsilon_1} \right) \left(\sum_{n_2} e^{-\beta n_2 \epsilon_2} \right) (\dots)(\dots)(\dots) \\ &= \left(\frac{1}{1 - e^{-\beta \epsilon_1}} \right) \left(\frac{1}{1 - e^{-\beta \epsilon_2}} \right) (\dots)(\dots) \\ &= \prod_{r=1}^{\infty} \left(\frac{1}{1 - e^{-\beta \epsilon_r}} \right) \quad \dots(7.3.3) \end{aligned}$$

Therefore

$$\ln Z = - \sum_{r=1}^{\infty} \ln(1 - e^{-\beta \epsilon_r}) \quad \dots(7.3.4)$$

where $\epsilon_r = \hbar \omega$.

The mean occupation number of photons in the state r is

$$\bar{n}_r(\omega) = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_r} = \frac{1}{e^{\beta \epsilon_r} - 1} = \frac{1}{e^{\beta \hbar \omega} - 1} \quad \dots(7.3.5)$$

The degeneracy of energy levels ϵ_r is given by

$$g(\omega) d\omega = 2 \left(\frac{V}{2\pi^2 c^3} \omega^2 \right) d\omega \quad \dots(7.3.6)$$

The factor 2 accounts for the two independent directions of polarization of photon.
Therefore

$$\begin{aligned}\ln Z &= -\sum_r \left(\frac{V}{\pi^2 c^3} \omega^2 \right) \ln(1 - e^{-\beta \hbar \omega_r}) \\ &= -\frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \ln(1 - e^{-\beta \hbar \omega}) d\omega \quad \dots(7.3.7)\end{aligned}$$

$$\begin{aligned}&= -\frac{V}{\pi^2 c^3} \left[\frac{\omega^3}{3} \ln(1 - e^{-\beta \hbar \omega}) \right]_0^\infty + \frac{V\beta \hbar}{3\pi^2 c^3} \int_0^\infty \frac{\omega^3 e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} d\omega \\ &= 0 + \frac{V\beta \hbar}{3\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega \\ &= \frac{V}{3\pi^2 c^3 (\beta \hbar)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \quad \text{where } \beta \hbar \omega = x \\ &= \frac{V\pi^2}{45} \left(\frac{kT}{\hbar c} \right)^3 \quad \dots(7.3.8)\end{aligned}$$

Average energy $\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = kT^2 \frac{\partial \ln Z}{\partial T} = \left(\frac{V\pi^2 k^4}{15\hbar^3 c^3} \right) T^4 \quad \dots(7.3.9)$

Mean pressure $\bar{P} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{\pi^2 k^4 T^4}{45\hbar^3 c^3} \quad \dots(7.3.10)$

$$\bar{P}V = \frac{1}{3} \bar{E} \quad \dots(7.3.11)$$

Entropy $S = k[\ln Z + \beta \bar{E}]$

$$= \frac{4V\pi^2 k^4 T^3}{45\hbar^3 c^3} \quad \dots(7.3.12)$$

Radiation density

$$\begin{aligned}
 u(\omega, T)d\omega &= g(\omega).n(\omega)d\omega(\hbar\omega) \\
 &= \left(\frac{\omega^2 d\omega}{\pi^2 c^3} \right) \left(\frac{1}{e^{\beta \hbar \omega} - 1} \right) (\hbar\omega) \\
 &= \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta \hbar \omega} - 1} d\omega \quad \dots(7.3.13)
 \end{aligned}$$

This is the Planck radiation law.

QUESTIONS AND PROBLEMS

1. With suitable examples, explain macrostates, microstates of a system. What are accessible states?
2. Explain the concept of ensemble in statistical mechanics. State the fundamental postulates of statistical mechanics.
3. What do you mean by micro-canonical, canonical and grand-canonical ensemble? Which one is more suitable for quantum particles and why?
4. What do you mean by phase space? How do you divide the phase space into cells? What is the minimum size of a cell according to classical and quantum mechanics?
5. Distinguish between μ -space and γ -space. Find an expression for density states of a system using the concept of phase space.
6. Derive an expression for the density of states using the concept of discrete energy levels and quantum states of a particle restricted to move in a three dimensional box.
7. Four distinguishable particles are distributed in two boxes with equal weights. State clearly (i) various possible microstates (ii) number of macrostates (iii) the probabilities of most probable and least probable states.
8. What do you mean by canonical system? Deduce the Boltzmann canonical distribution law and determine the expression for probability for a molecule having energy ϵ_i

$$P(\epsilon_i) = \frac{e^{-\epsilon_i / kT}}{\sum_i e^{-\epsilon_i / kT}}.$$

9. Define entropy and thermodynamic probability (statistical weight) and establish a relation between them.
10. Give statistical definition of entropy and prove that $S = k \ln \Omega$.
11. For a single particle of mass m enclosed in volume V , show that the number of accessible states in the energy range E to $E + dE$ is given by

$$\Omega(E)dE = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2} dE.$$

12. Derive the classical Maxwell-Boltzmann velocity distribution law. Discuss the effect of temperature on the distribution function.
13. Write down Maxwell velocity distribution function for an ideal gas and calculate average velocity, root mean square velocity and most probable velocity.

14. Write the basic assumptions of Maxwell-Boltzmann statistics and derive expression for Boltzmann distribution function.
15. What is difference between the classical and quantum statistics? Obtain the condition under which quantum statistics reduces to classical statistics.
16. Write the basic assumptions which form the basis of Bose-Einstein statistics. Derive B-E statistics.
17. State the conditions of Fermi-Dirac statistics. Derive F-D statistics. In what respect a F-D system differs from a B-E system?
18. Derive Planck's radiation law from B-E statistics.
19. What do mean by degenerate and non-degenerate system. Discuss the degeneration of Fermi gas and Bose gas.
20. What do you mean by B-E condensation? In what respect does it differ from conventional condensation of vapour into liquid.
21. Obtain expression for energy, pressure and entropy of a Fermi gas in degenerate and non-degenerate state.
22. Obtain expression for energy, pressure and entropy of a Bose gas in degenerate and non-degenerate state.
23. What do you mean by Fermi energy and Fermi temperature of an electron gas? Obtain an expression for Fermi energy at $T = 0$ and $T \neq 0$.
24. What do you mean by partition function of a particle? Show that the partition function of a monatomic gas is given by

$$Z = \frac{V}{h^3} (2\pi mkT)^{3/2}.$$

25. Give Einstein theory of specific heat of solids. Give comments about the draw back of the theory.
26. Giving the basic assumptions of Debye model for the specific heat of solids, derive Debye T^3 law.
27. What do you mean by grand canonical ensemble? Obtain F-D and B-E statistics from this formulation.
28. Give a comparative study of classical and quantum statistics. Under what conditions quantum statistics merge into classical statistics?

APPENDIX-A

A-1 Evaluation of integral $\int_{-\infty}^{\infty} e^{-x^2} dx$.

Let
$$I = \int_{-\infty}^{\infty} e^{-x^2} dx \quad \dots(1)$$

Also
$$I = \int_{-\infty}^{\infty} e^{-y^2} dy \quad \dots(2)$$

Multiplying (1) and (2)

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy \quad \dots(3)$$

The range of integration is over the entire x - y plane. The integral (3) can be evaluated in terms of polar coordinates (r, θ) .

$$x = r \cos \theta, \quad y = r \sin \theta, \quad x^2 + y^2 = r^2 \quad \text{and} \quad dx dy = r dr d\theta$$

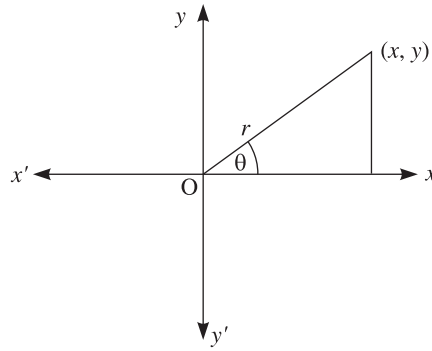


Fig. A-1 Relation between Cartesian and polar coordinates

The range of r is from 0 to ∞ and that of θ is from 0 to 2π . Therefore

$$\begin{aligned} I^2 &= \int_0^{\infty} \int_0^{2\pi} r e^{-r^2} dr d\theta \\ &= \int_0^{\infty} r e^{-r^2} dr \int_0^{2\pi} d\theta \\ &= 2\pi \int_0^{\infty} r e^{-r^2} dr = \pi \int_0^{\infty} e^{-u} du = \pi \quad (r^2 = u, \quad 2r dr = du) \end{aligned}$$

$$\therefore I = \sqrt{\pi}$$

Therefore $\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi} \quad \dots(4)$

and $\int_0^{\infty} e^{-x^2} dx = \frac{\sqrt{\pi}}{2} \quad \dots(5)$

A-2. Evaluation of Integral $I_n(a) = \int_0^{\infty} x^n e^{-ax^2} dx$

$$I_n(a) = \int_0^{\infty} x^n e^{-ax^2} dx \quad \dots(1)$$

These integrals are found by calculating $I_0(a)$ and $I_1(a)$.

$$I_0(a) = \int_0^{\infty} e^{-ax^2} dx = \frac{1}{\sqrt{a}} \int_0^{\infty} e^{-y^2} dy, \quad (\because ax^2 = y^2, \quad dx = \frac{1}{\sqrt{a}} dy)$$

$$I_0(a) = \frac{1}{2} \sqrt{\frac{\pi}{a}} \quad \dots(2)$$

$$\begin{aligned} I_1(a) &= \int_0^{\infty} x e^{-ax^2} dx = \frac{1}{2a} \int_0^{\infty} e^{-y} dy, \quad \text{where } ax^2 = y, \quad x dx = \frac{1}{2a} dy \\ &= \frac{1}{2a} \left[-e^{-y} \right]_0^{\infty} = \frac{1}{2a} \end{aligned}$$

$$I_1(a) = \frac{1}{2a} \quad \dots(3)$$

$$\begin{aligned} I_n(a) &= \int_0^{\infty} x^n e^{-ax^2} dx = -\frac{1}{2a} \int_0^{\infty} x^{n-1} d(e^{-ax^2}) \\ &= -\frac{1}{2a} \left[\left\{ x^{n-1} e^{-ax^2} \right\}_0^{\infty} - (n-1) \int_0^{\infty} x^{n-2} e^{-ax^2} dx \right] \\ &= 0 + \frac{n-1}{2a} \int_0^{\infty} x^{n-2} e^{-ax^2} dx \\ &= \frac{n-1}{2a} I_{n-2}(a) \end{aligned}$$

$$\therefore I_n(a) = \frac{n-1}{2a} I_{n-2}(a) \quad \dots(4)$$

From (4)

$$I_2(a) = \frac{1}{4a} \sqrt{\frac{\pi}{a}}, \quad I_3(a) = \frac{1}{2a^2}, \quad I_4(a) = \frac{3}{8a^2} \sqrt{\frac{\pi}{a}} \text{ etc.} \quad \dots(5)$$

A-3. Evaluation of $I = \int_0^{\infty} \frac{x^3}{e^x - 1} dx.$

This integral can be evaluated by expanding the integrand in a series. Since $e^x > 1$, throughout the range of integration, we can write

$$\begin{aligned} \frac{x^3}{e^x - 1} &= \frac{e^{-x} x^3}{1 - e^{-x}} = e^{-x} x^3 [1 + e^{-x} + e^{-2x} + \dots] \\ &= \sum_{n=1}^{\infty} e^{-nx} x^3 \end{aligned}$$

Hence

$$\begin{aligned} I &= \sum_{n=1}^{\infty} \int_0^{\infty} e^{-nx} x^3 dx \\ &= \sum_{n=1}^{\infty} \frac{1}{n^4} \int_0^{\infty} e^{-y} y^3 dy, \quad \text{where } nx = y, \\ &= \sum_{n=1}^{\infty} \frac{1}{n^4} \Gamma(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} (3!) = 6 \sum_{n=1}^{\infty} \frac{1}{n^4} = 6 \left(\frac{\pi^4}{90} \right) = \frac{\pi^4}{15}. \end{aligned}$$

A-4. Evaluation of $I = \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx.$

$$\begin{aligned} I &= - \int_0^{\infty} x^4 d \left(\frac{1}{e^x - 1} \right) = - \left[\left(x^4 \cdot \frac{1}{e^x - 1} \right) \Big|_0^{\infty} - 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx \right] \\ &= 4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx \\ &= 4 \left(\frac{\pi^4}{15} \right) = \frac{4}{15} \pi^4. \end{aligned}$$

A-5. Riemann Zeta Function $\zeta(x)$.

Riemann zeta function is defined as

$$\zeta(x) = 1 + \frac{1}{2^x} + \frac{1}{3^x} + \frac{1}{4^x} + \dots \quad \dots(1)$$

$$\zeta(2) = \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6} = 1.645$$

$$\zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90} = 1.082$$

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^2} = \frac{\pi^2}{12}.$$

A-6. Stirling's Approximation.

For large n ,

$$\ln n! = n \ln n - n = n \ln (n/e) \quad \dots(1)$$

By definition

$$n! = 1.2.3 \dots n$$

$$\ln n! = \ln 1 + \ln 2 + \ln 3 + \dots + \ln n$$

$$= \sum_{m=1}^n \ln m$$

This sum is exactly equal to the area under the step curve shown by broken line in the figure between $n = 1$ and $n = n$. This area may be approximated with the area under the smooth curve $y = \ln n$ between the same limits. For small values of n , the step curve differs appreciably from the smooth curve but the smooth curve becomes more and more nearly parallel to the n -axis as n increases.

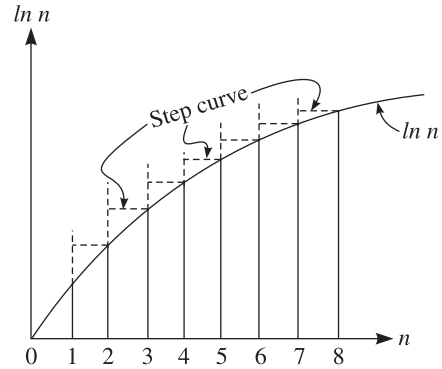


Fig. A-6

$$\ln n! = \int_1^n \ln x \, dx = (x \ln x)_1^n - \int_1^n x \cdot \frac{1}{x} \, dx$$

$$= n \ln n - n + 1$$

$$= n \ln n - n \quad \dots(2)$$

($n \gg 1$, we can neglect 1)

An exact analysis gives the following series for $n!$.

$$n! = \sqrt{2\pi n} \left(\frac{n}{e}\right)^n \left[1 + \frac{1}{12n} + \frac{1}{288n^2} - \frac{139}{51840n^3} + \dots\right]$$

Retaining the first term only we obtain

$$\ln n! = \frac{1}{2} \ln(2n\pi) + n \ln n - n \quad \dots(3)$$

n	$\ln n!$	$n \ln n - n$	$\frac{1}{2} \ln 2n\pi$
5	4.8	3.0	1.8
25	58.0	55.5	2.5
100	363.7	360.5	3.2

A-7. Gamma Function.

Gamma function is defined as

$$\Gamma n = \int_0^{\infty} x^{n-1} e^{-x} dx, \quad n > 0. \quad \dots(1)$$

Now

$$\begin{aligned} \Gamma(n) &= \int_0^{\infty} x^{n-1} e^{-x} dx = - \int_0^{\infty} x^{n-1} d(e^{-x}) \\ &= \left[- \left\{ x^{n-1} e^{-x} \right\}_0^{\infty} - \int_0^{\infty} (n-1) x^{n-2} (-e^{-x}) dx \right] \\ &= (n-1) \int_0^{\infty} x^{n-2} e^{-x} dx \\ &= (n-1) \Gamma(n-1) \end{aligned}$$

$$\text{So} \quad \Gamma(n) = (n-1) \Gamma(n-1) \quad \dots(2)$$

For $n = 1/2$ we have

$$\Gamma\left(\frac{1}{2}\right) = \int_0^{\infty} x^{-1/2} e^{-x} dx = 2 \int_0^{\infty} e^{-u^2} du = 2 \frac{\sqrt{\pi}}{2} = \sqrt{\pi} \quad \dots(3)$$

$$\Gamma(1) = \int_0^{\infty} e^{-x} dx = - \left(e^{-x} \right)_0^{\infty} = 1 \quad \dots(4)$$

If n is a positive integer then

$$\begin{aligned}
 \Gamma(n) &= (n-1)\Gamma(n-1) = (n-1)(n-2)\Gamma(n-2) \\
 &= (n-1)(n-2)(n-3)\dots\Gamma(1) \\
 &= (n-1)(n-2)(n-3)\dots\dots\dots 1 \\
 &= (n-1)!
 \end{aligned}
 \tag{5}$$

A-8. An useful integral associated with F-D distribution.

$$\int_0^\infty \frac{\epsilon^p d\epsilon}{1 + \exp(\epsilon - \epsilon_F)/kT} = \frac{1}{p+1} \left[\epsilon_F^{p+1} + \sum_{n=1}^\infty 2(kT)^{2n} \left(1 - \frac{1}{2^{2n-1}} \right) \zeta(2n) \frac{d^{2n}}{d\epsilon_F^{2n}} (\epsilon_F^{p+1}) \right]
 \tag{1}$$

For $p = 1/2$, $n = 1, 2, 3, \dots$, $\zeta(2) = \frac{\pi^2}{6} = 1.645$.

A-9. An useful integral associated with B-E distribution.

When working with B-E distribution function we often come across an integral of type

$\frac{1}{\Gamma s} \int_0^\infty \frac{x^{s-1}}{\eta^{-1}e^x - 1} dx$. This integral can be expressed as infinite series in the following form:

$$\frac{1}{\Gamma s} \int_0^\infty \frac{x^{s-1}}{\eta^{-1}e^x - 1} dx = F_s(\eta) = \eta + \frac{\eta^2}{2^s} + \frac{\eta^3}{3^s} + \frac{\eta^4}{4^s} + \dots\dots\dots
 \tag{1}$$

For $\eta = 1$,

$$F_s(1) = \frac{1}{\Gamma s} \int_0^\infty \frac{x^{s-1}}{e^x - 1} dx = 1 + \frac{1}{2^s} + \frac{1}{3^s} + \frac{1}{4^s} + \dots\dots\dots = \zeta(s)
 \tag{2}$$

For $s = 3/2$, $\eta = 1$,

$$F_{3/2}(1) = \frac{1}{\Gamma(3/2)} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \frac{1}{4^{3/2}} + \dots\dots = \zeta(3/2) = 2.612
 \tag{3}$$

For $s = 5/2$, $\eta = 1$,

$$F_{5/2}(1) = \frac{1}{\Gamma(5/2)} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx = 1 + \frac{1}{2^{5/2}} + \frac{1}{3^{5/2}} + \frac{1}{4^{5/2}} + \dots\dots = \zeta(5/2) = 1.342
 \tag{4}$$

UNIT

IV

ATOMIC SPECTRA

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ATOMIC SPECTRA-I

1.1 INTRODUCTION

The history of development of the understanding of atomic structure is of special significance because it was the first systematic attempt through which, the relationship between the macroscopic properties of matter and its microscopic structure was investigated. By 19th century, it was firmly established that the matter was composed of atoms and molecules. The kinetic theory of gases provided direct evidence and realistic information regarding mass and size of atoms and molecules. The kinetic theory was based on the application of ordinary laws of mechanics to the motion of molecules in gases and provided relationship between some structural properties of its molecules and the properties of gases. The discovery of electron by J.J. Thomson (1996) gave indication that the atom had inner structure. This led physicists to speculate about the internal structure of atom. Attempts made in this direction manifested in terms of various atomic models.

1.2 THOMSON'S MODEL

After the discovery of negatively charged electrons, it was realized that the electrons were the constituent particles of atom. Since atom is electrically neutral, Thomson proposed that the atom might be regarded as a sphere of positive charge in which negatively charged electrons were embedded in it. The magnitude of positive charge in the sphere was equal to the total charge carried by electrons. This model of atom, called *plum-pudding model*, received serious set back because it could not explain the experimental observations made in the famous *alpha-particle scattering experiment* conducted by Geiger and Marsden under the guidance of Lord Rutherford.

Figure 1.2.1 shows the schematic diagram of the experimental set up used by Rutherford. A collimated beam of α -particles from a radioactive substance was allowed to fall on a thin gold foil. The scattered α -particles were detected by a zinc sulphide screen placed behind the foil. When α -particles strike the screen, they give off visible flash of light.

It was found that majority of the particles suffered small deflection from their original direction but some of them suffered a deflection of 90° or more. One in ten thousand α -particles came off in backward direction after being scattered by gold foil. Let us see what does the Thomson's model

predict? Suppose that an alpha-particle is incident on the thin metallic film, which consists of many layers of atoms. If an alpha-particle while passing through the foil is outside the atom, it should suffer no deviation from its original path. If it penetrates inside the atom and interacts with electron, it should suffer small deviation because the electron is very light in comparison to the alpha-particle. On a foil there are many layers of atoms, the alpha-particle may be scattered in different ways depending upon its interaction with various atoms.

The problem of finding the deflection of alpha-particles after emerging from the foil is a statistical problem, which is similar to the random walk problem. In accordance with the prediction of this theory, the probability of scattering of alpha-particle by 90° or more is about 1 in every 10^{3500} alpha-particles whereas the experiment shows 1 in 10^4 . Therefore, the Thomson's model was subjected to serious objections. In an attempt to explain the results of alpha-particle scattering experiment, Rutherford suggested another model that is named after him.

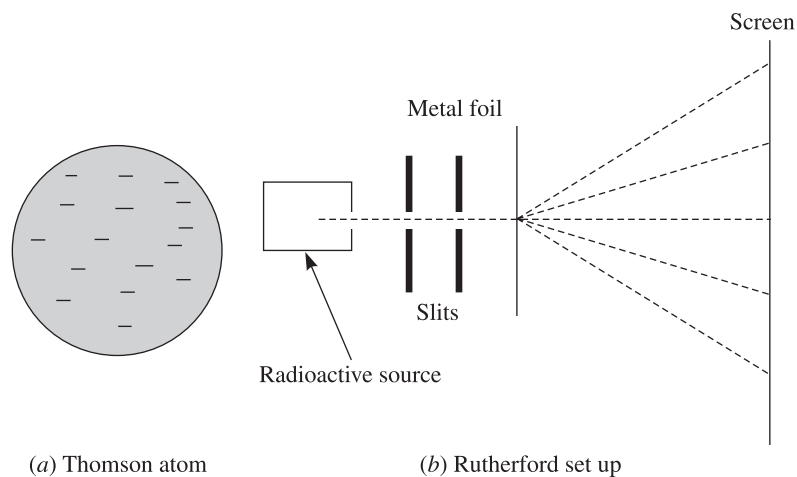


Fig. 1.2.1 Schematic diagram of Rutherford experiment

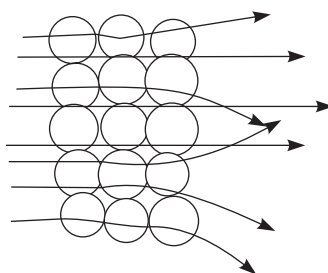


Fig. 1.2.2 Deflection of α -particles by atoms of the target foil

1.3 RUTHERFORD ATOMIC MODEL

On the basis of the results obtained from the scattering experiments, Rutherford suggested an atomic model, according to which *the entire positive charge in the atom is concentrated to a very small region, called nucleus. The entire mass of the atom is due to this nucleus. To explain the stability of the atom against the falling of electrons into the nucleus under the electrostatic attraction, he postulated that like solar system, electrons revolve around the nucleus in circular orbits; the centripetal force required for the circular motion is obtained from the electrostatic attraction of the nucleus on the electrons. This model is known as the planetary atomic model.*

Let us now consider the dynamics of the simplest atom, the hydrogen atom, consisting of a single electron revolving round the nucleus (proton). In accordance with the laws of classical mechanics, the equation of motion of the electron is

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} = \frac{mv^2}{r} \quad \dots(1.3.1)$$

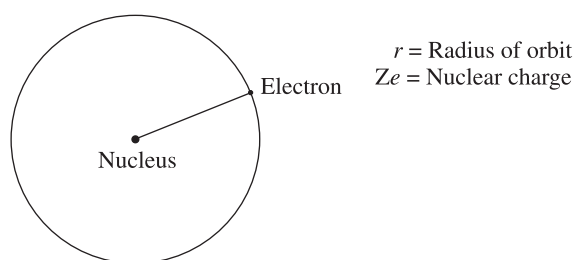


Fig. 1.3.1 Hydrogen atom according to Rutherford model

From this equation the kinetic energy of electron comes out to be

$$K = \frac{1}{2}mv^2 = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad \dots(1.3.2)$$

The total energy E of electron moving around the nucleus in circular orbit consists of two parts: kinetic and potential.

$$E = K + U = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + \frac{-e^2}{4\pi\epsilon_0 r} = -\frac{1}{2} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad \dots(1.3.3)$$

The negative total energy means that the electron in the atom is bound to the nucleus.

The motion of electron in the force field of a nucleus is governed by the two well-established laws of classical physics namely the Newton's law and the Coulomb's law. The electron moves in a circular orbit, which is an accelerated motion. According to classical electrodynamics an accelerated charge must radiate energy in the form of electromagnetic waves. The rate at which a particle having

charge e and moving with acceleration a radiates electromagnetic energy is given by

$$P = \frac{2}{3} \frac{1}{4\pi\epsilon_0} \frac{e^2 a^2}{c^3} \quad \dots(1.3.4)$$

Since the acceleration of electron in a circular orbit is $a = v^2/r$, the rate at which energy is radiated is given by

$$P = \frac{2}{3} \left(\frac{1}{4\pi\epsilon_0} \right)^3 \frac{e^6}{c^3 m^2 r^4} \quad \dots(1.3.5)$$

For hydrogen atom $r = 5.3 \times 10^{-11}$ m, the value of P comes out to be

$$P = 4.6 \times 10^{-9} \text{ J/s} = 2.9 \times 10^{10} \text{ eV/s}$$

Since the electron loses energy through emission of radiation, the total energy E becomes more and more negative, which implies that the radius becomes progressively shorter. It is apparent from Eqn. (1.3.5) that the rate of emission of energy is proportional to $1/r^4$, hence the rate of emission rapidly increases as the orbit becomes shorter and shorter, and if this process continues the electron must ultimately fall into the nucleus. This prediction of classical physics is in direct contradiction to the fact that the hydrogen atom is stable. Moreover, classical electrodynamics predicts that energy is continuously radiated and therefore the resulting spectrum of the emitted radiation must be continuous. This again contradicts the observations. These puzzling results led physicists to think that the classical laws of physics, which are valid in the macroscopic world, do not apply to the microscopic world.

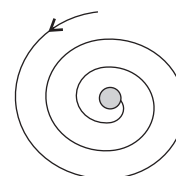


Fig. 1.3.2 Spiral path of electron

1.4 ATOMIC (LINE) SPECTRUM

To obtain line spectrum of a substance, it is transformed into gaseous (atomic) state and is then excited by an electric discharge. The atoms then emit light that contains only certain wavelengths. To observe spectrum we often allow the emitted light to pass through a fine rectangular aperture, called slit, and then through a dispersive device, such as prism or diffraction grating. The emergent radiation is received on a photographic film or can be seen through a telescope. The various wavelengths in the light appear as well-defined fine lines, which are the images of the slit. Each line corresponds to a definite wavelength present in the light. These lines taken together constitute what we call **atomic or line spectrum**. By 1823, the line spectrum of each element was found. The line spectrum is a characteristic property of the element. In other words, each element can be identified by its line spectrum.

By the middle of the 19th century the study of atomic spectra had held the interest of scientists because of their mysterious varieties. Using improved techniques and spectrographs of high resolving power, more and more finer details of atomic spectra were recorded and a wealth of fascinating but unexplained data on the spectral lines of various atoms was collected. The real theoretical work in

spectroscopy dates back from 1885 when a Swiss high school mathematics teacher Johann Balmer discovered an empirical rule governing the wavelengths of various spectral lines in the visible part of the spectrum of hydrogen atom. Balmer found that the wavelengths of spectral lines of hydrogen atom could be represented by formula

$$\lambda = b \frac{m^2}{m^2 - 4} = 3645.6 \times \frac{m^2}{m^2 - 4} \text{ \AA}$$

Substituting for $m = 3, 4, 5, 6, \dots$, we get the wavelength of the first, second, third, fourth lines beginning at the red end. Customarily the lines are denoted by wave number, which is reciprocal of wavelength. In terms of wave number the Balmer formula is represented as

$$\bar{\nu} = \frac{1}{\lambda} = 109678 \left(\frac{1}{2^2} - \frac{1}{m^2} \right) \text{ cm}^{-1} = R \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

where $R = 109678 \text{ cm}^{-1}$ is a constant now known as Rydberg constant.

A group of lines, whose wave numbers are represented by giving appropriate values to the variable integer m , constitute a spectral series. Since the pioneer work of Balmer, a large volume of work has been done on the analysis of atomic spectra. In the hydrogen spectrum many spectral series were discovered, which were named after their discoverer.

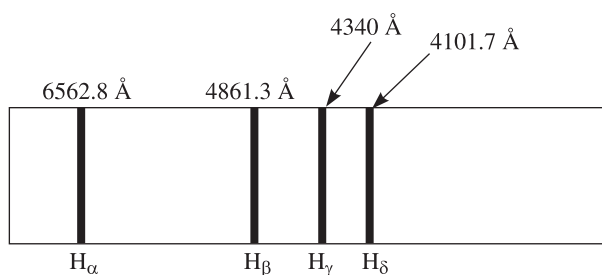


Fig. 1.4.1 Balmer lines of hydrogen spectrum

Spectral Series of Hydrogen Atom:

Lyman series (1906): It is found in ultraviolet region.

$$\bar{\nu} = R \left(\frac{1}{1^2} - \frac{1}{m^2} \right); \quad m = 2, 3, 4, \dots$$

$$\bar{\nu}_{\infty} = R \left(\frac{1}{1^2} - \frac{1}{\infty} \right) = R$$

$$\lambda_1 = 1216 \text{ \AA}, \quad \lambda_{\infty} = 912 \text{ \AA}.$$

Balmer series (1885): Four lines (H_{α} , H_{β} , H_{γ} , H_{δ}) are found in the visible region.

$$\bar{\nu} = R \left(\frac{1}{2^2} - \frac{1}{m^2} \right); \quad m = 3, 4, 5, \dots$$

$$\bar{\nu}_{\infty} = R \left(\frac{1}{2^2} - \frac{1}{\infty} \right) = \frac{R}{4}$$

$$\lambda_1 = 6563 \text{ Å}, \lambda_{\infty} = 3640 \text{ Å}.$$

Paschen series (1908): It is found in infrared region.

$$\bar{\nu} = R \left(\frac{1}{3^2} - \frac{1}{m^2} \right); \quad m = 4, 5, 6, \dots$$

$$\bar{\nu}_{\infty} = R \left(\frac{1}{3^2} - \frac{1}{\infty} \right) = \frac{R}{9}$$

$$\lambda_1 = 18760 \text{ Å}, \lambda_{\infty} = 8210 \text{ Å}.$$

Bracket series (1922): It is found in infrared region.

$$\bar{\nu} = R \left(\frac{1}{4^2} - \frac{1}{m^2} \right); \quad m = 5, 6, \dots$$

$$\bar{\nu}_{\infty} = R \left(\frac{1}{4^2} - \frac{1}{\infty} \right) = \frac{R}{16}$$

$$\lambda_1 = 40530 \text{ Å}, \lambda_{\infty} = 14590 \text{ Å}.$$

Pfund series: It is found in far infrared region.

$$\bar{\nu} = R \left(\frac{1}{5^2} - \frac{1}{m^2} \right); \quad m = 6, 7, \dots$$

$$\bar{\nu}_{\infty} = R \left(\frac{1}{5^2} - \frac{1}{\infty} \right) = \frac{R}{25}$$

$$\lambda_1 = 74620 \text{ Å}, \lambda_{\infty} = 22800 \text{ Å}.$$

The problem to which the physicists in the second decade of the 20th century were confronted was the problem of finding the possible mechanism responsible for the origin of discrete spectral lines. The only atomic model available at that time was that of Rutherford but that too was unstable according to the classical concepts of electrodynamics. The observed facts viz the existence of discrete spectral lines and the stability of the atom, were inexplicable in terms of classical physics. The reign of confusion was spread over the scientific world. No solution within the realm of classical physics was seen. At the same time, the departure from the concepts of classical physics was much too a daring step. On this cloudy scene a brilliant young man appeared like an angel who made a bold departure from the classical physics and cleared up the mystifying clouds—the man was Niels Hendrick David Bohr.

NIELS BOHR

Born in 1885 at Copenhagen in Denmark, Bohr studied at Copenhagen when Rutherford was performing his epoch making scattering experiment at the university of Manchester. Bohr received a fellowship to work at Cambridge and Manchester. There he became acquainted with the Rutherford's atomic model. After returning to his home city Copenhagen in the summer of 1913, he published his celebrated paper on the atomic structure in the Philosophical Magazine. As mentioned earlier the Rutherford's atomic model was not consistent with the laws of classical physics, Bohr's solution to this contradiction between the conclusions of the conventional laws of physics and the facts of nature was straightforward and bold. Since nature cannot be wrong, the conventional laws of physics must be wrong at least when applied to the dynamics of electron within the atom. In making his revolutionary statement regarding the motion of electron within the atom, he took a bold step in applying Planck-Einstein quantum hypothesis to the atomic system. Thus his theory of atomic structure was a hybrid of classical and quantum ideas. The way he proposed was too odd and unconventional that he kept the manuscript locked in his desk for almost two years before he decided to send it for publication. When this epoch making paper finally appeared (1913) it sent out a shock wave of amazement through the world of contemporary physics. For this outstanding work Bohr was awarded Nobel Prize in 1922.



In 1918, Bohr became professor of theoretical physics at the university of Copenhagen and in 1921 he established an institute in Copenhagen, which became an international center for theoretical work in quantum physics. At this institute, world's outstanding physicists spent some time. Wolfgang Pauli, P.A.M. Dirac, Werner Heisenberg, Landau, Bloch, Teller, Gamow, Heitler were all alumni of Bohr's institute, their names and accomplishments tell a large part of what happened in quantum mechanics during the crucial decade of the 1920's. Robert Oppenheimer wrote of this and Bohr's indispensable role in it. It was a heroic time. It was not the doing of one man: it involved the collaboration of scores of scientists from many different lands, though from the first to the last the deep creative and critical spirit of Niels Bohr guided, restrained, deepened and finally transmuted the enterprise.

1.5 BOHR'S THEORY OF HYDROGENIC ATOMS (H, He⁺, Li⁺⁺)

In 1913, Bohr proposed an atomic model, which explained with amazing accuracy the main features of the spectra of hydrogenic atoms. His model was based on the following postulates:

- (i) The electron in hydrogen atom moves in circular orbit around the nucleus. The dynamics of the electron is governed by the Newtonian mechanics *i.e.*, the centripetal force required for circular motion is provided by Coulomb attraction of nucleus on the electron.

$$\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r^2} = m\omega^2 r \quad \dots(1.5.1)$$

where r = Radius of the orbit, ω = Angular velocity of electron, m = Electronic mass, Z = Atomic number of atom.

- (ii) In contrast to classical physics where the radius of electronic orbit can assume any magnitude, Bohr asserted that only those orbits are allowed in which the angular momentum of electron is integral multiple of $\hbar$ ($= h/2\pi$).

$$mr^2\omega = n\hbar \quad \dots(1.5.2)$$

where n is an integer, called principal quantum number. $n = 1, 2, 3, \dots$ label the first, second, third orbits of the electron.

- (iii) Since the revolving electron around the nucleus is not a stable system under the laws of classical electrodynamics. Bohr assumed that the classical laws do not apply, at least, to the atomic phenomena. That is, the electron revolving in any one of the allowed orbits does not radiate. These non-radiating orbits are called *stationary orbits*. However, while making transition from a stationary orbit of higher energy to that of lower energy it does radiate. The electron may also go over from orbit of lower energy to that of higher energy by absorbing energy. If E_i and E_f are the energies of electron in the initial and final orbit, the frequency ν (or angular frequency ω) is given by

$$E_i - E_f = h\nu = \hbar\omega \quad \dots(1.5.3)$$

Let us calculate the radius of electron orbit, orbital frequency of revolution, energy of electron and the frequency (wavelength) of the radiation emitted in electronic transition.

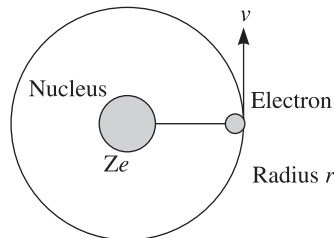


Fig. 1.5.1 Hydrogen atom

Radius of orbit: Eliminating ω from Eqns. (1.5.1) and (1.5.3) and solving the resulting equation for r , we have

$$r = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} \frac{n^2}{Z} \quad \dots(1.5.4)$$

For hydrogen atom $Z = 1$, the radius of the first orbit ($n = 1$), called Bohr orbit (a_0) comes out to be

$$r_1 = a_0 = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} \quad \dots(1.5.5)$$

Substituting $e = 1.6 \times 10^{-19}$ C, $m = 9.1 \times 10^{-31}$ kg, $\hbar = 1.054 \times 10^{-34}$ J s and $(1/4\pi\epsilon_0) = 9 \times 10^9$ m/F, we obtain

$$a_0 = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA}$$

In terms of Bohr radius a_0 , the radius of the n th orbit is given by

$$r_n = a_0 \frac{n^2}{Z} \quad \dots(1.5.6)$$

Rotational frequency of electron: Eliminating r from Eqns. (1.5.1) and (1.5.2) we obtain the frequency of rotation of electron in n th orbit.

$$\omega_n = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^3} \frac{Z^2}{n^3} = \omega_0 \frac{Z^2}{n^3} \quad \dots(1.5.7)$$

where $\omega_0 = 4.14 \times 10^{15}$ radian/s.

Linear velocity of electron: The linear velocity of electron in n th orbit is given by

$$v_n = \omega_n r_n = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar} \frac{Z}{n} = v_0 \frac{Z}{n} \quad \dots(1.5.8)$$

where $v_0 = 2.19 \times 10^6$ m/s.

The ratio of velocity of electron in the first orbit of hydrogen atom to the speed of light c is called the *fine structure constant* α and is given by

$$\alpha = \frac{v_1}{c} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} = \frac{1}{137} \quad \dots(1.5.9)$$

Energy of electron: The kinetic energy of electron is

$$K = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2 = \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{2r} \quad \dots(1.5.10)$$

Potential energy of electron is

$$U = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r} \quad \dots(1.5.11)$$

The total energy of electron is

$$E = K + U = -\frac{1}{4\pi\epsilon_0} \frac{Ze^2}{2r} \quad \dots(1.5.12)$$

Substituting the value of r from (1.5.4), we have

$$E_n = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4 Z^2}{2\hbar^2 n^2} = -(2.176 \times 10^{-18} \text{ J}) \frac{Z^2}{n^2} = -(13.6 \text{ eV}) \frac{Z^2}{n^2} \quad \dots(1.5.13)$$

Equation (1.5.13) can be rearranged as

$$E_n = -\left[\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi c\hbar^3}\right] (2\pi\hbar c) \frac{Z^2}{n^2} = -(2\pi\hbar c R) \frac{Z^2}{n^2} = -hcR \frac{Z^2}{n^2} \quad \dots(1.5.14)$$

where $R = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{4\pi c\hbar^3} = 1.097 \times 10^7 \text{ m}^{-1}$ is **Rydberg constant**.

From Eqns. (1.5.10), (1.5.11) and (1.5.12), we see that

$$K = |E_n| \quad \text{and} \quad U = 2E_n$$

Equation (1.5.13) gives the possible energy levels of electron in hydrogen atom. The electron in the first orbit ($n = 1$) of hydrogen atom ($Z = 1$) has energy equal to

$$E_1 = -13.6 \text{ eV}$$

The negative energy means that the electron is bound to the nucleus with this much energy. In order to remove the electron from the force field of nucleus, minimum energy equal to 13.6 eV must be imparted to it and therefore the **first ionization energy** of hydrogen atom is 13.6 eV.

Frequency of emitted radiation: If the electron makes transition from an orbit of quantum number n_i to the orbit of quantum number n_f , the frequency ω of the emitted radiation is given by

$$\hbar\omega = E_i - E_f = (2\pi\hbar c R) Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The wavelength ($\lambda = 2\pi c/\omega$) of the radiation is

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots(1.5.15)$$

This formula is known as the **Balmer formula**. It is remarkable to note that the value of Rydberg constant R calculated from fundamental constants comes out to be the same as that obtained from spectroscopic measurements. This gives the dramatic confirmation of Bohr's theory.

1.6 ORIGIN OF SPECTRAL SERIES

Lyman series: When the electron jumps from the energy levels labeled by $n_i = 2, 3, 4, \dots$ to the energy levels $n_f = 1$, a series of spectral lines are emitted. These lines constitute *Lyman series* after the name of its discoverer. The wavelengths of these lines are given by

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right); \quad n_i = 2, 3, 4, \dots \text{ (ultraviolet).}$$

Balmer series: When the electron makes transition from energy levels $n_i = 3, 4, 5, \dots$ to $n_f = 2$, the spectral lines of Balmer series are emitted. The wavelengths of these lines are represented by formula

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right); \quad n_i = 3, 4, 5, \dots$$

The first four lines of this series lie in the visible region and are denoted by H_α , H_β , H_γ , and H_δ .

Paschen series: The lines of Paschen series are emitted when the electron jumps from $n_i = 4, 5, 6, \dots$ to $n_f = 3$ and their wavelengths are given by the formula

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{3^2} - \frac{1}{n_i^2} \right); \quad n_i = 4, 5, 6, \dots \text{ (infrared)}$$

Bracket series: The wavelength of Bracket series are given by

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{4^2} - \frac{1}{n_i^2} \right); \quad n_i = 5, 6, 7, \dots \text{ (far-infrared).}$$

Pfund series: The wavelength of lines of this series are represented by formula

$$\frac{1}{\lambda} = \bar{\nu} = RZ^2 \left(\frac{1}{5^2} - \frac{1}{n_i^2} \right); \quad n_i = 6, 7, 8, \dots \infty$$

The criterion for the success of any new theory in physics is not only that it should give a correct interpretation of the previous observations but it should also provide new predictions, which can later be confirmed. At the time when Bohr presented his theory, the only spectral series known was Balmer series. Bohr's theory not only explained the origin of this series but also predicted the existence of other spectral series. In fact Lyman and other series were discovered much after the Bohr's theory was presented.

Energy level diagram : The energy level diagram of hydrogen atom corresponding to different values of principal quantum number n are shown in the Figure (1.6.1). The energy level for $n = 1$ is called the ground state and has energy equal to -13.6 eV . All other energy states are called the excited

states. The electronic transitions leading to various spectral series are shown on the diagram by vertical lines.

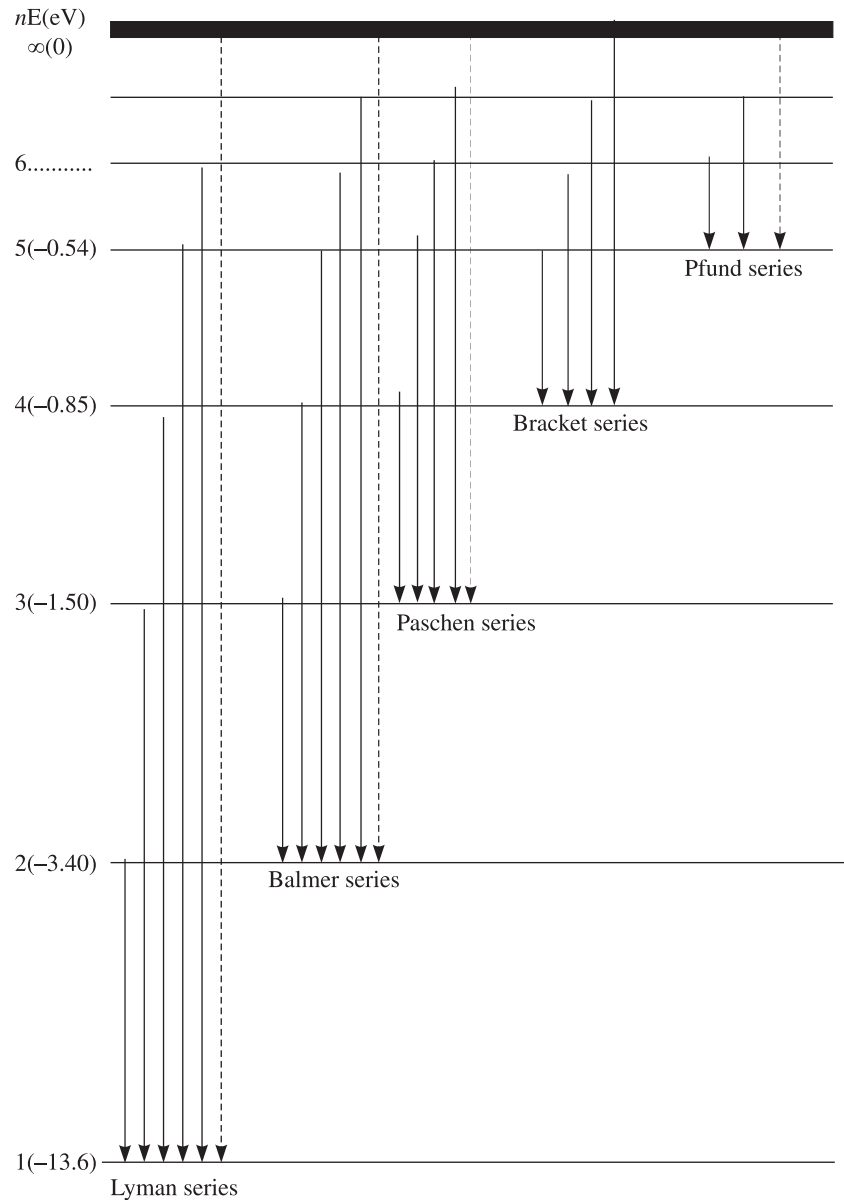


Fig. 1.6.1 Spectral series of hydrogen atom

Criticism of Bohr's theory: Although Bohr's theory met with spectacular success in explaining the hydrogen spectrum, nevertheless it was too revolutionary to get a warm reception. In order to save the stability of the atom from catastrophe Bohr threw away the only classical picture of mechanism

of emission of radiation by an accelerated charge. His postulates viz., only those orbits are allowed in which angular momentum of electron is integral multiple of $\hbar$ and the frequency of emitted radiation during electronic transition is given by $\omega = (E_i - E_f)/\hbar$, were taken from the quantum theory, which itself was questioned. Bohr's theory has nothing to say about the intensity of spectral lines. All attempts to construct a theory of helium atom (and other multi-electron atoms) failed. The weakest point of Bohr's theory was its internal logical contradiction. It was neither consistent classical theory nor a consistent quantum theory. It was a hybrid theory based on classical and quantum concepts both and so it was felt by many physicists to be unsatisfactory. In spite of all its deficiencies Bohr's theory brought a new light and hope for spectroscopy and for quantum theory as well. This theory may be regarded as a transition step on the path to the creation of a consistent theory of atomic phenomena. It provided the foundation on which theoretical physicists erected a vast structure of atomic and molecular physics.

1.7 CORRECTION FOR NUCLEAR MOTION

In the development of Bohr's theory the nucleus of the atom was assumed to be stationary. In fact, the motion of electron and nucleus under their mutual interaction is a two body problem. In hydrogen atom both the nucleus and the electron rotate with the same angular velocity, say ω about an axis passing through their center of mass and perpendicular to the line joining them. Let r be the distance between the nucleus and the electron and r_1 and r_2 be their distances from the center of mass. If M and m are the masses of the nucleus and the electron then

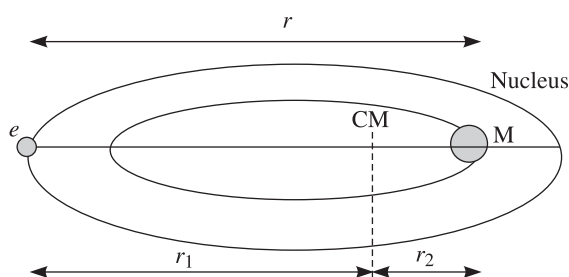


Fig. 1.7.1 Rotation of nucleus and electron about their center of mass

$$Mr_1 = mr_2 \quad \text{and} \quad r_1 + r_2 = r$$

From these two equations, we find

$$r_1 = \frac{m}{m+M}r \quad \text{and} \quad r_2 = \frac{M}{m+M}r$$

The total angular momentum of the system is

$$L = Mr_1^2\omega + mr_2^2\omega = \frac{mM}{m+M}r^2\omega = \mu r^2\omega$$

where μ is called the *reduced mass* of nucleus and electron and is given by $\mu = \frac{mM}{m+M}$ or $\frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}$. The above result shows that the angular momentum of electron–nucleus system rotating about their center of mass is the same as that of a fictitious particle of mass μ revolving in a circular orbit of radius r . Thus, the effect of taking the nuclear motion into consideration is equivalent to replacing electronic mass m by the *reduced mass* μ . In the special case: when $M \rightarrow \infty$, $\mu \rightarrow m$. Thus, the assumption that the nucleus is stationary is equivalent to assuming the nucleus to be infinitely heavy. When nuclear motion is taken into consideration, the formulas for orbital radius, angular frequency of rotation, energy and Rydberg constant become

$$r_n = 4\pi\epsilon_0 \frac{\hbar^2}{\mu e^2} \frac{n^2}{Z} = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} \left(\frac{m+M}{M} \right) \frac{n^2}{Z} = a_0 \left(\frac{m+M}{M} \right) \frac{n^2}{Z} \quad \dots(1.7.1)$$

$$\omega_n = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{\mu e^4}{\hbar^3} \frac{Z^2}{n^3} = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^3} \left(\frac{M}{m+M} \right) \frac{Z^2}{n^3} \quad \dots(1.7.2)$$

$$E = - \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{2\hbar^2} \left(\frac{M}{m+M} \right) \frac{Z^2}{n^2} \quad \dots(1.7.3)$$

$$R = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{4\pi c \hbar^3} \left(\frac{M}{m+M} \right) = R_\infty \left(\frac{M}{m+M} \right) = R_\infty \left(\frac{1}{1 + \frac{m}{M}} \right) \quad \dots(1.7.4)$$

where R_∞ is the value of Rydberg constant when nucleus is assumed to infinitely heavy. The Balmer formula now becomes

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_\infty \left(\frac{M}{m+M} \right) Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \dots(1.7.5)$$

Positronium atom: When an electron and positron come together, they form a short-lived atom positronium in which both the particles revolve about their center of mass. Since both the particles are equally massive, the center of mass lies mid-way between them. For positronium atom, reduced mass $\mu = m/2$ and $(M+m)/M = 2$. The radius of the circular path of either particle is

$$r_n = a_0 \left(\frac{M+m}{M} \right) = 2a_0 = 1.06 \text{ \AA}$$

The orbital frequency is

$$\omega_n = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^2} \left(\frac{M}{m+M} \right) = (4.14 \times 10^{15} \text{ rad/s})(2)$$

$$= 2.07 \times 10^{15} \text{ rad/s}$$

The energy of the atom is

$$\begin{aligned} E_n &= -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{2\hbar^2} \left(\frac{M}{M+m}\right) \frac{Z^2}{n^2} = -(13.6 \text{ eV}) \left(\frac{M}{m+M}\right) \frac{Z^2}{n^2} \\ &= -6.79 \text{ eV} \end{aligned}$$

Rydberg's constant

$$R = R_\infty \left(\frac{M}{M+m}\right) = \frac{1}{2} R_\infty$$

The wavelength of spectral line

$$\frac{1}{\lambda} = \frac{1}{2} R_\infty \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

Muonic (mesic) atom: In this atom a muon which has charge equal to that of electron and mass equal to 207 times the electronic mass, revolves around a proton. The reduced mass of the system is

$$\mu = \frac{m'M}{m'+M} = \frac{(207m)(1836m)}{207m + 1836m} = 186m$$

The orbital radius

$$r_n = 4\pi\epsilon_0 \frac{\hbar^2}{\mu e^2} \frac{n^2}{Z} = 4\pi\epsilon_0 \frac{\hbar^2}{me^2} \frac{n^2}{Z} \frac{1}{186} = \frac{a_0}{186} \frac{n^2}{Z}$$

For $n = 1$ and $Z = 1$,

$$r_1 = \frac{a_0}{186} = 2.84 \times 10^{-3} \text{ Å}$$

Orbital frequency

$$\begin{aligned} \omega_n &= \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu e^4}{\hbar^3} \frac{Z^2}{n^3} = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{\hbar^3} \frac{Z^2}{n^3} (186) \\ &= (4.14 \times 10^{15} \text{ rad/s})(186) \frac{Z^2}{n^3} \end{aligned}$$

For $n = 1$ and $Z = 1$,

$$\omega_1 = 7.70 \times 10^{17} \text{ rad/s}$$

Energy of atom

$$E_n = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{\mu e^4}{2\hbar^2} \frac{Z^2}{n^2} = -\left(\frac{1}{4\pi\epsilon_0}\right)^2 \frac{me^4}{2\hbar^2} \frac{Z^2}{n^2} (186)$$

For $n = 1$ and $Z = 1$

$$E_1 = -(13.6 \text{ eV}) (186) = -2530 \text{ eV}$$

$$\text{Rydberg's constant} \quad R = \frac{1}{4\pi\epsilon_0} \frac{\mu e^4}{4\pi c \hbar^3} = \frac{1}{4\pi\epsilon_0} \frac{m e^4}{4\pi c \hbar^3} (186) = 186 R_\infty = 204.04 \times 10^7 \text{ m}^{-1}$$

Wavelength of spectral line.

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The first line of Lyman series has wavelength $\lambda = 6.5 \text{ \AA}$ (x-ray region.)

1.8 DETERMINATION OF ELECTRON-PROTON MASS RATIO (m/M_H)

The Rydberg constant for hydrogen atom is

$$R_H = R_\infty \frac{1}{1 + (m/M_H)} \quad \dots(1.8.1)$$

and for helium atom is

$$R_{He} = R_\infty \frac{1}{1 + (m/M_{He})} \quad \dots(1.8.2)$$

where $M_{He} = 4 M_H$

From Eqns. (1.8.1) and (1.8.2), we have

$$\frac{R_H}{R_{He}} = \frac{1 + (m/M_{He})}{1 + (m/M_H)} = \frac{1 + (m/4M_H)}{1 + (m/M_H)}$$

$$\text{Or} \quad \frac{m}{M_H} = \frac{R_{He} - R_H}{R_H - (1/4)R_{He}} \quad \dots(1.8.3)$$

Substituting the experimental value of $R_H = 1096758 \text{ m}^{-1}$ and $R_{He} = 10972226 \text{ m}^{-1}$ we find that $m/M_H = 1/1848$ which agrees with other measurements.

1.9 ISOTOPIC SHIFT: DISCOVERY OF DEUTERIUM

The Rydberg's constant for an atom depends on nuclear mass hence it will have different values for different isotopes. The Rydberg's constants for ordinary hydrogen (${}_1H^1$) and deuterium (${}_1H^2$) are

$$R_{H_1} = R_\infty \frac{1}{1 + m/M_{H_1}} \quad R_{H_2} = R_\infty \frac{1}{1 + m/M_{H_2}}$$

The wavelengths of the first Balmer lines emitted by these two isotopes are given by

$$\frac{1}{\lambda_1}(\text{H}_\alpha^1) = R_{\text{H}_1} Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

$$\frac{1}{\lambda_1'}(\text{H}_\alpha^2) = R_{\text{H}_2} Z^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

Substituting the values of R_{H_1} and R_{H_2} , we get

$$\lambda_1(\text{H}_\alpha^1) = 6562.79\text{\AA} \text{ and } \lambda_1(\text{H}_\alpha^2) = 6561.00\text{\AA}.$$

Thus, the two Balmer lines should be separated by 1.79Å. Using a concave grating spectrograph Urey, Brickwedde and Murphy observed that the H_α lines emitted by these two isotopes were separated by this amount. In fact, the isotope deuterium was discovered in this way.

1.10 ATOMIC EXCITATION

According Bohr's theory, atomic energy levels are *quantized*. Normally the atom resides in its lowest energy state (ground state). By imparting energy to it from external agency, it can be raised to one of its excited states. There are many ways to cause excitation in the atom. One way is to make it collide with another particle possessing appropriate energy. If the kinetic energy of the colliding particle is less than the energy difference between the ground state and the first excited state of the atom, the collision is **elastic** and the particle bounces off (because of its much smaller mass in comparison to that of the atom). If the energy of the colliding particle is large, the atom may absorb some of its energy during collision and make a transition from ground state to one of its excited state. In such collisions, the kinetic energy is not conserved. Such types of collisions are called **inelastic collisions**. The excited atom returns to its ground state in an average time of 10^{-8} second by emitting one or more photons. These atomic processes can be realized in a discharge tube containing a gas at low pressure. Electrons and ions produced due to discharge are accelerated under the intense electric field produced by the applied voltage between the electrodes. The electrons acquire sufficient energy and are capable of causing excitation in the atoms, which come their way.

The atom can also make a transition from the ground state to one of its excited state by absorbing a photon whose energy is exactly equal to the energy difference between the ground state and the excited state. Absorption spectra have their origin because of this type of excitation.

At the time Bohr published his theory of atomic structure, two scientists James Franck and Gustav Hertz were performing experiments on the excitation of atoms. In 1914, they submitted their results, which gave striking evidence in the favour of quantization of atomic energy states. It is remarkable to note that Franck and Hertz were not aware of Bohr theory. If they had read it before collecting their results they would not have believed it which is evident from the Franck's candid remark *we had a colloquium at that time in Berlin at which all important papers were discussed. Nobody discussed Bohr's paper. Why not? The reason is that fifty years ago one was so convinced that nobody would, with the state of knowledge we had at that time, understand spectral lines emission, so that if somebody published a paper about it, one assumed, probably it is not right. So we did not know it (this statement of Franck was given in an interview in 1961).*

1.11 FRANCK-HERTZ EXPERIMENT

Franck and Hertz experiment provides strong and conclusive evidence in support of the existence of discrete energy states of atoms. The apparatus, as shown in the Fig. (1.11.1), consists of a glass tube filled with mercury vapor, a filament with heating arrangement, an anode plate for receiving electrons and a grid near the anode. On heating the filament electrons are emitted, which are accelerated towards the anode. When they pass through the grid, the retarding potential V_0 prevents them from reaching the plate. Thus, electrons having very small kinetic energy will not be able to reach the anode. An ammeter measures the current due to electrons reaching the plate. When the accelerating voltage is increased, the current increases. For a particular value of the accelerating voltage the current suddenly drops and then again increases with increasing voltage. At certain voltage again the current drops. It is observed that the current drops at equal interval of accelerating voltage. The results obtained are shown in the Fig. (1.11.2).

Interpretation of observed results: When the accelerating voltage is increased from its zero value, the kinetic energy of the electrons increases and therefore more and more electrons reach the anode overcoming the retarding potential thus the current increases. When the accelerating voltage becomes 4.9 volts, the electrons acquire kinetic energy equal to 4.9 eV on reaching the grid. In front of the grid, they suffer inelastic collisions with the mercury atoms and lose most of their kinetic energy and are unable to reach the anode because of the retarding potential. This explains the drop in current with increasing voltage. During the collisions with electrons the mercury atoms are raised to their first excited state. When the accelerating voltage is further increased above 4.9 volts, electrons acquire so much energy that even after suffering inelastic collision they are left with sufficient energy to overcome the retarding potential and thus reach the anode. This explains the reason for the increase in current after the first drop of current. Again when electrons acquire energy equal to 9.8 eV they suffer inelastic collisions with mercury atoms in their trip from cathode to anode and therefore current falls.

This simple experiment shows that the energy required to raise mercury atoms from their ground to their first excited state is 4.9 eV. Electrons of energy less than 4.9 eV do not excite the mercury atoms. Thus, the mercury atoms can exist in the ground state or in the first excited state which it has energy 4.9 eV relative to the ground state.

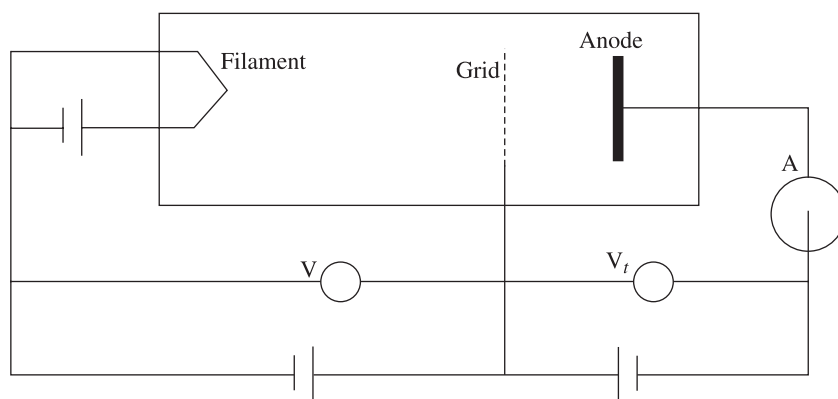


Fig. 1.11.1 Schematic sketch of Franck-Hertz experiment

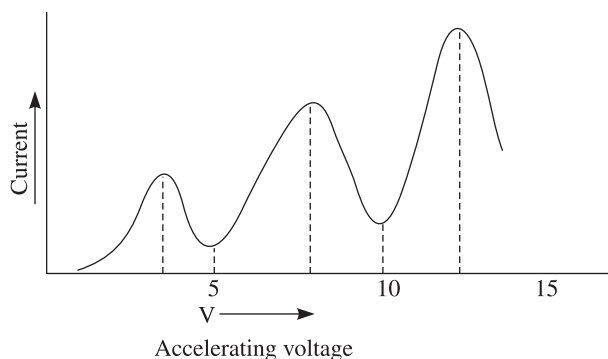


Fig. 1.11.2 Results of Franck-Hertz experiment

When an excited mercury atom returns to its ground state a photon of energy 4.9 eV is emitted. In order to find the energy of the emitted photon, Hertz observed the emission spectrum of mercury vapor filled in the tube. To his surprise, when the accelerating voltage was less than 4.9 volts, no spectral line appeared but when it was 4.9 volts a spectral line of wavelength 2536 Å was observed. The energy of this photon is

$$E = \frac{ch}{\lambda} = \frac{12400 \text{ eV} \cdot \text{Å}}{2536 \text{ Å}} = 4.89 \text{ eV}$$

which is in excellent agreement with the experiment.

1.12 BOHR'S CORRESPONDENCE PRINCIPLE

In 1923, Bohr pointed out that *quantum and classical theories yield identical result in the region of high quantum numbers*. This requirement is called the **Correspondence principle**. In the early development of the quantum theory, this principle played an important role in checking the formulae obtained from quantum principles. Let us verify this principle by taking hydrogen atom as an example.

According to classical electromagnetic theory; an electron revolving in circular orbit radiates electromagnetic radiation of frequency equal to the orbital frequency and to the harmonics of the orbital frequency. The orbital frequency of electron in the hydrogen atom is

$$\omega_n = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^3} \frac{Z^2}{n^3} = 4\pi cR \frac{Z^2}{n^3} \quad (\text{orbital}) \quad \dots(1.12.1)$$

The frequency of the emitted radiation when electron jumps from $(n + p)$ th orbit to n th orbit is

$$\begin{aligned} \omega &= \frac{2\pi c}{\lambda} = 2\pi cRZ^2 \left(\frac{1}{n^2} - \frac{1}{(n+p)^2} \right) \\ &= 2\pi cRZ^2 \left(\frac{(n+p)^2 - n^2}{n^2(n+p)^2} \right) \end{aligned}$$

$$= 2\pi c R Z^2 \left(\frac{(2n+p)p}{n^2(n+p)^2} \right)$$

In the limit of large quantum numbers $p \ll n$, we have

$$\omega = 2\pi c R Z^2 \frac{2p}{n^3} \quad \dots(1.12.2)$$

For $p = 1$, this frequency coincides with the orbital frequency of electron. Harmonics are obtained by letting $p = 2, 3, 4, \dots$. This illustrates that: *In the limit of large quantum numbers, classical and quantum physics provide identical results.*

1.13 SOMMERFELD THEORY OF HYDROGEN ATOM

Bohr's theory of hydrogen atom in its simplest form met with spectacular success in predicting the correct positions of the spectral lines in the hydrogen atom. Spectrographs of higher resolving power revealed that the spectral lines which were thought to be single, actually consisted of a group of lines very close together. This means that the energy levels corresponding to a principal quantum number possess fine structure *i.e.*, the energy level consists of a number of energy levels lying very close together. Michelson with his interferometer found that the H_α and H_β lines of Balmer series were close doublet with separation of only $0.14 \text{ \AA}$ and $0.48 \text{ \AA}$ respectively.

In an attempt to explain the existence of fine structure, Wilson and Sommerfeld proposed a general rule for quantum conditions, known as Wilson-Sommerfeld quantization rule. The Planck's quantum condition for a harmonic oscillator: *energy of a harmonic oscillator is integral multiple of $\hbar\omega$* and Bohr's condition: *angular momentum of an electron moving in circular orbit is integral multiple of $\hbar$* are the particular cases of this general quantum condition.

For a harmonic oscillator with momentum p and position q , the Wilson-Sommerfeld quantum condition states that

$$\oint p dq = nh \quad \dots(1.13.1)$$

where the integration is to be carried out over the complete cycle. The integer n is called the principal quantum number. The energy of a one-dimensional harmonic oscillator is

$$E = K + U = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 q^2$$

Above equation can be written as

$$\frac{p^2}{2mE} + \frac{q^2}{2E/m\omega^2} = 1 \quad \dots(1.13.2)$$

The state of harmonic oscillator is described by momentum coordinate p and position coordinate q . If we plot the instantaneous values of q and p on $q-p$ plane for one cycle we get an ellipse with

semi-major axis $a = \sqrt{\frac{2E}{m\omega^2}}$ and semi-minor axis $b = \sqrt{2mE}$. Each point on the ellipse represents some state of the oscillator. Such a two-dimensional space with position and momentum as its axes is called *phase space*. As the oscillator completes its one cycle, its representative point completes ellipse in phase space. The actual motion of the oscillator should not be confused with the motion of its representative point in phase space.

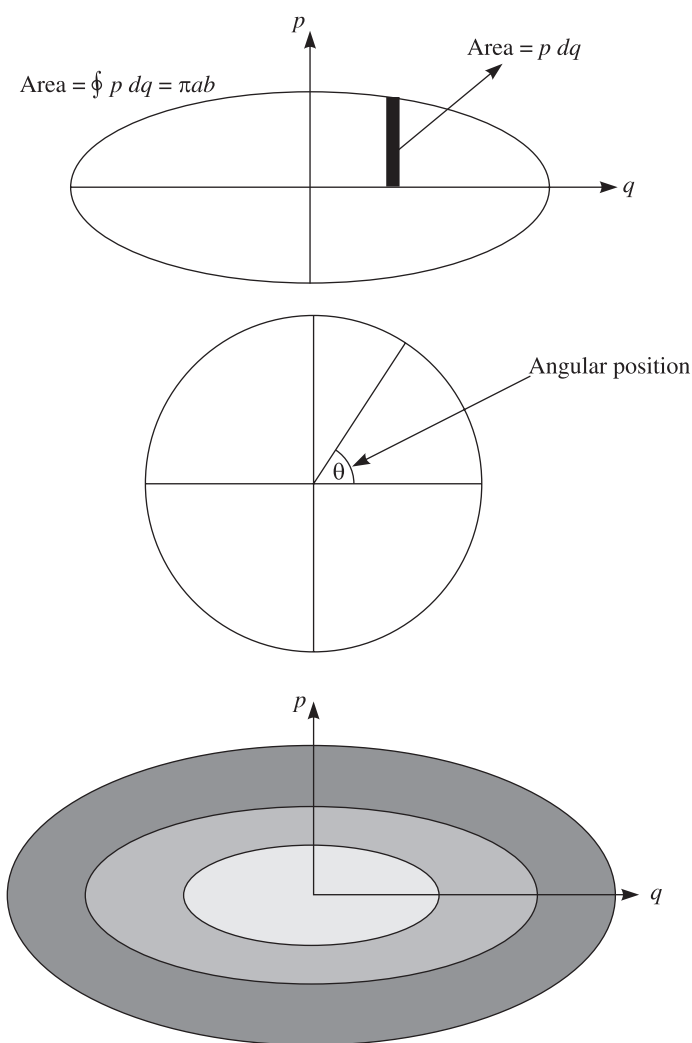


Fig. 1.13.1 Area between any two successive ellipses is h

In Wilson-Sommerfeld quantum condition $\oint p \, dq = nh$, the integral on the left hand side represents the area of the phase trajectory and is equal to πab . Thus, Eqn. (1.13.1) can be written as

$$\pi ab = nh$$

$$\pi \sqrt{\frac{2E}{m\omega^2}} \sqrt{2mE} = nh$$

$$E = n \frac{h}{2\pi} \omega = n\hbar\omega \quad \dots(1.13.3)$$

which is the Planck's quantization rule for harmonic oscillator. The states of oscillator with energies $E = \hbar\omega, 2\hbar\omega, 3\hbar\omega, \dots$ are described by a series of ellipses such that the area between two successive ellipses is equal to Planck's constant h .

The Wilson-Sommerfeld condition for electron moving in circular orbit around the nucleus is obtained by replacing linear momentum p with angular momentum L and position coordinate q with angular position θ . So the quantum condition in this case reduces to

$$\oint L d\theta = nh \quad \dots(1.13.4)$$

In Coulomb force (which is a central force) the angular momentum remains constant and therefore

$$L \oint d\theta = nh$$

$$L \cdot 2\pi = nh$$

$$L = n \frac{h}{2\pi} = n\hbar \quad \dots(1.13.5)$$

which is the Bohr quantum condition.

Sommerfeld Theory of Hydrogen Atom

In 1916, Arnold Sommerfeld presented a theory of hydrogen atom according to which the electron in hydrogen atom revolves round the nucleus in an elliptical orbit with nucleus at one of its foci. This system requires two coordinates for the description of motion. In polar coordinates it is specified by radial distance r and angular position θ . The Wilson-Sommerfeld quantum conditions in this case are

$$\oint p_r dr = n_r h \quad \dots(1.13.6)$$

$$\oint p_\theta d\theta = n_\theta h \quad \dots(1.13.7)$$

where p_r and p_θ are radial and angular momentum respectively. n_r and n_θ are radial and *azimuthal* quantum numbers.

In central force angular momentum of electron is a constant and therefore equation (1.13.7) simplifies to

$$p_\theta = n_\theta \frac{h}{2\pi} = n_\theta \hbar \quad \dots(1.13.8)$$

The total energy of electron is

$$\begin{aligned} E = K + U &= \frac{1}{2}mv^2 + \frac{-e^2}{4\pi\epsilon_0 r} = \frac{1}{2}m(\dot{r}^2 + (r\dot{\theta})^2) - \frac{e^2}{4\pi\epsilon_0 r} \\ &= \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \quad (\because p = m\dot{r}, p_\theta = mr^2\dot{\theta}) \end{aligned}$$

Solving for p_r we get

$$p_r = \sqrt{2mE + \frac{2me^2}{4\pi\epsilon_0} \frac{1}{r} - \frac{p_\theta^2}{r^2}} \quad \dots(1.13.9)$$

Substituting the expression for p_r in (1.13.7), we have

$$\oint \sqrt{2mE + \frac{1}{4\pi\epsilon_0} \frac{2me^4}{r} - \frac{n_\theta^2 \hbar^2}{r^2}} = n_r h$$

This integral on simplification gives

$$E = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{(n_r + n_\theta)^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}$$

where $n = n_r + n_\theta$ is called the total principal quantum number.

In polar coordinates, the equation of ellipse is

$$\frac{l}{r} = 1 + e \cos \theta$$

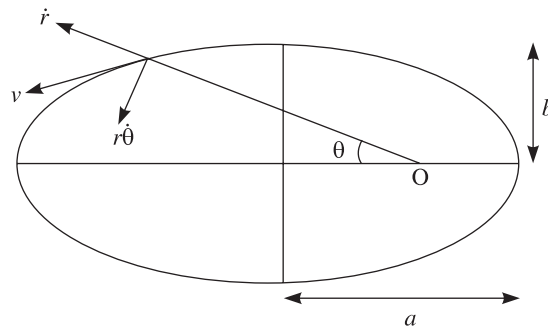


Fig. 1.13.2 Elliptical trajectory of electron

Taking logarithm and then differentiating, we get

$$\frac{1}{r} \frac{dr}{d\theta} = \frac{e \sin \theta}{1 + e \cos \theta} \quad \dots(1.13.10)$$

Now

$$\begin{aligned}
 p_r dr &= m \frac{dr}{dt} dr = m \frac{dr}{d\theta} \frac{d\theta}{dt} \frac{dr}{d\theta} d\theta = m \left(\frac{dr}{d\theta} \right)^2 \frac{d\theta}{dt} d\theta \\
 &= \left(\frac{1}{r} \frac{dr}{d\theta} \right)^2 p_\theta d\theta \quad \left(\because p_\theta = mr^2 \frac{d\theta}{dt} \right) \\
 &= \frac{e^2 \sin^2 \theta}{(1 + e \cos \theta)^2} p_\theta d\theta \quad \dots(1.13.11)
 \end{aligned}$$

In view of Eqn. (1.13.11), the quantum condition (1.13.7) becomes

$$\oint p_r dr = p_\theta \oint \frac{e^2 \sin^2 \theta}{(1 + e \cos \theta)^2} d\theta = n_r h \quad \dots(1.13.12)$$

or

$$\oint p_r dr = 2\pi p_\theta \left(\frac{1}{\sqrt{1 - e^2}} \right) = n_r h \quad \dots(1.13.13)$$

Since $p_\theta = n_\theta \hbar$, Eqn. (1.13.13) may be written as

$$1 - e^2 = \frac{n_\theta^2}{(n_r + n_\theta)^2} \quad \dots(1.13.14)$$

For ellipse, we know that

$$1 - e^2 = \frac{b^2}{a^2} \quad \dots(1.13.15)$$

where a and b are the semi-major and semi-minor axes of the ellipse. From Eqns. (1.13.14) and (1.13.15), we have

$$1 - e^2 = \frac{b^2}{a^2} = \frac{n_\theta^2}{(n_r + n_\theta)^2} = \frac{n_\theta^2}{n^2} \quad \dots(1.13.16)$$

Since n_r and n_θ are integers, the total quantum number n is also an integer. In ellipse $b < a$, so $n_\theta < n$. When $b = a$, the ellipse becomes circle and $n_\theta = n$. So the maximum value of *azimuthal quantum number* n_θ can be n . When $n_\theta = 0$, $b = 0$ and the ellipse a straight line. Physically this means that the electron would move along a straight line passing through the nucleus, which is not possible. So n_θ cannot be zero. Thus, allowed values n_θ are the integers between 1 and n , both values inclusive. For $n = 4$, n_θ can assume values 1, 2, 3, 4 and the radial quantum number n_r takes 3, 2, 1 and 0. Corresponding to these four values of n_θ we have four orbits with different eccentricities. The orbits with their usual notations are given in the table.

n	n_θ	n_r	Orbit notation (n_{n_θ})
4	1,2,3,4	3,2,1,0	$4_1, 4_2, 4_3, 4_4$

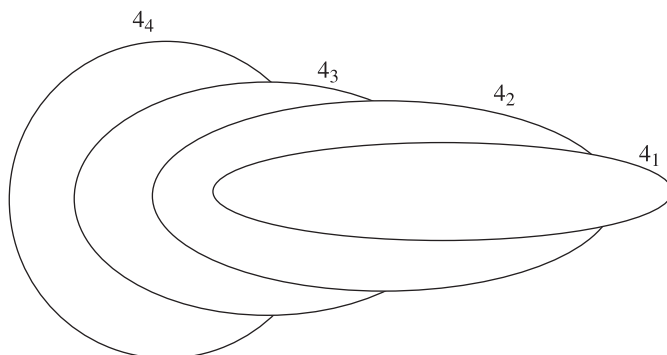


Fig. 1.13.3 Sommerfeld elliptical orbits

Since the total energy of the atom depends on the total quantum number n , which has the same value for all elliptical orbits, the introduction of elliptical orbit does not lead to the prediction of new energy levels for hydrogen atom. The orbits corresponding to a given total quantum number n with the same energy are said to be *degenerate*. Thus, the Sommerfeld theory as such is in no way superior to Bohr's theory.

1.14 SOMMERFELD'S RELATIVISTIC THEORY OF HYDROGEN ATOM

The revolving electron in an elliptical orbit around the nucleus of hydrogen atom has greater velocity when it is near the nucleus and has smaller velocity when it is relatively far away from the nucleus. According to the special theory of relativity, the mass of a moving body varies with velocity. When this result is applied to the motion of electron, its energy levels, except the ground level, are found to split into a number of closely spaced components called the **fine structure**, a term for the first time used by Sommerfeld. The orbit of electron now becomes a complicated curve — a *precessing ellipse* — similar to the orbit of the planet mercury about the sun.

According to Wilson-Sommerfeld, each degree of freedom of electron is quantized. So, we have two quantum conditions.

$$\oint p_{\theta} d\theta = n_{\theta} h \quad \dots(1.14.1)$$

$$\oint p_r dr = n_r h \quad \dots(1.14.2)$$

The first condition reduces to

$$p_{\theta} = n_{\theta} \hbar \quad \dots(1.14.3)$$

The total energy of electron is

$$E = K + U = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} \right) - \frac{e^2}{4\pi\epsilon_0 r} \quad \dots(1.14.4)$$

Making use of Eqns. (1.14.3) and (1.14.4) the total energy of electron can be found. The actual calculation is somewhat tedious. The final expression for the energy comes out to be

$$E = -\frac{2\pi\hbar c R}{n^2} - \frac{me^4\alpha^2}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^4} \left(\frac{n}{n_\theta} - \frac{3}{4} \right) \quad \dots(1.14.5)$$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$ is fine structure constant. The expression for E may be symbolically represented as

$$E = -E_{0n} - E_c(n, n_\theta) \quad \dots(1.14.6)$$

where E_{0n} stands for the first term on the right hand side of Eqn. (1.14.5) and represents the energy of electron as obtained from Bohr's theory. E_c is the relativistic correction term that depends on n and n_θ . Allowed values of n are 1, 2, 3, ... and of n_θ are 1, 2, ... n . The expression of Eqn. (1.14.6) is sufficient to explain the fine structure of H_α line of hydrogen atom.

The H_α line in the spectrum of hydrogen atom results from the transition from energy level $n = 3$ to the energy level $n = 2$. For $n = 3$, $n_\theta = 1, 2, 3$. And for $n = 2$, $n_\theta = 1, 2$. The energy levels corresponding to $n = 3$ are given by

$$E_3 = -E_{03} - E_c(3, 1)$$

$$E_3 = -E_{03} - E_c(3, 2)$$

$$E_3 = -E_{03} - E_c(3, 3)$$

The energy levels corresponding to the total quantum number $n = 2$ are:

$$E_2 = -E_{02} - E_c(2, 1)$$

$$E_2 = -E_{02} - E_c(2, 2)$$

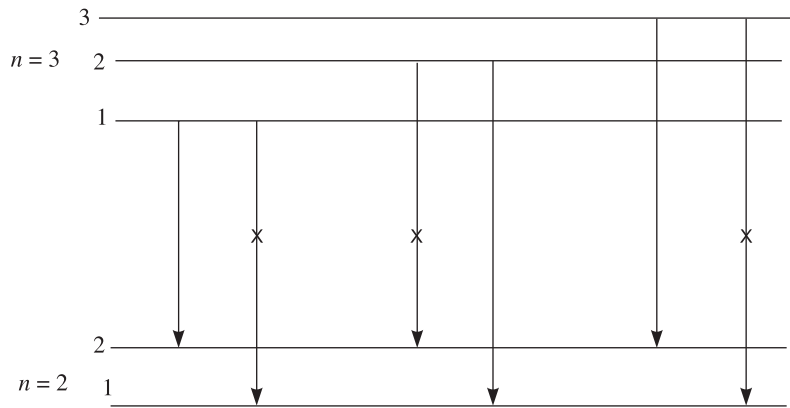


Fig. 1.14.1 Fine structure of H_α line. Transitions marked x are forbidden

These energy levels and the possible transitions are shown in the Figure (1.14.1). Theory shows that there should be six transitions. Experimentally H_α line is found to be a doublet. In order to explain the existence of only two lines out of six possibilities it was further assumed that certain

selection rules are obeyed in such transitions. Selection rules are statements that allow certain transitions and forbid others. In the present case only those transitions are allowed for which the quantum number n_0 changes by ± 1 .

$$\Delta n_0 = \pm 1 \quad (\text{allowed transitions})$$

Thus, the selection rule permits only three lines. The spectral lines resulting from the transitions $3_1 \rightarrow 2_2$ and $3_3 \rightarrow 2_2$ are so close together, that they cannot be resolved at normal temperature. The triplet character of H_α line was later observed using heavy hydrogen at low temperature.

The agreement between the prediction of Sommerfeld's relativistic theory and the observed fine structure of H_α line provided another remarkable confirmation of special theory of relativity and reinforces conviction of its universal validity. In fact one can visualize the slight change in energy for electrons of different *azimuthal* quantum number in the following way: It is apparent that the velocity of electron in an atom is comparable to the velocity of light and therefore relativistic effects are plausible. Since the electrons with the same principal quantum number n but different *azimuthal* quantum numbers have orbits of elliptical shape with varying eccentricity, electron possesses higher speed in the vicinity of nucleus for more eccentric orbit and therefore it can have different effective mass, different n_0 and hence different total energy.

SOLVED EXAMPLES

Ex. 1. Calculate for He^+ (i) radius of the first Bohr orbit (ii) velocity of electron moving in the first orbit (iii) orbital frequency in the first orbit (iv) kinetic energy and binding energy of electron in the ground state (v) ionization potential and the first excitation potential (vi) wavelength of the resonance line emitted in the transition $n = 2 \rightarrow n = 1$.

Sol. (i) For helium atom $Z = 2$.

$$\text{Radius of the first orbit} \quad r_n = a_0 \frac{n^2}{Z} \quad (n = 1)$$

$$r_1 = \frac{a_0}{2} = \frac{0.529 \text{ \AA}}{2} = 0.264 \text{ \AA}$$

$$(ii) \text{ Velocity of electron } v_n = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar} \frac{Z}{n} = (2.19 \times 10^6 \text{ m/s}) \frac{Z}{n}$$

$$v_1 = (2.19 \times 10^6 \text{ m/s}) \left(\frac{2}{1} \right) = 4.38 \times 10^6 \text{ m/s}$$

$$(iii) \text{ Orbital frequency } \omega_n = \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{me^4}{\hbar^3} \frac{Z^2}{n^3} = (4.14 \times 10^{15}) \frac{Z^2}{n^3}$$

$$\omega_1 = 16.56 \times 10^{15} \text{ rad/s}$$

(iv) Kinetic energy $K_n = |E_n| = (13.6 \text{ eV}) \frac{Z^2}{n^2}$

$$K_1 = 54.32 \text{ eV}$$

$$\text{Binding energy} = 54.32 \text{ eV}$$

(v) Ionization potential = 54.32 eV.

First excitation energy is equal to the energy required to raise the electron from ground state ($n = 1$) to the first excited state ($n = 2$).

$$\Delta E = E_2 - E_1 = (13.58 \text{ eV}) Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = 40.74 \text{ eV} \quad (Z = 2)$$

(vi) Wavelength of the resonance line

$$\frac{1}{\lambda} = R_\infty Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_\infty \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R_\infty Z^2$$

$$\lambda = \frac{4}{3 R_\infty Z^2} = \frac{4}{3 \times (1.097 \times 10^7 \text{ m}^{-1}) \times 4} = 303.8 \text{ \AA}.$$

Ex. 2. A stationary hydrogen atom emits photon corresponding to the first line of Lyman series. Calculate (i) recoil velocity of the atom, (ii) recoil kinetic energy of the atom and (iii) energy of emitted photon.

Sol. (i) When the electron makes transition from $n = 2$ to $n = 1$, the energy of transition is shared by photon and the atom. The energy emitted in the transition is given by

$$\Delta E = E_2 - E_1 = 2\pi\hbar c R Z^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{2} \pi\hbar c R Z^2 \quad \dots(1)$$

The conservation of momentum requires that:

Momentum of atom = Momentum of photon

$$P = \hbar\omega/c \quad \dots(2)$$

$$\text{Energy of recoil atom} \quad E = \frac{p^2}{2M} = \frac{(\hbar\omega)^2}{2Mc^2} \quad \dots(3)$$

The energy of transition is equal to the sum of energy of emitted photon and the recoil energy of atom.

$$\Delta E = \hbar\omega + \frac{(\hbar\omega)^2}{2Mc^2} \quad \dots(4)$$

whence

$$\hbar\omega = \frac{2\Delta E}{1 + \sqrt{2\Delta E/Mc^2}} \quad \dots(5)$$

For hydrogen atom, $\Delta E/Mc^2 \ll 1$ hence

$$\hbar\omega = \Delta E = \frac{3}{2}\pi\hbar cRZ^2 \quad \dots(6)$$

The velocity of recoil of the atom is given by

$$v = \frac{p}{M} = \frac{\hbar\omega}{Mc} = \frac{3\pi\hbar RZ^2}{2M} = 3.26 \text{ m/s} \quad \dots(7)$$

(ii) Recoil kinetic energy of atom

$$E_r = \frac{p^2}{2M} = \frac{(\hbar\omega)^2}{2Mc^2} = \frac{9}{8} \frac{\pi^2 \hbar^2 R^2 Z^4}{M} = 5.5 \times 10^{-8} \text{ eV}$$

(iii) Energy of emitted photon

$$\begin{aligned} E &= \Delta E - E_r \quad (E_r \ll \Delta E) \\ &= \Delta E = 10.20 \text{ eV.} \end{aligned}$$

Ex. 3. A stationary He^+ ion emits a photon corresponding to the first line of Lyman series. This photon, when strikes a stationary hydrogen atom in the ground state liberates the electron from the latter. Find the kinetic energy of the photoelectron.

Sol. The energy of the emitted photon

$$\hbar\omega = \Delta E = E_2 - E_1 = \frac{3}{2}\pi\hbar cRZ^2 = 6\pi\hbar cR \quad (Z = 2)$$

Ionization energy of hydrogen atom

$$\Delta E_0 = 2\pi\hbar cR$$

The excess energy of the photon will appear as the kinetic energy of photoelectron. The kinetic energy of photoelectron

$$K = \Delta E - \Delta E_0 = 6\pi\hbar cR - 2\pi\hbar cR = 4\pi\hbar cR = 27.2 \text{ eV.}$$

Ex. 4. What element has a hydrogen like spectrum whose lines have wavelengths four times shorter than those of atomic hydrogen?

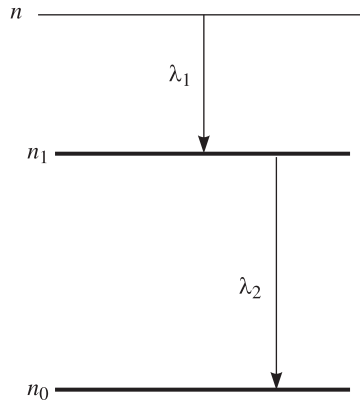
Sol. The reciprocal of wavelength ($1/\lambda$) emitted by hydrogen like atoms is proportional to Z^2 . Let λ_1 and λ_2 be the wavelengths of hydrogen atom and of unknown atom respectively. Then

$$\frac{\lambda_1}{\lambda_2} = \frac{Z_2^2}{Z_1^2} \quad \Rightarrow \quad Z_2 = 2 \text{ (helium).}$$

Ex. 5. Find the quantum number n corresponding to the excited state of He^+ if on transition to the ground state that ion emits two photons in succession with wavelengths 1.85 and 30.4 nm.

Sol. Let the n_0 and n_1 be the quantum number of the ground and intermediate state respectively and λ_1 and λ_2 be the wavelengths corresponding to transitions $n \rightarrow n_1$ and $n_1 \rightarrow n_0$.

$$\frac{1}{\lambda_1} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right), \quad \frac{1}{\lambda_2} = RZ^2 \left(\frac{1}{n_0^2} - \frac{1}{n_1^2} \right)$$



Adding these two equations, we have

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = RZ^2 \left(\frac{1}{n_0^2} - \frac{1}{n^2} \right) \quad n_0 = 1$$

Substituting $\lambda_1 = 108.5 \times 10^{-9} \text{ m}$, $\lambda_2 = 30.4 \times 10^{-9} \text{ m}$, $R = 1.097 \times 10^7 \text{ m}^{-1}$, $Z = 2$, $n_0 = 1$ we find $n = 5$.

Ex. 6. Calculate the Rydberg's constant R if He^+ ions are known to have the wavelength difference between the first (longest wavelength) lines of the Balmer and Lyman series equal to $\Delta\lambda = 133.7 \text{ nm}$.

Sol. Wavelength of the first line of Balmer series

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \Rightarrow \lambda = \frac{9}{5R}$$

Wavelength of the first line of Lyman series

$$\frac{1}{\lambda'} = RZ^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \Rightarrow \lambda' = \frac{1}{3R}$$

Therefore

$$\Delta\lambda = \lambda - \lambda' = \frac{22}{15R}$$

$$\Rightarrow R = \frac{22}{15\Delta\lambda} = 1.097 \times 10^7 \text{ m}^{-1}$$

Ex. 7. What hydrogen—like ion has the wavelength difference between the first lines of the Balmer and Lyman series equal to 59.3 nm?

Sol.
$$\Delta\lambda = \frac{36}{5RZ^2} - \frac{4}{3RZ^2} = \frac{88}{15RZ^2}$$

Whence

$$Z = \sqrt{\frac{88}{15R\Delta\lambda}} = \sqrt{\frac{88}{15 \times 1.097 \times 10^7 \text{ m}^{-1} \times 59.3 \times 10^{-9} \text{ m}}} = 3.$$

Ex. 8. Determine the separation of the first line of the Balmer series in a spectrum of mixture of ordinary hydrogen and tritium. $R_\infty = 1.097 \times 10^7 \text{ m}^{-1}$.

Sol. Rydberg's constant of ordinary hydrogen is

$$R_H = \frac{R_\infty}{1 + m/M}$$

and that of tritium is

$$R_T = \frac{R_\infty}{1 + m/3M}$$

Let λ_1 and λ_2 be the wavelengths of the first lines of Balmer series of the two isotopes. Then

$$\frac{1}{\lambda_1} = R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_H \Rightarrow \lambda_1 = \frac{36}{5R_H}$$

$$\frac{1}{\lambda_2} = R_T \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R_T \Rightarrow \lambda_2 = \frac{36}{5R_T}$$

The wavelength difference

$$\begin{aligned} \Delta\lambda = \lambda_1 - \lambda_2 &= \frac{36}{5} \left(\frac{1}{R_H} - \frac{1}{R_T} \right) = \frac{36}{5R_\infty} \left[\left(1 + \frac{m}{M} \right) - \left(1 + \frac{m}{3M} \right) \right] \\ &= \frac{36}{5R_\infty} \frac{2}{3} \frac{m}{M} = \frac{36 \times 2}{5 \times 1.0973 \times 10^7 \text{ m}^{-1} \times 3} \left(\frac{1}{1836} \right) = 2.4 \times 10^{-10} \text{ m} = 2.4 \text{ \AA}. \end{aligned}$$

QUESTIONS AND PROBLEMS

1. Describe Rutherford scattering experiment of alpha particles. What were the conclusions drawn the results of this experiment? How did Rutherford calculate the nuclear dimensions? Describe Rutherford atomic model. What were the objections raised against this model?
2. Describe Bohr's theory of hydrogen atom. How does this theory explain the various spectral series observed in the spectrum of hydrogen atom? What are the shortcomings of Bohr's theory?

3. Find expression for the Rydberg constant for hydrogen atom taking nuclear motion into consideration. How will you find the ratio of electron to proton mass?
4. Describe an experiment gives experimental evidence for the existence of discrete energy levels of atomic system. State and explain Bohr correspondence principle.
5. Describe non-relativistic Sommerfeld theory of hydrogen atom. Why does this theory not explain the fine structure of H_{α} line?
6. Give an outline of relativistic Sommerfeld's theory of hydrogen atom. How does this theory explain the fine structure of H_{α} line? Mention the shortcomings of this theory.
7. Calculate for doubly ionized lithium (Li^{++})
 - (i) radius of the first Bohr orbit.
 - (ii) velocity of electron in the first orbit.
 - (iii) orbital frequency of electron in the first orbit.
 - (iv) ground state energy of electron.
 - (v) first ionization potential.
 - (vi) the wavelengths of first line of Lyman and Balmer series.
8. Calculate the longest and the shortest wavelength in Lyman and Balmer series of
 - (i) hydrogen atom.
 - (ii) singly ionized helium atom.
9. What minimum energy must an electron have for all lines of all the series of the hydrogen spectrum to appear when the hydrogen atoms are excited by impacts of the electrons? What is the minimum velocity of these electrons? [Ans. 13.58 eV, 2.2×10^6 m/s]
10. Within what limits (in eV) should the energy of bombarding electrons be for the hydrogen spectrum to have only one spectral line when hydrogen atoms are excited by impacts of these electrons?

[Hint: First excitation energy is 10.2 eV, second excitation energy is 12.1 eV. To obtain only one spectral line the bombarding electrons must have energy E such that $10.2 \leq E \leq 1212.1$ eV].
11. How many revolutions does an electron in the state $n = 2$ of hydrogen atom make before dropping to $n = 1$? The average life-time of excited atom is 10^{-8} s.

[Hint: $\omega = (4.14 \times 10^{15} \text{ rad/s})(1/8)$]

[Ans. Required number of revolutions $N = \omega \tau / 2\pi = 8.2 \times 10^5$ rev.]
12. How many spectral lines are emitted when hydrogen atom are excited to the fourth energy level?

[Hint: Number of spectral lines $N = {}^nC_2 = {}^4C_2 = n(n-1)/2 = 6$]
13. Calculate for He^+ and Li^{++} the following quantities:
 - (i) Radius of the first orbit.
 - (ii) Frequency of revolution of electron in the first Bohr orbit.
 - (iii) Velocity of the electron in the first orbit.
 - (iv) Kinetic energy, potential energy and total energy of electron.

- (v) Ionization energy in the ground state.
 - (vi) First three excitation potentials.
 - (vii) Wavelengths of spectral lines when electron jumps from $n = 3$ to $n = 2$.
- 14.** For positronium atom calculate
- (i) the radius of the first Bohr orbit.
 - (ii) ground state energy.
 - (iii) Rydberg constant.
 - (iv) wavelengths of the first line of Lyman and Balmer series.
- 15.** Calculate the following for mesic atom:
- (i) Radius of the first Bohr orbit.
 - (ii) Ground state energy of the atom.
 - (iii) Binding energy in the ground state.
 - (iv) Wavelengths of the first lines of Lyman and Balmer series.
 - (v) In what region of electromagnetic spectrum do these radiations lie?
- 16.** For atom of light and heavy hydrogen find the difference between
- (i) the binding energies of their electrons in the ground state.
 - (ii) the wavelengths of the first lines of the Lyman series.

[Ans. (i) $E_D - E_H = 3.7 \times 10^{-3} \text{ eV}$, (ii) $\lambda_D - \lambda_H = 0.33 \text{ \AA}$]

ATOMIC SPECTRA-II

2.1 ELECTRON SPIN

In an attempt to explain the doublet character of spectral lines emitted by alkali atoms and the phenomenon of anomalous Zeeman effect, two Dutch physicists Samuel Goudsmit and George Uhlenbeck in 1925 postulated that electron might be rotating about its own axis. The name ‘spin’ was given to this kind of motion of the electron. The angular momentum associated with the spin motion of the electron is called intrinsic spin angular momentum. In classical picture electron is regarded as a charged sphere, which rotates about its own axis. The motion of the electron in an atom may be compared with that of earth’s motion. The angular momentum of the earth due to its rotation about its own axis corresponds to the intrinsic spin angular momentum. The hypothesis of spinning electron was proposed before the discovery of Schrodinger equation and had no theoretical basis. It was merely an ad-hoc hypothesis introduced to explain experimental observations. The concept of electron spin was missing in Schrodinger theory. Later in 1928, English physicist P.A.M. Dirac, showed that in relativistic formulation of Schrodinger equation for hydrogen atom the intrinsic angular momentum of electron appeared in a natural way and the concept of electron spin got theoretical basis. In quantum picture, the spin is regarded as an intrinsic property characterizing an electron in the same way as its charge and mass do.

2.2 QUANTUM NUMBERS AND THE STATE OF AN ELECTRON IN AN ATOM

When Schrodinger equation is applied to the motion of electron in an atom, it is found that the quantum state or the wave function ψ of an electron is characterized by four numbers, called *quantum numbers*. They are: **principal quantum number n** , **orbital quantum number l** , **magnetic quantum number m_l** and **spin quantum number m_s** . The solution ψ of Schrodinger wave equation, called *wave function*, gives all kind of information about the electron in the atom. The important characteristics and significance of these quantum numbers are as follows.

Principal Quantum Number (n): This quantum number determines the total energy of electron in the atom and the average distance of electron from nucleus. It can take integral values 1, 2, 3, ... The greater the value of n ; greater is the energy of electron.

Orbital (azimuthal) quantum number (l): This quantum number determines the orbital angular momentum of electron. The magnitude of orbital angular momentum of electron is given by

$$|l| = \sqrt{l(l+1)} \hbar \quad \dots(2.2.1)$$

where l is a number, called *orbital quantum number*. For a given value of principal quantum number n , the orbital quantum number can take integral values $0, 1, 2, \dots, (n-1)$. The quantum number l also gives the shape of probability distribution curve. The electrons with $l = 0, 1, 2, 3, \dots$ are called *s, p, d, f* electrons respectively.

Magnetic Quantum Number (m_l): The angular momentum vector l cannot take all orientations in space; only certain directions are allowed. This feature of vector l is called *space quantization*. The allowed orientations of vector l are such that its components along any fixed direction, say z -axis, are given by

$$|l_z| = m_l \hbar \quad \dots(2.2.2)$$

where m_l is an integer called *magnetic quantum number*. For a given value of l , the quantum number m_l can take integrally spaced values from $-l$ to $+l$.

The other components of vector l are uncertain which is in accord with the uncertainty principle. This means that the vector l traces out a cone in space about z -axis such that its projection onto z -axis is $m_l \hbar$. The average values of x and y -components of l turn out to be zero.

Spin quantum number (m_s): Relativistic quantum mechanics shows that electron possesses an intrinsic angular momentum S whose magnitude is given by

$$|s| = \sqrt{s(s+1)} \hbar \quad \dots(2.2.3)$$

where s is spin quantum number. It assumes only one value $1/2$. The vector s can have only two directions. The projection of vector s onto any fixed axis, say z -axis, are given by

$$|s_z| = m_s \hbar = \pm \frac{1}{2} \hbar \quad \dots(2.2.4)$$

where $m_s = \pm 1/2$ is called the magnetic spin quantum number.

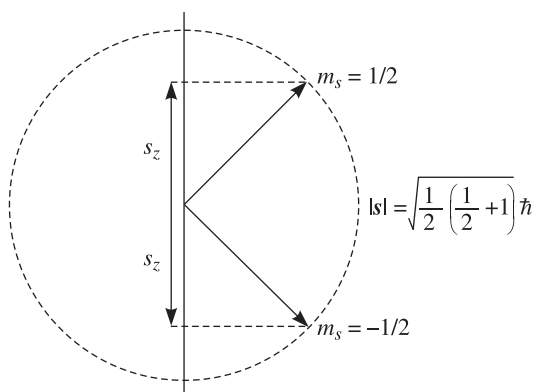


Fig. 2.2.1 The allowed values of quantum number m_s are $\pm 1/2$

Thus, the state of an electron, in an atom is described by four quantum numbers n , l , m_l and m_s . Now we shall find the number of quantum states corresponding to various values of principal quantum number n .

Corresponding to the principal quantum number $n = 1$, we have $l = 0$, $m_l = 0$, $m_s = \pm 1/2$. Thus, for $n = 1$, there are 2 states defined by the quantum numbers

$$n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$$

$$n = 1, l = 0, m_l = 0, m_s = -\frac{1}{2}$$

According to *Pauli principle*, each state is occupied by a single electron. The quantum states having the same value of principal quantum number n are said to constitute a shell. Shells are designated according to the following scheme

n	1	2	3	4	5
Shell	K	L	M	N	O

Thus, K shell contains two quantum states and hence two electrons. The quantum states, which have the same value of l are said to constitute a **sub-shell**. The above two states have the same value of l ($= 0$) and therefore form a sub-shell. The sub-shells are designated according to the following scheme:

Azimuthal quantum number l	0	1	2	3	4	5	...
Sub-shell	s	p	d	f	g	h	

The K shell contains only one sub-shell denoted by s .

For $n = 2$, $l = 0, 1$. For $l = 0$, the allowed value of m_l is 0. For $l = 1$, the allowed values m_l are $-1, 0, 1$. For each value of m_l , $m_s = \pm 1/2$. Thus, the quantum states for $n = 2$ are as follows.

n	l	m_l	m_s	Quantum states
2	0	0	$+ 1/2$	$(2, 0, 0, 1/2)$
			$- 1/2$	$(2, 0, 0, - 1/2)$
2	1	-1	$+ 1/2$	$(2, 1, -1, 1/2)$
			$- 1/2$	$(2, 1, -1, - 1/2)$
		0	$1/2$	$(2, 1, 0, 1/2)$
			$- 1/2$	$(2, 1, 0, - 1/2)$
		1	$1/2$	$(2, 1, 1, 1/2)$
			$- 1/2$	$(2, 1, 1, - 1/2)$

Thus, the L shell ($n = 2$) contains one s sub-shell and three p sub-shells. In all there are eight quantum states. The pair of quantum states of a sub-shell differing in spin quantum numbers only, are called **orbital**. The s sub-shell contains one orbital and p sub-shell contains three orbitals, usually designated as p_x, p_y, p_z . Each orbital can accommodate two electrons with opposite spins.

The quantum states corresponding to principal quantum number $n = 3$ are shown in the table given below.

The M shell ($n = 3$) contains one s sub-shell, three p sub-shells and five d sub-shells and in all eighteen quantum states. Thus, it can accommodate 18 electrons.

The number of electrons that can be accommodated in shell can be calculated as follows. Consider a shell characterized by a principal quantum number n . For this value of n , the orbital (*azimuthal*) quantum number l can take integral values from 0 to $n - 1$. For each value of l , magnetic quantum number m_l assumes integrally spaced values from $-l$ to $+l$ i.e., in all $2l + 1$ values. For each value of m_l , the spin quantum number takes two values $+\frac{1}{2}$ and $-\frac{1}{2}$. Thus, the total number of quantum states is given by

$$\sum_{l=0}^{n-1} 2(2l + 1) = 2[1 + 3 + 5 + \dots + (2n - 1)]$$

$$= 2 \left[\frac{n}{2} (1 + (2n - 1)) \right] = 2n^2$$

n	l	m_l	m_s	Quantum states
3	0	0	$+1/2$	$(3, 0, 0, 1/2)$
			$-1/2$	$(3, 0, 0, -1/2)$
	1	-1	$1/2$	$(3, 1, -1, 1/2)$
			$-1/2$	$(3, 1, -1, -1/2)$
		0	$1/2$	$(3, 1, 0, 1/2)$
			$-1/2$	$(3, 1, 0, -1/2)$
		1	$1/2$	$(3, 1, 1, 1/2)$
			$-1/2$	$(3, 1, 1, -1/2)$
	2	-2	$1/2$	$(3, 2, -2, 1/2)$
			$-1/2$	$(3, 2, -2, -1/2)$
		-1	$1/2$	$(3, 2, -1, 1/2)$
			$-1/2$	$(3, 2, -1, -1/2)$
		0	$1/2$	$(3, 2, 0, 1/2)$
			$-1/2$	$(3, 2, 0, -1/2)$
		1	$1/2$	$(3, 2, 1, 1/2)$
			$-1/2$	$(3, 2, 1, -1/2)$
		2	$1/2$	$(3, 2, 2, 1/2)$
			$-1/2$	$(3, 2, 2, -1/2)$

2.3 ELECTRONIC CONFIGURATION OF ATOMS

The electronic configuration of atoms are governed by following rules:

Aufbau's principle: The word *Aufbau* means *build up*. According to this principle *the first electron in an atom occupies the quantum state with lowest possible energy and then the second electron*

goes to the next quantum state having higher energy. The sequence of energy levels in increasing order of energy is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d.$$

Pauli's exclusion principle: In 1925, A German Physicist Wolfgang Pauli enunciated this fundamental principle, which governs the electronic configuration of complex atoms. This principle, known as **Pauli's Exclusion Principle states that "no two electrons in an atom can exist in the same quantum state or each quantum state is occupied by a single electron."**

Hund's rule: The filling of electron in various orbitals of a sub-shell take place according to Hund's rule. This rule states that electrons prefer to occupy separate orbitals so that they have parallel spins. In other words, the pairing of electrons will occur in any orbital of a given sub-shell when all the available orbitals have one electron each. According to this rule the electronic configuration of carbon, nitrogen and oxygen atom will be as follows:

${}^6\text{C}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	
	1s	2s	$2p_x$	$2p_y$	$2p_z$
${}^7\text{N}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
	1s	2s	$2p_x$	$2p_y$	$2p_z$
${}^8\text{O}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
	1s	2s	$2p_x$	$2p_y$	$2p_z$

2.4 MAGNETIC MOMENT OF ATOM

When a charged particle moves along a closed path or rotates about its own axis, an electric current is associated with it. This current loop has magnetic moment. The magnetic moments of electron due to orbital and spin motions are related to their corresponding angular momenta.

Consider an electron moving with velocity v in a circular orbit of radius r . The orbital current associated with this motion is

$$I = -\frac{ev}{2\pi r} \quad \dots(2.4.1)$$

The magnetic moment associated with orbital motion is

$$|\vec{\mu}| = IA = -\left(\frac{ev}{2\pi r}\right)(\pi r^2) = -\left(\frac{e}{2m}\right)(mvr) = -\left(\frac{e}{2m}\right)|\mathbf{L}| \quad \dots(2.4.2)$$

where $|\mathbf{L}| = mvr$ is the orbital angular momentum of electron. Eqn. (2.4.2) expresses the fact that magnetic moment is associated with angular momentum of micro-particle. The minus sign indicates that the direction of the magnetic moment is opposite to that of the angular momentum. It is a remarkable fact that this classical result is also valid in quantum mechanics. The ratio of magnetic

moment to the angular momentum $\frac{\mu}{|L|} = \frac{e}{2m}$ is called the *gyromagnetic ratio*. The magnetic moment associated with orbital motion of electron can be written as

$$|\vec{\mu}_L| = -\frac{e\hbar}{2m} \frac{|L|}{\hbar} = -\mu_\beta \sqrt{l(l+1)} = -g_l \mu_\beta \sqrt{l(l+1)} \quad \dots(2.4.3)$$

where $g_l = 1$, called orbital *g-factor* and

$$\mu_\beta = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T} = 5.79 \times 10^{-5} \text{ eV/T}$$

is *Bohr Magnetron*, a unit for measuring magnetic moment of atom.

For purely quantum mechanical reason, the magnetic moment associated with spin motion is related to its intrinsic (spin) angular momentum. The relation between them is

$$|\vec{\mu}| = -\frac{e}{m} |s| 2 \left(\frac{e\hbar}{2m} \right) \frac{|s|}{\hbar} = -g_s \mu_\beta \sqrt{s(s+1)} \quad \dots(2.4.4)$$

where $g_s = 2$, *spin g-factor*. Notice that the *gyromagnetic ratio* of spin motion is not $(-e/2m)$ but twice of it. For this reason the spin is said to have *double magnetism*.

2.5 LARMOR THEOREM

Consider an electron moving in a circular orbit. The orbital angular momentum l and corresponding magnetic moment μ are mutually related through the relation

$$\mu = - \left(\frac{e}{2m} \right) l \quad \dots(2.5.1)$$

Let a magnetic field $\mathbf{B}$ be applied to the electron. In the magnetic field the electron experiences a torque $\tau = \mu B \sin \alpha$, where α is angle between vector l and $\mathbf{B}$. This torque cause the vector l and μ to precess about the direction of the magnetic field $\mathbf{B}$. The angular velocity of precession of l or μ about $\mathbf{B}$ is called *Larmor frequency* (ω_l).

Let the torque τ cause a change in angular momentum l by amount dl in time dt . Then

$$dl = \tau dt \quad \dots(2.5.2)$$

Now refer to the Fig. (2.5.1). The magnitude of change dl is given by

$$dl = l \sin \alpha d\theta$$

or

$$\tau dt = l \sin \alpha d\theta$$

or

$$\mu B \sin \alpha dt = l \sin \alpha d\theta$$

whence

$$\frac{d\theta}{dt} = \frac{\mu}{l} B$$

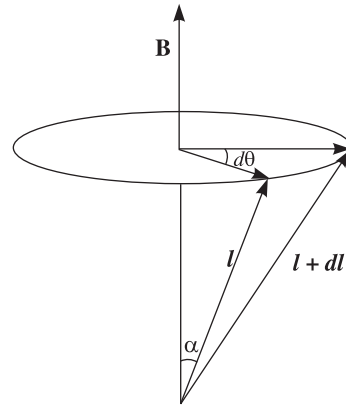


Fig. 2.5.1 Precession of vector l about $\mathbf{B}$

$$\frac{d\theta}{dt} = \frac{eB}{2m}$$

$$\omega_l = \frac{eB}{2m} \quad \dots(2.5.3)$$

The result Eqn. (2.5.3) is known as *Larmor theorem*.

2.6 THE MAGNETIC MOMENT AND LANDE *g*-FACTOR FOR ONE VALENCE ELECTRON ATOM

Electrons in an atom are distributed in various sub-shells according to *Pauli's principle* and *Hund's rule*. Every electron has orbital angular momentum and spin angular momentum. In a closed sub-shell, every electron is matched by another electron with opposite orbital and spin angular momenta. So the resultant angular momentum of a closed sub-shell is zero. Only the valence electrons outside the closed sub-shell contribute to the total angular momentum and the magnetic moment of the atom. The optical properties of atoms are all due to valence electrons only.

The magnetic moment of an atom with one valence electron is due to the single valence electron. Magnetic moments are associated with orbital and spin motion both and are given by

$$\mu_l = - \left(\frac{e}{2m} \right) l \quad \dots(2.6.1)$$

$$\mu_s = - \left(\frac{e}{2m} \right) s \quad \dots(2.6.2)$$

A schematic vector diagram of magnetic moments μ_l and μ_s and vectors l and s is shown in the figure. Due to double spin magnetism the resultant magnetic moment μ_{ls} is not collinear with the resultant j . The *spin-orbit interaction* causes vectors l and s to combine to form resultant vector j . The vectors l and s precess about the direction of their resultant j . The frequency of precession is equal to the Larmor frequency.

The consequence of precession is that only the component of μ_{ls} parallel to j contributes to the magnetic moment of atom. The perpendicular component averages out to zero

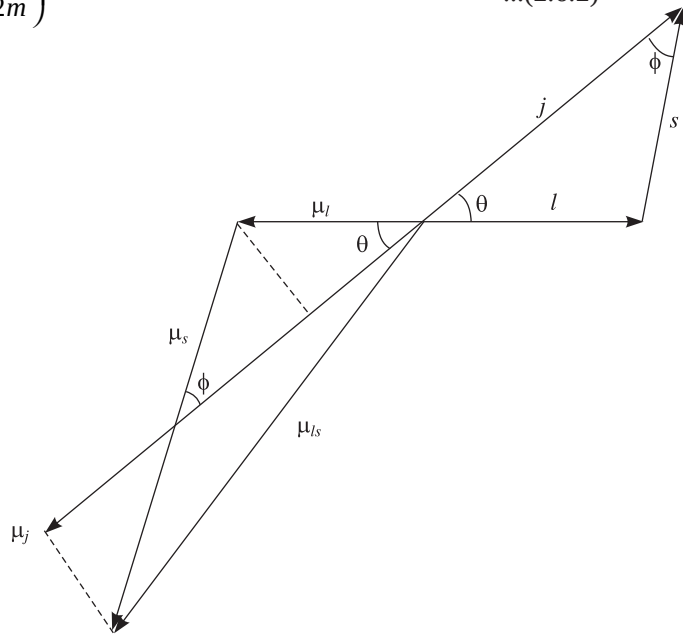


Fig. 2.6.1. Vector addition of l , s , and m_l , m_s

Therefore

$$\begin{aligned}
 \mu_j &= \mu_l \cos \theta + \mu_s \cos \phi \\
 &= \left(-\frac{e}{2m} \right) |l| \cos \theta + \left(-2\frac{e}{2m} \right) |s| \cos \phi \\
 &= -\left(\frac{e}{2m} \right) \left[\sqrt{l(l+1)} \hbar \cos \theta + 2\sqrt{s(s+1)} \hbar \cos \phi \right] \quad \dots(2.6.3)
 \end{aligned}$$

The cosine formula for angles θ and ϕ are

$$\cos \theta = \frac{|j|^2 + |l|^2 - |s|^2}{2|j||l|} = \frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)}\sqrt{l(l+1)}} \quad \dots(2.6.4)$$

$$\cos \phi = \frac{|j|^2 + |s|^2 - |l|^2}{2|j||s|} = \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}\sqrt{s(s+1)}} \quad \dots(2.6.5)$$

Substituting the expressions of $\cos \theta$ and $\cos \phi$ in Eqn. (2.6.3), we have

$$\begin{aligned}
 \mu_j &= -\frac{e\hbar}{2m} \left[\frac{j(j+1) + l(l+1) - s(s+1)}{2\sqrt{j(j+1)}} + 2 \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}} \right] \\
 &= -\frac{e\hbar}{2m} \left[\frac{3j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}} \right] \sqrt{j(j+1)} \\
 &= -\frac{e\hbar}{2m} \left[1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2\sqrt{j(j+1)}} \right] \sqrt{j(j+1)} \\
 &= -\frac{e\hbar}{2m} g \sqrt{j(j+1)} \\
 &= -\mu_B g \sqrt{j(j+1)} \quad \dots(2.6.6)
 \end{aligned}$$

where

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad \dots(2.6.7)$$

Thus the magnetic moment of an atom can be written as

$$\mu_j = -\frac{e}{2m} g |\mathbf{j}| = -\frac{e\hbar}{2m} g \sqrt{j(j+1)} = -\mu_B g \sqrt{j(j+1)} \quad \dots(2.6.8)$$

The projection of μ_j onto z-direction is given by

$$(\mu_j)_z = -\frac{e}{2m}g|\mathbf{j}_z| = -\frac{e\hbar}{2m}gm_j = -\mu_B gm_j \quad \dots(2.6.9)$$

where $m_j = 0, \pm 1, \pm 2, \pm 3, \dots$ i.e., m_j can take on integrally spaced values from $-j$ to $+j$. m_j is called the *magnetic quantum number* of the atom.

2.7 VECTOR MODEL OF ATOM

The quantum mechanical theory of atom is capable of providing satisfactory explanation of all atomic phenomena but the application of this theory to the interpretation of puzzling features of atomic spectra presents great mathematical complications. Before the advent of quantum mechanics, *Lande* developed an atomic model, called *Vector Model*, to explain the experimental observations made about atomic spectra and the behaviour of atom in magnetic field. This model is based on many concepts and empirical rules, which had no theoretical justification at that time, but later after the advent of quantum mechanics they got theoretical basis. This model not only provided the satisfactory explanation of many features of atomic spectra with amazing accuracy but also predicted many phenomena that were discovered later.

Electrons in an atom are distributed in various sub-shells according to Pauli's principle and Hund's rule. Every electron has orbital angular momentum and spin angular momentum. In a closed sub-shell, every electron is matched by another electron with opposite orbital and spin angular momenta. So the resultant angular momentum of closed sub-shell is zero. Only the valence electrons outside the closed sub-shell contribute to the total angular momentum and the magnetic moment of the atom. Only valence electrons are responsible for the optical properties of atoms.

In this model, the orbital angular momenta and spin angular momenta and associated magnetic moments of valence electrons are treated as vectors. These angular momenta combine under the influence of two kinds of interactions to form resultant angular momentum for the atom as a whole. Since the interactions responsible for the coupling of angular momenta are of two types therefore there are two types of coupling between the angular momenta.

Russell-Saunders Coupling or L-S Coupling

When the mutual repulsion between electrons due to their electrical charge is treated quantum mechanically an unexpected result is found. The energy of the system contains two terms: one corresponding to classical Coulomb interaction and the other is known as *exchange interaction*. The exchange forces have no classical analogue but play an important role in atomic theory. One effect of exchange forces is to couple together the various spin vectors $\mathbf{s}_i$ to form a resultant $\mathbf{S}$ vector. The orbital momenta $\mathbf{l}_i$ couple under the influence of electrostatic forces to form a resultant $\mathbf{L}$. This method of coupling of angular momenta is known as Russell-Saunders or L-S coupling. Finally, under the action of *spin-orbit interaction*, the resultant orbital angular momentum $\mathbf{L}$ and resultant spin vector $\mathbf{S}$ couple to form resultant angular momentum $\mathbf{J}$ for the atom as a whole. The L-S coupling may be summarized as follows.

(i) Coupling of orbital angular momenta

In light atoms containing many valence electrons, the electrostatic interaction between the electrons is large and by virtue of this interaction the individual orbital angular momenta of valence electrons add up to form a resultant $\mathbf{L}$.

$$l_1 + l_2 + l_3 + \dots = \sum l_i = \mathbf{L} \quad \dots(2.7.1)$$

where l_i are the orbital angular momenta of valence electrons and are given by

$$|l_1| = \sqrt{l_1(l_1+1)} \hbar, \quad |l_2| = \sqrt{l_2(l_2+1)} \hbar \text{ etc.}$$

The magnitude of vector $\mathbf{L}$ is quantized and is given by

$$|\mathbf{L}| = \sqrt{L(L+1)} \hbar$$

where L is *total orbital quantum number* and is determined by

$$L = l_1 \oplus l_2 \oplus l_3 \oplus \dots \quad \dots(2.7.2)$$

Here l_1, l_2, l_3 stand for *orbital quantum number* of valence electrons and $\oplus$ for quantized vector addition. For example, consider an atom with two valence electrons both in p sub-shell i.e., $l_1 = 1, l_2 = 1$. Then

$$L = l_1 \oplus l_2 = 1 \oplus 1 = 0, 1, 2$$

Here $(l_1 \oplus l_2)$ takes on all integrally spaced values from $|l_1 - l_2|$ to $(l_1 + l_2)$. The allowed values of magnitude of the total orbital angular momentum $\mathbf{L}$ of these two valence electrons are:

$$|\mathbf{L}| = \sqrt{0(0+1)} \hbar = 0$$

$$|\mathbf{L}| = \sqrt{1(1+1)} \hbar = \sqrt{2} \hbar$$

$$|\mathbf{L}| = \sqrt{2(2+1)} \hbar = \sqrt{6} \hbar$$

The geometrical addition of orbital angular momenta of the two electrons with $l_1 = 1$ and $l_2 = 1$ is shown in the Fig. (2.7.1).

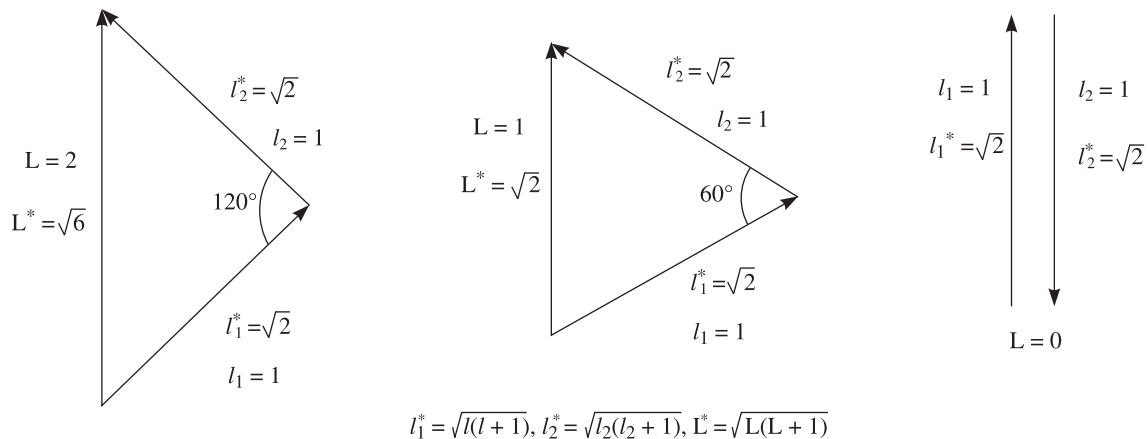


Fig. 2.7.1 Addition of orbital angular momenta of two electrons with $l_1=1$ and $l_2 = 1$. Symbols with star as superscript denote magnitude of corresponding vectors in units of $\hbar$

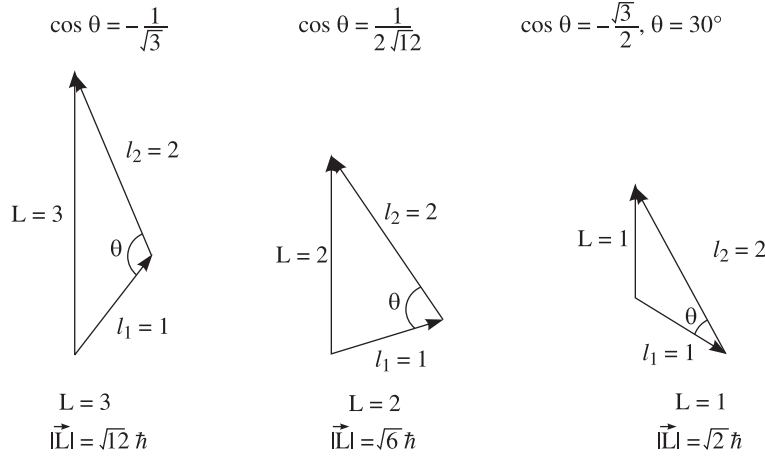


Fig. 2.7.2 Addition of orbital angular momenta of two electrons with $l_1 = 1$ and $l_2 = 2$

If one of the valence electrons is in p sub-shell and the other is in d sub-shell *i.e.*, $l_1 = 1$, $l_2 = 2$ then

$$\mathbf{L} = l_1 \oplus l_2 = 1 \oplus 2 = 1, 2, 3$$

$$|\mathbf{L}| = \sqrt{L(L+1)} \hbar = \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar$$

The geometrical addition of angular momenta are shown in the Fig. (2.7.2).

The total orbital angular momentum vector $\mathbf{L}$ can have only certain orientations in space. This implies that its projection along any fixed direction (z -axis) can have only discrete values given by

$$|\mathbf{L}_Z| = M_L \hbar \quad \dots(2.7.3)$$

where M_L , called *total orbital magnetic quantum number*, can take on integrally spaced values from $-L$ to L . In all M_L can take $(2L + 1)$ values.

(ii) Coupling of Spin Angular Momenta

Each electron has spin angular momentum. Because of strong quantum mechanical effect, known as exchange interaction, which has no classical analogue, the spin angular momenta of valence electrons are coupled to form a resultant spin angular momentum vector $\mathbf{S}$.

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \dots \quad \dots(2.7.4)$$

The magnitude of vector $\mathbf{S}$ is quantized and is given by

$$|\mathbf{S}| = \sqrt{S(S+1)} \hbar$$

where S is *total spin quantum number* and is obtained from the following quantum sum:

$$\begin{aligned} S &= s_1 \oplus s_2 \oplus s_3 \oplus \dots \\ &= \frac{1}{2} \oplus \frac{1}{2} \oplus \frac{1}{2} \oplus \dots \end{aligned} \quad \dots(2.7.5)$$

The direction of vector $\mathbf{S}$ is quantized and its projection along any fixed direction has discrete values given by

$$|S_z| = M_S \hbar \quad \dots(2.7.6)$$

where M_S , called *total magnetic spin quantum number*, can take integrally spaced values from $-S$ to S .

Let there be five valence electrons in an atom. The possible orientations of spin and the corresponding values of total spin quantum number S are shown below.

$$\begin{aligned} \uparrow\uparrow\uparrow\uparrow\uparrow \quad S &= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{5}{2} \\ \uparrow\uparrow\uparrow\uparrow\downarrow \quad S &= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = \frac{3}{2} \\ \uparrow\uparrow\uparrow\downarrow\downarrow \quad S &= \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = \frac{1}{2} \end{aligned}$$

Corresponding to $S = 5/2$, the allowed values of M_S are $-5/2, -3/2, -1/2, 1/2, 3/2, 5/2$. Similarly the values of M_S for $S = 3/2$ and $S = 1/2$ can be written.

(iii) Coupling of $\mathbf{L}$ and $\mathbf{S}$

Now the total orbital angular momentum vector $\mathbf{L}$ and total spin angular momentum vector $\mathbf{S}$ interact magnetically through their associated magnetic moments and form a resultant $\mathbf{J}$ called the total angular momentum vector of the atom. This coupling is called spin-orbit coupling.

$$\mathbf{L} + \mathbf{S} = \mathbf{J} \quad \dots(2.7.7)$$

The magnitude of vector $\mathbf{J}$ is quantized and is specified by

$$|\mathbf{J}| = \sqrt{J(J+1)} \hbar$$

where J is *total angular momentum quantum number* of the atom. The allowed values of J are given by

$$J = L \oplus S \quad \dots(2.7.8)$$

i.e., J can take on integrally spaced values from $L + S$ down to $|L - S|$.

The direction of vector $\mathbf{J}$ is quantized. Its projection onto any axis is given by

$$|J_z| = M_J \hbar \quad \dots(2.7.9)$$

where M_J called *total magnetic quantum number* of the atom. It can take integrally spaced values from $-J$ to $+J$. In absence of external magnetic field, the total angular momentum $\mathbf{J}$ is conserved in magnitude and direction. The effect of the internal torques can be only produce precession of $\mathbf{L}$ and $\mathbf{S}$ around the direction of their resultant $\mathbf{J}$. However, in presence of external magnetic field $\mathbf{B}$, the resultant vector $\mathbf{J}$ precesses about $\mathbf{B}$ while $\mathbf{L}$ and $\mathbf{S}$ continue to precess about their resultant $\mathbf{J}$. If we calculate the component of $\mathbf{J}$ along a specified direction, say z -direction, then z -component has a well-defined value but the other components of $\mathbf{J}$ viz. J_x and J_y are uncertain. This means that vectors $\mathbf{L}$ and $\mathbf{S}$ precess about their resultant $\mathbf{J}$ as shown in the figure.

If $L = 2$, and $S = 1$ then $J = L \oplus S = 2 \oplus 1 = 1, 2, 3$.

If $L = 2$, $S = 3/2$ then $J = L \oplus S = 2 \oplus 3/2 = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$.

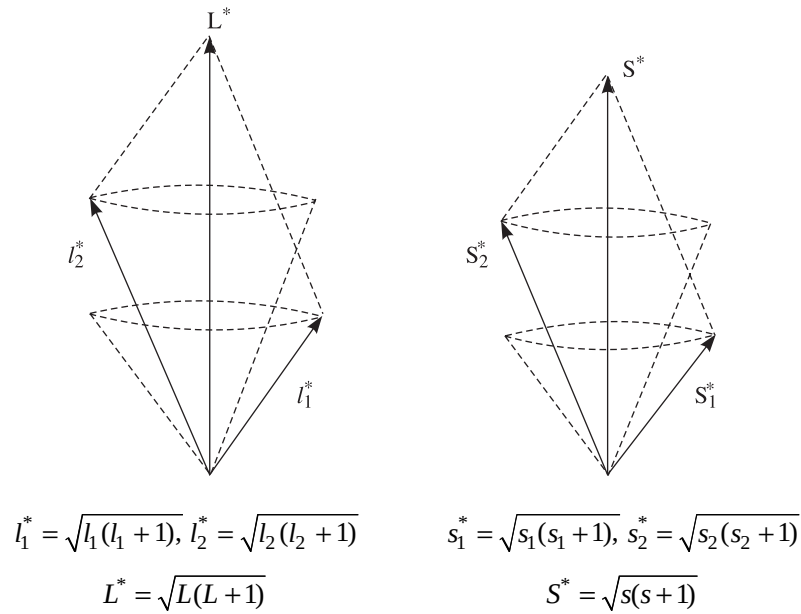


Fig. 2.7.3 Vectors l_1 and l_2 precess about their resultant L . Vectors s_1 and s_2 precess about their resultant S

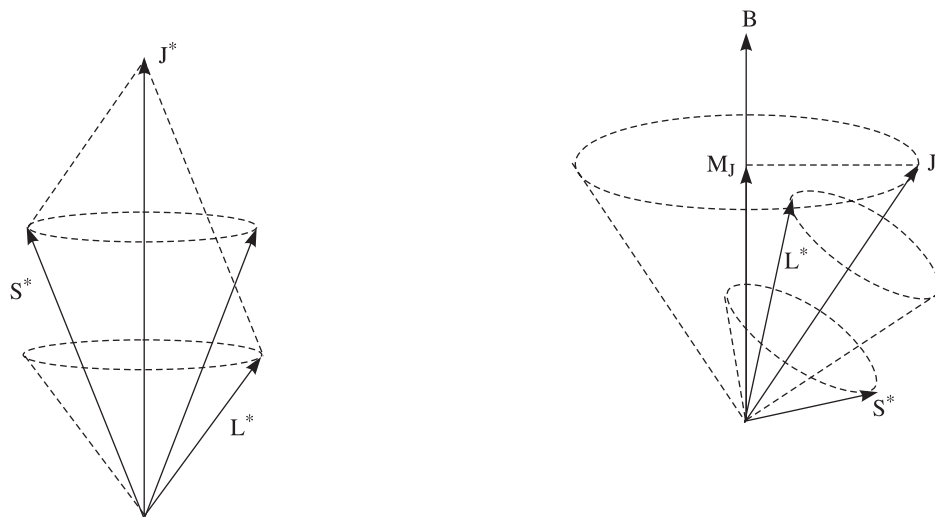


Fig. 2.7.4 Vectors L and S precess about their resultant J . Vector J precesses about external magnetic field B

j-j Coupling

As the nuclear charge increases the magnetic spin orbit forces become stronger which dominate the electrostatic interactions. The L-S coupling now breaks down. Under the influence of large *spin orbit interaction*, the orbital and the spin angular momenta of each electron couple to form a resultant angular momentum $\mathbf{j}$. The resultant angular momentum $\mathbf{j}$ of each electron combine to form a resultant $\mathbf{J}$ called total angular momentum vector of the atom. The spin-orbit coupling is primarily magnetic in origin and arises from the magnetic moments of the orbital and spin motion of electrons. This coupling is known as *j-j* coupling and is summarized below

$$\mathbf{l}_i + \mathbf{s}_i = \mathbf{j}_i$$

$$\mathbf{j}_i + \mathbf{j}_2 + \dots = \Sigma \mathbf{j}_i = \mathbf{J}$$

For illustration of *j-j* coupling consider the electron configuration *pd*. For *p* electron, $l_1 = 1$, $s_1 = 1/2$, therefore $j = 1/2, 3/2$. Similarly, for *d* electron, $l_2 = 2$, $s_2 = 1/2$, and $j = 3/2, 5/2$. Now j_1 and j_2 may combine in four ways as describe below.

$$(i) \quad j_1 = 1/2, j_2 = 3/2, \quad \therefore J = j_1 \oplus j_2 = 1, 2.$$

$$(ii) \quad j_1 = 1/2, j_2 = 5/2, \quad \therefore J = j_1 \oplus j_2 = 2, 3.$$

$$(iii) \quad j_1 = 3/2, j_2 = 3/2, \quad \therefore J = \mathbf{j}_1 \oplus \mathbf{j}_2 = 0, 1, 2, 3.$$

$$(iv) \quad j_1 = 3/2, j_2 = 5/2, \quad \therefore J = j_1 \oplus j_2 = 1, 2, 3, 4.$$

It should be noted that L-S and *j-j* coupling both give the same number of terms and the same *J* values. The spectral term arising from *j-j* coupling are designated as (j_1, j_2) .

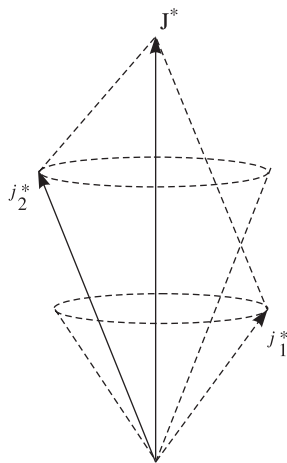


Fig. 2.7.5 Precession of $\mathbf{j}_1$ and $\mathbf{j}_2$ about their resultant $\mathbf{J}$

For *j-j* coupling, L and S lose their meaning. The selection rules that operate in transitions between terms arising from this type of coupling are:

$$\Delta j = 0, \pm 1, \quad \Delta j = 0, \pm 1.$$

2.8 ATOMIC STATE OR SPECTRAL TERM SYMBOL

The state of an atom is characterized by quantum numbers L , S and J and is represented by a symbol according to the following scheme

L	0	1	2	3	4	5
Symbol	S	P	D	F	G	H

Here S is not to be confused with total spin quantum number. The value of J is written as post subscript and the multiplicity r ($= 2S + 1$ if $S \leq L$ and $= 2L + 1$ if $L < S$) as pre-superscript. For example if an atom is characterized by $L = 2$, $S = 3/2$ and $J = 5/2$ then it is designated as

$${}^4D_{5/2} \quad (r = 2S + 1 = 3 + 1 = 4)$$

2.9 GROUND STATE OF ATOMS WITH ONE VALENCE ELECTRON (HYDROGEN AND ALKALI ATOMS)

The ground state configuration of valence electron is $n s^1$. The valence shell has only one electron with $l = 0$.

$$L = l = 0$$

$$S = s = 1/2$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

$$\text{Multiplicity} \quad r = 2L + 1 = 1$$

The multiplicity is equal to the number of sub-levels differing in their values of J . The ground state symbol should be ${}^1S_{1/2}$ but it is written as ${}^2S_{1/2}$ because this term belongs to a system, which is doublet. (In the excited state the valence goes to p or some other sub-shell. In all excited states $L > S$ and the multiplicity $r = 2S + 1 = 2$. To specify this fact that these terms belong the system whose excited states are doublet ($r = 2$) we write the ground state as ${}^2S_{1/2}$.

Excited states of alkali atoms: In the excited state the valence electron in an alkali atom goes from s to p state or other higher states. If it is in p state then

$$L = l_1 = 1$$

$$S = s_1 = 1/2$$

$$r = 2S + 1 = 2$$

$$J = 1 \oplus \frac{1}{2} = \frac{3}{2}, \frac{1}{2}$$

$$\text{Spectroscopic symbol } {}^2P_{1/2}, {}^2P_{3/2}.$$

If the valence electron is promoted to d state then

$$L = 2, S = 1/2, J = 2 \oplus \frac{1}{2} = \frac{5}{2}, \frac{3}{2}.$$

$$\text{Multiplicity} \quad r = 2S + 1 = 2$$

$$\text{Spectroscopic symbol } {}^2D_{3/2}, {}^2D_{5/2}.$$

Multiplet

Due to spin-orbit interaction each level characterized by an L value splits into a group of sub-levels called fine-structure levels. The collection of fine-structure levels belonging to a given L value is called a multiplet.

2.10 SPECTRAL TERMS OF TWO VALENCE ELECTRONS SYSTEMS (HELIUM AND ALKALINE-EARTHS)

I. L-S Coupling

Two non-equivalent electrons (n, l different)

In such atoms all the four quantum numbers of the two electrons are not identical. The method of writing the spectral terms will be illustrated with examples.

(1) sp configuration

$$\text{In this case} \quad l_1 = 0, l_2 = 1, L = l_1 \oplus l_2 = 0 \oplus 1 = 1,$$

$$s_1 = 1/2, s_2 = 1/2, S = s_1 \oplus s_2 = 1/2 \oplus 1/2 = 0, 1$$

Singlet states ($S = 0$): $J = L \oplus S = 1 \oplus 0 = 1$. Spectral term is ${}^1P_1$.

Triplet states ($S = 1$): $J = L \oplus S = 1 \oplus 1 = 0, 1, 2$. Spectral terms are ${}^3P_{0, 1, 2}$

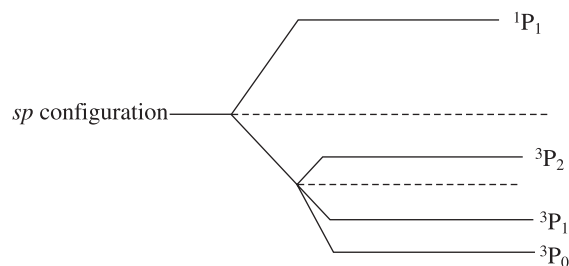


Fig. 2.10.1 Fine structure levels of sp configuration

Breit's scheme: The same spectral terms can be obtained with the help of Breit's scheme as illustrated below.

For the first electron, $l_1 = 0, m_{l_1} = 0, m_{s_1} = 1/2, -1/2$.

For the second electron, $l_2 = 1$, $m_{l_2} = 1, 0, -1$. $m_{s_2} = 1/2, -1/2$.

Write the values of m_l of the two electrons in row and in column as shown in the table. In the similar way write the values of m_s of the two electrons in row and in column.

$m_{l_1} \rightarrow$	1	0	-1	$m_{l_2} \downarrow$
M_L	1	0	-1	0

Allowed values of $M_L = 1, 0, -1$

$m_{s_1} \rightarrow$	1/2	-1/2	$m_{s_2} \downarrow$
M_S	1	0	1/2
	0	-1	-1/2

$M_S = 0$

$M_S = 1, 0, -1$

From the table on the left we see that $M_L = 1, 0, -1$. This implies that $L = 1$. The L-shaped dotted line in the right table separates the two sets of values of M_S , viz. $M_S = 0$ and $M_S = 1, 0, -1$. From the values of M_S we obtain the value of S which are $S = 0$ and $S = 1$.

Thus, we have $L = 1$ and $S = 0$ and 1 . Therefore,

Singlet states ($S = 0$): $J = L \oplus S = 1 \oplus 0 = 1$. Spectral term is $^1P_1$.

Triplet states ($S = 1$): $J = L \oplus S = 1 \oplus 1 = 0, 1, 2$. Spectral terms are $^3P_{0, 1, 2}$

(2) *pd configuration*

In this case $l_1 = 1$, $l_2 = 2$, $L = 1 \oplus 2 = 1, 2, 3$. (P, D, F terms)

$$s_1 = 1/2, s_2 = 1/2, S = 1/2 \oplus 1/2 = 0, 1$$

Singlet states ($S = 0$):

(i) $J = L \oplus S = 1 \oplus 0 = 1$

(ii) $J = L \oplus S = 2 \oplus 0 = 2$

(iii) $J = L \oplus S = 3 \oplus 0 = 3$

The spectral terms are: $^1P_1, ^1D_2, ^1F_3$.

Triplet states ($S = 1$):

(i) $J = L \oplus S = 1 \oplus 1 = 0, 1, 2$. The spectral terms are: $^3P_{0, 1, 2}$

(ii) $J = 2 \oplus 1 = 1, 2, 3$. The spectral terms are: $^3D_{1, 2, 3}$

(iii) $J = 3 \oplus 1 = 2, 3, 4$. The spectral terms are: $^3F_{2, 3, 4}$.

Breit's scheme

$l_1 = 1$, $m_{l_1} = 1, 0, -1$ and $l_2 = 2$, $m_{l_2} = 2, 1, 0, -1, -2$. $m_{s_1} = 1/2, -1/2$, $m_{s_2} = 1/2, -1/2$.

$m_{l_1} \rightarrow$	1	0	-1	$m_{l_2} \downarrow$
	3	2	1	2
	2	1	0	1
M_L	1	0	-1	0
	0	-1	-2	-1
	-1	-2	-3	-2
	L = 1	L = 2	L = 3	

$m_{s_1} \rightarrow$	1/2	-1/2	$m_{s_2} \downarrow$
	1	0	1/2
	0	-1	-1/2
	S = 0	S = 1	

In table on the left, the L-shaped dotted line separates the values of M_L . From the allowed values of M_L we find $L = 1, 2, 3$. Similarly from the table on the right, we get $S = 0, 1$. From the values of L and S we can easily find the J values and the spectral terms $^1P_1$, $^1D_2$, $^1F_3$, $^3P_{0,1,2}$, $^3D_{1,2,3}$ and $^3F_{2,3,4}$.

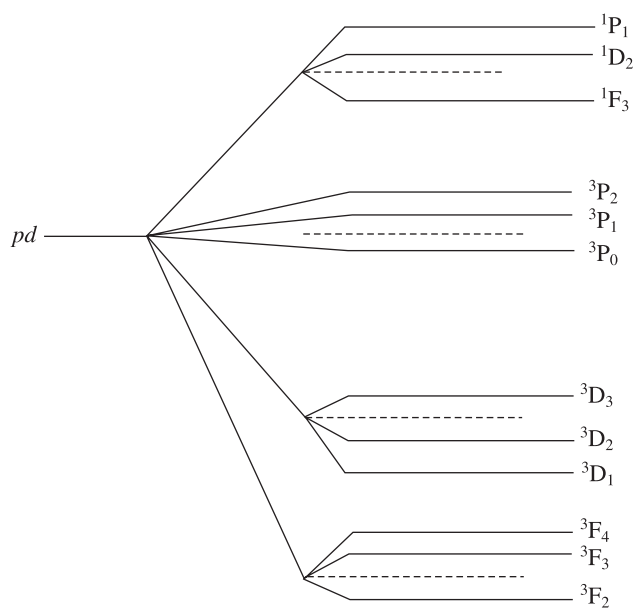


Fig. 2.10 .2 Spectral terms of pd configuration

(3) $np\ n'\ p$ configuration (non-equivalent electron)

In this case the principal quantum number n is different for the two electrons hence they are non-equivalent electrons.

Here $l_1 = 1, l_2 = 1, s_1 = 1/2, s_2 = 1/2$.

$m_{l_1} \rightarrow$	1	0	-1	$m_{l_2} \downarrow$
	2	1	0	1
M_L	1	0	-1	0
	0	-1	-2	-1
	$L = 0$	$L = 1$	$L = 2$	

$m_{s_1} \rightarrow$	$1/2$	$-1/2$	$m_{s_2} \downarrow$
	1	0	$1/2$
M_S	0	-1	$-1/2$
	$S = 0$	$S = 1$	

Allowed values of $L = 0, 1, 2$.

Allowed values of $S = 0, 1$.

Singlet states ($S = 0$):

(i) $J = 0 \oplus 0 = 0$

(ii) $J = 1 \oplus 0 = 1$

(iii) $J = 2 \oplus 0 = 2$

Singlet states are: $^1S_0, ^1P_1, ^1D_2$.

Triplet states ($S = 1$):

(i) $J = 0 \oplus 1 = 1$

(ii) $J = 1 \oplus 1 = 0, 1, 2$

(iii) $J = 2 \oplus 1 = 1, 2, 3$.

The spectral terms are: $^3S_1, ^3P_{0, 1, 2}, ^3D_{1, 2, 3}$.

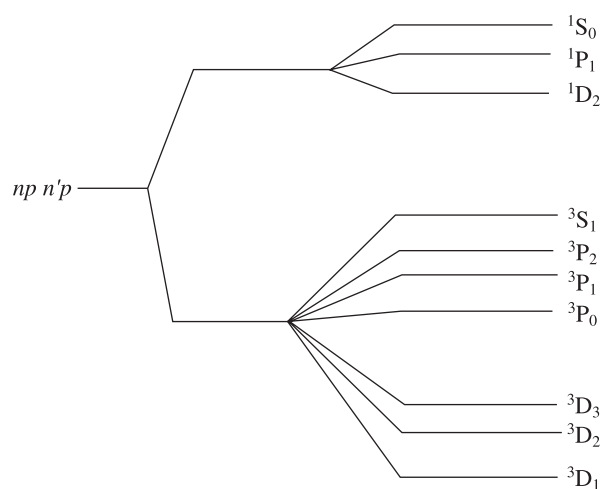


Fig. 2.10.3 Spectral terms of non-equivalent p - p configuration

Two equivalent electrons (n, l same)

p - p configuration: Two electrons having the same n and l quantum numbers are called equivalent electrons. In the ground state of **carbon atom** (${}_6\text{C} = 1s^2 2s^2 2p^2$), the two p -electrons are equivalent electrons. In this case

$$l_1 = 1, m_{l_1} = 1, 0, -1, m_{s_1} = 1/2, -1/2.$$

$$l_2 = 1, m_{l_2} = 1, 0, -1, m_{s_2} = 1/2, -1/2.$$

The Breit's scheme for obtaining spectral terms is shown in the following tables.

$m_{l_1} \rightarrow$	1	0	-1	$m_{l_2} \downarrow$
M_L	2 1 0	1 0 -1	0 -1 -2	1 0 -1

$m_{s_1} \rightarrow$	1/2	-1/2	$m_{s_2} \downarrow$
M_S	1 0	0 -1	1/2 -1/2
	S = 0	S = 1	

According to Pauli's principle, if (i) $m_{s_1} = m_{s_2}$ then $m_{l_1} \neq m_{l_2}$ and if (ii) $m_{l_1} = m_{l_2}$ then $m_{s_1} \neq m_{s_2}$. We consider the two cases one by one.

- (i) $m_{s_1} = m_{s_2}$ (parallel spins) and $m_{l_1} \neq m_{l_2}$. In the left table, the numbers (2, 0, -2) along the diagonal, enclosed in the dotted curve, correspond to the case $m_{l_1} = m_{l_2}$. So they must be excluded. The remaining values of M_L are 1, 0, -1. This gives $L = 1$ (P state). The table on the right gives $S = 0$ and 1. The value $S = 0$ is excluded because this corresponds to opposite spins of electrons whereas we are considering the case of parallel spins ($m_{s_1} = m_{s_2}$). The allowed values of J are given by

$$J = L \oplus S = 1 \oplus 1 = 0, 1, 2.$$

The spectral terms are: ${}^3P_{0, 1, 2}$.

- (ii) $m_{l_1} = m_{l_2}$ and $m_{s_1} \neq m_{s_2}$ (opposite spins). Allowed values of M_L fall along the diagonal of the left table and these are 2, 0, -2. This gives $L = 0, 2$. To exclude the values of M_S corresponding to parallel spins we omit the values $M_S = 1, -1$. The remaining value of M_S is zero. This gives $S = 0$. The values of J are given by

(i) $J = L \oplus S = 0 \oplus 0 = 0$. The spectral term is ${}^1S_0$.

(ii) $J = 2 \oplus 0 = 2$. The spectral term is ${}^1D_2$.

So the spectral terms of pp configuration of equivalent electrons are

$${}^1S_0, {}^1D_2, {}^3P_{0, 1, 2}.$$

II. Spectral Terms in J-J Coupling

(1) *p-d* configuration of non-equivalent electrons

In this case

$$l_1 = 1, s_1 = 1/2, j_1 = l_1 \oplus s_1 = 1 \oplus 1/2 = \frac{1}{2}, \frac{3}{2}$$

$$l_2 = 2, s_2 = 1/2, j_2 = l_2 \oplus s_2 = 2 \oplus 1/2 = \frac{3}{2}, \frac{5}{2}$$

$$(i) J = j_1 \oplus j_2 = \frac{1}{2} \oplus \frac{3}{2} = 1, 2$$

$$(ii) J = \frac{1}{2} \oplus \frac{5}{2} = 2, 3$$

$$(iii) J = \frac{3}{2} \oplus \frac{3}{2} = 0, 1, 2, 3.$$

$$(iv) J = \frac{3}{2} \oplus \frac{5}{2} = 1, 2, 3, 4.$$

Spectral terms are:

$$\left(\frac{1}{2}, \frac{3}{2}\right)_{1,2}, \left(\frac{1}{2}, \frac{5}{2}\right)_{2,3}, \left(\frac{3}{2}, \frac{3}{2}\right)_{0,1,2,3}, \left(\frac{3}{2}, \frac{5}{2}\right)_{1,2,3,4}. \text{ There are 12 states.}$$

(2) *p-p* configuration of non-equivalent electrons

$$l_1 = 1, s_1 = 1/2, j_1 = 1 \oplus 1/2 = 1/2, 3/2.$$

$$l_2 = 1, s_2 = 1/2, j_2 = 1 \oplus 1/2 = 1/2, 3/2.$$

$$(i) J = j_1 \oplus j_2 = 1/2 \oplus 1/2 = 0, 1$$

$$(ii) J = 1/2 \oplus 3/2 = 1, 2$$

$$(iii) J = 3/2 \oplus 1/2 = 1, 2$$

$$(iv) J = 3/2 \oplus 3/2 = 0, 1, 2, 3$$

Spectral states are:

$$\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1}, \left(\frac{1}{2}, \frac{3}{2}\right)_{1,2}, \left(\frac{3}{2}, \frac{1}{2}\right)_{1,2}, \left(\frac{3}{2}, \frac{3}{2}\right)_{0,1,2,3}$$

(3) *p-p* configuration of equivalent electrons

$$l_1 = 1, s_1 = 1/2, j_1 = l_1 \oplus s_1 = 1 \oplus 1/2 = 1/2, 3/2.$$

$$l_2 = 1, s_2 = 1/2, j_2 = 1 \oplus 1/2 = 1/2, 3/2.$$

In *j-j* coupling the state of an electron is described by four quantum numbers n, l, j and m_j . According to Pauli's principle, at least one of the four quantum numbers of the two electrons must be different. The values of m_j ($m_{l_1} \oplus m_{s_1}$) may be obtained from Breit's scheme.

m_{l_1}	1	0	-1	m_{s_1}
m_{j_1}	3/2	1/2	-1/2	1/2
	1/2	-1/2	-3/2	-1/2
	$j_1 = 1/2$		$j_1 = 3/2$	

m_{l_2}	1	0	-1	m_{s_2}
m_{j_2}	3/2	1/2	-1/2	1/2
	1/2	-1/2	-3/2	-1/2
	$j_2 = 1/2$		$j_2 = 3/2$	

From the left table $m_{j_1} = 1/2, -1/2$ and $m_{j_1} = 3/2, 1/2, -1/2, -3/2$. These values of m_{j_1} give $j_1 = 1/2$ and $3/2$. Similarly, the right table gives $j_2 = 1/2$ and $3/2$.

Possible combinations of j_1 and j_2 are

$$\left(\frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{3}{2}\right), \left(\frac{3}{2}, \frac{1}{2}\right), \left(\frac{3}{2}, \frac{3}{2}\right)$$

Of the four combinations, the two in the middle give identical terms and one of these must be omitted. So we are left with only three combinations

$$\left(\frac{1}{2}, \frac{1}{2}\right), \left(\frac{1}{2}, \frac{3}{2}\right), \left(\frac{3}{2}, \frac{3}{2}\right).$$

Determination of J for state $\left(\frac{1}{2}, \frac{1}{2}\right)$ with $j_1 = j_2$ and $m_{j_1} \neq m_{j_2}$, (Pauli's principle)

m_{j_1}	1/2	-1/2	m_{j_2}
M_j	1	0	1/2
	0	-1	-1/2
$M_j = 0$			
$J = 0$			

Diagonal terms must be excluded.

Spectral term is $\left(\frac{1}{2}, \frac{1}{2}\right)_0$.

Determination of J for the state $\left(\frac{1}{2}, \frac{3}{2}\right)$ with $j_1 \neq j_2$ (no need of Pauli's principle)

m_{j_1}	$\frac{1}{2}$	$-\frac{1}{2}$	m_{j_2}
	2	1	$\frac{3}{2}$
M_J	1	0	$\frac{1}{2}$
	0	-1	$-\frac{1}{2}$
	-1	-2	$-\frac{3}{2}$

$M_J = 2, 1, 0, -1, -2$ gives $J = 2$.

$M_J = 1, 0, -1$, gives $J = 1$.

The spectral term is $\left(\frac{1}{2}, \frac{3}{2}\right)_{1,2}$.

Determination of J for $\left(\frac{3}{2}, \frac{3}{2}\right)$ when $j_1 = j_2$ and $m_{j_1} \neq m_{j_2}$ (Pauli's principle)

m_{j_1}	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	m_{j_2}
	3	2	1	0	$\frac{3}{2}$
M_J	2	1	0	-1	$\frac{1}{2}$
	1	0	-1	-2	$-\frac{1}{2}$
	0	-1	-2	-3	$-\frac{3}{2}$

Diagonal terms must be excluded.

$M_J = 0$, gives $J = 0$ and $M_J = 2, 1, 0, -1, -2$ gives $J = 2$

Spectral term is $\left(\frac{3}{2}, \frac{3}{2}\right)_{0,2}$.

2.11 HUND'S RULE FOR DETERMINING THE GROUND STATE OF AN ATOM

(i) Of the terms belonging to a given electronic configuration, the term with the greatest possible value of S (highest multiplicity) and greatest possible value of L at this S will have the lowest energy.

- (ii) The multiplet formed by equivalent electrons are normal i.e., the energy of the state grows with increase in the value of J if not more than half of the sub-shell is filled.
- (iii) The multiplet formed by equivalent electrons are inverted i.e., the energy diminishes with an increase in J if more than half of the sub-shell is filled.

In other words when not more than half of a sub-shell is filled, the component of the multiplet with having minimum value of J has the lowest energy.

Equivalent Electrons with Closed Sub-shell

When the valence sub-shell of an atom is closed the atom has only one term symbol for which $S = 0$, $L = 0$, $J = 0$. The spectral term is $^1S_0$.

For a closed sub-shell, $\sum m_l = 0$, $\sum m_s = 0$. (Example: for p^6 , $m_l = 1, 1, 0, 0, -1, -1$ and $m_s = 1/2, -1/2, 1/2, -1/2, 1/2, -1/2$.) That is, $M_L = 0$, and $M_S = 0$. This implies that $L = 0$, $S = 0$ and $J = 0$.

The spectral terms of p^4 , and p^5 are same as those of $p^{6-4} = p^2$ and $p^{6-5} = p^1$. Similarly, terms of d^6 , d^7 , d^8 are same as those of $d^{10-6} = d^4$, $d^{10-7} = d^3$, $d^{10-8} = d^2$.

2.12 LANDE g -FACTOR IN L-S COUPLING

In light element containing more than one valence electron, the electrostatic interaction between electrons is larger than the spin orbit interaction. As a result of electrostatic interaction the individual orbital angular momenta of electrons combine vectorially to give a resultant L . The electrons in the closed shells do not contribute towards the resultant L . So only valence electrons need to be considered.

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \dots \dots \dots \quad \dots(2.12.1)$$

Where $|\mathbf{l}_1| = [l_1(l_1 + 1)]^{1/2} \hbar$, $|\mathbf{l}_2| = [l_2(l_2 + 1)]^{1/2} \hbar, \dots l_1, l_2$ are the orbital angular quantum numbers of valence electrons. The magnitude of resultant orbital angular momentum of atom is given by

$$|\mathbf{L}| = \sqrt{L(L+1)} \hbar \quad \dots(2.12.2)$$

where $L = l_1 \oplus l_2 \oplus \dots$. The symbol $\oplus$ stands for quantized sum.

Similarly, the spin angular momenta of valence electrons add up vectorially to form a resultant S .

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \dots \dots \dots \quad \dots(2.12.3)$$

where $|\mathbf{s}_1| = [s_1(s_1 + 1)]^{1/2} \hbar$, $|\mathbf{s}_2| = [s_2(s_2 + 1)]^{1/2} \hbar$, $s_1 = 1/2$, $s_2 = 1/2$. The magnitude of $\mathbf{S}$ is given by

$$|\mathbf{S}| = [S(S + 1)]^{1/2} \hbar \quad \dots(2.12.4)$$

The total spin quantum number S is given by

$$S = s_1 \oplus s_2 \dots \dots = \frac{1}{2} \oplus \frac{1}{2} \oplus \dots \quad \dots(2.12.5)$$

Now total orbital angular momentum $\mathbf{L}$ and total spin angular momentum $\mathbf{S}$ combine to form a resultant angular momentum $\mathbf{J}$.

$$\mathbf{L} \oplus \mathbf{S} = \mathbf{J} \quad \dots(2.12.6)$$

The magnitude of $\mathbf{J}$ is given by

$$|\mathbf{J}| = \sqrt{J(J+1)} \hbar \quad \dots(2.12.7)$$

where the total angular quantum number J is given by

$$J = L \oplus S \quad \dots(2.12.8)$$

This type of coupling of angular momentum is called L-S or Russell-Saunders coupling. Like L and S , the associated magnetic moments also add up to form a resultant. The magnetic moment of an atom is given by

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = -\frac{e}{2m}(\mathbf{L} + 2\mathbf{S}) = -\frac{e}{2m}(\mathbf{J} + \mathbf{S}) \quad \dots(2.12.9)$$

The projection of $\vec{\mu}$ onto $\mathbf{J}$ is

$$\mu_J = \frac{\vec{\mu} \cdot \mathbf{J}}{|\mathbf{J}|} = \left(-\frac{e}{2m}\right) \frac{(\mathbf{J} + \mathbf{S}) \cdot \mathbf{J}}{|\mathbf{J}|} = \left(-\frac{e}{2m}\right) \frac{\mathbf{J} \cdot \mathbf{J} + \mathbf{J} \cdot \mathbf{S}}{|\mathbf{J}|} \quad \dots(2.12.10)$$

Now

$$\mathbf{L} \cdot \mathbf{L} = (\mathbf{J} - \mathbf{S}) \cdot (\mathbf{J} - \mathbf{S}) = \mathbf{J} \cdot \mathbf{J} + \mathbf{S} \cdot \mathbf{S} - 2 \mathbf{J} \cdot \mathbf{S}$$

$$\mathbf{J} \cdot \mathbf{S} = \frac{\mathbf{J} \cdot \mathbf{J} + \mathbf{S} \cdot \mathbf{S} - \mathbf{L} \cdot \mathbf{L}}{2}$$

$$\begin{aligned} \mu_J &= \frac{\vec{\mu} \cdot \mathbf{J}}{|\mathbf{J}|} = -\frac{e}{2m} \frac{\mathbf{J} \cdot \mathbf{J} - \frac{1}{2}(\mathbf{J} \cdot \mathbf{J} + \mathbf{S} \cdot \mathbf{S} - \mathbf{L} \cdot \mathbf{L})}{|\mathbf{J}|} \\ &= -\frac{e}{2m} \frac{J(J+1)\hbar^2 - \frac{1}{2}\{J(J+1)\hbar^2 + S(S+1)\hbar^2 - L(L+1)\hbar^2\}}{\sqrt{J(J+1)} \hbar} \\ &= -\frac{e}{2m} \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \sqrt{J(J+1)} \hbar \\ &= -\frac{e}{2m} g \sqrt{J(J+1)} \hbar \\ &= -\frac{e\hbar}{2m} g \sqrt{J(J+1)} \\ &= -\mu_B g \sqrt{J(J+1)} \quad \dots(2.12.11) \end{aligned}$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \dots(2.12.12)$$

g is called Lande g -factor or spectroscopic splitting factor.

The g -factor depends on the atomic state (*i.e.*, on L , S , J). For pure orbital motion $S = 0$, $L = J$ and hence $g = 1$. For pure spin motion $L = 0$, $S = J$ and hence $g = 2$. The g -factor can also be calculated as follows.

Aliter

The relation between orbital angular momentum vector $\mathbf{L}$, spin angular momentum vector $\mathbf{S}$ and their resultant total angular momentum vector $\mathbf{J}$ is depicted by vector diagram as shown in the figure. Also shown are the associated magnetic moments on the same diagram. Because of double magnetism of spin motion, the resultant of μ_L and μ_S , which has been depicted as μ_{atom} , is not collinear with $\mathbf{J}$. The projection of μ_{atom} onto the direction of $\mathbf{J}$ is μ_J . Let θ_{LJ} and ϕ_{SJ} be the angles defined in the figure. From the geometry of the figure we have

$$\begin{aligned} \mu_J &= |\mu_L| \cos \theta_{LJ} + |\mu_S| \cos \phi_{SJ} \\ &= -\frac{e}{2m} |\mathbf{L}| \cos \theta_{LJ} - 2\frac{e}{2m} |\mathbf{S}| \cos \phi_{SJ} \\ &= -\frac{e}{2m} \left[\sqrt{L(L+1)} \hbar \cos \theta_{LJ} + 2\sqrt{S(S+1)} \hbar \cos \phi_{SJ} \right] \quad \dots(2.12.13) \end{aligned}$$

The cosine formula for angles θ_{LJ} and ϕ_{SJ} are

$$\cos \theta_{LJ} = \frac{|\mathbf{J}|^2 + |\mathbf{L}|^2 - |\mathbf{S}|^2}{2|\mathbf{J}||\mathbf{L}|} = \frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)}\sqrt{L(L+1)}} \quad \dots(2.12.14)$$

$$\cos \phi_{SJ} = \frac{|\mathbf{J}|^2 + |\mathbf{S}|^2 - |\mathbf{L}|^2}{2|\mathbf{J}||\mathbf{S}|} = \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}\sqrt{S(S+1)}} \quad \dots(2.12.15)$$

Substituting the expressions of $\cos \theta_{LJ}$ and $\cos \phi_{SJ}$ in Eqn. (2.12.13), we have

$$\begin{aligned} \mu_J &= -\frac{e\hbar}{2m} \left[\frac{J(J+1) + L(L+1) - S(S+1)}{2\sqrt{J(J+1)}} + 2 \frac{J(J+1) + S(S+1) - L(L+1)}{2\sqrt{J(J+1)}} \right] \\ &= -\frac{e\hbar}{2m} \left[\frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \sqrt{J(J+1)} \end{aligned}$$

$$\begin{aligned}
&= -\frac{e\hbar}{2m} \left[1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \right] \sqrt{J(J+1)} \\
&= -\frac{e\hbar}{2m} g \sqrt{J(J+1)} \\
&= -\mu_B g \sqrt{J(J+1)} \quad \dots(2.12.16)
\end{aligned}$$

where

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Thus, the magnetic moment of an atom can be written as

$$\mu_J = -\frac{e}{2m} g |J| = -\frac{e\hbar}{2m} g \sqrt{J(J+1)} = -\mu_B g \sqrt{J(J+1)} \quad \dots(2.12.17)$$

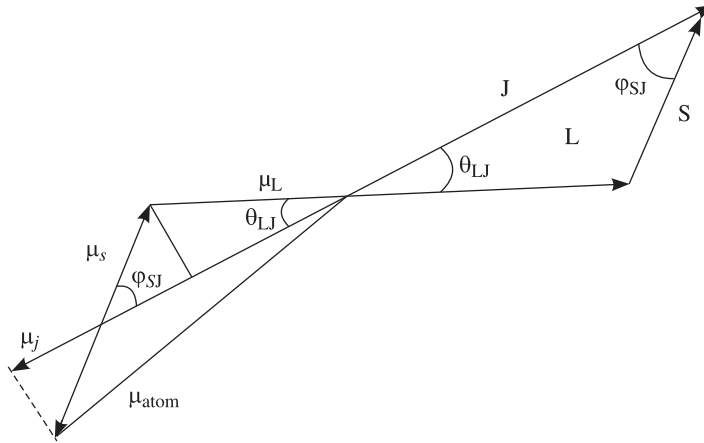


Fig. 2.12.1 Addition of μ_L and μ_S to form μ_{atom}

The projection of μ_J onto z-direction is given by

$$(\mu_J)_z = -\frac{e}{2m} g |J_z| = -\frac{e\hbar}{2m} g M_J = -\mu_B g M_J \quad (2.12.18)$$

where $M_J = 0, \pm 1, \pm 2, \pm 3, \dots$ i.e., M_J can take on integrally spaced values from $-J$ to $+J$. M_J is called the magnetic quantum number of the atom.

2.13 LANDE g -FACTOR IN J-J COUPLING

In heavy atoms, the spin-orbit interaction between magnetic moments associated with orbital and spin motion of an electron is greater than the electrostatic interaction between orbital magnetic moments of valence electrons and that between spin magnetic moments. As a result of this the orbital angular momentum l and spin angular momentum s of the same electron combine to form a resultant j . Now these j 's of valence electrons combine to form a resultant J . This type of coupling of angular momenta is called j - j coupling.

$$l_1 + s_1 = j_1, l_2 + s_2 = j_2, \dots \dots \dots \quad \dots(2.13.1)$$

$$j_1 + j_2 + \dots \dots = J \quad \dots(2.13.2)$$

Consider two valence electrons with angular momentum j_1 and j_2 and associated magnetic moments μ_1 and μ_2 . The resultant magnetic moment in the direction of J is equal to the sum of components of μ_1 and μ_2 parallel to J .

$$\begin{aligned} \mu_J &= \mu_1 \cos(j_1, J) + \mu_2 \cos(j_2, J) \\ &= \frac{e}{2m} [g_1 |j_1| \cos(j_1, J) + g_2 |j_2| \cos(j_2, J)] \\ &= \frac{e}{2m} \left[g_1 |j_1| \frac{J^2 + j_1^2 - j_2^2}{2 |j_1| |J|} + g_2 |j_2| \frac{J^2 + j_2^2 - j_1^2}{2 |j_2| |J|} \right] \\ &= \frac{e}{2m} \left[g_1 \frac{J^2 + j_1^2 - j_2^2}{2 |J|} + g_2 \frac{J^2 + j_2^2 - j_1^2}{2 |J|} \right] \\ &= \frac{e}{2m} \left[g_1 \frac{J^2 + j_1^2 - j_2^2}{2 |J|^2} + g_2 \frac{J^2 + j_2^2 - j_1^2}{2 |J|^2} \right] |J| \\ &= \frac{e}{2m} \left[g_1 \frac{J^2 + j_1^2 - j_2^2}{2 |J|^2} + g_2 \frac{J^2 + j_2^2 - j_1^2}{2 |J|^2} \right] \sqrt{J(J+1)} \hbar \\ &= \frac{e\hbar}{2m} \left[g_1 \frac{J^2 + j_1^2 - j_2^2}{2 |J|^2} + g_2 \frac{J^2 + j_2^2 - j_1^2}{2 |J|^2} \right] \sqrt{J(J+1)} \\ &= \mu_B \left[g_1 \frac{J^2 + j_1^2 - j_2^2}{2 |J|^2} + g_2 \frac{J^2 + j_2^2 - j_1^2}{2 |J|^2} \right] \sqrt{J(J+1)} \end{aligned}$$

$$= \mu_B g \sqrt{J(J+1)} \quad \dots(2.13.3)$$

where

$$g = g_1 \frac{J^2 + \mathbf{j}_1^2 - \mathbf{j}_2^2}{2|\mathbf{J}|^2} + g_2 \frac{J^2 + \mathbf{j}_1^2 - \mathbf{j}_2^2}{2|\mathbf{J}|^2} \quad \dots(2.13.4)$$

where g_1 and g_2 are the Lande g -factors of individual electrons and are given by

$$g_1 = 1 + \frac{j_1(j_1 + 1) + s_1(s_1 + 1) - l_1(l_1 + 1)}{2j_1(j_1 + 1)}.$$

$$g_2 = 1 + \frac{j_2(j_2 + 1) + s_2(s_2 + 1) - l_2(l_2 + 1)}{2j_2(j_2 + 1)}.$$

2.14 ENERGY OF AN ATOM IN MAGNETIC FIELD

When an atom possessing magnetic moment is placed in a uniform magnetic field, it experiences a torque equal to $\boldsymbol{\mu} \cdot \mathbf{B}$. Referred to a zero of potential energy when $\boldsymbol{\mu}$ and $\mathbf{B}$ are perpendicular to each other, the potential energy in an arbitrary orientation is given by $-\boldsymbol{\mu} \cdot \mathbf{B}$. Thus, in the magnetic field an atom acquires an extra energy $-\boldsymbol{\mu} \cdot \mathbf{B}$. If E_0 is the energy of an atom in absence of magnetic field, the energy in presence of magnetic field is

$$E = E_0 - \boldsymbol{\mu} \cdot \mathbf{B} \quad \dots(2.14.1)$$

If z -axis is chosen in the direction of the magnetic field *i.e.*, $\mathbf{B} = B\hat{z}$, then the energy of the atom can be written as

$$\begin{aligned} E &= E_0 - \mu_z B \\ &= E_0 - \left(-\frac{e}{2m}\right) g |\mathbf{J}_z| B \\ &= E_0 + g \left(\frac{e}{2m}\right) M_J \hbar B \\ &= E_0 + g \frac{e\hbar}{2m} B M_J \\ &= E_0 + g \mu_B B M_J \end{aligned} \quad \dots(2.14.2)$$

where $M_J = J, J - 1, \dots, 0, \dots, -(J - 1), -J$. Since M_J can take on $2J + 1$ values, an atomic energy level is splits into $2J + 1$ equally spaced sub-levels as shown in the Fig. (2.14.1). The splitting of an energy level results from the interaction of magnetic field with the magnetic moment of the atom. It is evident from Eqn. (2.14.2) that an atomic level with $g = 0$ does not split at all. For example, the

state $^4D_{1/2}$ has $L = 0$, $S = 3/2$, $J = 1/2$ and $g = 0$. Similarly for a state with $S = 0$ (called *singlet*), no splitting occurs. ^1S state is an example of this case. In magnetic field the separation of two adjacent sub-levels is $g\mu_B B$ and the total splitting is given by

$$\Delta E = 2g\mu_B B J \quad \dots(2.14.3)$$

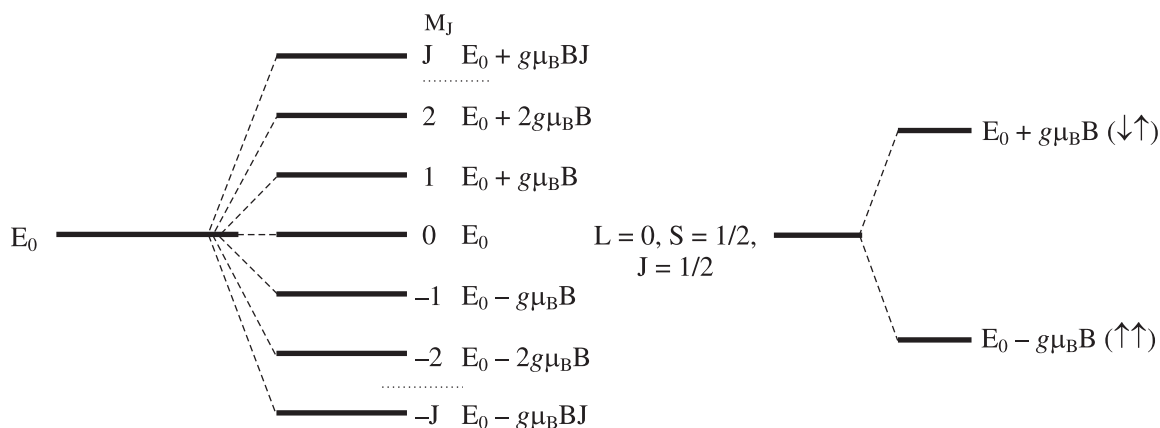


Fig. 2.14.1 Splitting of an energy level in magnetic field

An energy level characterized by $L = 0$, $S = 1/2$, $J = 1/2$ splits into two levels, one with μ is parallel and the other with μ anti-parallel to field B . The level with μ parallel to B has minimum energy and lies deepest.

2.15 STERN AND GERLACH EXPERIMENT (SPACE QUANTIZATION): EXPERIMENTAL CONFIRMATION FOR ELECTRON SPIN CONCEPT

The confirming evidence of space quantization of angular momentum (and hence of magnetic moment) came from the celebrated atomic beam experiment of Stern and Gerlach (1922), which was originally devised to measure the magnetic moment of individual silver atoms. This experiment also provides an evidence for the spin hypothesis of electron. A well-defined beam of silver atoms was obtained by evaporating silver in a hot oven and letting the atoms through a series of holes as shown in the Fig. (2.15.1). The beam of silver atoms was allowed to pass through an *inhomogeneous* magnetic field B , which was produced between a sharp edged and a flat faced pole piece of a magnet. The emergent beam was received on photographic plate. The geometry of the experimental set up is shown in the figure. The magnetic field acts in z -direction and the atomic beam enters the field along x -axis.

In silver atom, the angular momentum and hence the magnetic moment comes from the spin of valence electron. Let μ be the magnetic moment of silver atom. In an *inhomogeneous* magnetic field having gradient in z -direction a magnetic dipole with magnetic moment μ experiences a translational force F_z in z -direction.

$$F_z = \mu_z \frac{\partial B}{\partial z} = \mu \cos \theta \cdot \frac{\partial B}{\partial z} \quad \dots(2.15.1)$$

where θ is the angle that magnetic moment vector makes with the field B . Classically the magnetic moment μ can take all possible orientations and hence θ is a continuous variable. Atoms for which $\cos \theta$ is positive, will be pulled up and those for which $\cos \theta$ is negative, will be pulled downward. Atoms whose magnetic moments are perpendicular to the magnetic field will be subjected to no force and hence they will go straight. Atoms with μ parallel to B will suffer maximum upward deflection and those with μ anti-parallel to B will suffer maximum downward deflection. Thus, the beam of silver atoms, after emerging the field B will spread out; the spreading of atoms will be proportional to the z -component of μ . Thus, the classical physics predicts a *smeared out* pattern in vertical direction on the photographic plate. Stern and Gerlach, however, observed that the beam of silver atoms was split into two distinct parts giving two separate lines arranged symmetrically with respect to the trace of the beam obtained in absence of magnetic field.

A beam of ions cannot be used because the ions will be acted upon by Lorentz force in magnetic field and hence the beam will suffer deflection due to this force also and unnecessary complication will arise.

Quantum Mechanical Explanation

As stated the entire magnetic moment of silver atom comes from the spin of its valence electron. The spin of silver atom is $1/2$. In magnetic field, the angular momentum and hence the magnetic moment can have only two orientations, parallel and anti-parallel to B . Atoms with μ parallel to B are deflected upward and those with μ anti-parallel to B are deflected downward and hence the beam gets split into two parts. Thus, only two traces are expected. This is observed in the experiment. The number of traces on the photographic plate depends on the angular momentum (spin) of the atom. In experiments with beams of aluminium, copper and alkali metals two traces were obtained. Vanadium, nitrogen, halogens gave four, oxygen five, manganese six, iron nine and cobalt 10 traces. Mercury and magnesium gave a single trace at the central position. This means that these atoms have no magnetic moments.

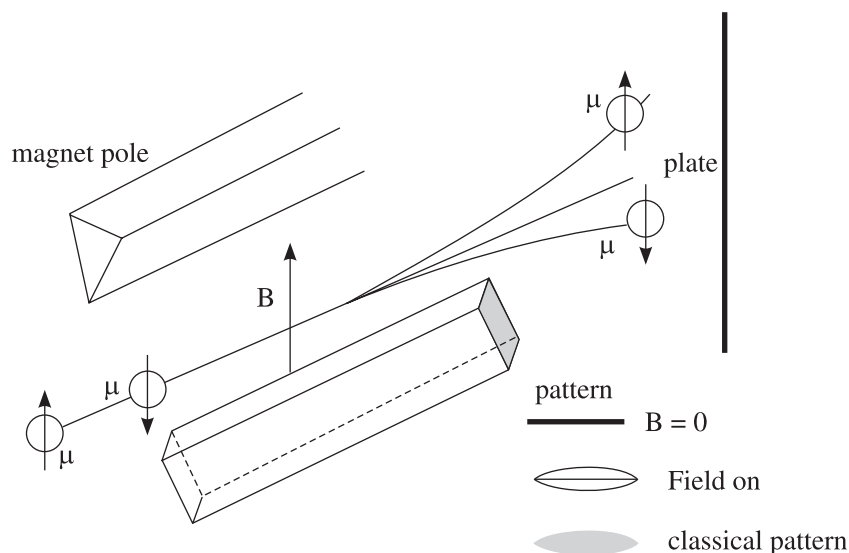


Fig. 2.15.1 Stern-Gerlach experiment

2.16 SPIN ORBIT INTERACTION ENERGY

The classical theory of atom assumes that the electron moves in the Coulomb field of the stationary nucleus. In electron's rest frame, the nucleus moves around the electron. The circulation of nucleus around the electron is equivalent to a current loop, which produces a magnetic field $\mathbf{B}$ at the site of electron. The intrinsic magnetic moment ($\boldsymbol{\mu} = -(e/m) \mathbf{s}$) of electron interacts with the magnetic field $\mathbf{B}$. This interaction is known as the *spin-orbit interaction* and leads to a structure in energy spectrum, known as *fine structure*. The change in energy of atom due to this interaction is called spin orbit interaction energy. We shall now derive an expression for this energy.

The spin-orbit interaction causes the orbital angular momentum $\mathbf{l}$ and spin angular momentum $\mathbf{s}$ of electron to combine to form a resultant $\mathbf{j}$ and this type of coupling is called L-S coupling. We shall see that spin orbit interaction causes splitting of energy levels, and hence the splitting of spectral lines.

Consider an electron moving in a circular orbit of radius r around the nucleus with velocity $\mathbf{v}$. In electron's rest frame, the nucleus is moving in a circular orbit of radius r in the direction opposite to that of the electron with the velocity $-\mathbf{v}$. The current associated with the motion of nucleus produces magnetic field at the location of electron. This magnetic field $\mathbf{B}$ is given by

$$\mathbf{B} = -\mu_0 \epsilon_0 (\mathbf{v} \times \mathbf{E}) = -\frac{\mathbf{v} \times \mathbf{E}}{c^2} \quad \dots(2.16.1)$$

where $\mathbf{E}$ is electric field of nucleus, $\mathbf{v}$ is velocity of electron. Making use of the result

$$\mathbf{E} = -\frac{1}{r} \frac{\partial V}{\partial r} \mathbf{r}, \quad V = \frac{Ze}{4\pi\epsilon_0 r}$$

We can write

$$\mathbf{B} = -\frac{1}{c^2 r} \frac{\partial V}{\partial r} (\mathbf{r} \times \mathbf{v}) = -\frac{1}{mc^2 r} \frac{\partial V}{\partial r} \mathbf{l} \quad \dots(2.16.2)$$

where $\mathbf{l} = \mathbf{r} \times m\mathbf{v}$ is orbital angular momentum of electron. The electron possesses spin magnetic moment given by

$$\boldsymbol{\mu} = -\frac{e}{m} \mathbf{s} \quad \dots(2.16.3)$$

The spin magnetic moment interacts with magnetic field $\mathbf{B}$, the corresponding magnetic energy is

$$E_{ls} = -\boldsymbol{\mu} \cdot \mathbf{B}$$

We call this energy *spin orbit interaction energy*. Substituting the values of $\mathbf{B}$ and $\boldsymbol{\mu}$, we have

$$E_{ls} = \left(\frac{1}{4\pi\epsilon_0} \right) \left(\frac{Ze^2}{m^2 c^2} \right) \left(\frac{1}{r^3} \right) (\mathbf{l} \cdot \mathbf{s}) \quad \dots(2.16.4)$$

where we have put $V = \frac{Ze}{4\pi\epsilon_0 r}$.

So far our calculation was non-relativistic. The relativistic correction imparts the electron a precessional motion about the nucleus. The effect of this precession, called *Thomas Precession*, is that the magnetic field seen by electron is only half as large as the one assumed in the forgoing derivation. With this correction, the spin orbit interaction energy becomes

$$\Delta E_{ls} = \frac{1}{2} \left(\frac{Ze^2}{4\pi\epsilon_0} \right) \frac{1}{m^2 c^2} \left(\frac{1}{r^3} \right) (\mathbf{l} \cdot \mathbf{s}) \quad \dots(2.16.5)$$

The magnitude of spin-orbit energy correction is very small in comparison with the total energy of the electron. It may be regarded as a small perturbation. The Hamiltonian operator corresponding to this spin-orbit correction is

$$\hat{H} = \frac{1}{2} \cdot \frac{1}{4\pi\epsilon_0} \cdot \frac{Ze^2}{m^2 c^2} \cdot \frac{\hat{\mathbf{l}} \cdot \hat{\mathbf{s}}}{r^3}$$

If the wave function of electron for the state characterized by quantum numbers n, l, j is $\psi_{n,l,j}$ then the average value of spin-orbit energy is given by

$$\langle \Delta E_{ls} \rangle = \frac{1}{2(4\pi\epsilon_0)} \cdot \frac{Ze^2}{m^2 c^2} \int \psi_{n,l,j}^* \frac{\hat{\mathbf{l}} \cdot \hat{\mathbf{s}}}{r^3} \psi_{n,l,j} d\tau \quad \dots(2.16.6)$$

Now

$$(\mathbf{l} + \mathbf{s})^2 = \mathbf{j} \cdot \mathbf{j}$$

$$|\mathbf{l}|^2 + |\mathbf{s}|^2 + 2\mathbf{l} \cdot \mathbf{s} = |\mathbf{j}|^2$$

The average values of $\mathbf{l}^2$, $\mathbf{s}^2$ and $\mathbf{j}^2$ are $l(l+1)\hbar^2$, $s(s+1)\hbar^2$ and $j(j+1)\hbar^2$. Therefore

$$\mathbf{l} \cdot \mathbf{s} = \frac{|\mathbf{j}|^2 - |\mathbf{l}|^2 - |\mathbf{s}|^2}{2} = \frac{j(j+1) - l(l+1) - s(s+1)}{2} \hbar^2 \quad \dots(2.16.7)$$

The average value of $1/r^3$ in a state characterized by quantum numbers n, l, j is given by

$$\left\langle \frac{1}{r^3} \right\rangle = \int \psi_{n,l,j}^* \left(\frac{1}{r^3} \right) \psi_{n,l,j} d\tau = \frac{Z^3}{a_0^3 n^3 l(l + \frac{1}{2})(l+1)} \quad \dots(2.16.8)$$

In view of results Eqns. (2.16.7) and (2.16.8) the expression for spin orbit interaction energy becomes

$$\Delta E_{ls} = \frac{1}{4} \frac{e^2 \hbar^2 Z^4}{4\pi\epsilon_0 m^2 c^2 a_0^3} \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l + \frac{1}{2})(l+1)}$$

$$= \frac{1}{2} Rch\alpha^2 Z^4 \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l + \frac{1}{2})(l+1)}, \quad l \neq 0, \quad \dots(2.16.9)$$

The corresponding change in term value is

$$\Delta T_{ls} = -\frac{\Delta E_{ls}}{hc} = -\frac{1}{2} \frac{R\alpha^2 Z^4}{n^3 l(l + \frac{1}{2})(l + 1)} [j(j + 1) - l(l + 1) - s(s + 1)] \quad \dots(2.16.10)$$

or
$$\Delta T_{ls} = -\frac{a}{2} [j(j + 1) - l(l + 1) - s(s + 1)] \quad \dots(2.16.11)$$

where
$$a = \frac{R\alpha^2 Z^4}{n^3 l(l + \frac{1}{2})(l + 1)} \quad \dots(2.16.12)$$

The term value of an energy level, taking spin orbit energy into consideration, is

$$T = T_0 + \Delta T_{ls}$$

where T_0 is the term value of some reference level (or hypothetical level). If ΔT_{ls} is positive, the shift of level is downward and if ΔT_{ls} is negative, the shift is upward with respect to the reference level. *The splitting of states with the same n is called fine structure.*

We shall illustrate it with the help of examples.

1. Fine Structure of Doublet ${}^2P_{1/2}$ and ${}^2P_{3/2}$

For the first spectral term, $l = 1$, $s = 1/2$, $j = 1/2$.

$$\Delta T = -\frac{a}{2} \left[\frac{1}{2} \cdot \frac{3}{2} - 1(1 + 1) - \frac{1}{2} \cdot \frac{3}{2} \right] = a(\downarrow)$$

For the second spectral term, $l = 1$, $s = 1/2$, $j = 3/2$.

$$\Delta T = -\frac{a}{2} \left[\frac{3}{2} \cdot \frac{5}{2} - 1(1 + 1) - \frac{1}{2} \cdot \frac{3}{2} \right] = -\frac{a}{2}(\uparrow)$$

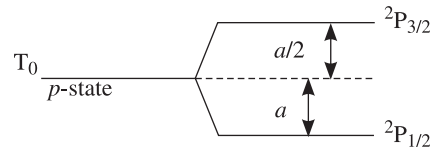


Fig. 2.16.1

2. Fine Structure of Doublet ${}^2D_{3/2}$ and ${}^2D_{5/2}$

For state ${}^2D_{3/2}$, $s = 1/2$, $l = 2$, $j = 3/2$.

Therefore $\Delta T = 3a/2(\downarrow)$

For the state ${}^2D_{5/2}$, $s = 1/2$, $l = 2$, $j = 5/2$.

Therefore $\Delta T = -a(\uparrow)$

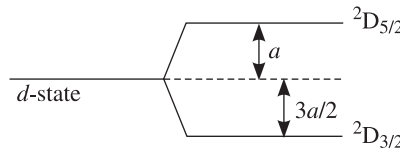


Fig. 2.16.2

3. Fine Structure of Doublet ${}^2F_{5/2}$ and ${}^2F_{7/2}$

For the state ${}^2F_{5/2}$ $s = 1/2$, $l = 3$, $j = 5/2$.
 Therefore $\Delta T = 2a$ ($\downarrow$)
 For state ${}^2F_{7/2}$ $s = 1/2$, $l = 3$, $j = 7/2$.
 Therefore $\Delta T = -3a/2$ ($\uparrow$)

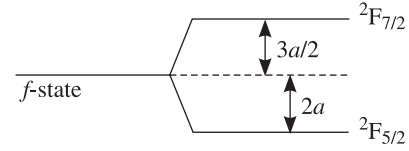


Fig. 2.16.3

2.17 FINE STRUCTURE OF ENERGY LEVELS IN HYDROGEN ATOM

The spin orbit interaction energy is

$$\Delta E_{ls} = \frac{1}{2} Rch\alpha^2 Z^4 \frac{j(j+1) - l(l+1) - s(s+1)}{n^3 l(l+\frac{1}{2})(l+1)}, \quad l \neq 0 \quad \dots(2.17.1)$$

For one electron atom, $s = 1/2$, $j = l \oplus s = l \oplus 1/2 = l + 1/2$ and $l - 1/2$. Therefore,

$$\Delta E_{ls, j=l+1/2} = \frac{1}{2} Rch\alpha^2 Z^4 \frac{1}{n^3 (l+\frac{1}{2})(l+1)} \quad \dots(2.17.2)$$

$$\text{and} \quad \Delta E_{ls, j=l-1/2} = -\frac{1}{2} Rch\alpha^2 Z^4 \frac{1}{n^3 l(l+\frac{1}{2})} \quad \dots(2.17.3)$$

The spin orbit interaction is not the only effect that contributes to the fine structure. Two other factors which add to the spin orbit energy are: relativistic effect and self-energy effect. The relativistic effect arises due to increase in electron mass and the self-energy effect due to interaction of electron with its own electromagnetic field. The change in energy due to latter effect is called *Lamb shift*.

The relativistic increase in electron mass gives rise to the following expression for the change in energy.

$$\Delta E_r = -\frac{Rch\alpha^2 Z^4}{n^3} \left[\frac{1}{l+\frac{1}{2}} - \frac{3}{4n} \right] \quad \dots(2.17.4)$$

n and l are the principal and orbital quantum number of electron.

The total energy shift due to spin orbit interaction and relativistic effect for $j = l + 1/2$ is

$$\begin{aligned} \Delta E &= \Delta E_{ls} + \Delta E_r \\ &= \frac{Rch\alpha^2 Z^4}{n^3} \left[\frac{1}{2(l+\frac{1}{2})(l+1)} - \left(\frac{1}{l+\frac{1}{2}} - \frac{3}{4n} \right) \right] \\ &= -\frac{Rch\alpha^2 Z^4}{n^3} \left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right] \end{aligned} \quad \dots(2.17.5)$$

The expression for the total energy shift for state $j = l - 1/2$ also comes out to be the same.

The corresponding term value is

$$\Delta T = \frac{R\alpha^2 Z^4}{n^3} \left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n} \right] \quad \dots(2.17.6)$$

where $j = 1/2, 3/2, 5/2, \dots, n - 1/2$.

Equation (2.17.6) shows that for a given value of n , the total correction term depends on j and each level with $l > 0$ is split into two levels, the level of higher j having the higher energy. Therefore, the states having the same value of j but different l values have the same energy. For example, the states $2^2S_{1/2}$ and $2^2P_{1/2}$ are degenerate. Other degenerate pairs are ($3^2S_{1/2}$, $3^2P_{1/2}$) and ($3^2P_{3/2}$, $3^2D_{3/2}$). The spin orbit energy shift and relativistic corrections add up in such a way that finally the states $2^2S_{1/2}$ and $2^2P_{1/2}$ are degenerate for a given $n = 2, 3, 4, \dots$

In 1947, Lamb and Rutherford observed a very small splitting of 0.033 cm^{-1} between the energies of $2^2S_{1/2}$ and $2^2P_{1/2}$ in hydrogen atom. This shift is called Lamb shift. The cause of this shift is the interaction of the electron with its own electromagnetic field (self energy).

Since $R\alpha^2 = 1.097 \times 10^5 \text{ cm}^{-1} \times (1/137)^2 = 5.84 \text{ cm}^{-1}$, the shift of energy level $n = 1$, ($l = 0, s = 1/2$) $1^2S_{1/2}$ is given by

$$\Delta T = \frac{5.84}{n^3} \left[\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right]$$

$$= 1.46 \text{ cm}^{-1}$$

For $n = 2, l = 0, 1, s = 1/2$. For $l = 0, j = 1/2$, and for $l = 1, j = 1/2$ and $3/2$. Therefore, there are three states $2^2S_{1/2}$, $2^2P_{1/2}$, $2^2P_{3/2}$. The states $2^2S_{1/2}$ and $2^2P_{1/2}$ shift by equal amount given by

$$\Delta T = \frac{5.84}{8} \left[\frac{1}{\frac{1}{2} + \frac{1}{2}} - \frac{3}{8} \right] = 0.456 \text{ cm}^{-1}$$

The state $2^2P_{3/2}$ shifts by amount

$$\Delta T = \frac{5.84}{8} \left[\frac{1}{\frac{3}{2} + \frac{1}{2}} - \frac{3}{8} \right] = 0.09125 \text{ cm}^{-1}$$

For $n = 3, l = 0, 1, 2$ and $s = 1/2$. There are five states $3^2S_{1/2}$, $3^2P_{1/2}$, $3^2P_{3/2}$, $3^2D_{3/2}$ and $3^2D_{5/2}$. The states $3^2S_{1/2}$ and $3^2P_{1/2}$ shift by equal amount given by

$$\Delta T_{j=1/2} = \frac{5.84}{27} \left[\frac{1}{\frac{1}{2} + \frac{1}{2}} - \frac{3}{12} \right] = 0.1622 \text{ cm}^{-1}$$

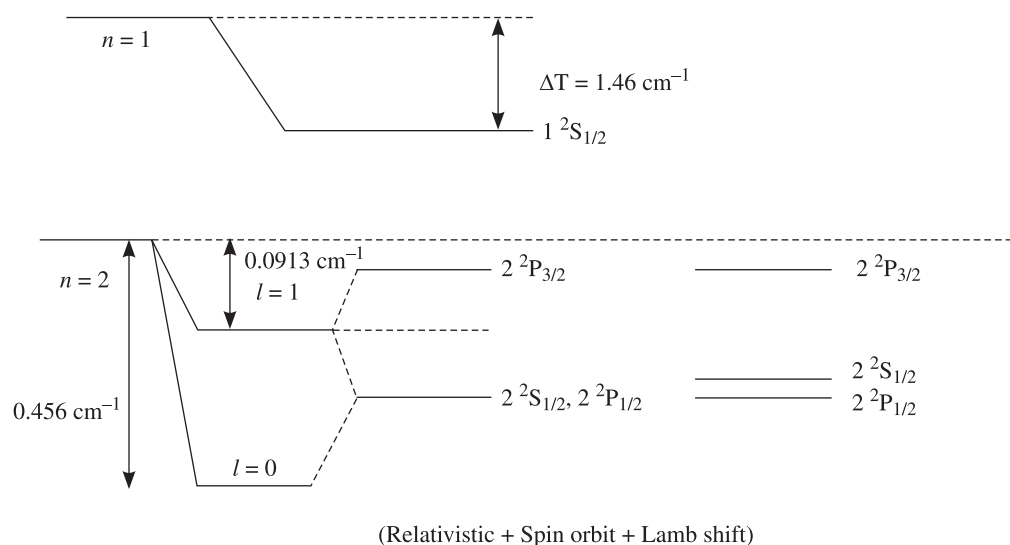
Without Lamb shift these states are degenerate. The states $3^2P_{3/2}$ and $3^2D_{3/2}$ also shift by equal amount and hence are degenerate without Lamb shift. The energy shift is given by

$$\Delta T_{j=3/2} = \frac{5.84}{27} \left[\frac{1}{\frac{3}{2} + \frac{1}{2}} - \frac{3}{12} \right] = 0.054 \text{ cm}^{-1}$$

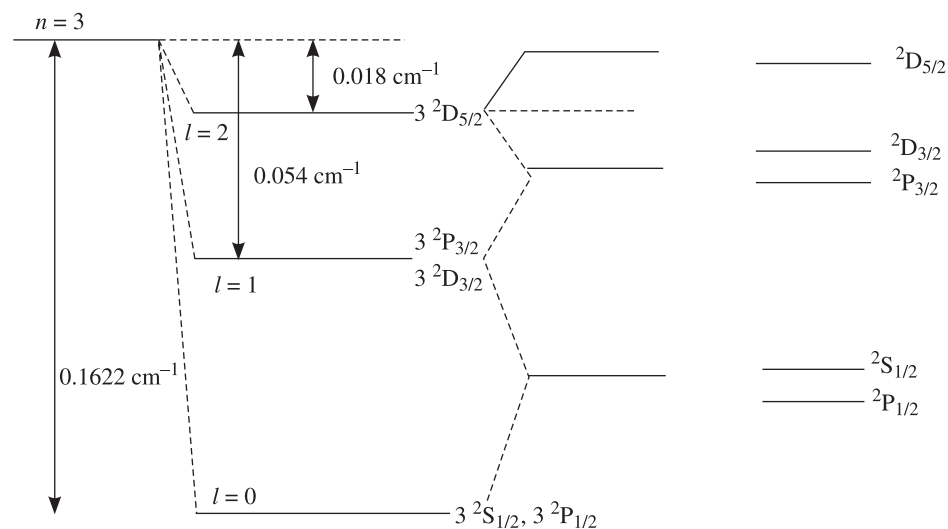
Similarly, the state $3^2D_{5/2}$ shifts by amount

$$\Delta T = -0.018 \text{ cm}^{-1}$$

The fine structure splitting of energy levels $n = 1, n = 2$ and $n = 3$ for hydrogen atom are shown in the figure.



The cumulative effect of these corrections is to split the energy level $n=2$ into three components ($2^2P_{1/2}, 2^2S_{1/2}, 2^2P_{3/2}$).



The cumulative effect of these corrections is to split the energy level $n=3$ into five components ($3^2S_{1/2}, 3^2P_{1/2}, 3^2P_{3/2}, 3^2D_{3/2}, 3^2D_{5/2}$).

Fig. 2.17.1 Fine structure of first three energy levels of hydrogen atom

2.18 FINE STRUCTURE OF H_α LINE

The H_α line of hydrogen spectrum results from the transition of electron from the energy level corresponding to $n = 3$ to the energy level $n = 2$. The entire state of the atom is determined by its single valence electron.

Corresponding to $n = 2$, there are two sub-levels, s sub-level ($l = 0$) and p sub-level ($l = 1$). When electron is in s sub-level ($l = 0$).

$$L = l = 0$$

$$S = s = 1/2$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

This state is represented by $^2S_{1/2}$.

When the electron is in p sub-level ($l = 1$)

$$L = l = 1$$

$$S = s = 1/2$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

This state is represented by $^2P_{3/2}, ^2P_{1/2}$.

Corresponding to $n = 3$ there are three sub-levels, s , p and d sub-levels. When the electron is in s sub-level ($l = 0$)

$$L = l = 0$$

$$S = s = 1/2$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

The corresponding state is $^2S_{1/2}$.

When the electron is in p sub-level ($l = 1$)

$$L = l = 1$$

$$S = s = 1/2$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

and the corresponding states are $^2P_{3/2}$ and $^2P_{1/2}$.

When the electron is in d sub-level ($l = 2$)

$$L = l = 2$$

$$S = s = 1/2$$

$$J = L \oplus S = 2 \oplus 1/2 = 5/2, 3/2.$$

The corresponding states are $^2D_{5/2}, ^2D_{3/2}$.

The energy levels corresponding to $n = 3$ and $n = 2$ are shown in the Fig. (2.18.1). It can be shown that a state with lower value of J has smaller energy than the state with higher value of J . In all fifteen transitions are possible but selection rules limit their number. Allowed transitions are those in which L changes by ± 1 or J changes by 0 or ± 1 , i.e.,

$$\Delta L = \pm 1, \Delta J = 0, \pm 1 \quad (\text{allowed})$$

The selection rules permit only seven transitions. The allowed transitions are:

$$^2D_{5/2} \rightarrow ^2P_{3/2}, \quad ^2D_{3/2} \rightarrow ^2P_{1/2}, \quad ^2P_{1/2} \rightarrow ^2S_{1/2}, \quad ^2D_{3/2} \rightarrow ^2P_{3/2},$$

$$^2P_{3/2} \rightarrow ^2S_{1/2}, \quad ^2S_{1/2} \rightarrow ^2P_{3/2}, \quad ^2S_{1/2} \rightarrow ^2P_{1/2}.$$

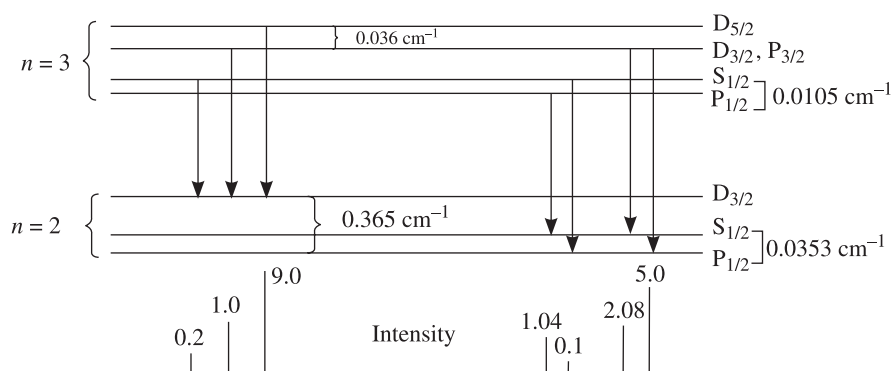


Fig. 2.18.1 Fine Structure of H_α line (6563 Å). Lines marked 4, 4 are coincident. This is also true for lines marked 5, 5.

It was Lamb who in collaboration with Rutherford in 1947, discovered that in hydrogen-like atom, for a given value of n , the levels with the same value of J but L values differing by unity are non-degenerate. In fact, he detected a small difference of 0.0353 cm^{-1} between the levels $2^2S_{1/2}$ and $2^2P_{1/2}$. This shift in energy is called *Lamb Shift*. Lamb shift of amount 0.0105 cm^{-1} is also observed between levels $3^2S_{1/2}$ and $3^2P_{1/2}$. Because of very small magnitude of Lamb shift, the resulting splitting of spectral lines is normally not observed.

2.19 FINE STRUCTURE OF SODIUM D LINES

The D lines of sodium spectrum result from the transitions of electron from $3p$ to $3s$ level. In the ground state of Na atom the valence electron lies in $3s$ level. In this state

$$L = l = 0$$

$$S = s = 1/2$$

$$J = L \oplus S = 0 \oplus 1/2 = 1/2$$

The ground state is denoted by $^2S_{1/2}$. When the valence electron is excited to $3p$ level

$$L = l = 1$$

$$S = s = 1/2$$

$$J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$$

This state is denoted by $^2P_{3/2}, ^2P_{1/2}$.

The energy level diagram of $3s$ and $3p$ levels are shown in the Fig. (2.19.1). Three transitions from upper level to lower level are possible. Selection rules $\Delta L = \pm 1, \Delta J = 0, \pm 1$ allow only two transitions. The D_1 line ($\lambda = 5896 \text{ Å}$) originates from the transition $^2P_{1/2} \rightarrow ^2S_{1/2}$ and D_2 line ($\lambda = 5890 \text{ Å}$) from the transition $^2P_{3/2} \rightarrow ^2S_{1/2}$.

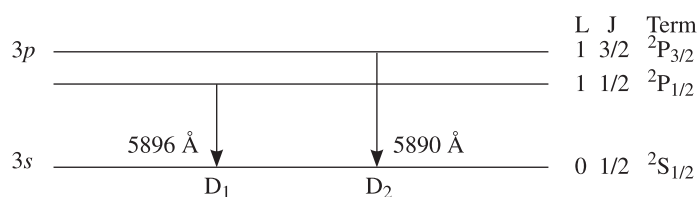


Fig. 2.19.1 Fine Structure of sodium spectrum (origin of D_1 and D_2 lines)

2.20 INTERACTION ENERGY IN L-S COUPLING IN ATOM WITH TWO VALENCE ELECTRONS

In an atom with two valence electrons there are four angular momenta l_1, s_1, l_2 and s_2 and hence there are six terms for interaction energy corresponding to six combinations of these momenta viz. $(s_1, s_2), (l_1, l_2), (l_1, s_1), (l_2, s_2), (l_1, s_2)$ and (l_2, s_1) . The general expression for interaction energy Γ in l - s coupling is

$$\Gamma = -\Delta T_{ls} = a |\mathbf{I}_{ls}| \cos(l, s) = \frac{a}{2} j^2 - l^2 - s^2 = \frac{a}{2} [j(j+1) - l(l+1) - s(s+1)] \quad \dots(2.20.1)$$

where $|\mathbf{l}| = \sqrt{l(l+1)}\hbar, |\mathbf{s}| = \sqrt{s(s+1)}\hbar, |\mathbf{j}| = \sqrt{j(j+1)}\hbar$

$$\text{and} \quad a = \frac{R\alpha^2 Z^2}{n^3 l(l + \frac{1}{2})(l+1)} \quad \dots(2.20.2)$$

For convenience we shall make a change in notation as given below.

$$l^* = \sqrt{l(l+1)}, \quad s^* = \sqrt{s(s+1)}, \quad j^* = \sqrt{j(j+1)}$$

$$L^* = \sqrt{L(L+1)}, \quad S^* = \sqrt{S(S+1)}, \quad J^* = \sqrt{J(J+1)}$$

Thus, the symbols l^*, s^* and j^* represent the magnitude of orbital, spin and total angular momenta in unit of $\hbar$ and so on. In terms of new symbols the general expression for interaction energy is

$$\Gamma = -\Delta T_{ls} = a l^* s^* \cos(l^*, s^*) = \frac{1}{2} a (j^{*2} - l^{*2} - s^{*2}) \quad \dots(2.20.3)$$

Now the interaction energies for two valence electrons can be expressed as

$$\Gamma_1 = a_1 s_1^* s_2^* \cos(s_1^*, s_2^*) = \frac{a_1}{2} (S^{*2} - s_1^{*2} - s_2^{*2}) \quad \dots(2.20.4)$$

$$\Gamma_2 = a_2 l_1^* l_2^* \cos(l_1^*, l_2^*) = \frac{a_2}{2} (L^{*2} - l_1^{*2} - l_2^{*2}) \quad \dots(2.20.5)$$

$$\Gamma_3 = a_3 l_1^* s_1^* \cos(l_1^*, s_1^*) = \frac{a_3}{2} (j_1^{*2} - l_1^{*2} - s_1^{*2}) \quad \dots(2.20.6)$$

$$\Gamma_4 = a_4 l_2^* s_2^* \cos(l_2^*, s_2^*) = \frac{a_4}{2} (j_2^{*2} - l_2^{*2} - s_2^{*2}) \quad \dots(2.20.7)$$

$$\Gamma_5 = a_5 l_1^* s_2^* \cos(l_1^*, s_2^*) = \frac{a_5}{2} (j_{12}^{*2} - l_1^{*2} - s_2^{*2}) \quad \dots(2.20.8)$$

$$\Gamma_6 = a_6 l_2^* s_1^* \cos(l_2^*, s_1^*) = \frac{a_6}{2} (j_{21}^{*2} - l_2^{*2} - s_1^{*2}) \quad \dots(2.20.9)$$

The terms Γ_5 and Γ_6 are negligibly small and will be omitted. The spin-spin and orbital-orbital interactions are electrostatic in nature whereas spin-orbit interaction is magnetic in origin.

In L-S coupling the quantum mechanical exchange interactions between spin vectors s_1 and s_2 and between orbital vectors l_1 and l_2 predominate over the spin-orbit interactions between vectors l and s . A consequence of this is that orbital vectors l_1 and l_2 precess more rapidly about their resultant L . This result also holds for spin vectors s_1 and s_2 . Due to weaker spin orbit interaction, vectors L and S precess slowly about their resultant J . This means that Γ_1 and Γ_2 are greater than Γ_3 and Γ_4 . The interaction energies Γ_1 and Γ_2 can be calculated from Eqns. (2.20.4) and (2.20.5).

To calculate Γ_3 and Γ_4 , let us transform Eqns. (2.20.6) and (2.20.7) into a convenient form. The angles between l_1 and s_1 and between l_2 and s_2 continuously change. The average values of cosine terms are then given by

$$\langle \cos(l_1^*, s_1^*) \rangle = \cos(l_1^*, L^*) \cos(L^*, S^*) \cos(S^*, s_1^*) \quad \dots(2.20.10)$$

$$\langle \cos(l_2^*, s_2^*) \rangle = \cos(l_2^*, L^*) \cos(L^*, S^*) \cos(S^*, s_2^*) \quad \dots(2.20.11)$$

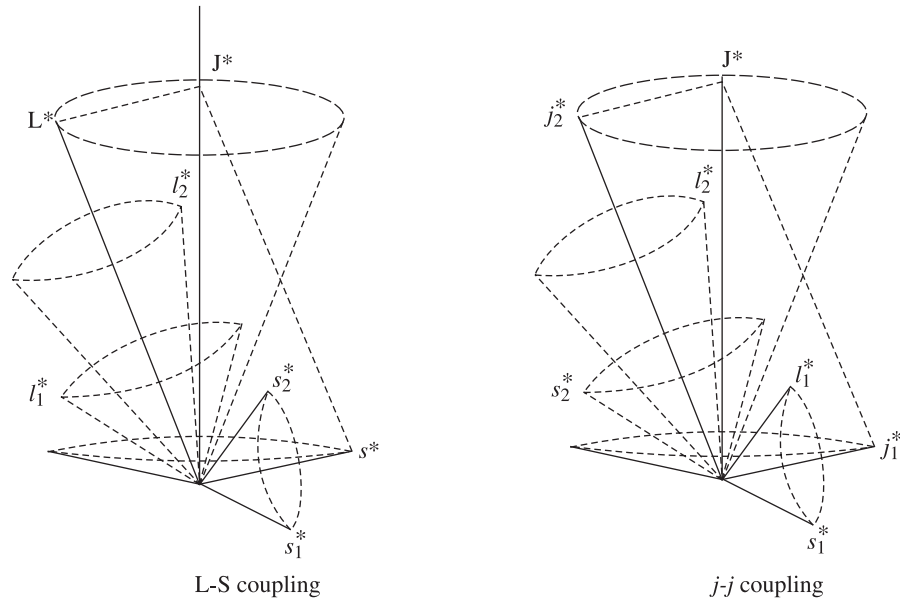


Fig. 2.20.1

$$\begin{aligned} \Gamma_3 &= a_3 l_1^* s_1^* \cos(l_1^*, s_1^*) = a_3 l_1^* s_1^* \cos(l_1^*, L^*) \cos(L^*, S^*) \cos(S^*, s_1^*) \\ &= a_3 l_1^* s_1^* \left(\frac{L^{*2} + l_1^{*2} - l_2^{*2}}{2 l_1^* L^*} \right) \left(\frac{J^{*2} - L^{*2} - S^{*2}}{2 L^* S^*} \right) \left(\frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2 s_1^* S^*} \right) \\ &= \frac{a_3}{8} \left[\left(\frac{L^{*2} + l_1^{*2} - l_2^{*2}}{L^{*2}} \right) \left(\frac{S^{*2} + s_1^{*2} - s_2^{*2}}{S^{*2}} \right) (J^{*2} - L^{*2} - S^{*2}) \right] \end{aligned}$$

Similarly,

$$\begin{aligned}
 \Gamma_4 &= \frac{a_4}{8} \left[\left(\frac{L^{*2} + l_2^{*2} - l_1^{*2}}{L^{*2}} \right) \left(\frac{S^{*2} + s_2^{*2} - s_1^{*2}}{S^{*2}} \right) (J^{*2} - L^{*2} - S^{*2}) \right] \\
 \Gamma_3 + \Gamma_4 &= \frac{1}{2} \left[a_3 \left(\frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}} \right) \left(\frac{L^{*2} + l_1^{*2} - l_2^{*2}}{2L^{*2}} \right) + a_4 \left(\frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}} \right) \left(\frac{L^{*2} + l_2^{*2} - l_1^{*2}}{2L^{*2}} \right) \right] (J^{*2} - L^{*2} - S^{*2}) \\
 &= \frac{1}{2} [a_3 \alpha_3 + a_4 \alpha_4] (J^{*2} - L^{*2} - S^{*2}) \\
 &= \frac{A}{2} (J^{*2} - L^{*2} - S^{*2}) \quad \dots(2.20.12)
 \end{aligned}$$

where

$$A = a_3 \alpha_3 + a_4 \alpha_4 \quad \dots(2.20.13)$$

and

$$\alpha_3 = \left(\frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}} \right) \left(\frac{L^{*2} + l_1^{*2} - l_2^{*2}}{2L^{*2}} \right) \quad \dots(2.20.14)$$

$$\alpha_4 = \left(\frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}} \right) \left(\frac{L^{*2} + l_2^{*2} - l_1^{*2}}{2L^{*2}} \right) \quad \dots(2.20.15)$$

The term value of the state is

$$\begin{aligned}
 T &= T_0 + \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 \\
 &= T_0 + \frac{a_1}{2} (S^{*2} - s_1^{*2} - s_2^{*2}) + \frac{a_2}{2} (L^{*2} - l_1^{*2} - l_2^{*2}) + \frac{A}{2} (J^{*2} - L^{*2} - S^{*2}) \\
 &\quad \dots(2.20.16)
 \end{aligned}$$

where T_0 is the hypothetical (reference) level from which the shift of energy levels are measured.

Heisenberg, on the basis of quantum mechanical analysis, showed that a_1 and a_2 are negative, a_3 and a_4 are positive.

Splitting of *sp* Configuration in L-S Coupling

For this configuration

$$\begin{aligned}
 l_1 &= 0, l_2 = 1, s_1 = 1/2, s_2 = 1/2. \\
 L &= 0 \oplus 1 = 1, \\
 S &= 1/2 \oplus 1/2 = 0, 1, \\
 J &= L \oplus S
 \end{aligned}$$

For singlet state ($S = 0$), $J = 1 \oplus 0 = 1$. $^1P_1$.

For triplet state ($S = 1$), $J = 1 \oplus 1 = 0, 1, 2$. $^3P_{0, 1, 2}$.

(i) For singlet state $S = 0$

Calculation of $\Gamma_1 + \Gamma_2$: ($S = 0, l_1 = 0, l_2 = 1, s_1 = 1/2, s_2 = 1/2$)

$$\begin{aligned}\Gamma_1 &= \frac{a_1}{2} (S^{*2} - s_1^{*2} - s_2^{*2}) \\ &= \frac{a_1}{2} (0.1 - \frac{1}{2} \cdot \frac{3}{2} - \frac{1}{2} \cdot \frac{3}{2}) = -\frac{3a_1}{4}\end{aligned}$$

and

$$\Gamma_2 = \frac{a_2}{2} (L^{*2} - l_1^{*2} - l_2^{*2}) = \frac{a_2}{2} (1.2 - 0.1 - 1.2) = 0$$

It is worth to notice that for any configuration involving s -electron ($l = 0$) the interaction energy Γ_2 always comes out be zero.

General observations show that the singlet level lies above the corresponding triplet level. This indicates that the coefficient a_1 in Γ_1 should be negative. This was also shown by Heisenberg by quantum mechanical calculations. Therefore,

$$\therefore \Gamma_1 + \Gamma_2 = -\frac{3a_1}{4}$$

So the singlet level ($S = 0$) shifts upward by $-\frac{3a_1}{4}$ from the hypothetical reference level T_0 .

This is also supported by Hund's rule: A term with highest multiplicity (hence highest value of S) will lie deepest, and of these the term with largest value of L will lie deepest.

Calculation of $\Gamma_3 + \Gamma_4$: ($S = 0, l_1 = 0, l_2 = 1, s_1 = 1/2, s_2 = 1/2$.)

The coefficients α_3 and α_4 are given by

$$\alpha_3 = \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2S^{*2}} \cdot \frac{L^{*2} + l_1^{*2} - l_2^{*2}}{2L^{*2}}, \quad \alpha_4 = \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2S^{*2}} \cdot \frac{L^{*2} + l_2^{*2} - l_1^{*2}}{2L^{*2}}$$

Obviously, $\alpha_3 = \alpha_4 = 0$

Therefore, for the singlet state $\Gamma_3 + \Gamma_4 = 0$. Hence this state does not split into components due to spin-orbit interaction.

(ii) For triplet state $S = 1$

$$\Gamma_1 = \frac{a_1}{4}, \quad \Gamma_2 = 0. \quad \therefore \Gamma_1 + \Gamma_2 = \frac{a_1}{4}, \quad a_1 \text{ is negative.}$$

The triplet states shift downward by amount $\frac{a_1}{4}$.

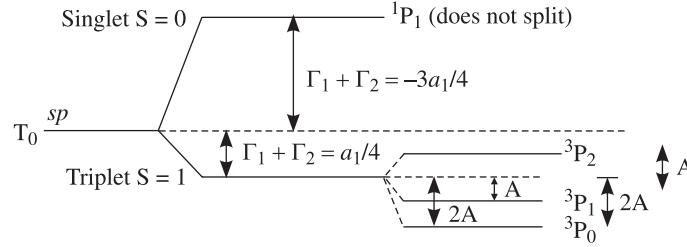


Fig. 2.20.2

Now we shall calculate the splitting of this state due to spin-orbit interaction.

(i) $J = 0, L = 1, S = 1, {}^3P_0$

$$\Gamma_3 + \Gamma_4 = \frac{A}{2} (J^2 - L^2 - S^2) = \frac{A}{2} (0 \cdot 1 - 1 \cdot 2 - 1 \cdot 2) = -2A = -a_4$$

(ii) $J = 1, L = 1, S = 1, {}^3P_1$

$$\Gamma_3 + \Gamma_4 = \frac{A}{2} (J^2 - L^2 - S^2) = \frac{A}{2} (1 \cdot 2 - 1 \cdot 2 - 1 \cdot 2) = -A = -\frac{a_4}{2}$$

(iii) $J = 2, L = 1, S = 1, {}^3P_2$

$$\Gamma_3 + \Gamma_4 = \frac{A}{2} (2 \cdot 3 - 1 \cdot 2 - 1 \cdot 2) = A = \frac{a_4}{2}, \quad a_3 \text{ and } a_4 \text{ are positive.}$$

Splitting of triplet level is shown in Fig. (2.20.2).

2.21 INTERACTION ENERGY IN J-J COUPLING IN ATOM WITH TWO VALENCE ELECTRONS

For j - j coupling the interaction energies are given by

$$\Gamma_1 = a_1 s_1^* s_2^* \cos(s_1^* s_2^*) \quad \dots(2.21.1)$$

$$\Gamma_2 = a_2 l_1^* l_2^* \cos(l_1^* l_2^*) \quad \dots(2.21.2)$$

$$\Gamma_3 = a_3 l_1^* s_1^* \cos(l_1^* s_1^*) \quad \dots(2.21.3)$$

$$\Gamma_4 = a_4 l_2^* s_2^* \cos(l_2^* s_2^*) \quad \dots(2.21.4)$$

$$\Gamma_5 = a_5 l_1^* s_2^* \cos(l_1^* s_2^*) \quad \dots(2.21.5)$$

$$\Gamma_6 = a_6 l_2^* s_1^* \cos(l_2^* s_1^*) \quad \dots(2.21.6)$$

The terms Γ_5 and Γ_6 are negligibly small and will be omitted. In j - j coupling the spin-orbit interaction are much stronger than spin-spin and orbit-orbit interaction and therefore the interaction energies Γ_3 and Γ_4 predominate over the terms Γ_1 and Γ_2 . The angle between l_1 and s_1 and between

l_2 and s_2 are fixed but the angle between s_1 and s_2 and between l_1 and l_2 continuously change. So the average values of the changing angles should be taken.

$$\langle \cos(s_1, s_2) \rangle = \cos(s_1, j_1) \cos(j_1, j_2) \cos(j_2, s_2) \quad \dots(2.21.7)$$

$$\langle \cos(l_1, l_2) \rangle = \cos(l_1, j_1) \cos(j_1, j_2) \cos(j_2, l_2) \quad \dots(2.21.8)$$

Now,

$$\begin{aligned} \Gamma_1 &= a_1 s_1^* s_2^* \left[\frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2s_1^* j_1^*} \cos(j_1^* j_2^*) \frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2s_2^* j_2^*} \right] \\ \Gamma_2 &= a_2 l_1^* l_2^* \left[\frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2l_1^* j_1^*} \cos(j_1^* j_2^*) \frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2l_2^* j_2^*} \right] \\ \Gamma_1 + \Gamma_2 &= \left[a_1 \frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2j_1^*} \frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2j_2^*} + a_2 \frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2j_1^*} \frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2j_2^*} \right] \cos(j_1^* j_2^*) \\ &= \left[a_1 \frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2j_1^{*2}} \frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2j_2^{*2}} + a_2 \frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2j_1^{*2}} \frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2j_2^{*2}} \right] \frac{J^{*2} - j_1^{*2} - j_2^{*2}}{2} \end{aligned}$$

$$\text{or} \quad \Gamma_1 + \Gamma_2 = \frac{B}{2} [J^{*2} - j_1^{*2} - j_2^{*2}] \quad \dots(2.21.9)$$

where

$$B = a_1 \left(\frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2j_1^{*2}} \right) \left(\frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2j_2^{*2}} \right) + a_2 \left(\frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2j_1^{*2}} \right) \left(\frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2j_2^{*2}} \right) \quad \dots(2.21.10)$$

$$\text{or} \quad B = a_1 \beta_1 + a_2 \beta_2 \quad \dots(2.21.11)$$

$$\text{where} \quad \beta_1 = \left(\frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2j_1^{*2}} \right) \left(\frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2j_2^{*2}} \right) \quad \dots(2.21.12)$$

$$\text{and} \quad \beta_2 = \left(\frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2j_1^{*2}} \right) \left(\frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2j_2^{*2}} \right) \quad \dots(2.21.13)$$

The interaction energies Γ_3 and Γ_4 are given by

$$\Gamma_3 = a_3 l_1^* s_1^* \cos(l_1^* s_1^*) = \frac{a_3}{2} (j_1^{*2} - l_1^{*2} - s_1^{*2}) \quad \dots(2.21.14)$$

$$\Gamma_4 = a_4 l_2^* s_2^* \cos(l_2^* s_2^*) = \frac{a_4}{2} (j_2^{*2} - l_2^{*2} - s_2^{*2}) \quad \dots(2.21.15)$$

The total shift is

$$\Delta T = \frac{1}{2} (a_1 \beta_1 + a_2 \beta_2) (J^{*2} - j_1^{*2} - j_2^{*2}) + \frac{a_3}{2} (j_1^{*2} - l_1^{*2} - s_1^{*2}) + \frac{a_4}{2} (j_2^{*2} - l_2^{*2} - s_2^{*2}) \quad \dots(2.21.16)$$

Interaction Energy in sp Configuration (j - j coupling)

$$l_1 = 0, s_1 = 1/2, j_1 = 0 \oplus 1/2 = 1/2.$$

$$l_2 = 1, s_2 = 1/2, j_2 = 1 \oplus 1/2 = 1/2, 3/2.$$

$$J = j_1 \oplus j_2$$

$$(i) J = 1/2 \oplus 1/2 = 0, 1$$

$$(ii) J = 1/2 \oplus 3/2 = 1, 2.$$

The spectral terms are $\left(\frac{1}{2}, \frac{1}{2}\right)_{0,1}$ and $\left(\frac{1}{2}, \frac{3}{2}\right)_{1,2}$

$$\begin{aligned} \text{For } \left(\frac{1}{2}, \frac{1}{2}\right), \quad \Gamma_3 + \Gamma_4 &= \frac{a_3}{2} (j_1^{*2} - l_1^{*2} - s_1^{*2}) + \frac{a_4}{2} (j_2^{*2} - l_2^{*2} - s_2^{*2}) \\ &= \frac{a_3}{2} \left(\frac{1}{2} \cdot \frac{3}{2} - 0 - \frac{1}{2} \cdot \frac{3}{2}\right) + \frac{a_4}{2} \left(\frac{1}{2} \cdot \frac{3}{2} - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2}\right) = -a_4 \end{aligned}$$

$$\text{For } \left(\frac{1}{2}, \frac{3}{2}\right), \quad \Gamma_3 + \Gamma_4 = \frac{a_4}{2}$$

(i) Calculation of $\Gamma_1 + \Gamma_2$ for state $\left(\frac{1}{2}, \frac{1}{2}\right)_0$

$$s_1 = 1/2, s_2 = 1/2, l_1 = 0, l_2 = 1, j_1 = 1/2, j_2 = 1/2, J = 0$$

$$\begin{aligned} \Gamma_1 + \Gamma_2 &= \left[a_1 \frac{j_1^{*2} + s_1^{*2} - l_1^{*2}}{2j_1^{*2}} \frac{j_2^{*2} + s_2^{*2} - l_2^{*2}}{2j_2^{*2}} + a_2 \frac{j_1^{*2} + l_1^{*2} - s_1^{*2}}{2j_1^{*2}} \frac{j_2^{*2} + l_2^{*2} - s_2^{*2}}{2j_2^{*2}} \right] \left(\frac{J^{*2} - j_1^{*2} - j_2^{*2}}{2} \right) \\ &= \frac{a_1}{4} \end{aligned}$$

(ii) Calculation of $\Gamma_1 + \Gamma_2$ for state $\left(\frac{1}{2}, \frac{1}{2}\right)_1$

$$s_1 = 1/2, s_2 = 1/2, l_1 = 0, l_2 = 1, j_1 = 1/2, j_2 = 1/2, J = 1$$

$$\Gamma_1 + \Gamma_2 = -\frac{a_1}{12}, \quad a_1 \text{ is negative}$$

(iii) Calculation of $\Gamma_1 + \Gamma_2$ for state $\left(\frac{1}{2}, \frac{3}{2}\right)_1$

$$s_1 = 1/2, s_2 = 1/2, l_1 = 0, l_2 = 1, j_1 = 1/2, j_2 = 3/2, J = 1$$

$$\Gamma_1 + \Gamma_2 = -\frac{5a_1}{12}, \quad a_1 \text{ is negative.}$$

(iv) Calculation of $\Gamma_1 + \Gamma_2$ for state $\left(\frac{1}{2}, \frac{3}{2}\right)_2$

$$s_1 = 1/2, s_2 = 1/2, l_1 = 0, l_2 = 1, j_1 = 1/2, j_2 = 3/2, J = 2$$

$$\Gamma_1 + \Gamma_2 = \frac{a_1}{4}, \quad a_1 \text{ is negative.}$$

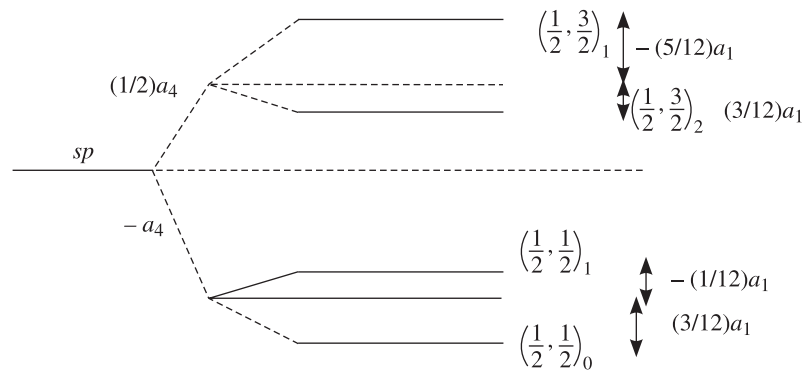


Fig. 2.21.1

2.22 LANDE INTERVAL RULE

Spin-orbit interaction energy is given by

$$\Delta E_{ls} = a \cdot \mathbf{L} \cdot \mathbf{S}, \quad \text{where } a \text{ is a constant.}$$

Now, $\mathbf{L} \cdot \mathbf{S}$ is given by

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} [\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2] = \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \hbar^2$$

Therefore interaction energy becomes

$$\Delta E_{ls} = \frac{a}{2} [J(J+1) - L(L+1) - S(S+1)] \hbar^2 = A [J(J+1) - L(L+1) - S(S+1)]$$

where A is a constant. The fine structure levels are characterized by the same value of L and S but

differ in J values. The energy difference between two fine structure levels corresponding to two values of J viz. J and $J + 1$ is

$$E_{J+1} - E_J = A[(J+1)(J+2) - J(J+1)] = 2A[J+1]$$

This is the mathematical statement of Lande interval rule. It can be stated as follows:

The energy interval (spacing) between two fine structure levels of a multiplet characterized by J and $J + 1$ is proportional to the larger of the two J -values of the levels.

Let us find the ratio of intervals between the fine structure levels $^3P_0$, $^3P_1$, $^3P_2$. The interval between the first pair of levels is proportional to larger J -value 1 and the interval between the last pair of levels is proportional to 2. Thus, the ratio of energy interval is 1 : 2.

Similarly, the ratio of intervals between the levels $^3D_1$, $^3D_2$, $^3D_3$ is 2 : 3 and that between the levels $^4D_{1/2}$, $^4D_{3/2}$, $^4D_{5/2}$, $^4D_{7/2}$ is 3 : 5 : 7.

SOLVED EXAMPLES

Ex. 1. Write down the spectral designations of the terms of the hydrogen atom whose electron is in the state with principal quantum number $n = 3$.

Sol. Hydrogen atom has a single electron. For $n = 3$, $l = 0, 1, 2$ and $s = 1/2$. Therefore

$$L = l = 0, 1, 2.$$

$$S = 1/2,$$

$$J = L \oplus S$$

$$= (0 \oplus 1/2), (1 \oplus 1/2), (2 \oplus 1/2)$$

$$= 1/2, (3/2, 1/2), (5/2, 3/2).$$

$$\text{Multiplicity, } r = 2S + 1 = 2 \text{ (except for } L = 0)$$

$$\text{Spectral terms } ^2S_{1/2}, ^2P_{1/2}, ^2P_{3/2}, ^2D_{3/2}, ^2D_{5/2}.$$

Ex. 2. Write the spectroscopic notation of the following states:

(a) $L = 0$, $S = 0$, $J = 0$ (b) $L = 2$, $S = 0$, $J = 5/2$, (c) $L = 3$, $S = 1/2$, $J = 5/2$, (d) $L = 4$, $S = 1$, $J = 5$.

Sol. (a) $^1S_0$, (b) $^1D_2$, (c) $^2F_{5/2}$ (d) $^3G_5$.

Ex. 3. Find the values of S , L and J in the following states. $^1S_0$, $^3P_2$, $^2D_{3/2}$, $^5F_5$, $^6H_{5/2}$.

Sol.

State	L	$S = (r - 1)/2$	J
$^1S_0$	0	0	0
$^3P_2$	1	1	2
$^2D_{3/2}$	2	1/2	3/2
$^5F_5$	3	2	5
$^6H_{5/2}$	5	5/2	5/2

Ex. 4. Find the allowed values of total angular momenta of electron shells of atom in the states ^4P and ^5D .

Sol.

State	r	$S = (r - 1)/2$	L	$J = L \oplus S$	$ J = \sqrt{J(J+1)}\hbar$
^4P	4	3/2	1	5/2, 3/2, 1/2	$\frac{\sqrt{35}}{2}, \frac{\sqrt{15}}{2}, \frac{\sqrt{3}}{2}$
^5D	5	2	2	4, 3, 2, 1, 0	$\sqrt{20}, \sqrt{12}, \sqrt{6}, \sqrt{2}, 0$

Ex. 5. Write the spectral terms of atoms possessing besides filled shells

(a) two electrons, one in s and the other in p

(b) two electrons one in p and the other in d .

Sol. (a) for s electron $l_1 = 0$, and for p electron $l_2 = 1$.

$L = l_1 \oplus l_2$	$S = s_1 \oplus s_2$	$r = 2S + 1$	$J = L \oplus S$	Spectral Terms
$0 \oplus 1 = 1$	$1/2 \oplus 1/2$ $= 0, 1$	1, 3	$1 \oplus 0 = 1$ $1 \oplus 1 = 2, 1, 0$	$^1P_1$ $^3P_2, ^3P_1, ^3P_0$

(b) For p electron $l_1 = 1$ and for d electron $l_2 = 2$

$$L = 1 \oplus 2 = 1, 2, 3$$

$$S = 1/2 \oplus 1/2 = 0, 1$$

$$J = L \oplus S$$

(i) $J = 1 \oplus 0 = 1, r = 2S + 1 = 1, ^1P_1$

(ii) $J = 2 \oplus 0 = 2, r = 2S + 1 = 1, ^1D_2$

(iii) $J = 3 \oplus 0 = 3, r = 2S + 1 = 1, ^1F_3$

(iv) $J = 1 \oplus 1 = 2, 1, 0, r = 2S + 1 = 3, ^3P_0, ^3P_1, ^3P_2$

(v) $J = 2 \oplus 1 = 3, 2, 1, r = 2S + 1 = 3, ^3D_1, ^3D_2, ^3D_3$

(vi) $J = 3 \oplus 1 = 4, 3, 2, r = 2S + 1 = 3, ^3F_2, ^3F_3, ^3F_4$.

Ex. 6. How many different types of terms can a two electron system consisting of d and f electrons possess?

Sol. For d electron $l_1 = 2$, and that for f electron $l_2 = 3$.

$$L = l_1 \oplus l_2 = 2 \oplus 3 = 5, 4, 3, 2, 1.$$

$$S = s_1 \oplus s_2 = 1/2 \oplus 1/2 = 0, 1$$

$$r = 2S + 1 = 1, 3.$$

$$J = L \oplus S$$

- (i) $J = 5 \oplus 0 = 5$
(ii) $J = 4 \oplus 0 = 4$
(iii) $J = 3 \oplus 0 = 3$
(iv) $J = 2 \oplus 0 = 2$
(v) $J = 1 \oplus 0 = 1$. These are singlet terms.
(vi) $J = 5 \oplus 1 = 6, 5, 4$.
(vii) $J = 4 \oplus 1 = 5, 4, 3$.
(viii) $J = 3 \oplus 1 = 4, 3, 2$.
(ix) $J = 2 \oplus 1 = 3, 2, 1$.
(x) $J = 1 \oplus 1 = 2, 1, 0$.

These are triplet terms.

Ex. 7. What is the ground state of atoms composed of filled sub-shells?

Sol. The z -component of total orbital angular momentum of an atom is given by

$$|L_z| = M_L \hbar$$

where $M_L = \sum m_l$, summation is carried over all electrons. Since the values of m_l lie in the range $-l, (-l+1), \dots, -1, 0, 1, \dots, (l-1), l$,

therefore $\sum m_l = 0$. Thus $|L_z| = 0$. This implies that $L = 0$.

Similarly, the z -component of total spin angular momentum is given by

$$|S_z| = M_S \hbar$$

where $M_S = \sum m_s$. In a closed sub-shell, electron are paired with opposite spins hence $M_S = \sum m_s = 0$. This means that $S = 0$.

Thus, for a closed sub-shell, $L = 0$, $S = 0$ and hence $J = 0$. So, the ground state of the atom is $^1S_0$.

Ex. 8. Obtain $L \cdot S$ in terms of L, S, J . Calculate the possible values of $L \cdot S$ for $L = 1$ and $S = 1/2$.

Sol.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

$$|\mathbf{J}|^2 = (\mathbf{L} + \mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) = |\mathbf{L}|^2 + 2\mathbf{L} \cdot \mathbf{S} + |\mathbf{S}|^2$$

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (|\mathbf{J}|^2 - |\mathbf{L}|^2 - |\mathbf{S}|^2)$$

$$= \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \hbar^2$$

For $L = 1$, $S = 1/2$, $J = L \oplus S = 1 \oplus 1/2 = 3/2, 1/2$.

$$\text{For } J = 3/2, \mathbf{L} \cdot \mathbf{S} = \frac{1}{2} \hbar^2$$

$$\text{For } J = 1/2, \mathbf{L} \cdot \mathbf{S} = -\frac{1}{2} \hbar^2$$

Ex. 9. Find the angle between vectors $\mathbf{l}$ and $\mathbf{s}$ in $^2P_{3/2}$ state of one electron atom.

$$\text{Sol. } \cos \theta = \frac{j^{*2} - l^{*2} - s^{*2}}{2l^{*}s^{*}} = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)s(s+1)}}$$

Given that $l = 1, s = 1/2, j = 3/2$.

$$\cos \theta = \frac{\frac{3}{2} \cdot \frac{5}{2} - 1 \cdot 2 - \frac{1}{2} \cdot \frac{3}{2}}{2\sqrt{1 \cdot 2 \cdot \frac{1}{2} \cdot \frac{3}{2}}} = \frac{1}{\sqrt{6}}$$

Ex. 10. An atom in the state $^2P_{3/2}$ is located in an external magnetic field of 1.0 kg. Find g-factor, difference of energies of adjacent levels after splitting and frequency of Larmor precession.

Sol. For the state $^2P_{3/2}$, $L = 0, S = 1/2, J = 3/2, g = 4/3$. Possible values of M_j are $-3/2, -1/2, 1/2, 3/2$. The level splits into 4 sub-levels. The spacing of adjacent sub-levels is

$$\Delta E = g\mu_B B = \frac{4}{3} \times (0.1 \text{ Wb/m}^2) \mu_B = 0.133\mu_B$$

where

$$\mu_B = 9.27 \times 10^{-24} \text{ J/T.}$$

$$\text{Larmor frequency } \nu_L = \frac{eB}{4\pi m} = \frac{1.6 \times 10^{-19} \text{ C} \times 0.1 \text{ Wb/m}^2}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ kg}} = 1.4 \times 10^9 \text{ Hz.}$$

Ex. 11. Determine the maximum separation of a beam of hydrogen atoms that moves a distance of 20 cm with a speed of $2 \times 10^5 \text{ m/s}$ perpendicular to a magnetic field whose gradient is $2 \times 10^2 \text{ T/m}$. Neglect the magnetic moment of proton.

Sol. For hydrogen atom $s_z = m_s \hbar$.

Resolved part of magnetic moment in the direction of magnetic field

$$\mu_z = -g_s \left(\frac{e}{2m} \right) m_s \hbar = -2 \left(\frac{e\hbar}{2m} \right) m_s = -2\mu_B \left(\frac{1}{2} \right) = -\mu_B$$

$$\begin{aligned} \text{Force on the atom } |F_z| &= \mu_z \frac{dB}{dz} = \mu_B \frac{dB}{dz} = (9.27 \times 10^{-24} \text{ J/T})(2 \times 10^2 \text{ T/m}) \\ &= 1.85 \times 10^{-21} \text{ N} \end{aligned}$$

$$\begin{aligned} \text{Displacement of beam } \Delta z &= \pm \frac{1}{2} a_z t^2 = \pm \frac{1}{2} \left(\frac{F_z}{m} \right) \left(\frac{l}{v} \right)^2 \\ &= \pm \frac{1}{2} \left(\frac{1.85 \times 10^{-21} \text{ N}}{1.67 \times 10^{-27} \text{ kg}} \right) \left(\frac{0.20 \text{ m}}{2 \times 10^5 \text{ m/s}} \right)^2 \\ &= 5.54 \times 10^{-7} \text{ m} \end{aligned}$$

$$\text{Total separation} = 2 \Delta z = 1.11 \times 10^{-6} \text{ m.}$$

Ex. 12. Calculate the magnitudes of orbital, spin and total angular momenta and also the angle between l and s for a p electron in a one-electron atom.

Sol. For p electron $l = 1$, $s = 1/2$.

$$|\vec{l}| = \sqrt{l(l+1)} \hbar = \sqrt{2} \hbar, \quad |s| = \sqrt{s(s+1)} \hbar = \sqrt{\frac{3}{4}} \hbar$$

$$j = l \oplus s = 1 \oplus \frac{1}{2} = \frac{1}{2}, \frac{3}{2}$$

$$|j| = \sqrt{j(j+1)} \hbar = \sqrt{\frac{3}{4}} \hbar, \quad \sqrt{\frac{15}{4}} \hbar$$

Angle between l and s

$$\cos \theta = \frac{|j|^2 - |l|^2 - |s|^2}{2|l||s|} = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)}\sqrt{s(s+1)}}$$

$$\text{For } l = 1, s = 1/2, j = 3/2. \quad \cos \theta = \frac{1}{\sqrt{6}}, \quad \theta = 66^\circ$$

$$\text{For } l = 1, s = 1/2, j = 1/2 \quad \cos \theta = -2\sqrt{\frac{1}{6}}, \quad \theta = 145^\circ.$$

Ex. 13. Calculate the two possible orientations of spin vector of an electron in a magnetic field of 0.5 T. Also calculate the separation of the energy levels.

Sol. Magnitude of spin vector $|s| = \sqrt{s(s+1)} \hbar = \sqrt{\frac{1}{2}(\frac{1}{2}+1)} \hbar = \sqrt{\frac{3}{4}} \hbar$

Projection of s onto the magnetic field

$$s_z = s \cos \theta = \pm \frac{1}{2} \hbar$$

$$\cos \theta = \frac{s_z}{|s|} = \frac{\pm \frac{1}{2} \hbar}{\sqrt{\frac{3}{4}} \hbar} = \pm \frac{1}{\sqrt{3}}, \quad \Rightarrow \quad \theta = 54.7^\circ \quad \text{and} \quad \theta = 125.3^\circ$$

In magnetic field, the energy level of electron is split into two components with separation

$$\Delta E = 2g\mu_B B = 2 \times 2 \times (0.5)\mu_B = 2\mu_B.$$

Ex. 14. Show that for hydrogen atom (or one electron atom) the term separation of spin-orbit doublet is given by

$$\Delta T = 5.84 \frac{Z^4}{n^3 l(l+1)}$$

Sol. The term value of spin-orbit interaction energy is given by

$$\Delta T_{ls} = \frac{-\Delta E_{ls}}{hc} = -\frac{R\alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})(l+1)} [j^{*2} - l^{*2} - s^{*2}]$$

For one electron atom, $s = 1/2$, $j = l \oplus s = l \pm 1/2$.

$$\text{For } j = l + 1/2, \quad j^{*2} - l^{*2} - s^{*2} = l$$

$$\text{For } j = l - 1/2, \quad j^{*2} - l^{*2} - s^{*2} = -(l + 1)$$

$$\therefore [\Delta T_{ls}]_{j=l+1/2} = -\frac{R\alpha^2 Z^4}{2n^3(l+\frac{1}{2})(l+1)}$$

$$\text{And } [\Delta T_{ls}]_{j=l-1/2} = \frac{R\alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})}$$

The separation of the doublet is

$$\delta(\Delta T_{ls}) = \frac{R\alpha^2 Z^4}{n^3 l(l+1)} = 584 \frac{Z^4}{n^3 l(l+1)} \text{ m}^{-1} = 5.84 \frac{Z^4}{n^3 l(l+1)} \text{ cm}^{-1}$$

Thus, the *level splitting* for one electron atom (H and alkali atoms)

- (i) increases with increasing atomic number Z
- (ii) decreases with increasing principal quantum number
- (iii) decreases with increasing l value

The splitting is zero for $l = 0$ (s -state).

Ex. 15. If the doublet splitting of the first excited state, $2^2P_{3/2} - 2^2P_{1/2}$ of He^+ is 5.84 cm^{-1} .

Calculate the corresponding separation for hydrogen atom.

Sol. The term separation (doublet splitting) of a state in one electron atom due to spin-orbit interaction is given by

$$\delta(\Delta T) = \frac{R\alpha^2 Z^4}{n^3 l(l+1)}$$

Since $\delta(\Delta T) \propto Z^4$ we have

$$\frac{\delta(\Delta T)_{\text{H}}}{\delta(\Delta T)_{\text{He}^+}} = \frac{Z_{\text{H}}^4}{Z_{\text{He}^+}^4} = \frac{1}{2^4} \Rightarrow \delta(\Delta T)_{\text{H}} = \frac{\delta(\Delta T)_{\text{He}}}{16} = \frac{5.84}{16} \text{ cm}^{-1} = 0.365 \text{ cm}^{-1}.$$

Ex. 16. Calculate the spin-orbit interaction splitting of a level corresponding to $n = 2$, $l = 1$ of the hydrogen atom.

$$\text{Sol. } \delta(\Delta T) = 5.84 \frac{Z^4}{n^3 l(l+1)} \text{ cm}^{-1} = \frac{5.84 \times 1}{8 \times 1(1+1)} \text{ cm}^{-1} = 0.365 \text{ cm}^{-1}.$$

Ex. 17. Write down the spectral terms of carbon atom in the normal and first excited state. Indicate the allowed transitions.

Sol. In the normal state (${}^6\text{C } 1s^2 2s^2 2p^2$) the carbon atom has two equivalent optical electrons. The spectral terms are ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, ${}^1D_2$, ${}^1S_0$. In the excited ($2p 3s$) the spectral terms are ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, ${}^1P_1$. The allowed transitions are shown in the Fig. E-17.

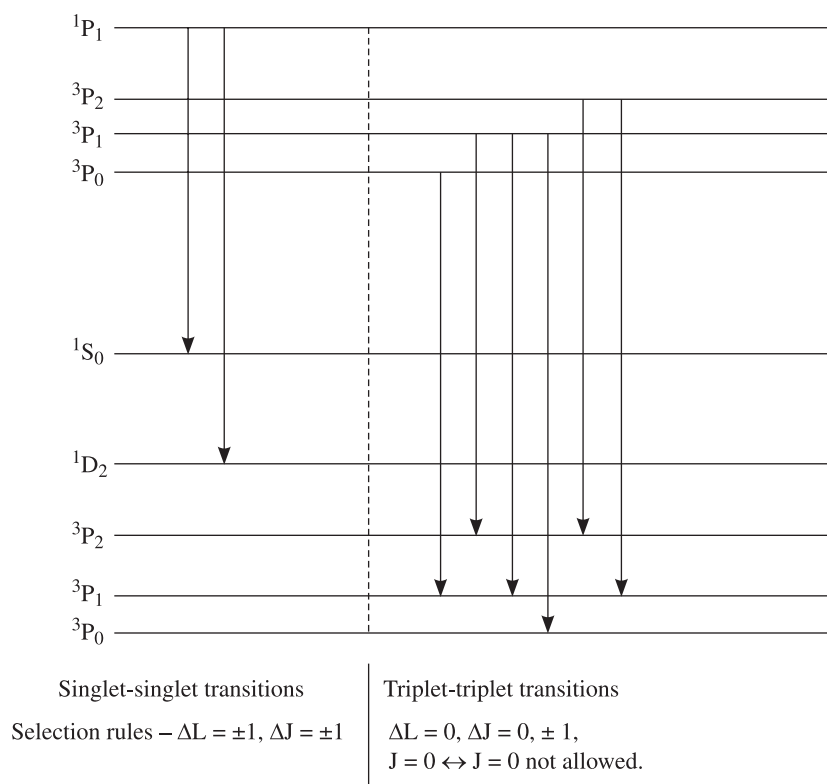


Fig. E-17

Ex. 18. In an atom obeying L - S coupling, the components of a normal triplet state have separations 20 cm^{-1} and 40 cm^{-1} between adjacent components. There is a higher state for which the separations are 22 cm^{-1} and 33 cm^{-1} respectively. Determine the terms for the two states and show with the help of an energy level diagram the allowed transitions and the pattern of the spectrum.

Sol. Calculation of L , S , J for the lower triplet state.

Let the J values of the lower triplet state are J , $J + 1$ and $J + 2$. According to Lande interval rule,

$$\frac{J+1}{J+2} = \frac{20}{40}$$

From this we get $J = 0$. Therefore, the J -values of the lower triplet state are $J = 0, 1, 2$. Now the values of J are given by

$$|L - S|, |L - S| + 1, \dots, (L + S)$$

This implies that $|L - S| = 0$ and $L + S = 2$.

(i) Let $L > S$, then $L - S = 0$ and $L + S = 2$. This gives $L = 1$ and $S = 1$ and multiplicity $r = 2S + 1 = 3$ (triplet). The states are ${}^3P_{0, 1, 2}$.

(ii) Let $S > L$, then $S - L = 0$ and $L + S = 2$. This gives $L = 1$, and $S = 1$.

Calculation of L, S, J for the Higher State

According to Lande rule $\frac{J+1}{J+2} = \frac{22}{33}$. This gives $J = 1$. Therefore, the J-values of the successive states of higher level are $J = 1, 2, 3$.

Since J-values are given by

$$|L - S|, \dots, L + S$$

If $L > S$ then $|L - S| = 1$ and $L + S = 3$. From these equations, we get $L = 2$ and $S = 1$.

The states are ${}^3D_{1, 2, 3}$.

If $S > L$ then $S - L = 1$ and $L + S = 3$. From these equations, we get $S = 2$, and $L = 1$. Given that the higher state is triplet ($S = 1$). So this state does not exist.

Allowed transitions and pattern of spectrum are shown in the Fig. E-18.

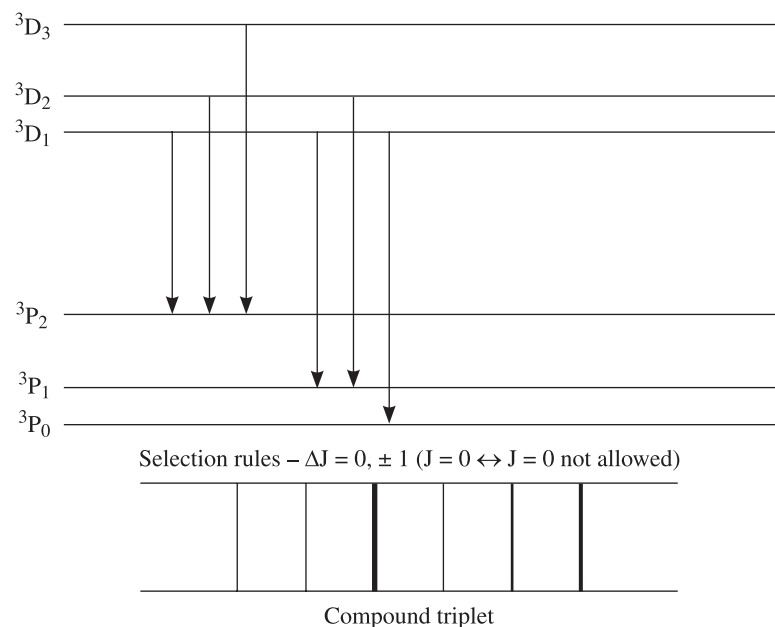


Fig. E-18

Ex. 19. Assuming j - j coupling derive the spectral terms of $4p4d$ configuration.

Sol. For p electron: $l_1 = 1, s_1 = 1/2, j_1 = 1/2, 3/2$.

For d electron: $l_2 = 2, s_2 = 1/2, j_2 = 3/2, 5/2$.

Possible combination of j_1 and j_2 are $(1/2, 3/2), (1/2, 5/2), (3/2, 3/2), (3/2, 5/2)$.

Of these, $(1/2, 3/2)$ lies lowest and $(3/2, 5/2)$ highest. Each of these four levels is further splits by residual electrostatic interaction and spin-spin correlation into a number of J-levels. The J-values of the four levels are given below.

$(1/2, 3/2) \quad J = 1, 2$

$(1/2, 5/2) \quad J = 2, 3$

$(3/2, 3/2) \quad J = 0, 1, 2, 3$

$(3/2, 5/2) \quad J = 1, 2, 3, 4$

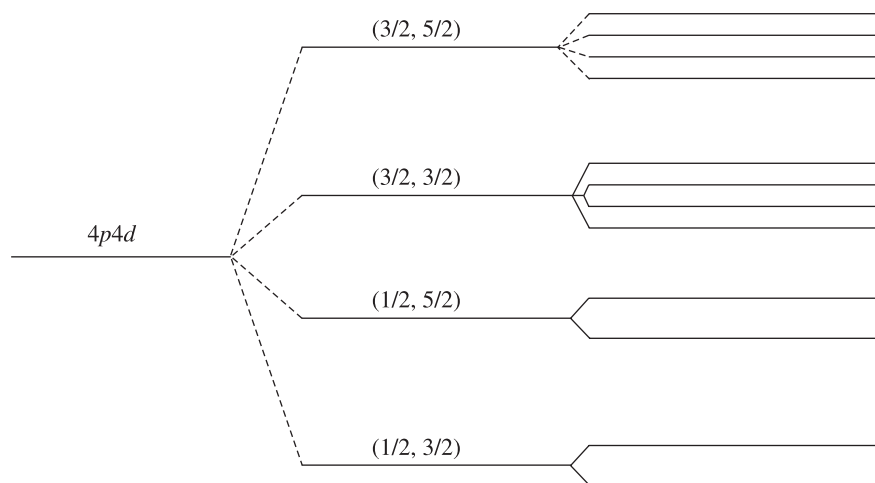


Fig. E-19

Ex. 20. Derive the spectral terms of oxygen atom in normal state.

Sol. $O_8 : 1s^2 2s^2 2p^4$

The terms of p^4 configuration are the same as those of p^2 configuration.

The terms are $^1S_0$, $^1D_2$ and $^3P_{0, 1, 2}$.

According to Hund's rule, the terms of highest multiplicity lie lowest. These are $^3P_{0, 1, 2}$.

Since the valence sub-shell is more than half filled, the terms of the triplet will be **inverted**.

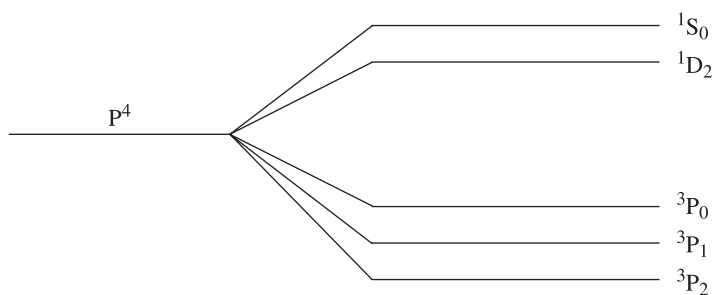


Fig. E-20

QUESTIONS AND PROBLEMS

1. Calculate Lande g -factor for the energy levels $^1S_0$, $^1P_1$, $^2S_{1/2}$, $^2P_{3/2}$.
2. Discuss L-S coupling scheme for a two valence electron system and find the expression for the interaction energy. Show schematically the fine structure for the electron configuration sp .
3. Write the normal electronic configuration of carbon atom and obtain spectral terms arising from it. Also write the first excited configuration of C atom and obtain the resulting spectral terms.

4. Find the angle between l and s vectors in $^2P_{3/2}$, $^2D_{5/2}$ states of one electron system.
5. Find out the different angular momentum states for a $d-s$ electron configuration in L-S and $j-j$ coupling in ground state.
6. The ground state of Cl is $^2P_{3/2}$. Find its magnetic moment.
7. Deduce an expression for the change in energy due to spin-orbit interaction.
Explain that the relative splitting of ^2P level is greater than ^2D level.
8. (a) Explain what is meant by L-S and $j-j$ coupling in atoms having more than one electron.
(b) The quantum numbers of two electrons in a two-valence electron atom are $n_1 = 6$, $l_1 = 3$, $s_1 = 1/2$ and $n_2 = 5$, $l_2 = 1$, $s_2 = 1/2$. Assuming (i) L-S coupling find the possible values of L and J . (ii) $j-j$ coupling find the possible values of J .
9. Calculate the values of l , s , j for d electron of sodium atom. What are the spectroscopic symbols for d electron?
10. Deduce an expression for spin-orbit interaction energy for D lines of sodium atom.
11. Describe the different types of coupling schemes found in the spectra of two valence electron system. Find expressions for their interaction energies.
12. Show that for $p-s$ configuration the total ^3P separation is the same in both L-S and $j-j$ coupling schemes.
13. Deduce the spectral terms for a $3p4p$ configuration in both L-S and $j-j$ couplings. Show that the same number of states is obtained under both coupling schemes.
14. Calculate the spectral terms arising from p^2 configuration in L-S coupling.
15. (a) In a lithium atom the valence electron is in the state $n = 3$. What is the maximum value of angular momentum in this state?
(b) For a p^2 configuration in L-S coupling, $^1S_0$, $^1D_2$, and $^3P_{0,1,2}$ states are obtained. Which one is ground state?
(c) In a certain state, the angular momentum of the atom is $\sqrt{2}\hbar$, spin is 2 and the Lande g -factor is zero. Find the term symbol.
16. Calculate the energy states for p^2 configuration in $j-j$ coupling.
17. (a) In a lithium atom the valence electron is in the state $n = 3$. What is the angular momentum of electron in this state?
[Ans. $\frac{\sqrt{35}}{4\pi}h$]
(b) For a p^2 configuration in L-S coupling, $^1S_0$, $^1D_2$, and $^3P_{0,1,2}$ states are obtained. Which one is the ground state?
(c) Amongst the following transitions, which one is forbidden?
 $^2S_{1/2} \rightarrow ^2P_{1/2}$, $^1S_0 \rightarrow ^1D_2$, $^1P_1 \rightarrow ^1D_2$, $^3S_1 \rightarrow ^3P_0$
[Ans. $^1S_0 \rightarrow ^1D_2$ (Selection rules: $\Delta L = \pm 1$, $\Delta J = 0, \pm 1$)]
(d) In a state the angular momentum of the atom is $\sqrt{2}\hbar$, spin is 2 and Lande's g -factor is zero. Write down the state.
[Ans. $^5F_1$]
18. Calculate the energy states for p^2 configuration in $j-j$ coupling.
19. From a two electron configuration $^3F_4$ state is obtained. What is the magnetic moment of the atom in this state?
[Ans. $\frac{5\sqrt{5}}{2}\mu_B$, $\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T}$]

20. Using Breit scheme derive the spectral terms arising from p^2 configuration in L-S coupling.
21. In sodium atom the first member of principal series consisting of two lines of wavelengths 5890 and 5896 Å arises from $3p \rightarrow 3s$ transition. This happens due to splitting of $3p$ level into two levels $3^2P_{3/2}$ and $3^2P_{1/2}$ due to spin orbit interaction. Find the value of spin orbit coupling coefficient in cm^{-1} .
22. Write out the allowed terms for the atoms possessing, in addition to filled sub-shells, two p electrons with different principal quantum numbers. [Ans. $^1D_2, ^1P_1, ^1S_0, ^3D_1, ^3D_2, ^3D_3, ^3P_0, ^3P_1, ^3P_2, ^3S_1$]
23. D term consists of five components. What are the multiplicities of this term? [Ans. 5, 6, 7...]
24. Find the possible multiplicities of the terms $S_0, P_2, D_{3/2}, F_{1/2}$. [Ans. (1), (3, 5, 7), (2, 4, 6, 8), (6, 8)]
25. Write out the possible terms of atoms with following configurations:
 (i) $2s^2$ (ii) $2p3s$ [Ans. (i) $^1S_0$ (ii) $^1P_1, ^3P_2, ^3P_1, ^3P_0$]
26. What is the minimum possible value of total angular momentum of lithium atom whose valence electron is in a state $n = 3$. Write the symbol of the corresponding state. [Ans. $\frac{\sqrt{35}}{2} \hbar, ^2D_{5/2}$]
27. An atom is in a state whose multiplicity is 4 and has angular momentum $|\mathbf{J}| = \frac{\sqrt{63}}{2} \hbar$. What values can the quantum number L of this state have? [Ans. $L = 2, 3, 4, 5$]
28. Find the Lande g -factor in the following states: $^4D_{1/2}, ^5F_1, ^7H_2$. [Ans. $g = 0$ in all the states]
29. Obtain the magnetic moment of the atom in the following states: $^3S_1, ^1P_0, ^1P_1, ^4D_{1/2}, ^5F_1, ^7H_2$ [Ans. $\sqrt{2}\mu_B, 0, 2\sqrt{2}\mu_B, 0, 0, 0$]
30. Calculate the magnetic moment of hydrogen atom in the ground state. Hint: $L = 0, S = 1/2, J = 1/2, g = 2$. [Ans. $\sqrt{3}\mu_B$]
31. Find μ and the allowed values of the projection of an atom in the state ^1F and $^2D_{3/2}$.
 [Hint: In the first case $L = 3, S = 0, J = 3, g = 1, \mu = 2\sqrt{3}\mu_B$
 In the second case $L = 2, S = 1/2, J = 3/2, g = 4/5, \mu = 2\sqrt{\frac{3}{5}}\mu_B$].
32. Write the spectral terms of atom with (i) $S = 1/2, J = 5/2, g = 6/7$ [Ans. (i) $^2F_{5/2}$ (ii) $^3D_3$]
 (ii) $S = 1, L = 2, g = 4/3$
33. Calculate the Lande g -factor for atom (i) with one valence electron in S, P, D states (ii) with one electron in 3P state (iii) with one electron in S state (iv) in the singlet state.
 [Ans. (i) 2, (2/3, 4/3), (4/5, 6/5) (ii) 0/0 in $^3P_0$ state, 3/2 in $^3P_1$ and $^3P_{3/2}$ state
 (iii) 2 except in the singlet state for which $g = 0/0$ (iv) 1]
34. The valence electron of a sodium atom is in a state with $n = 4$. The values of other quantum numbers of the electron are such that the atom has maximum possible value of the total angular momentum $|\mathbf{J}|$. Determine the magnetic moment of the atom.
 [Hint: $n = 4, l = 0, 1, 2, 3, L_{\max} = 3, S_{\max} = 1/2, J_{\max} = 7/2, g = 8/7$. Hence $\mu = \frac{4\sqrt{63}}{7}\mu_B$].

35. A carbon atom with electronic configuration $1s^2 2s^2 2p 3d$ has maximum possible total angular momentum at such a configuration. What is the magnetic moment of the atom in this state?

[Hint: $L = 1 \oplus 2 = 3, 2, 1$. $S_{\max} = 1$, $L_{\max} = 3$, $J_{\max} = 4$. Hence $\mu = \frac{5\sqrt{5}}{2} \mu_B$]

36. Into how many components will the following terms split in magnetic field? ^1S , ^1P , ^1D , $^2D_{5/2}$.

[Ans. 3, 3, 5, 6]

37. A magnetic field of 1.0 T is switched on an atom in the following states: (i) ^1P (ii) $^2D_{5/2}$. Find the total splitting in electron volt.

[Hint: (i) $J = 1$, $g = 1$. This state splits into three components.

$$\Delta E = 2 g \mu_B B = 1.6 \times 10^{-4} \text{ eV}$$

(ii) $J = 5/2$, $g = 6/5$. This state splits into six components.

$$\Delta E = 5 g \mu_B B = 3.47 \times 10^{-4} \text{ eV}.$$

38. Derive the Russel-Saunders terms for the configuration $2s 2p$.

[Ans. $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$]

39. Derive the spectral terms for the configuration $2p 3p$.

[Ans. ($^3D_3$, $^3D_2$, $^3D_1$), ($^1D_2$), ($^3P_2$, $^3P_1$, $^3P_0$), ($^1P_1$), ($^1S_0$)]

40. The quantum numbers of two electrons in a two valence electron atom are

$$n_1 = 6, l_1 = 3, s_1 = 1/2$$

$$n_2 = 5, l_2 = 1, s_2 = 1/2$$

Find the possible values of J (i) assuming L-S coupling scheme (ii) assuming j - j coupling scheme.

[Hint: (i) $L = 2, 3, 4$. $S = 0, 1$. For $S = 0$, $J = 2, 3, 4$ and for $S = 1$, $J = 1, 2, 3; 2, 3, 4; 3, 4, 5$.

(ii) $j_1 = 5/2, 7/2, j_2 = 1/2, 3/2$.

$$j_1 + j_2 = (2, 3), (3, 4), (1, 2, 3, 4), (2, 3, 4, 5)].$$

41. Write down the electronic configuration of an atom with $Z = 21$. Determine the values of l, s, j, L, S and J for the electron in the ground state.

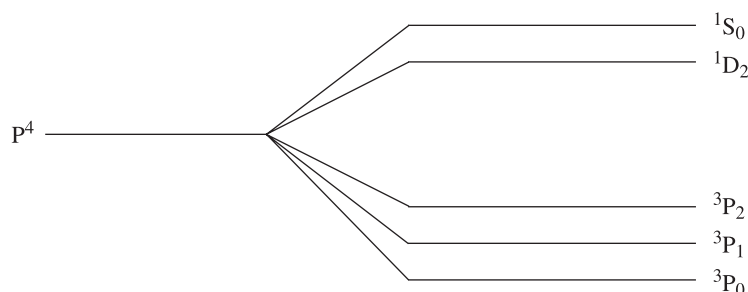
[Hint: $\text{Sc (21)} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

For $3d$ electron $n=3$, $l=2$, $s=\pm 1/2$. Hence $j=2 \pm 1/2 = 5/2, 3/2$.

$$L = l \oplus s = 5/2, 3/2, S = 1/2, J = L \oplus S = 3/2 \oplus 1/2 \text{ and } 5/2 \oplus 1/2]$$

42. Derive the spectral terms of carbon atom in the normal state.

[Hint: The spectral terms are: $^3P_0$, $^3P_1$, $^3P_2$, $^1D_2$, $^1S_0$. Since the outermost sub-shell is less than half filled, the triplet in normal. The terms of maximum multiplicity lie lowest. The ground state is $^3P_0$.]



ATOMIC SPECTRA-III

3.1 SPECTRA OF ALKALI METALS

Like the spectrum of hydrogen atom the emission spectrum of alkali metals consists of discrete lines as shown in the figure. The analysis of spectra requires diligent and patient study of a large mass of wavelength data. Spectroscopists of 19th century were able to isolate four kinds of spectral series in the spectrum of alkali metals. These are: *Principal Series*, *Sharp Series*, *Diffuse Series* and *Fundamental (Bergmann) Series*.

3.2 ENERGY LEVELS OF ALKALI METALS

A comparison of energy levels of an alkali metal with those of hydrogen atom shows that the energy states of former with higher values of l (viz, d and f) are nearly equal to those of their equivalents in hydrogen atom but there are considerable discrepancies at the lower values of l (such as S and P states). This can be seen in the energy level diagram. This discrepancy can be explained by using Gauss's law and radial probability of valence electron by taking sodium as an example.

The electronic configuration of sodium is $[1s^2 2s^2 2p^6]3s^1$. The electric field at the location of valence electron due to nucleus (11 protons) and the remaining 10 electrons in the inner closed sub-shells is given by $E = (1/4\pi\epsilon_0) (q_{eff}/r^2)$ where q_{eff} is the charge inside the Gaussian surface enclosing 11 protons and 10 core electrons. Obviously $q_{eff} = 11e - 10e = +e$. Thus, the valence electron of sodium atom experiences the electric field of effective nuclear charge $+e$. In other words, we can say that 10 electrons of the closed sub-shells screen the 10 protons of nucleus, leaving an effective net charge of $+e$, so $Z_{eff} = 1$. In this model, the ionization potential of sodium would be

$$I = \frac{RchZ_{eff}^2}{n^2} = \frac{(13.6\text{eV}) \times 1}{3^2} = 1.5 \text{ eV}.$$

This value of ionization potential is much lower than the observed value 5.1 eV. In order to remove this large discrepancy and to retain the idea of principal quantum number, a new term, Δ , called **quantum defect**, is introduced in the expression for energy of electron. That is, the concept

of quantum defect is used to explain the increased binding energy of the electron. In terms of quantum defect the energy of valence electron in alkali metals is written as

$$E = -\frac{Rch}{(n-\Delta)^2} = -\frac{Rch}{n_{eff}^2} \quad \text{or} \quad T = \frac{R}{(n-\Delta)^2} = \frac{R}{n_{eff}^2} \quad \dots(3.2.1)$$

The value of Δ depends on the value of l of valence electron and is greatest for s -state ($l = 0$). The quantum defect is a measure of the penetration of electron into the sub-shells of inner electrons. For a given value of n , the value of Δ decreases rapidly with increasing value of l . For this reason the state with larger value of l approaches to the corresponding state of hydrogen. The quantum defect also depends on n but its variation with n is very slow. All these facts can be understood by following arguments.

The variation of radial probability density $P(r)$ of valence electron with distance r from nucleus for electrons with different l is shown in the figure. We see that for $l = n - 1$, the maximum possible value of l , $P(r)$ has one peak, which gives the most probable distance of valence electron from the nucleus. For the electron with $l = n - 2$, $P(r)$ has two peaks, and for the electron with $l = n - 3$, $P(r)$ has three peaks and so on. In sodium atom $P(r)$ has one peak for d electron ($l = 2$), two peaks, for p electron ($l = 1$) and three peaks for s electron ($l = 0$).

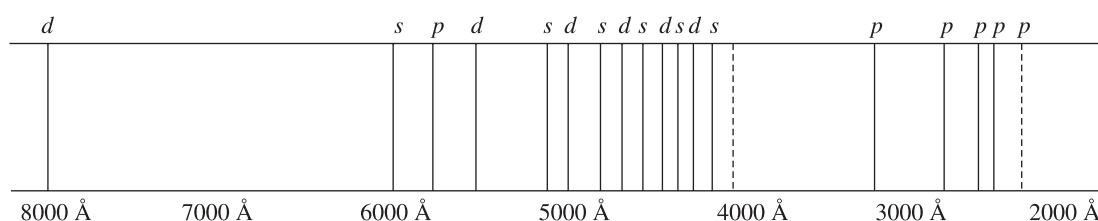


Fig. 3.2.1 Line spectrum of sodium : p principal series, s sharp series, d diffuse series. Dotted line indicates the position of series limit

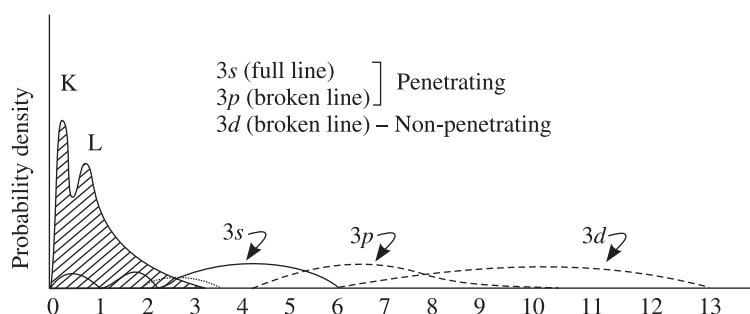


Fig. 3.2.2 Radial probability density of valence electron in sodium atom. The shaded area represents the probability for the ten core electrons. The $3d$ electron spends almost 100% of its time outside the core atom. A $3p$ electron spends less time outside and an s electron even less.

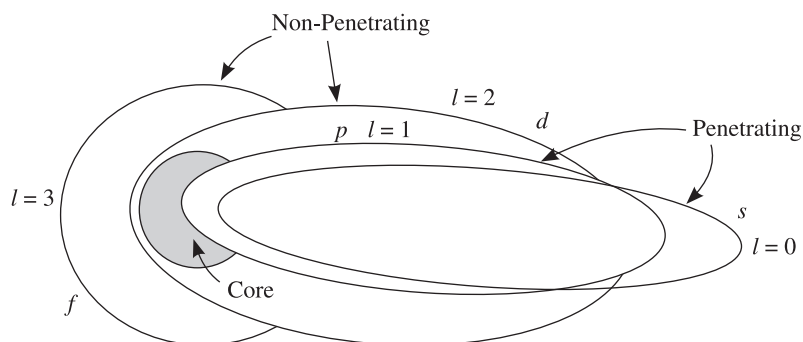


Fig. 3.2.3 Penetrating and non-penetrating orbits of valence electron

Thus, for a given value of n , the smaller the value of l , the valence electron has higher the probability of finding itself closer to the nucleus. That is the probability of penetrating the core of inner electrons is maximum when the valence electron is in s state. The valence electron in p state has less chance of penetrating the inner core of electrons and d electron has lesser chance to do so. In other words, the s electron finds itself most often within the inner electron sub-shells. Therefore s electron is least shielded from nucleus and hence experiences highest effective nuclear charge and is most tightly bound to the nucleus. This makes the energy of s electron most negative *i.e.*, least. For this reason the s state in alkali atom is displaced downward by large amount from its equivalent in hydrogen atom. The p electron spends some of its time within the inner closed sub-shells and is shielded less and its energy is less negative. The d electron spends least of its time inside the core of inner electrons so it is most shielded and hence experiences least effective nuclear charge. This is why as l increases, the downward shift of energy levels relative to their equivalents in hydrogen decreases.

We can arrive at the same conclusion by making use of the classical picture of electron orbits. The s electron moves in most eccentric elliptical orbit and penetrates all the inner orbits and it finds itself most often in the vicinity of the nucleus and hence it is most tightly bound. This causes its energy most negative. The p electron moves in less eccentric elliptical orbit and finds itself less often close to the nucleus. So it is less tightly bound and hence its energy is less negative. The energy of p state is greater than that of s state. The d electron moves in almost circular orbit and it finds itself least often near the nucleus and is least tightly bound. The energy of d electron is least negative *i.e.*, greater than that of p electron.

In the last decade of 19th century Rydberg showed that the wave number ($1/\lambda$) of a spectral line of a spectral series can be written as the difference of two spectral terms, of which one is fixed and the other is variable (running). [A term T and energy E of an atom are mutually related through the relation $T = -E/ch$]. In terms of principal quantum number n of valence electron, the term value is expressed by Eqn.(3.2.1).

Table 3.2.1: The values of quantum defect Δ for sodium atom

State	$n = 3$	$n = 4$	$n = 5$	$n = 6$
S	1.373	1.357	1.352	1.350
P	0.883	0.867	0.862	0.859
D	0.010	0.011	0.013	0.011
F	————	0.000	0.001	0.008

Since the value of Δ depends on the value of l , we shall denote its values by symbols Δ_S , Δ_P , Δ_D , Δ_F respectively.

3.3 SPECTRAL SERIES OF ALKALI ATOMS

The spectral lines of an alkali atom can be classified into four groups: *Principal series*, *sharp series*, *diffuse series* and *fundamental series*.

Principal series: The lines of principal series are observed in emission and absorption both and are the brightest lines in the spectrum. The lines of this series are emitted when the optical electron makes transition from P states to the ground state $3^2S_{1/2}$. The wave numbers of lines of this series are given by

$$\bar{\nu}^P = \frac{R}{(3 - \Delta_s)^2} - \frac{R}{(n - \Delta_p)^2}, \quad n = 3, 4, 5, \dots \quad \dots(3.3.1)$$

The wave number of the series limit is

$$\bar{\nu}_\infty^P = \frac{R}{(3 - \Delta_s)^2} \quad \dots(3.3.2)$$

Therefore
$$\bar{\nu}^P = \bar{\nu}_\infty^P - \frac{R}{(n - \Delta_p)^2}. \quad \dots(3.3.3)$$

Sharp series: The spectral lines of this series are very sharp in physical appearance and hence their name. These lines are emitted when the valence electron makes transition from higher S states to the lowest P state. Their wave numbers are given by

$$\bar{\nu}^S = \frac{R}{(3 - \Delta_p)^2} - \frac{R}{(n - \Delta_s)^2}, \quad n = 4, 5, 6, \dots \quad \dots(3.3.4)$$

$$\bar{\nu}_\infty^S = \frac{R}{(3 - \Delta_p)^2} \quad \dots(3.3.5)$$

$$\bar{\nu}^S = \bar{\nu}_\infty^S - \frac{R}{(n - \Delta_s)^2} \quad \dots(3.3.6)$$

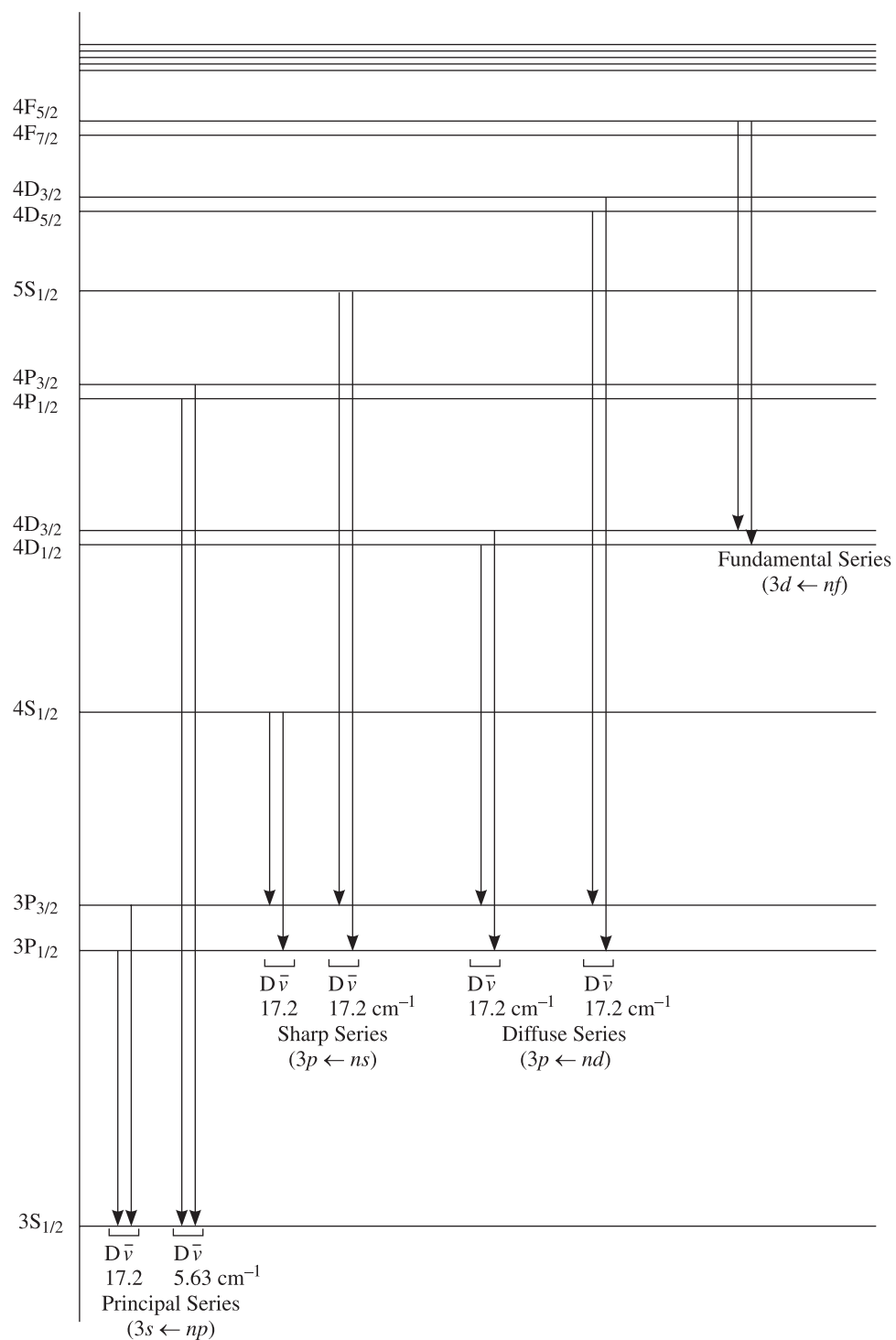


Fig. 3.3.1(a) Spectral series of sodium

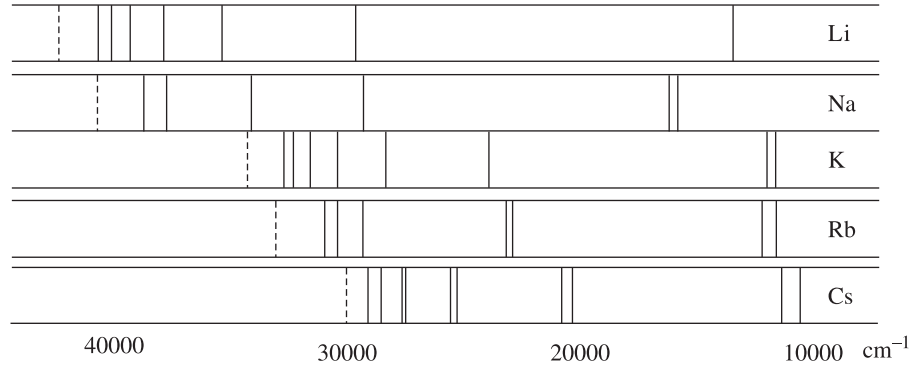


Fig. 3.3.1(b) Principal series doublets in alkali atoms

Diffuse series: The lines of this series are blurred in comparison to the lines of other series. These are emitted when the valence electron undergoes transition from higher D states to 3P states. Their wave numbers are given by

$$\bar{\nu}^d = \frac{R}{(3 - \Delta_p)^2} - \frac{R}{(n - \Delta_d)^2}, \quad n = 3, 4, 5, \dots \quad \dots(3.3.7)$$

$$\bar{\nu}_\infty^d = \frac{R}{(3 - \Delta_p)^2} \quad \dots(3.3.8)$$

$$\bar{\nu}^d = \bar{\nu}_\infty^d - \frac{R}{(n - \Delta_d)^2} \quad \dots(3.3.9)$$

Each line of this series consists of three components but under low resolution it appears as doublet. It is in fact called compound doublet. The weakest component is called satellite.

Fundamental series: The lines of this series are very much like those of hydrogen spectrum and hence called fundamental. The wave numbers of these lines are given by

$$\bar{\nu}^f = \frac{R}{(3 - \Delta_d)^2} - \frac{R}{(n - \Delta_f)^2}, \quad n = 4, 5, 6, \dots \quad \dots(3.3.10)$$

$$\bar{\nu}_\infty^f = \frac{R}{(3 - \Delta_d)^2} \quad \dots(3.3.11)$$

$$\bar{\nu}^f = \bar{\nu}_\infty^f - \frac{R}{(n - \Delta_f)^2} \quad \dots(3.3.12)$$

Selection rules: Out of many possible transitions, only those are allowed which obey the selection rules.

$$\Delta L = \pm 1, \quad \Delta S = 0, \quad \Delta J = 0, \pm 1, \quad (J = 0 \rightarrow J = 0 \text{ is forbidden})$$

3.4 SALIENT FEATURES OF SPECTRA OF ALKALI ATOMS

Some of the important features of alkali spectra are as follows:

- (i) The separation of spectral line of a particular series regularly decreases and ultimately the lines converge.
- (ii) The sharp and diffuse series have a common limit ($\bar{\nu}_{\infty}^s = \bar{\nu}_{\infty}^d = \frac{R}{(3 - \Delta_p)^2}$). This common limit is equal to the first running term of the principal series.
- (iii) The wave number difference between the limit of principal series and the common limit of sharp or diffuse series is equal to the wave number of first line of principal series.

$$\bar{\nu}_{\infty}^p - \bar{\nu}_{\infty}^{s,d} = \bar{\nu}_1^p$$

This is called **Rydberg-Schuster** law.

- (iv) The wave number difference of series limit of diffuse series and fundamental series is equal to the wave number of first line of diffuse series.

$$\bar{\nu}_{\infty}^d - \bar{\nu}_{\infty}^f = \bar{\nu}_1^d$$

This is called Runge's law.

- (v) When the spectra of alkali atoms are examined with instruments of high resolving power, it is found that each line of principal and sharp series of a particular atom consists of a narrow doublet and each line of diffuse series consists of a group of three lines (triplet). For example, the sodium D line, which a member of principal series, is actually a doublet (two closely spaced lines) with wavelength 5890 and 5896 Å. The spectral line is said to have a *fine-structure*. The complex lines consisting of several components are called *multiplets*.
- (vi) On going from Li to Cs, the wave number separation of principal doublet increases.
- (vii) The wave number separation of principal doublets decreases with increasing principal quantum number n .
- (viii) The wave number separation of sharp doublet remains constant ($=17.2 \text{ cm}^{-1}$).
- (ix) The wave number separation of diffuse series doublet remains constant ($=17.2 \text{ cm}^{-1}$).

3.5 ELECTRON SPIN AND FINE STRUCTURE OF SPECTRAL LINES

The concept of electron spin plays fundamental role in determining the state of an atom. The spin is quantum as well as relativistic property of electron. Its theoretical justification came in a natural way from relativistic formulation of Schrodinger wave equation by Dirac. According to this theory electron possesses intrinsic angular momentum s whose magnitude is given by

$$|s| = \sqrt{s(s+1)} \hbar, \quad s = 1/2 \quad \dots(3.5.1)$$

s is called spin quantum number and has value $1/2$. The magnetic moment associated with spin angular momentum is

$$\boldsymbol{\mu} = -g_s \left(\frac{e}{2m} \right) \mathbf{s} \quad \dots(3.5.2)$$

$$|\boldsymbol{\mu}_s| = -g_s \mu_B \frac{|\mathbf{s}|}{\hbar} = -g_s \mu_B \sqrt{s(s+1)} \quad \dots(3.5.3)$$

where g_s is spin g factor and has value $g_s = 2.00230$. Roughly it is taken equal to 2.

Alkali metals have a single electron outside closed sub-shells. The angular momentum of closed sub-shell is zero. So the angular momentum of an alkali atom is due to its single valence electron. The angular momentum of valence electron has two components: *the orbital angular momentum* $\mathbf{L}$ and *spin angular momentum* $\mathbf{S}$. The resultant of these two angular momenta gives the total angular momentum $\mathbf{J}$. The magnitude of $\mathbf{L}$, $\mathbf{S}$ and $\mathbf{J}$ are given by

$$|\mathbf{L}| = \sqrt{L(L+1)}\hbar$$

$$|\mathbf{S}| = \sqrt{S(S+1)}\hbar$$

$$|\mathbf{J}| = \sqrt{J(J+1)}\hbar$$

where $L = l$ = total orbital angular quantum number, $S = s$ = total spin quantum number and J = total angular momentum quantum number, and is given by

$$J = L \oplus S = L + S, L + S - 1, \dots, |L - S|$$

i.e., J can take integrally spaced values. The orbital magnetic moment (μ_L) and spin magnetic moment (μ_S) interact with each other like magnetic dipoles. This interaction is called spin-orbit interaction and the energy of interaction depends on the mutual orientation of the magnetic moments.

The spectral terms of sodium atom in ground and excited states are given below:

Ground state: $3s^1$.

Here $n = 3$, $L = 0$, $S = 1/2$, $J = 1/2$.

Spectral term: $3^2 S_{1/2}$.

Excited states: $3s 3p^1$ $3^2 P_{1/2, 3/2}$

$3s 3d^1$ $3^2 D_{3/2, 5/2}$

$3s 4s^1$ $4^2 S_{1/2}$

$3s 4p^1$ $4^2 P_{1/2, 3/2}$

$3s 4d^1$ $4^2 D_{3/2, 5/2}$

$3s 4f^1$ $4^2 F_{5/2, 7/2}$

In the ground state of alkali atom $L = 0$, $S = 1/2$, $J = 1/2$. The term symbol is $^2S_{1/2}$. The number of J value is one. So the ground state is *singlet i.e.*, it has no fine structure. If the valence electron is excited to p state, then $L = 1$, $S = 1/2$, $J = 1/2, 3/2$. The term symbols are $^2P_{1/2}$, and $^2P_{3/2}$. The spin-orbit interaction splits the P level into two components *i.e.*, P state has doublet structure. In this way, we can show D level splits into two sub-levels $^2D_{3/2}$ and $^2D_{5/2}$, F level splits into two sub-levels $^2F_{5/2}$ and $^2F_{7/2}$. Thus each level, except S , splits into two sub-levels *i.e.*, all the

excited states of alkali atoms have doublet structure. The multiple splitting of D and F terms for sodium is very small and therefore the sub-levels of D and F differing in their J values are shown as coincident lines. As one goes from Li to Cs the multiplet splitting increases.

Fine Structure of Spectral Lines

In alkali metals, due to spin-orbit interaction the s vector of valence electron combines with l vector of the same electron to form a resultant vector j . In one-electron atom vectors s , l and j represent the respective quantities for the atom as a whole hence we represent them by S , L and J . The effect of spin-orbit interaction is to the energy levels and hence the spectral terms into two components (except the S term) one with $J = L + 1/2$ and other with $J = L - 1/2$. The S term does not split, the P term ($L = 1$) splits into $P_{1/2}$ and $P_{3/2}$, D term ($L = 2$) splits into $D_{3/2}$ and $D_{5/2}$, F term ($L = 3$) splits into $F_{5/2}$ and $F_{7/2}$ etc.

Doublet Structure of Principal Series in Sodium

The transitions leading to the emission of first doublet of principal series of sodium viz., the well-known sodium D-lines is shown in the figure. Let $\bar{\nu}_1$ and $\bar{\nu}_2$ are the wave numbers of the lines of a doublet emitted in transitions $3^2S_{1/2} \leftarrow n^2P_{1/2}$ and $3^2S_{1/2} \leftarrow n^2P_{3/2}$ where $n = 3, 4, 5, \dots$

Table 3.5.1: The first doublet separation of the principal series in spectra of alkali metals

<i>Metal</i>	<i>Atomic number</i>	<i>Wave number separation cm⁻¹</i>	$\Delta\lambda$ Å
Li	3	0.34	0.15
Na	11	17.2	6
K	19	58	34
Rb	37	238	147
Cs	55	554	422

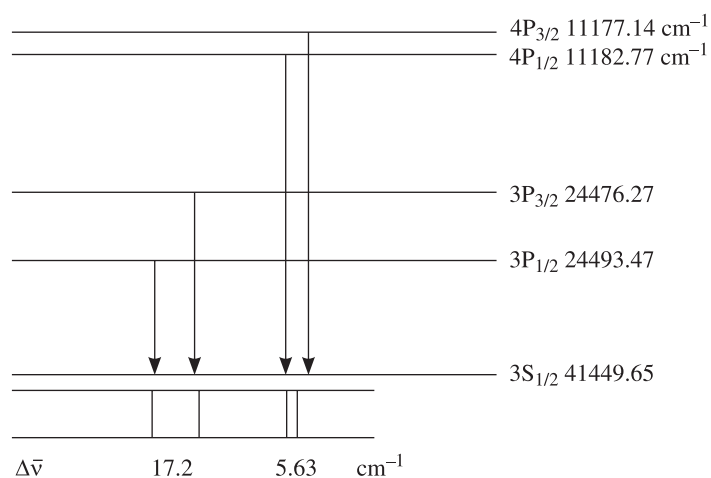


Fig. 3.5.1 Principal series doublets

Sharp series doublet in sodium: The doublets of this series are emitted in the transitions

$$3P_{1/2} \leftarrow nS_{1/2}, \text{ and } 3P_{3/2} \leftarrow nS_{1/2}$$

where $n = 4$ for first doublet, $n = 5$ for second doublet and so on.

Diffuse series doublet: The lines of the first doublet of diffuse series in sodium are emitted in the transitions

$$3P_{1/2} \leftarrow nD_{3/2}, 3P_{3/2} \leftarrow nD_{3/2}, 3P_{3/2} \leftarrow nD_{5/2}$$

where $n = 3, 4, 5, \dots$ (The transition $3P_{1/2} \leftarrow 3D_{5/2}$ is forbidden by selection rule $\Delta J = \pm 1$).

The fine structure of diffuse series consists of three lines instead of two. The transitions leading to these lines in cesium atom are shown below:

$$\begin{aligned} 6\ ^2P_{3/2} &\leftarrow 5\ ^2D_{3/2} & \lambda &= 36127\ \text{\AA} \\ 6\ ^2P_{3/2} &\leftarrow 5\ ^2D_{5/2} & \lambda &= 34892\ \text{\AA} \\ 6\ ^2P_{1/2} &\leftarrow 5\ ^2D_{3/2} & \lambda &= 30100\ \text{\AA} \end{aligned}$$

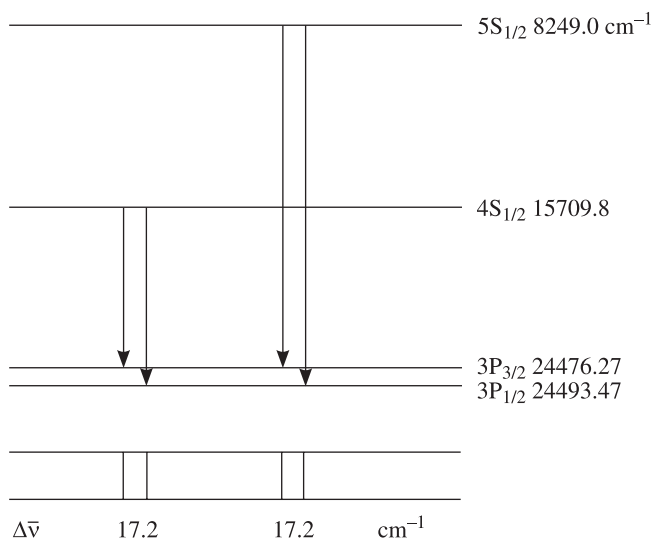


Fig. 3.5.2 First two doublets of sharp series

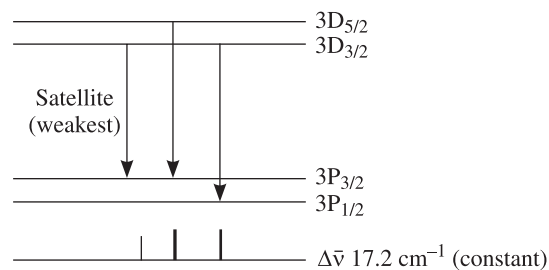


Fig. 3.5.3 Compound doublet of diffuse series

One of the three lines is very weak and is not observed under low resolution. Such a group of lines is called not a triplet but a compound doublet.

Fundamental series doublet: The transitions leading to the origin of compound doublet are shown in the Fig. (3.5.4).

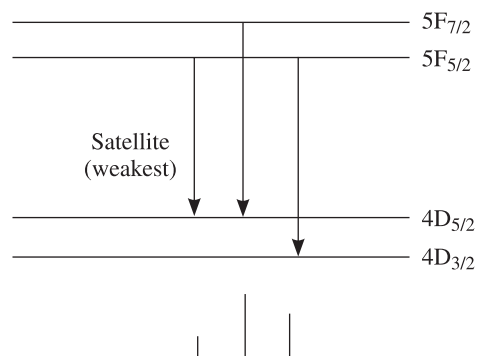


Fig. 3.5.4 First doublet of fundamental series (compound doublet)

It can be seen that the separation $\Delta\bar{\nu}$ of the doublets increases rapidly with increasing atomic number Z . In the following table the approximate separation of the first doublet of principal series of alkali metals are shown:

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
Z	3	11	19	37	55
$\Delta\bar{\nu}$ (cm^{-1})	0.34	17	58	238	554

3.6 INTENSITY OF SPECTRAL LINES

The qualitative idea about the relative intensities of spectral lines can be obtained from the following rules:

1. In any doublet, the spectral line resulting from transition in which L and J both either increase or both decrease (i.e., both change in the same way) is strongest.

If there are more than one line satisfy this condition, the strongest is one which involves largest J value.

A spectral line resulting from the transition in which L and J both change in opposite ways is not allowed. For example, the transition accompanied by $\Delta L = -1$, $\Delta J = +1$ and that with $\Delta L = +1$, $\Delta J = -1$ are not allowed.

Consider the principle series doublet $^2S_{1/2} \leftarrow ^2P_{1/2}$ and $^2S_{1/2} \leftarrow ^2P_{3/2}$. For the first line $\Delta L = -1$, $\Delta J = 0$ and for the second line $\Delta L = -1$, $\Delta J = -1$. For the second line L and J both decrease hence it stronger than the first line.

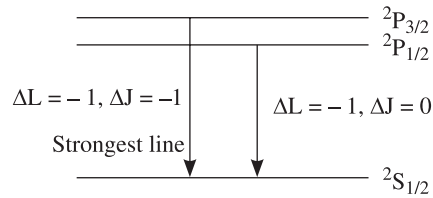


Fig. 3.6.1

Consider the diffuse series compound doublet.

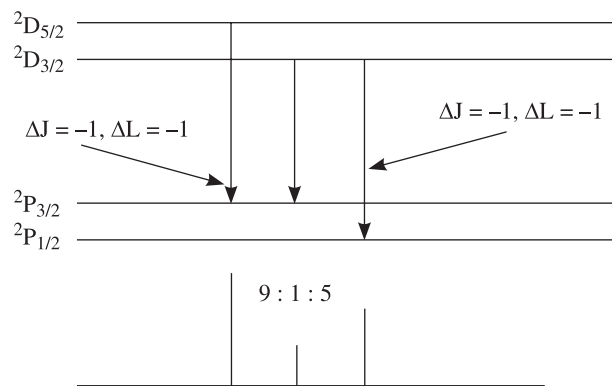


Fig. 3.6.2 The line arising from transition $D_{5/2} \rightarrow P_{3/2}$ involves largest J and hence is strongest

2. The relative intensities of lines of a compound doublet may be calculated from the **Burger-Dorgello-Ornstein sum rule**.
 - (i) The sum of the intensities of all the lines of a multiplet, which arise from the transition originating from same initial state is proportional to the statistical weight $2J + 1$ of the initial state.
 - (ii) The sum of the intensities of all the lines of a multiplet, which arise from the transition ending on same final state is proportional to the statistical weight $2J + 1$ of the final state.

Now consider the compound doublet of diffuse series.

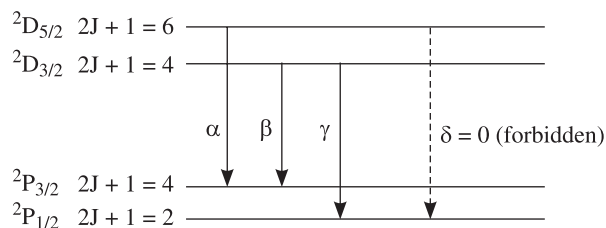


Fig. 3.6.3

Let α , β , γ , and δ denote the intensities of the lines as shown in the Fig. (3.6.3). The intensity of forbidden line $\delta = 0$. In the following table the spectral terms with their statistical weights are shown.

	${}^2P_{3/2} [4]$	${}^2P_{1/2} [2]$
${}^2D_{5/2} [6]$	α	$\delta = 0$
${}^2D_{3/2} [4]$	β	γ

Now, $\alpha + \delta$ is the sum of intensities of lines with the same initial state ${}^2D_{5/2} [2J + 1 = 6]$. Similarly, $\beta + \gamma$ is the sum of intensities of lines with the same initial state ${}^2D_{3/2} [2J + 1 = 4]$. Therefore,

$$\frac{\alpha + \delta}{\beta + \gamma} = \frac{6}{4} \Rightarrow \frac{\alpha}{\beta + \gamma} = \frac{3}{2} \quad \dots(i)$$

$\alpha + \beta$ is the sum of intensities of lines with the same final state ${}^2P_{3/2} [2J + 1 = 4]$ and $\delta + \gamma$ is the sum of intensities of lines with the same final state ${}^2P_{1/2} [2J + 1 = 2]$. Therefore,

$$\frac{\alpha + \beta}{\delta + \gamma} = \frac{4}{2} \Rightarrow \frac{\alpha + \beta}{\gamma} = \frac{2}{1} \quad \dots(ii)$$

From Eqns. (i) and (ii), we have $\alpha = 9\beta$ and $\gamma = 5\beta$. Hence

$$\alpha : \beta : \gamma = 9 : 1 : 5$$

Consider the compound doublet of fundamental series. The possible transitions are shown in the Fig. (3.6.4).

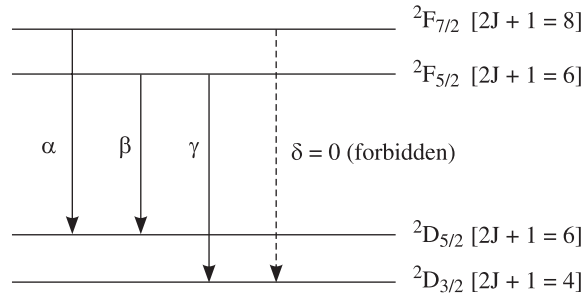


Fig. 3.6.4

According to the intensity rule,

$$\frac{\alpha + \delta}{\beta + \gamma} = \frac{8}{6} \Rightarrow \frac{\alpha}{\beta + \gamma} = \frac{4}{3} \quad \dots(i)$$

$$\frac{\alpha + \beta}{\delta + \gamma} = \frac{6}{4} \Rightarrow \frac{\alpha + \beta}{\gamma} = \frac{3}{2} \quad \dots(ii)$$

From Eqns. (i) and (ii), $\alpha = 20\beta$, $\gamma = 14\beta$.

$$\alpha : \beta : \gamma = 20 : 1 : 14.$$

SOLVED EXAMPLES

Ex. 1. If the valence electron in sodium is excited to the 4^2D state, what are the different routes open for electron in returning to the normal state?

Sol. Subject to the selection rules $\Delta L = \pm 1$, the following are the possible routes for electronic transitions.

1. $4^2D \rightarrow 4^2P \rightarrow 3^2D \rightarrow 3^2P \rightarrow 3^2S$
2. $4^2D \rightarrow 4^2P \rightarrow 3^2S$
3. $4^2D \rightarrow 3^2P \rightarrow 3^2S$
4. $4^2D \rightarrow 4^2P \rightarrow 4^2S \rightarrow 3^2P \rightarrow 3^2S$.

Ex. 2. Obtain an expression for the doublet separation caused by spin orbit interaction in alkali atoms. Interpret the results so obtained.

Sol. In alkali atoms the splitting of levels and hence the splitting of spectral lines due to spin orbit interaction is more important than that due to relativistic effects. All the energy levels of optical electron except $l = 0$ (s -state) are split into two components. One level corresponds to $J = l + 1/2$ and the other to $J = l - 1/2$. The change in term value due to spin orbit interaction is

$$\Delta T_{ls} = -\frac{\Delta E_{ls}}{hc} = -\frac{1}{2} R\alpha^2 Z^4 \frac{[j(j+1) - l(l+1) - s(s+1)]}{n^3 l(l + \frac{1}{2})(l+1)}, \quad l \neq 0$$

For one electron atom, $s = 1/2$, $j = l \oplus s = l \oplus 1/2 = l + 1/2$ and $l - 1/2$. Therefore,

$$\Delta T'_{ls} = -\frac{\Delta E_{ls, j=l+1/2}}{hc} = -\frac{1}{2} R\alpha^2 Z^4 \frac{1}{n^3 l(l + \frac{1}{2})(l+1)} l$$

and

$$\Delta T''_{ls} = -\frac{\Delta E_{ls, j=l-1/2}}{hc} = \frac{1}{2} R\alpha^2 Z^4 \frac{1}{n^3 l(l + \frac{1}{2})(l+1)} (l+1)$$

Doublet separation

$$\delta T_{ls} = \Delta T''_{ls} - \Delta T'_{ls} = \frac{R\alpha^2 Z^4}{n^3 l(l+1)} = 584 \frac{Z^4}{n^3 l(l+1)} m^{-1}.$$

Thus, the doublet separation is (i) proportional to Z^4 (ii) inversely proportional to n^3 . With increasing value of l , the doublet separation decreases.

Ex. 3. Show that the doublet separation in sharp series of alkali atoms is constant.

Sol. Wave numbers of the lines of n th doublet of sharp series are:

$$\bar{\nu}_1 = T_2(nP_{1/2}) - T_1(3S_{1/2}), \quad \bar{\nu}_2 = T_2(nP_{3/2}) - T_1(3S_{1/2})$$

Wave number separation of sharp series doublet

$$\Delta \bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 = T_2(3P_{3/2}) - T_2(3P_{1/2}) = \text{independent of } n = \text{constant}.$$

Ex. 4. The principal and sharp series for Li atom converge to continuum at 43487 and 28583 cm^{-1} respectively. Calculate the quantum defect for the common term in each series.

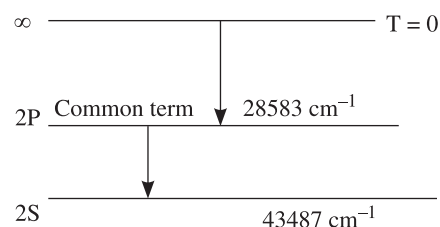
($R = 109729 \text{ cm}^{-1}$)

Sol. For common term $T = 28583 \text{ cm}^{-1}$.

$$\text{Now } T = \frac{R}{(n - \Delta)^2}$$

$$\therefore n - \Delta = \sqrt{\frac{R}{T}} = \sqrt{\frac{109729}{28583}} = \sqrt{3.83896} = 1.9593$$

$$\Delta = n - 1.9593 = 2 - 1.9593 = 0.0407.$$



Ex. 5. The effective quantum number for the ground state of rubidium is 1.805 . Determine the ionization potential of the atom. $R = 109737 \text{ cm}^{-1}$.

$$\text{Sol. } T = \frac{R}{n_{\text{eff}}^2} = \frac{109737}{(1.805)^2} = 33682 \text{ cm}^{-1} = \frac{33682}{8065} \text{ eV} = 4.176 \text{ eV} \quad (1 \text{ eV} = 8065 \text{ cm}^{-1}).$$

Ex. 6. The ionization potential of hydrogen is 2.5 times the ionization potential of sodium. Calculate the effective atomic number of sodium.

$$\text{Sol. Energy of atom } E = -\frac{RZ_{\text{eff}}^2}{n^2}$$

Ionization potential I is equal to $|E|$. Therefore,

$$\frac{I_{\text{Na}}}{I_{\text{H}}} = \left(\frac{Z_{\text{eff}}^2}{n^2} \right)_{\text{Na}} \left(\frac{n^2}{Z_{\text{eff}}^2} \right)_{\text{H}} = \frac{(Z_{\text{eff}}^2)_{\text{Na}}}{3^2} \cdot \frac{1}{1}$$

$$\frac{1}{2.5} = \frac{(Z_{\text{eff}}^2)_{\text{Na}}}{9} \Rightarrow (Z_{\text{eff}})_{\text{Na}} = \sqrt{3.6} = 1.89.$$

Ex. 7. The first member of principal series of sodium has a wavelength of 5890 Å . The first excited S -state of sodium lies 3.18 eV above the ground state. Find the wavelength of the first member of sharp series.

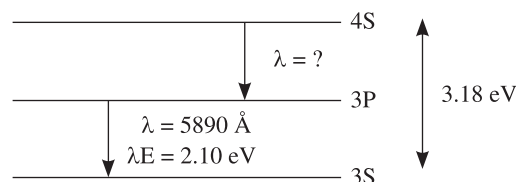
$$\text{Sol. The separation of } 3S \text{ and } 3P \text{ levels } \Delta E = \frac{hc}{\lambda} = \frac{12400 \text{ eV} \cdot \text{Å}}{5890 \text{ Å}} = 2.10 \text{ eV}$$

Separation of $4S$ and $3P$ level

$$\Delta E = 3.18 - 2.10 = 1.08 \text{ eV}$$

Wavelength of the first line of sharp series

$$\lambda = \frac{hc}{\Delta E} = \frac{12400 \text{ eV} \cdot \text{Å}}{1.08 \text{ eV}} = 11481 \text{ Å}.$$



Ex. 8. Calculate the doublet separation of the 3p state of sodium atom. The wavelengths of the principal series doublet are $\lambda_1 = 5890 \text{ \AA}$ and $\lambda_2 = 5896 \text{ \AA}$.

$$\text{Sol. } \bar{\nu} = \frac{1}{\lambda} \Rightarrow |\Delta\bar{\nu}| = \frac{\Delta\lambda}{\lambda^2} = \frac{\Delta\lambda}{\lambda_1\lambda_2} = \frac{6\text{ \AA}}{5890\text{ \AA} \times 5896\text{ \AA}} = 1.73 \times 10^{-7} \frac{1}{\text{\AA}}$$

$$\Delta\bar{\nu} = \frac{1.73 \times 10^{-7}}{10^{-8} \text{ cm}} = 17.3 \text{ cm}^{-1}$$

Separation of corresponding energy levels in wave number units is

$$\Delta E = hc\Delta\bar{\nu} = 6.63 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1} \times 1730 \text{ m}^{-1} = 3.43 \times 10^{-22} \text{ J}$$

$$\Delta E = 2.14 \times 10^{-3} \text{ eV.}$$

Ex. 9. The sodium yellow line $5893\text{ \AA}$ arises from the transition $3p \rightarrow 3s$. The p-level is split by spin orbit interaction into two components separated by $2.1 \times 10^{-3} \text{ eV}$. Evaluate the wavelength separation between the two components of the yellow line.

$$\text{Sol. } \Delta\bar{\nu} = \Delta T = 2.1 \times 10^{-3} \text{ eV} = \left(2.1 \times 10^{-3} \text{ eV}\right) \left(8065 \frac{\text{cm}}{\text{eV}}\right) = 16.9 \text{ cm}^{-1}$$

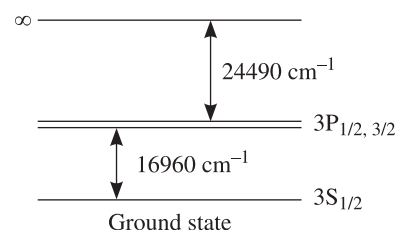
$$\text{Now } \Delta\bar{\nu} = \frac{\Delta\lambda}{\lambda^2} \therefore \Delta\lambda = \lambda^2 \Delta\bar{\nu} = (5893 \times 10^{-8} \text{ m})^2 (16.9 \text{ cm}^{-1}) = 5.87 \times 10^{-8} \text{ cm.}$$

Ex. 10. The mean position of the levels giving the first pair of principal series of sodium atom is 16960 cm^{-1} . The convergence limit of sharp series is 24490 cm^{-1} . Calculate the ionization potential of sodium atom.

Sol. Ionization energy of sodium atom

$$I = (16960 + 24490) \text{ cm}^{-1} = 41450 \text{ cm}^{-1}$$

$$= \frac{41450}{8065} \text{ eV} = 5.1395 \text{ eV.}$$

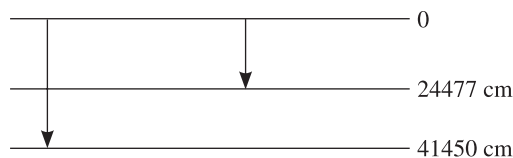


Ex. 11. The principal and sharp series for sodium atom converge to continuum at 41450 and 24477 cm^{-1} respectively. Calculate the ionization potential of sodium atom.

Sol. Ionization energy

$$I = 41450 \text{ cm}^{-1}$$

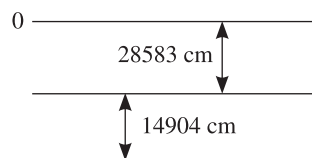
$$= \frac{41450}{8065} \text{ eV} = 5.139 \text{ eV.}$$



Ex. 12. The mean position of first pair of lines of the principal series of Li is 14904 cm^{-1} . If the convergence limit of the sharp series is at 28583 cm^{-1} , calculate the ionization potential of Li.

Sol. Ionization energy

$$I = (14904 + 28583) \text{ cm}^{-1} = 43487 \text{ cm}^{-1} \\ = 5.39 \text{ eV.}$$



Ex. 13. Calculate the quantum defect for 3p configuration of sodium. The term value for this state is 24477 cm^{-1} . ($R = 109734 \text{ cm}^{-1}$).

Sol. $T = \frac{RZ_{eff}^2}{n_{eff}^2} = \frac{RZ_{eff}^2}{(n - \Delta)^2}, Z_{eff} = 1, n = 3$

$$n - \Delta = \sqrt{\frac{R}{T}} = \sqrt{\frac{109734}{24477}} = 2.117$$

$$\Delta = 3 - 2.117 = 0.883.$$

Ex. 14. If the doublet splitting of the first excited state 2^2P state in an atom with $Z = 2$ is 5.84 cm^{-1} . Calculate the corresponding separation in hydrogen atom.

Sol. $\delta(\Delta T) \propto Z^4$

$$\frac{\delta(\Delta T)_{Z=2}}{\delta(\Delta T)_{Z=1}} = \frac{Z_2^4}{Z_1^4} \Rightarrow \frac{5.84}{\delta(\Delta T)} = \frac{2^4}{1^4} \Rightarrow \delta(\Delta T) = 0.365 \text{ cm}^{-1}.$$

3.7 SPECTRA OF ALKALINE EARTHS

The elements of Group II of periodic table viz., Be, Mg, Ca, Sr, Cd, Ba, Hg are called alkaline earths. The atoms of these elements have two valence electrons outside a closed shell. The helium atom also has two electrons in its outermost shell. Hence, the spectra of alkaline earths resemble with that of helium atom. The spectrum of an element of the group II consists of two systems—*singlet* and *triplet*, and each system can be grouped into four kinds of series, sharp, principal, diffuse and fundamental. The valence electrons determine the entire optical properties of these elements. When one or both electrons go to higher energy levels, the atom is said to be in excited state. It is found that the chief series of spectral lines result from the electronic transitions in which *only one of the valence electrons is involved*, the other electron remains in the ground state. When both electrons are excited and participate in electronic transitions, the resulting spectrum is complex in nature.

An alkaline earth atom has two valence electrons and hence there are two orbital angular momenta I_1 and I_2 and two spin angular momenta s_1 and s_2 . These angular momenta can combine in two ways: (i) L-S coupling and (ii) j-j coupling. In light atoms electrostatic interaction (electron-electron repulsion) and spin-spin exchange interaction predominate over the spin-orbit interaction. As a consequence of this, vectors I_1 and I_2 combine to form a resultant L . Similarly, vectors s_1 and s_2

combine to form a resultant **S**. Next, the spin orbit interaction causes the vectors **L** and **S** to combine to form a resultant **J**. These couplings may be summarized as follows:

$$\mathbf{l}_1 + \mathbf{l}_2 = \mathbf{L} \quad (\text{electrostatic interaction})$$

$$|\mathbf{l}_1| = \sqrt{l_1(l_1 + 1)}\hbar, \quad |\mathbf{l}_2| = \sqrt{l_2(l_2 + 1)}\hbar, \quad l_1, l_2 = 0, 1, 2, 3, \dots$$

$$|\mathbf{L}| = \sqrt{L(L + 1)}\hbar, \quad L = l_1 \oplus l_2 = |l_1 - l_2|, \dots, (l_1 + l_2)$$

$$\mathbf{s}_1 + \mathbf{s}_2 = \mathbf{S} \quad (\text{exchange interaction})$$

$$|\mathbf{s}_1| = \sqrt{s_1(s_1 + 1)}\hbar, \quad |\mathbf{s}_2| = \sqrt{s_2(s_2 + 1)}\hbar, \quad s_1 = 1/2, \quad s_2 = 1/2$$

$$|\mathbf{S}| = \sqrt{S(S + 1)}\hbar, \quad S = s_1 \oplus s_2 = 1/2 \oplus 1/2 = 0, 1$$

$$\mathbf{L} + \mathbf{S} = \mathbf{J}, \quad |\mathbf{J}| = \sqrt{J(J + 1)}\hbar, \quad J = L \oplus S = |L - S| \dots \text{integrally spaced values} \\ \dots L + S.$$

Explanation of Essential Features of Spectra of Alkaline-Earths

In an alkaline earth atom there are two valence electrons and hence there are four angular momenta $\mathbf{l}_1, \mathbf{l}_2, \mathbf{s}_1$ and $\mathbf{s}_2$, which may couple in two ways to form their resultant.

(i) L-S Coupling (ii) j-j Coupling

In light atoms, the electron-electron electrostatic interaction and spin-spin correlation predominate over the weak spin-orbit interaction. Owing to strong electrostatic interaction, the orbital angular momenta $\mathbf{l}_1$ and $\mathbf{l}_2$ couple to form their resultant **L**. Similarly, spin angular momenta $\mathbf{s}_1$ and $\mathbf{s}_2$ couple to form their resultant **S**. Then the spin-orbit interaction causes the vectors **L** and **S** to couple to form their resultant **J**. The magnitudes of the various angular momenta are determined by their respective quantum numbers. This type of coupling may be summarized as follows:

$$\mathbf{l}_1 + \mathbf{l}_2 = \mathbf{L}, \quad \mathbf{s}_1 + \mathbf{s}_2 = \mathbf{S}, \quad \mathbf{L} + \mathbf{S} = \mathbf{J}$$

$$|\mathbf{l}_1| = \sqrt{l_1(l_1 + 1)}\hbar, |\mathbf{l}_2| = \sqrt{l_2(l_2 + 1)}\hbar, |\mathbf{L}| = \sqrt{L(L + 1)}\hbar, |\mathbf{S}| = \sqrt{S(S + 1)}\hbar$$

$$|\mathbf{J}| = \sqrt{J(J + 1)}\hbar$$

Where

$$L = l_1 \oplus l_2, S = s_1 \oplus s_2, J = L \oplus S$$

The spin-orbit interaction splits each level characterized by L-value into a number of components (**fine structure**) each characterized by J-value. The group of fine structure levels constitutes a **multiplet**.

Ground state: In the normal state (ns^2) of alkaline earths both electrons have the same orbital quantum numbers as well as the same spin quantum numbers ($l_1 = 0, l_2 = 0, s_1 = 1/2, s_2 = 1/2$). If both electrons have parallel spins ($\uparrow\uparrow$), then all the four quantum numbers will be identical. This state is not allowed by Pauli's exclusion principle. Thus, the state in which valence electrons with parallel spin that leads to $S = 1$, is not permitted. Consequently the state $^3S_1$ does not exist. Therefore, the ground state of alkaline earth atom is one in which the valence electrons have opposite spins ($\uparrow\downarrow$). In this state $L = 0, S = 0, J = L \oplus S = 0$. This state is singlet and is designated as $^1S_0$.

Excited states: Assuming that only one electron is promoted to higher energy state, the term symbol and their multiplet nature of excited states can be deduced as explained in the following table.

Thus, we see that the spectral terms of elements of group II of periodic table consists of singlet and triplet energy states corresponding to one value of J and three values of J respectively for each value of L. The singlet and triplet energy states of calcium are shown in the Fig. (3.7.1a).

	l_1	l_2	L	s_1	s_2	S	J	Symbol
ss	0	0	0	$1/2 \uparrow$	$1/2 \uparrow$	1	1	$^3S_1$ does not exist
ss	0	0	0	$1/2 \uparrow$	$1/2 \downarrow$	0	0	$^1S_0$
sp	0	1	1	$1/2 \uparrow$	$1/2 \uparrow$	1	2, 1, 0	$^3P_{0, 1, 2}$
sp	0	1	1	$1/2 \uparrow$	$1/2 \downarrow$	0	1	$^1P_1$
sd	0	2	2	$1/2 \uparrow$	$1/2 \uparrow$	1	3, 2, 1	$^3D_{1, 2, 3}$
sd	0	2	2	$1/2 \uparrow$	$1/2 \downarrow$	0	2	$^1D_2$
sf	0	3	3	$1/2 \uparrow$	$1/2 \uparrow$	1	4, 3, 2	$^3F_{2, 3, 4}$
sf	0	3	3	$1/2 \uparrow$	$1/2 \downarrow$	0	3	$^1F_3$

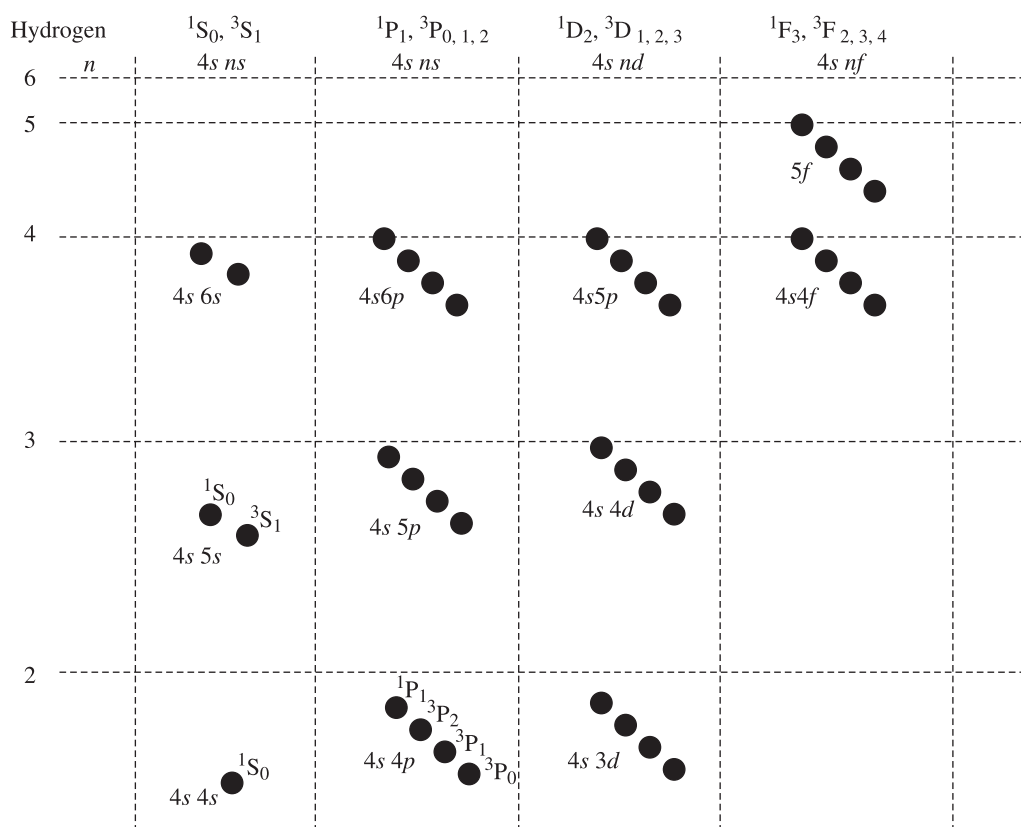
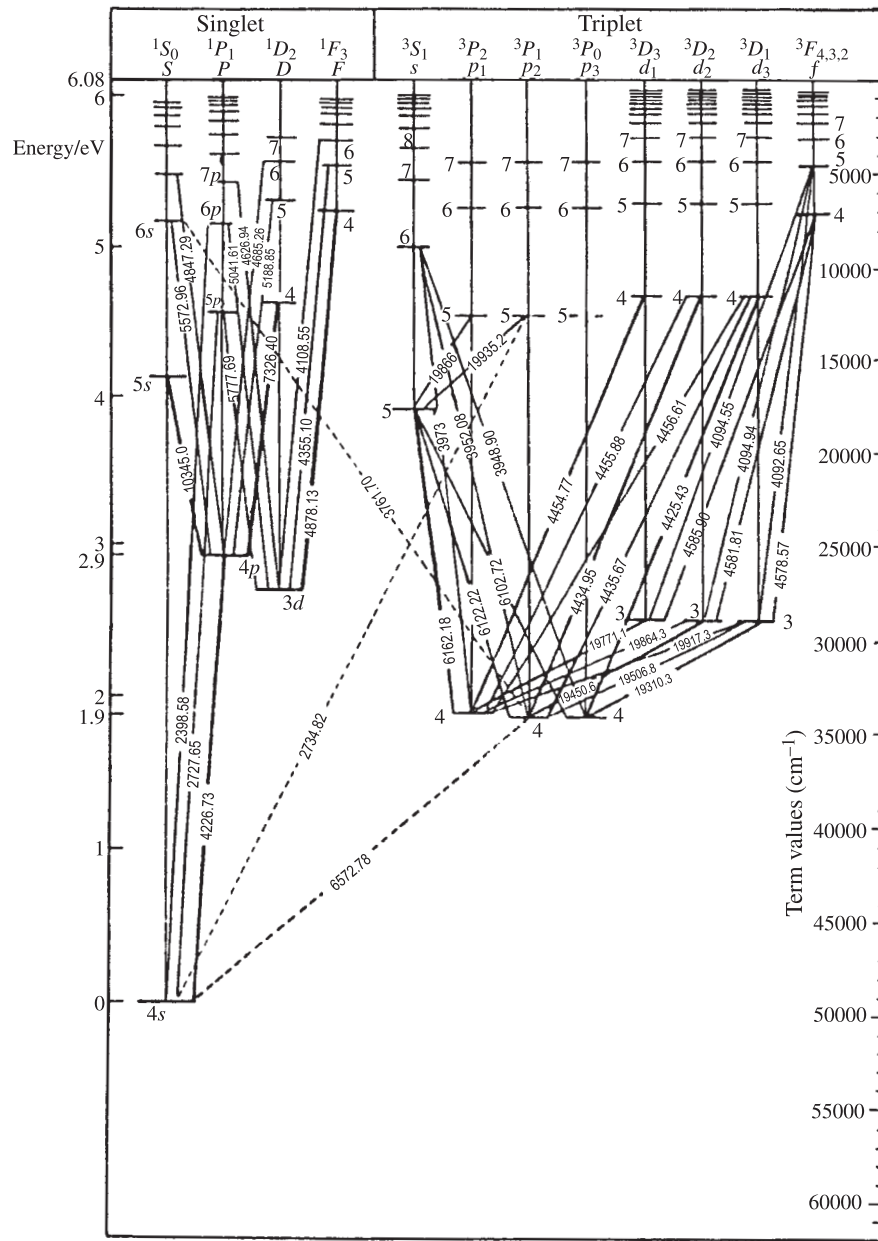


Fig. 3.7.1(a) Energy level diagram of calcium



Emission Spectrum of Ca Atom

Ca
(20) $1s^2$ $2s^2p^6$ $3s^2p^6$ $4s^2$

Fig. 3.7.1 (b)

Chief Series Resulting from Transitions Between Singlet Levels

The allowed transitions between the singlet levels give rise to chief series of spectral lines. No splitting of spectral lines occurs in these transitions.

Principal series: In calcium, the spectral lines of this series originate from the transitions $4s\ 4s \leftarrow 4s\ np$, $n = 4, 5, \dots$ that is, from n^1P levels to the ground state $^1S_0$.

Sharp series: The lines of this series are emitted from electronic transitions $4s\ 4p \leftarrow 4s\ ns$, $n = 5, 6, \dots$ that is, from ^1S levels to the lowest ^1P level.

Singlet sharp and singlet diffuse series have a common convergence limit.

$$\bar{\nu}_{\infty}^s = \bar{\nu}_{\infty}^d$$

Diffuse series: The lines of this series appear in electronic transitions $4s\ 4p \leftarrow 4s\ nd$, $n = 4, 5, \dots$ that is, from ^1D levels to the lowest ^1P level.

Fundamental Series: The electronic transitions $4s\ 3d \leftarrow 4s\ nf$, $n = 4, 5, \dots$ that is, from ^1F levels to the lowest ^1D level give rise to the lines of this series.

The wave numbers difference between the common limit of singlet sharp and diffuse series and the limit of singlet principal series is equal to the wave number of the first line of principal series. This is also observed in triplet series.

$$\bar{\nu}_{\infty}^s \text{ (or } \bar{\nu}_{\infty}^d) \sim \bar{\nu}_{\infty}^p = \bar{\nu}_1^p \quad (\text{in singlet and triplet both})$$

This result is called *Rydberg-Schuster law*.

The wave number difference between the common limit of singlet sharp and diffuse series and the limit of singlet fundamental series is equal to the wave number of the first line of diffuse series. This is also found in triplet series.

$$\bar{\nu}_{\infty}^s \text{ (or } \bar{\nu}_{\infty}^d) - \bar{\nu}_{\infty}^f = \bar{\nu}_1^f \quad (\text{in singlet and triplet both})$$

This result is known as *Runge's law*.

Chief Series Resulting from Transitions between Triplet Levels

Principal series: Lines of this series are emitted from the transitions from ^3P levels to the lowest ^3S level. Each line of this series consists of three components with decreasing separation. The lines approach a single series limit.

Sharp series: The transitions from ^3S levels to the lowest ^3P levels give rise to the lines of sharp series. The lines of this series also consist of three components but with constant separation. The triplet of principal and sharp series are called simple triplet. The triplet sharp and triplet diffuse have a common limit.

Diffuse and fundamental series: The diffuse series originates from transitions from ^3D levels to lowest ^3P level and fundamental series from transitions from ^3F to the lowest ^3D level. The lines of both series have six components — three strong and three satellites. The multiplet of lines is called compound triplet.

The intervals between $^3P_{0,1,2}$ states are greater than those of the $^3D_{1,2,3}$ states. Similarly, $^3D_{1,2,3}$ intervals are greater than those of $^3F_{2,3,4}$. These intervals obey the Lande interval rule. The order of these levels is regular (normal) that is, the energy of a level increases with increasing J

value. According to Lande interval rule, the intervals ${}^3P_2 - {}^3P_1$ and ${}^3P_1 - {}^3P_0$ are in the ratio 2 : 1. The intervals ${}^3D_3 - {}^3D_2$ and ${}^3D_2 - {}^3D_1$ are in the ratio 3 : 2.

Those components of the triplet fine structure are more intense for which L and J change in the same way and of these, the one involving larger value of J is strongest.

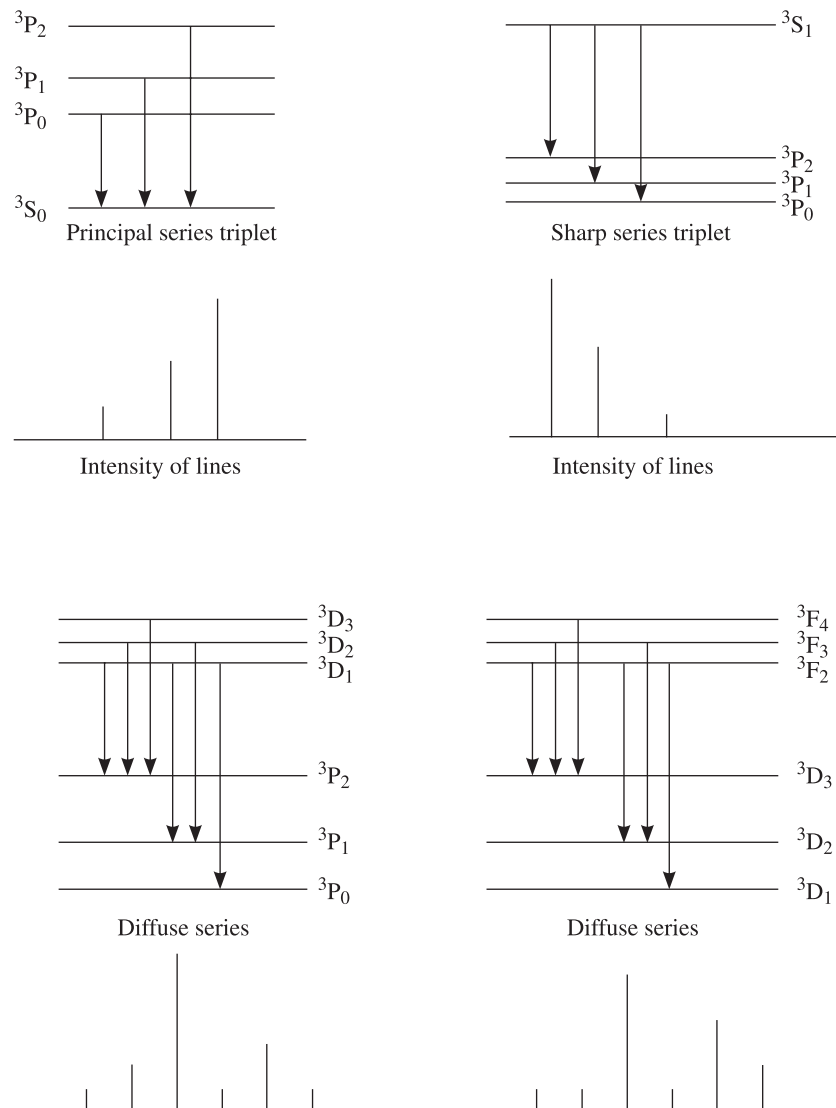


Fig. 3.7.2

3.8 TRANSITIONS BETWEEN TRIPLET ENERGY STATES

Series	Number of components	Transitions
Sharp	3	$4^3P_2 \leftarrow n^3S_1$ $4^3P_1 \leftarrow n^3S_1$ $4^3P_0 \leftarrow n^3S_1$
Principal	3	$5^3S_1 \leftarrow n^3P_2$ $5^3S_1 \leftarrow n^3P_1$ $5^3S_1 \leftarrow n^3P_0$
Diffuse	6	$4^3P_2 \leftarrow n^3D_3$ $4^3P_2 \leftarrow n^3D_2$ $4^3P_2 \leftarrow n^3D_1$ $4^3P_1 \leftarrow n^3D_2$ $4^3P_1 \leftarrow n^3D_1$ $4^3P_0 \leftarrow n^3D_1$
Fundamental	3	$3^3D_3 \leftarrow n^3F_{4,3,2}$ $3^3D_2 \leftarrow n^3F_{4,3,2}$ $3^3D_1 \leftarrow n^3F_{4,3,2}$

The allowed transitions amongst the triplet levels also produce the four chief series—sharp, principal, diffuse and fundamental. The transitions leading to these series and the number of components of each line are given in the table.

These transitions obey the selection rules:

$$\Delta S = 0, \Delta L = 0, \pm 1, \Delta J = 0, \pm 1, \quad (0 \rightarrow 0 \text{ excluded})$$

There is no restriction on the change in value of n .

In some cases transitions between singlet and triplet levels are also observed. These lines are called *inter-combination lines*.

3.9 INTENSITY RULES

The lines resulting from the transitions, in which changes in L and J are in the same sense, are stronger. Among these, the transition involving by largest values of L and J gives rise to the strongest line.

3.10 THE GREAT CALCIUM TRIADS

Calcium, strontium and barium emit three prominent groups of lines which do not belong to the chief series of singlet and triplets. These three groups of lines are called the great calcium triads. In calcium, these lines arise from the transitions which start from the three triplet terms $^3P_{0,1,2}$,

$^3D_{1,2,3}$ and $^3F_{2,3,4}$ and end to the triplet term $^3D_{1,2,3}$. The upper levels arise when both electrons are excited, one to $4p$ and the other to $3d$ level. The lower terms arise from the state $4s\ 3d$.

Each spectral line of the triad consists of three strong lines and three or four faint lines. The spectral lines of the triads are shown in the Figure 3.10.1.

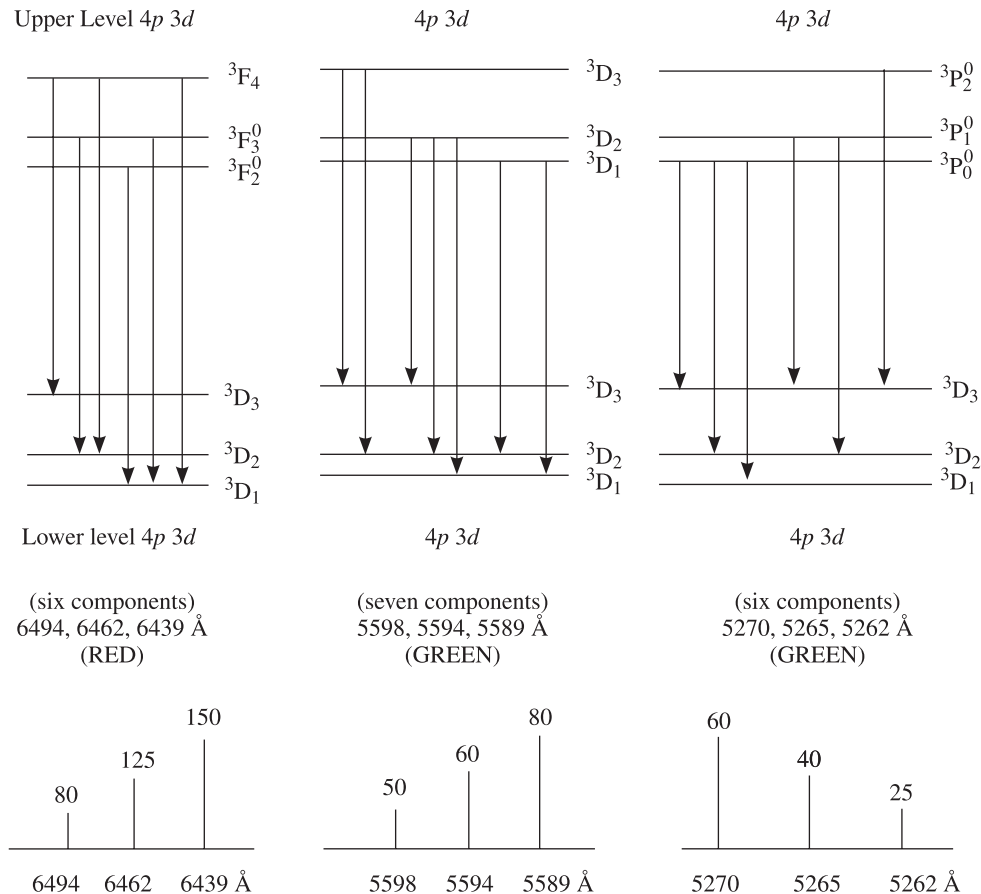


Fig. 3.10.1 The great triads of calcium

3.11 SPECTRUM OF HELIUM ATOM

Helium atom has two electrons in first shell. In many respects its spectrum resembles with that of an alkaline earth metal. Assuming L-S coupling to be in operation, we will first write the ground state of helium atom. In the normal state, the atom has configuration $1s\ 1s$. The helium atom whose both the electrons have opposite spins ($\uparrow\downarrow$) has total spin quantum number $S = s_1 \oplus s_2 = 0$ and is called *parahelium*. In the ground state ($1s\ 1s$) of *parahelium*, $l_1 = 0$, $l_2 = 0$, $L = 0$, $s_1 = 1/2$ ($\uparrow$), $s_2 = 1/2$ ($\downarrow$), $S = 0$, $J = L \oplus S = 0$. Its term symbol is 1^1S_0 (singlet). The term symbols for excited state of *parahelium* can be deduced as follows:

Configuration	l_1	l_2	L	s_1	s_2	S	J	Symbol
$1s\ 2s$	0	0	0	$1/2\ \uparrow$	$1/2\ \downarrow$	0	0	$2\ ^1S_0$
$1s\ 2p$	0	1	1	$1/2\ \uparrow$	$1/2\ \downarrow$	0	1	$2\ ^1P_1$
$1s\ 3s$	0	0	0	$1/2\ \uparrow$	$1/2\ \downarrow$	0	0	$3\ ^1S_0$
$1s\ 3p$	0	1	1	$1/2\ \uparrow$	$1/2\ \downarrow$	0	1	$3\ ^1P_1$
$1s\ 3d$	0	2	2	$1/2\ \uparrow$	$1/2\ \downarrow$	0	2	$3\ ^1D_2$
$1s\ 4s$	0	0	0	$1/2\ \uparrow$	$1/2\ \downarrow$	0	0	$4\ ^1S_0$

So the states of parahelium are singlets *i.e.*, J has only one value for each value of L .

The state $1s\ 1s$ of helium atom in which the two electrons have parallel spins ($\uparrow\uparrow$) has total spin quantum number $S = 1$ and is called *orthohelium*. In this configuration all the four quantum numbers of both the electrons are identical, which violates the Pauli's exclusion principle. This state, which has $L = 0$, $S = 1$, $J = 1$, $r = 3$, is designated by $^3S_1$. Pauli's principle forbids the existence of this state ($^3S_1$). Therefore, the lowest state $1s1s$ of *orthohelium* does not exist. Its first excited state is $1s\ 2s$.

The spectral terms of excited states of *orthohelium* can be deduced as explained below.

Configuration	l_1	l_2	L	s_1	s_2	S	J	Symbol
$1s\ 2s$	0	0	0	$1/2\uparrow$	$1/2\uparrow$	1	1	$2\ ^3S_1$ (lowest excited state)
$1s\ 2p$	0	1	1	$1/2\uparrow$	$1/2\uparrow$	1	0, 1, 2	$2\ ^3P_0, 2\ ^3P_1, 2\ ^3P_2$
$1s\ 3s$	0	0	0	$1/2\uparrow$	$1/2\uparrow$	1	1	$3\ ^3S_1$
$1s\ 3p$	0	1	1	$1/2\uparrow$	$1/2\uparrow$	1	0, 1, 2	$3\ ^3P_0, 3\ ^3P_1, 3\ ^3P_2$
$1s\ 3d$	0	2	2	$1/2\uparrow$	$1/2\uparrow$	1	1, 2, 3	$3\ ^3D_1, 3\ ^3D_2, 3\ ^3D_3$

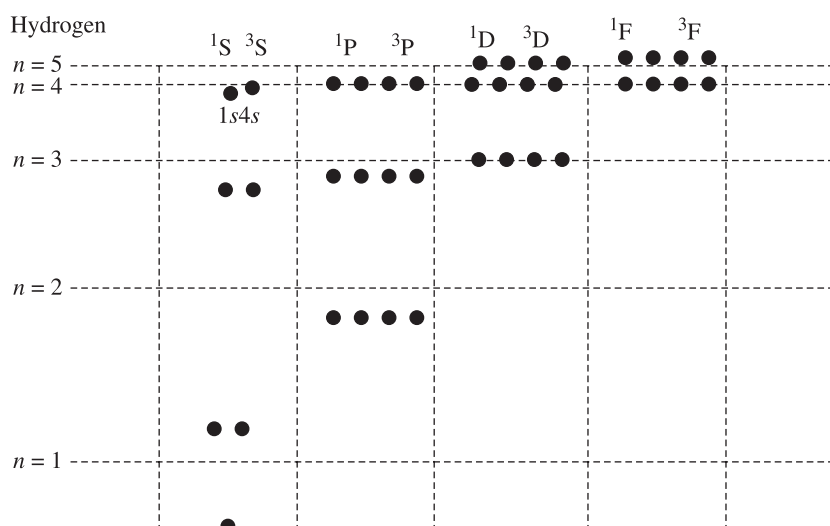


Fig. 3.11.1 Energy levels of helium atom

The excited states of *orthohelium* are triplet. Thus, the energy states of helium divide into singlet (*parahelium*) and triplet (*orthohelium*) states. *Parahelium* has additional energy level corresponding to the configuration $1s\ 1s$. The corresponding level does not exist in *orthohelium*.

The four chief series (sharp, principal, diffuse and fundamental) are observed in both singlet and triplet systems. Both the principal series in the two systems lie in visible and near and far ultraviolet regions. In *parahelium* the principal series arises as a result of transitions from higher P states to the ground state.

The energy level diagram and the transitions obeying selection rules

$$\begin{aligned}\Delta L &= 0, \pm 1, & \Delta S &= 0, \\ \Delta J &= 0, \pm 1 \quad (0 \rightarrow 0 \text{ excluded})\end{aligned}$$

are depicted in the figure. Because of selection rule $\Delta S = 0$, no transitions between singlet states and triplet states can occur and hence no inter-combination lines are observed in helium spectrum. The helium spectrum results from the transitions taking place in one set or the other.

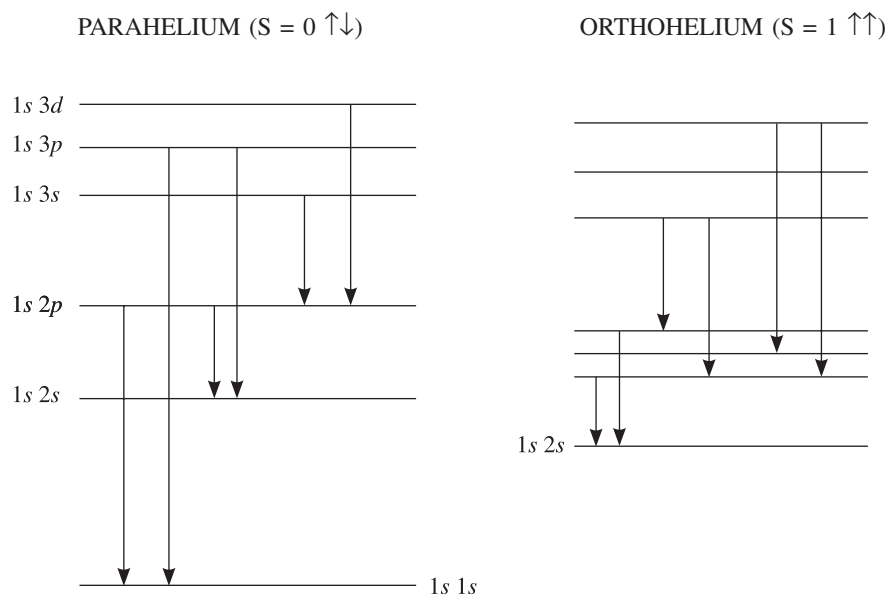


Fig. 3.11.2 Spectrum of helium atom

The ΔS rule forbids the triplet states ($S = 1$) from decaying to the ground state ($S = 0$). These transitions can thus only occur by violating these selection rules and since that is a very unlikely event, these transitions occur with very low probability. Energy levels that have a low probability of decay must live for a long time before they decay. Such states are known as *metastable states*.

An orthohelium atom ($\uparrow\uparrow$) can lose its excitation energy by collision to become a parahelium atom and a parahelium ($\uparrow\downarrow$) atom can be excited by collision to become an orthohelium atom. Ordinary helium is mixture of the two forms.

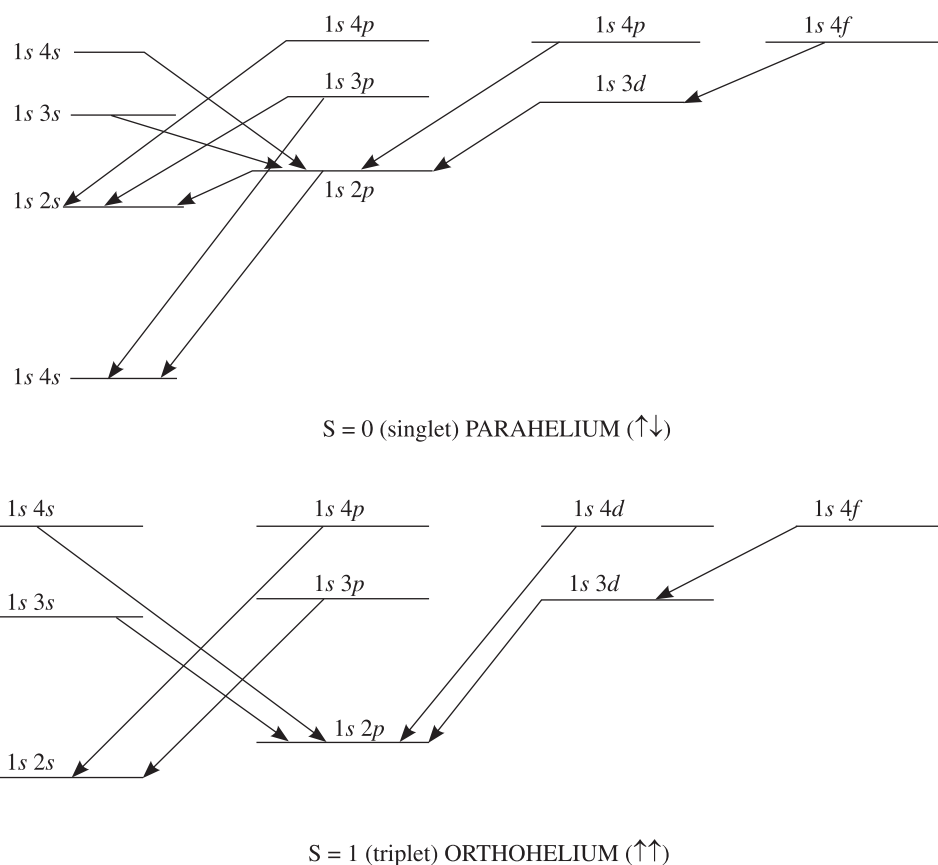


Fig. 3.11.3 Origin of helium spectrum

QUESTIONS AND PROBLEMS

1. Draw an energy level diagram of sodium atom and using this discuss the salient features of the spectra of alkali metals.
2. (a) Why does one get only principal series of lines in the absorption spectrum of alkali metals, while all the four series are observed in their emission spectra.
 (b) Describe the doublet fine structure in the spectra of alkali elements and interpret on the basis of spin orbit interaction model.
3. If the valence electron in sodium atom is excited to 4^2D state, what are the different routes open for the electron in returning to the normal $3^2S_{1/2}$ state? Draw energy level diagram to show the transitions.
4. Doublet structure of spectral lines is a characteristic feature of the spectra of all alkali metals. How is it explained by introducing the concept of electron spin?
5. Write down the expression for the energy levels of alkali atoms and explain the reason of introducing quantum defect term in it.

Name the different series of sodium atom have quantum defect 1.37 and 0.88 respectively. Obtain the wavelength of the spectral line for the transition $3p-3s$.

6. What is meant by fine structure of spectral lines? Describe how does electron spin coupled with orbital motion explain the fine structure of alkali spectra?
7. Differentiate between penetrating and non-penetrating orbit. Prove that the quantum defect for an atom depends upon azimuthal quantum number and is independent of principal quantum number.
8. Discuss the salient features of the spectra of alkaline earth elements.
9. What are calcium triads? What are their origins? Using a tentative energy level diagram, draw the transitions for the three calcium triads appearing in the visible region around 6500, 5600 and 5270 Å.
10. Explain the singlet and triplet series in two valence electron system.
11. Explain diagrammatically the singlet and triplet series of lines in the spectra of helium atom.
12. Draw the energy level diagram of calcium atom on the basis of one electron excitation. Using this diagram outline the essential features of the spectra of alkaline earth element.

MAGNETO-OPTIC AND ELECTRO-OPTIC PHENOMENA

4.1 ZEEMAN EFFECT

In 1896 Peter Zeeman discovered that when a light source is placed in a magnetic field, the spectral lines emitted by the atoms split into a number of components. This phenomenon is called the *Zeeman Effect*. Suppose that a source emits a spectral line of frequency ν_0 in absence of magnetic field. When a magnetic field is switched on and the light emitted by the source is viewed transverse to the field, three equally spaced spectral lines of frequencies $\nu_0 - \Delta\nu$, ν_0 , and $\nu_0 + \Delta\nu$ are observed. The change in frequency of emitted light is called Zeeman shift.

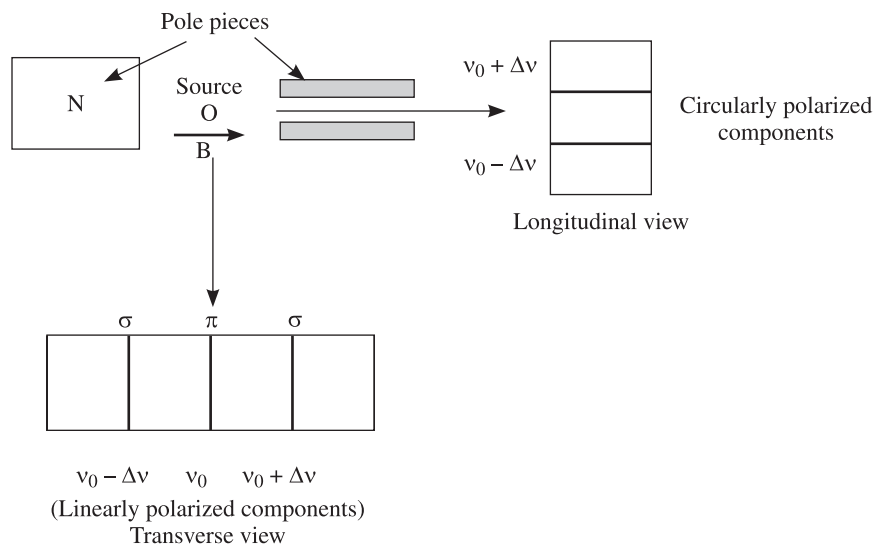


Fig. 4.1.1 Zeeman effect

In transverse view, the central line is designated as π component and the outer lines as σ components. The plane of vibration (electric vector) of the central line (π component) is parallel to

the magnetic field B and that of the outer lines (σ components) is perpendicular to the magnetic field. When viewed parallel to the magnetic field (longitudinal view) only two spectral lines with frequencies $\nu_0 - \Delta\nu$ and $\nu_0 + \Delta\nu$ are observed. Both of the lines are circularly polarized, the line of higher frequency shows left hand polarization and that with lower frequency shows right hand polarization.

Quantum Mechanical Explanation

Normal Zeeman effect occurs in atoms having zero spin ($S = 0$). In an atom having even number of electrons, the spins can pair off and cancel, so that the atom behaves like a spin-less particle. So the normal Zeeman effect is observed only in atoms with even number of valence electrons. In other words, the condition for normal Zeeman effect to occur is that the pair of energy levels involved in the transitions leading to emission of spectral lines must be singlet *i.e.*, $S = 0$ and $g = 1$ for initial and final levels both.

When an atom possessing magnetic moment is subjected to a magnetic field, its energy levels are split into a number of components, called magnetic sub-levels (or Zeeman levels). Obviously, the transitions between the two sets of sub-levels will result in splitting of spectral lines. Suppose that the atom is placed in a magnetic field B acting in z -direction. The change in energy of an energy level of the atom due to magnetic field is

$$\Delta E = -\vec{\mu} \cdot \vec{B} = -\mu_z B = -\left(-\frac{e}{2m}\right)gJ_z B = g\frac{e\hbar}{2m}BM_J = g\mu_B BM_J \quad \dots(4.1.1)$$

where J is total angular quantum number and M_J is total magnetic quantum number of atom. M_J can take on integrally spaced values from $J, J-1, \dots, 0, \dots, -J$. Thus, the energy level characterized by quantum number J is split into $2J+1$ equally spaced sub-levels. The amount of splitting depends on the Lande g -factor (*i.e.*, L, S, J). In absence of magnetic field, the sub-levels with different M_J have the same energy *i.e.*, they were degenerate. Application of the magnetic field removes the degeneracy and the sub-levels with different M_J now possess different energies.

For illustration we first consider the splitting of spectral line resulting from the transition $^1P_1 \rightarrow ^1S_0$ (These levels are involved in emission of lines of principal series in alkaline earth atom). For lower level ($^1S_0$), $L = 0, S = 0, g = 1, M_J = 0$. This level does not split in the magnetic field. For the upper level ($^1P_1$), $L = 1, S = 0, J = 1, g = 1, M_J = -1, 0, 1$. This level splits into three sub-levels. The allowed transitions are shown in the Fig. (4.1.2). It is evident from the figure that the original line will split into three components.

Let E_1 and E_2 be the energies of the lower and upper level in absence of magnetic field. The wave number of the spectral line emitted from the transition between these energies levels is

$$\bar{\nu}_0 = \frac{E_2 - E_1}{hc} \quad \dots(4.1.2)$$

In presence of external magnetic field B , the lower level does not split whereas the upper level splits into three sub-levels with different energies. The energies of the upper and lower levels are given by

$$E'_2 = E_2 + \Delta E = E_2 + \mu_B BM_J, \quad M_J = -1, 0, 1$$

$$E'_1 = E_1$$

The wave numbers of the lines resulting from transitions between these levels are given by

$$\bar{\nu} = \frac{E'_2 - E'_1}{hc} = \frac{E_2 - E_1}{hc} + \frac{\mu_\beta B M_J}{hc}, \quad M_J = -1, 0, 1$$

$$\bar{\nu} = \bar{\nu}_0 + \left(\frac{\mu_\beta B}{hc} \right) M_J \quad \dots(4.1.3)$$

The number $\frac{\mu_\beta B}{hc} = \frac{eB}{4\pi mc} = L_0 = 46.7 \text{ B m}^{-1}$ is called Lorentz number. In terms of Lorentz number we can write Eqn. (4.1.3) as

$$\bar{\nu} = \bar{\nu}_0 + L_0 M_J \quad \dots(4.1.4)$$

Putting $M_J = -1, 0, 1$ we obtain three wave numbers $\bar{\nu}_0 - L_0$, $\bar{\nu}_0$, $\bar{\nu}_0 + L_0$ of the spectral lines into which the original line is split under the action of magnetic field. The Zeeman shift in wave number units is

$$\Delta\bar{\nu} = \bar{\nu} - \bar{\nu}_0 = L_0 = \frac{eB}{4\pi mc} \quad \dots(4.1.5)$$

The corresponding shift in wavelength ($|\Delta\lambda| = \lambda^2 \cdot \Delta\bar{\nu}$) is

$$\Delta\lambda = \frac{eB\lambda^2}{4\pi mc} \quad \dots(4.1.6)$$

Thus, the normal Zeeman pattern consists of three lines of wave numbers $\bar{\nu}_0 - \Delta\bar{\nu}$, $\bar{\nu}_0$, $\bar{\nu}_0 + \Delta\bar{\nu}$ or wavelengths $\lambda + \Delta\lambda$, λ and $\lambda - \Delta\lambda$.

Polarization: Quantum mechanical analysis shows that the spectral line with σ polarization results from the transitions in which $\Delta M_J = \pm 1$ and π polarization from the transitions in which $\Delta M_J = 0$ (excluding $0 \rightarrow 0$ transitions).

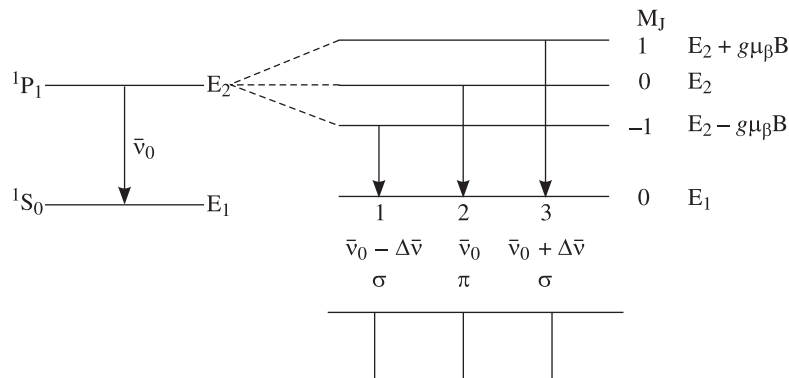


Fig. 4.1.2 Normal Zeeman effect

For another example let us consider the normal Zeeman splitting of the spectral line of *diffuse series* in cadmium resulting from the transition $^1D_2 \rightarrow ^1P_1$ between singlet levels.

For the lower level $L = 1, S = 0, J = 1, g = 1, M_J = -1, 0, 1$. This level splits into three sub-levels.

For the upper level, $L = 2, S = 0, J = 2, g = 1, M_J = -2, -1, 0, 1, 2$. This level splits into five components.

The selection rules for allowed transitions are

$$\Delta M_J = 0, \pm 1$$

The transitions for which $\Delta M_J = 0$ lead to emission line of a single line with wave number $\bar{\nu}_0$; that for which $\Delta M_J = 1$ leads to a single of wave number $\bar{\nu}_0 - \Delta\bar{\nu}$ and that for which $\Delta M_J = -1$ corresponds to wave number $\bar{\nu}_0 + \Delta\bar{\nu}$. These transitions with their frequencies are shown in the Fig. (4.1.3)

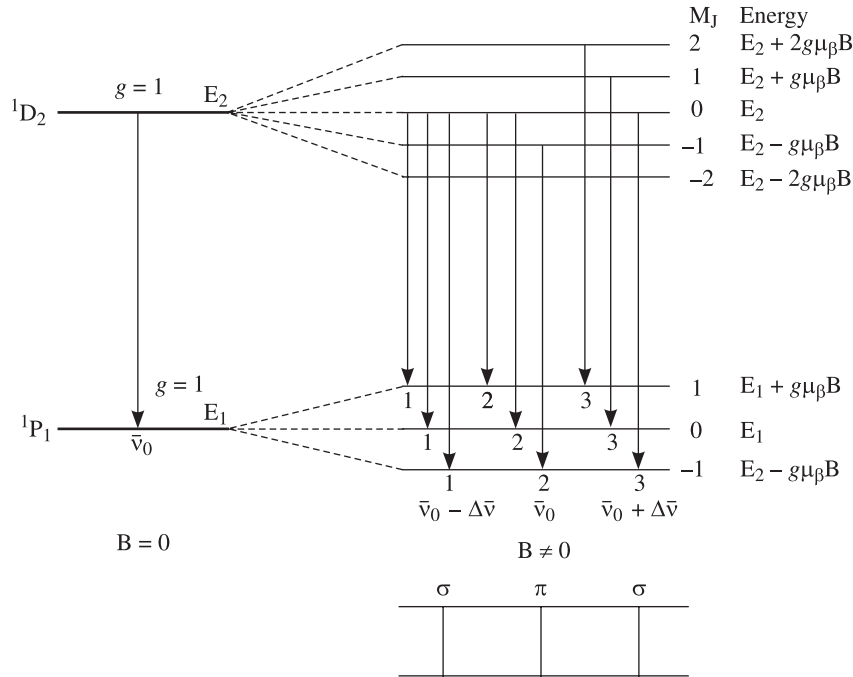


Fig. 4.1.3 Normal Zeeman splitting of a spectral line

The transitions marked 1 on the diagram are accompanied by equal amount of energy change and hence give rise to a single spectral line. Its wave number is given by

$$\bar{\nu} = \frac{E_2 - E_1}{hc} - \frac{\mu_B B}{hc} = \bar{\nu}_0 - \Delta\bar{\nu} \quad \dots(4.1.7)$$

Where $\Delta\bar{\nu}$ represents the Zeeman shift and is given by

$$\Delta\bar{\nu} = \frac{\mu_B B}{hc} = L_0 = \frac{eB}{4\pi mc} \text{ is Lorentz number}$$

or
$$\Delta\bar{\nu} = \frac{eB}{4\pi mc} \quad \dots(4.1.8)$$

The transitions marked 2 on the diagram are accompanied by a change in energy $E_2 - E_1$, which give rise to a line of wave number

$$\bar{\nu}_0 = \frac{E_2 - E_1}{hc}$$

Similarly, the transitions marked 3 on the diagram lead to a single line of wave number

$$\bar{\nu} = \bar{\nu}_0 + \Delta\bar{\nu}$$

The corresponding shift in wavelength is given by

$$\Delta\lambda = \frac{eB\lambda^2}{4\pi mc} \quad \dots(4.1.9)$$

Polarization Rules

Viewed perpendicular to B: The spectral line originating from the transition obeying the selection rule $\Delta M_J = 0$, have the plane of vibration parallel to the magnetic field B and that obeying the selection rule $\Delta M_J = \pm 1$, have the plane of vibration perpendicular to B.

Viewed parallel to B: The transition obeying $\Delta M_J = \pm 1$ gives spectral lines with circular polarization. Transitions for which $\Delta M_J = 0$ are forbidden.

4.2 ANOMALOUS ZEEMAN EFFECT

When an atom is placed in an external magnetic field, the behaviour of the angular momentum vector in general will be very complicated. The reason is that each of the magnetic moments associated with orbital and spin motion interact with each other as well as with the external field. No simple description of the motion is possible when these fields are of the order of the same magnitude. However, when one is much larger than the other an approximate treatment is possible.

Weak field approximation: When the external magnetic field is small compared with the field due to the spin-orbit coupling, the coupling between **L** and **S** remains intact. The resultant of **L** and **S** viz. **J** has physical significance. The vectors **L** and **S** precess around **J** at much faster rate than **J** precesses around external field **B**. The space quantization of vector **J** allows it to have only discrete values of its projection onto the direction of magnetic field **B** given by

$$|J_z| = M_J \hbar, \quad M_J = -j, -j+1, \dots, +j.$$

The magnetic interaction energy is given by

$$\Delta E = -\vec{\mu} \cdot \vec{B} = g\mu_B M_J \quad \dots(4.2.1)$$

[In case of one valence electron atom, we replace the vectors L, S, J by l, s, j and quantum numbers L, S, J , and M_J by l, s, j and m_j .]

In 1907 *Runge* observed that when a spectral line was split into more than three components, the magnitude of splitting was a rational fraction of the normal Zeeman splitting.

$$\Delta\bar{\nu} = \left(\frac{p}{q}\right) \Delta\bar{\nu}_{\text{normal}}, \quad p \text{ and } q \text{ being integers. (Runge's Law)} \quad \dots(4.2.2)$$

We shall explain the **anomalous Zeeman effect** with two examples; the splitting of sodium D lines. The D_1 line $5896 \text{ \AA}$ arises from the transition ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ and the D_2 line $5890 \text{ \AA}$ from the transition ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$. The values of L, S, J, g, M_J and gM_J for the levels involved in these transitions are given in the following table:

Table

Term	L	S	J	g	M_J	gM_J
${}^2P_{3/2}$	1	1/2	3/2	4/3	3/2, 1/2 -1/2, -3/2	2, 2/3 -2/3, -2
${}^2P_{1/2}$	1	1/2	1/2	2/3	1/2, -1/2	1/3, -1/3
${}^2S_{1/2}$	0	1/2	1/2	2	1/2, -1/2	1, -1

The allowed transitions obey the selection rules: $\Delta M_J = 0, \pm 1$.

The level ${}^2S_{1/2}$ (for which $L = 0, S = 1/2, J = 1/2, g' = 2$) splits into two sub-levels. The level ${}^2P_{1/2}$ (for which $L = 1, S = 1/2, J = 1/2, g'' = 2/3$.) splits into two sub-levels.

The level ${}^2P_{3/2}$ splits into four Zeeman levels.

Let E_1, E_2 and E_3 be the energies of the levels ${}^2S_{1/2}, {}^2P_{1/2}$, and ${}^2P_{3/2}$ in absence of magnetic field. The corresponding energies in presence of magnetic field will be denoted by prime. The wave numbers of lines in absence of B are

$$\bar{\nu}_0 = \frac{E_2 - E_1}{hc}, \quad D_1 \text{ - line}$$

$$\bar{\nu}_0 = \frac{E_3 - E_1}{hc}, \quad D_2 \text{ - line}$$

The energies of the levels in presence of magnetic field are

$$E'_1 = E_1 + \mu_B B g' M'_J$$

$$E'_2 = E_2 + \mu_B B g'' M''_J$$

$$E'_3 = E_3 + \mu_B B g''' M'''_J$$

The wave numbers of lines arising from transitions ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ are given by

$$\begin{aligned} \bar{\nu} &= \frac{E'_2 - E'_1}{hc} = \frac{E_2 - E_1}{hc} + \frac{(g'' M''_J - g' M'_J)}{hc} \mu_B B \\ &= \bar{\nu}_0 + (g'' M''_J - g' M'_J) L_0 \end{aligned} \quad \dots(4.2.3)$$

The value of $(g''M_J'' - g'M_J')$ for each line is given beside the vertical line showing the transitions in the Fig. (4.2.1). See that the original line disappears when the magnetic field is switched on. Substituting the values of g , and M_J we get the wave numbers of the four lines resulting from transitions between the two levels.

$$\bar{\nu}_1 = \bar{\nu}_0 - \frac{4}{3}L_0, \quad \bar{\nu}_2 = \bar{\nu}_0 - \frac{2}{3}L_0, \quad \bar{\nu}_3 = \bar{\nu}_0 + \frac{2}{3}L_0, \quad \bar{\nu}_4 = \bar{\nu}_0 + \frac{4}{3}L_0$$

Thus

$$\Delta\bar{\nu} = -\frac{4}{3}L_0 = -\frac{4}{3}\Delta\bar{\nu}_{\text{normal}}, \quad -\frac{2}{3}\Delta\bar{\nu}_{\text{normal}}, \quad \frac{2}{3}\Delta\bar{\nu}_{\text{normal}}, \quad \frac{4}{3}\Delta\bar{\nu}_{\text{normal}}.$$

This is Runge Law.

The wave numbers of the lines originating from the transitions $^2P_{3/2} \rightarrow ^2S_{1/2}$ are given by

$$\begin{aligned} \bar{\nu} &= \frac{E'_3 - E'_1}{hc} = \frac{E_2 - E_1}{hc} + \frac{(g'''M_J''' - g'M_J')}{hc} \mu_B B \quad \dots(4.2.4) \\ &= \bar{\nu}_0 + (g'''M_J''' - g'M_J') L_0 \end{aligned}$$

Substituting the values of g , and M_J , we get the wave numbers of the six lines resulting from transitions between the two levels.

$$\begin{aligned} \bar{\nu}_1 &= \bar{\nu}_0 - \frac{5}{3}L_0, \quad \bar{\nu}_2 = \bar{\nu}_0 - \frac{3}{3}L_0, \quad \bar{\nu}_3 = \bar{\nu}_0 - \frac{1}{3}L_0 \\ \bar{\nu}_4 &= \bar{\nu}_0 + \frac{1}{3}L_0, \quad \bar{\nu}_5 = \bar{\nu}_0 + \frac{3}{3}L_0, \quad \bar{\nu}_6 = \bar{\nu}_0 + \frac{5}{3}L_0 \end{aligned}$$

The wave number shift can be expressed as

$$\Delta\bar{\nu} = \left(-\frac{5}{3}, -\frac{3}{3}, -\frac{1}{3}, \frac{1}{3}, \frac{3}{3}, \frac{5}{3} \right) L_0 = \left(-\frac{5}{3}, -\frac{3}{3}, -\frac{1}{3}, \frac{1}{3}, \frac{3}{3}, \frac{5}{3} \right) \Delta\bar{\nu}_{\text{normal}}$$

This is Runge law.

Polarization Rules: If viewed perpendicular to B , the selection rule $\Delta M_J = 0$ leads to π polarization and $\Delta M_J = \pm 1$ to σ polarization.

If viewed parallel to B , the selection rule $\Delta M_J = \pm 1$ leads to circular polarization of spectral line.

Intensity Rules

The transition $J \rightarrow J$, $\Delta M_J = \pm 1$, gives the intensity of line given by

$$I = I_0 (J \pm M_J + 1)(J \mp M_J) \quad \dots(4.2.5)$$

And $\Delta M_J = 0$ gives the intensity

$$I = 4I_0 M_J^2 \quad \dots(4.2.6)$$

The transition $J \rightarrow J + 1$, $\Delta M_J = \pm 1$, gives the intensity of line given by

$$I = I_0 (J \pm M_J + 1)(J \pm M_J + 2) \quad \dots(4.2.7)$$

And

$$\begin{aligned} \Delta M_J = 0 \text{ gives the intensity} \\ I = 4I_0 (J + M_J + 1)(J - M_J + 1) \quad \dots(4.2.8) \end{aligned}$$

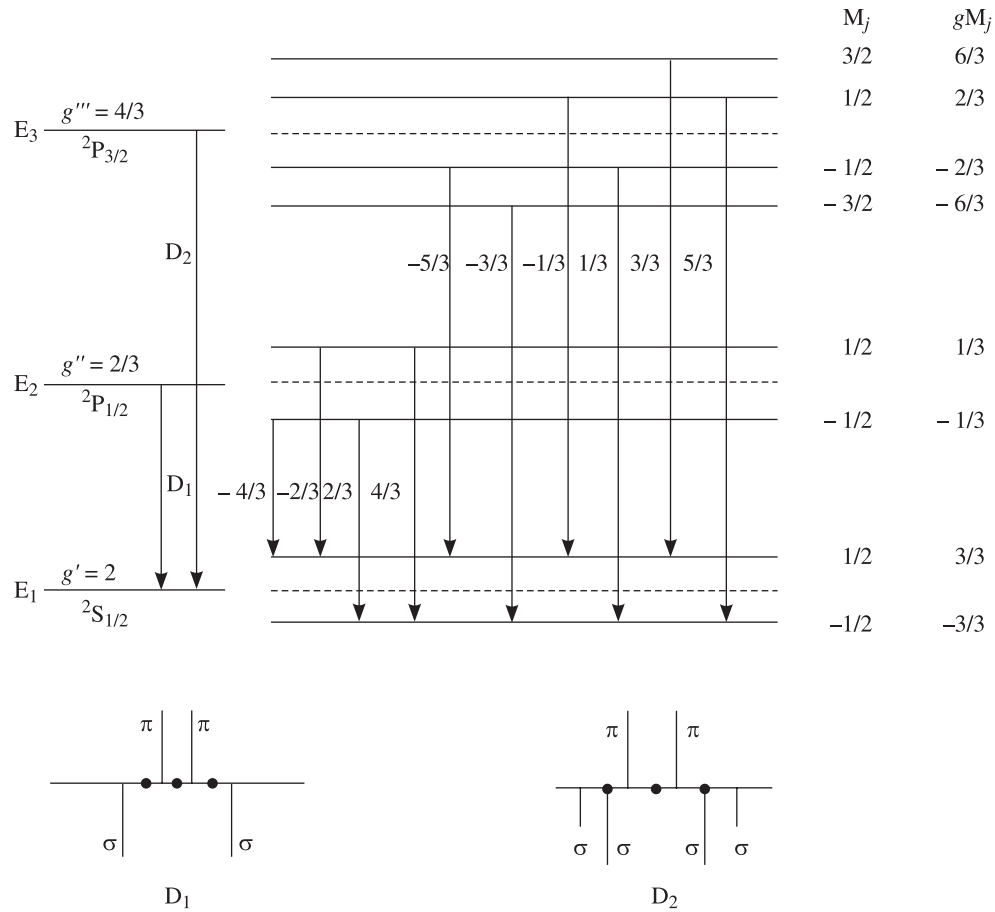


Fig. 4.2.1 Anomalous Zeeman effect with principal series doublet (Sodium D_1 and D_2 lines)
Dots represents the position of normal triplet

4.3 PASCHEN-BACK EFFECT

(i) For one valence electron atom

When a very strong magnetic field is applied to an atom, such that the interaction energy of the external field with the atom becomes larger than the spin-orbit interaction, the coupling between vectors $\mathbf{l}$ and $\mathbf{s}$ breaks down and the individual vectors $\mathbf{l}$ and $\mathbf{s}$ precess around the magnetic field independent of each other. In this condition the complicated anomalous Zeeman pattern transform into a simple Zeeman pattern. This phenomenon is called the Paschen-Back effect.

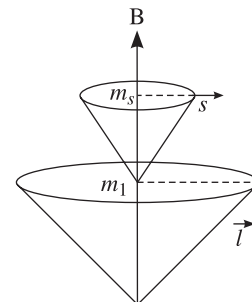


Fig. 4.3.1

In the strong magnetic field, the total interaction energy of the atom is equal to the sum of three parts.

- (i) The energy due to the precession of vector $\mathbf{l}$ around $\mathbf{B}$
- (ii) The energy due to the precession of vector $\mathbf{s}$ around $\mathbf{B}$
- (iii) The energy due to interaction between $\mathbf{l}$ and $\mathbf{s}$.

Thus

$$\begin{aligned}\Delta E &= \Delta E_{lB} + \Delta E_{sB} + \Delta E_{ls} \\ \Delta E &= g_l \mu_B B m_l + g_s \mu_B B m_s + a l^* s^* \cos(l^* s^*)\end{aligned}\quad \dots(4.3.1)$$

where m_l and m_s are orbital and spin magnetic quantum numbers.

In absence of magnetic field B , the angle between l^* and s^* is constant but in presence of B it changes continually. So its average value must be calculated.

$$\text{Now,} \quad \langle \cos(l^* s^*) \rangle = \cos(l^* B) \cos(s^* B)$$

$$\begin{aligned}\therefore \quad a l^* s^* \cos(l^* s^*) &= a l^* \cos(l^* B) \cdot s^* \cos(s^* B) \\ &= a m_l m_s\end{aligned}\quad \dots(4.3.2)$$

The total energy of atom in magnetic field can be expressed as

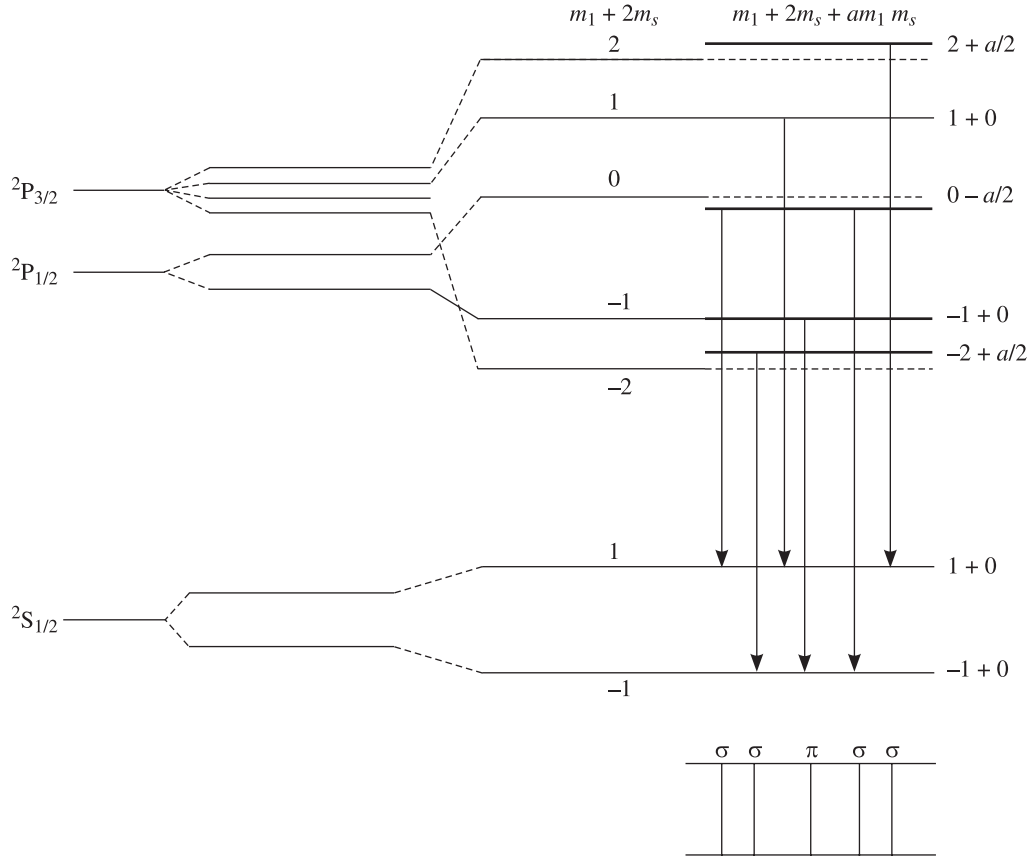
$$\Delta E = \mu_B B (m_l + 2m_s) + a m_l m_s, \quad g_l = 1, g_s = 2 \quad \dots(4.3.3)$$

As an example we consider the *Paschen-Back* effect with principal series doublet $^2S_{1/2} \leftarrow ^2P_{1/2, 3/2}$. The following table displays the computation of magnetic energies in strong magnetic field for the levels involved in the transitions. Fig. (4.3.2) shows the allowed transitions and resulting spectral lines.

The selection rules for the allowed transitions are

$$\Delta M_L = 0, \pm 1, \text{ and } \Delta M_S = 0.$$

Term	m_l	m_s	$m_l + 2m_s$	$a m_l m_s$
$^2P_{3/2}$	1	1/2	2	$a/2$
	0	1/2	1	0
	-1	1/2	0	$-a/2$
	1	-1/2	0	$-a/2$
$^2P_{1/2}$	0	-1/2	-1	0
	-1	-1/2	-2	$a/2$
$^2S_{1/2}$	0	1/2	1	0
	0	-1/2	-1	0



$$\Delta m_l = 0 \quad \pi\text{-components}, \quad \Delta m_l = \pm 1 \quad \sigma\text{-components}$$

Fig. 4.3.2 Magnetic energy levels and Paschen-Back pattern for a principal series doublet

If we neglect the spin-orbit interaction energy term $am_l m_s$ the expression for total energy becomes

$$\Delta E = \mu_B B(m_l + 2m_s) \quad \dots (4.3.4)$$

The quantity $(m_l + 2m_s)$ is an integer and thus the splitting of energy levels is integral multiples of the normal splitting ($\Delta\omega_0 = \mu_B B$). In terms of frequency the shift is

$$\Delta\omega = \Delta\omega_0 \Delta(m_l + 2m_s) = \Delta\omega_0 [(m_l + 2m_s)_{\text{upper}} - (m_l + 2m_s)_{\text{lower}}] \quad \dots (4.3.5)$$

The splitting of principal series doublet terms $^2P_{0, 1, 2}$ and $^2S_{1/2}$ in strong field are shown in Fig. (4.3.3). Since energy shift ΔE depend on $(m_l + 2m_s)$, the terms having the same value of $(m_l + 2m_s)$ now coincide. Thus, there are five P-states and two s-states. The selection rules for allowed transitions are

$$\Delta(m_l + 2m_s) = 0, \pm 1$$

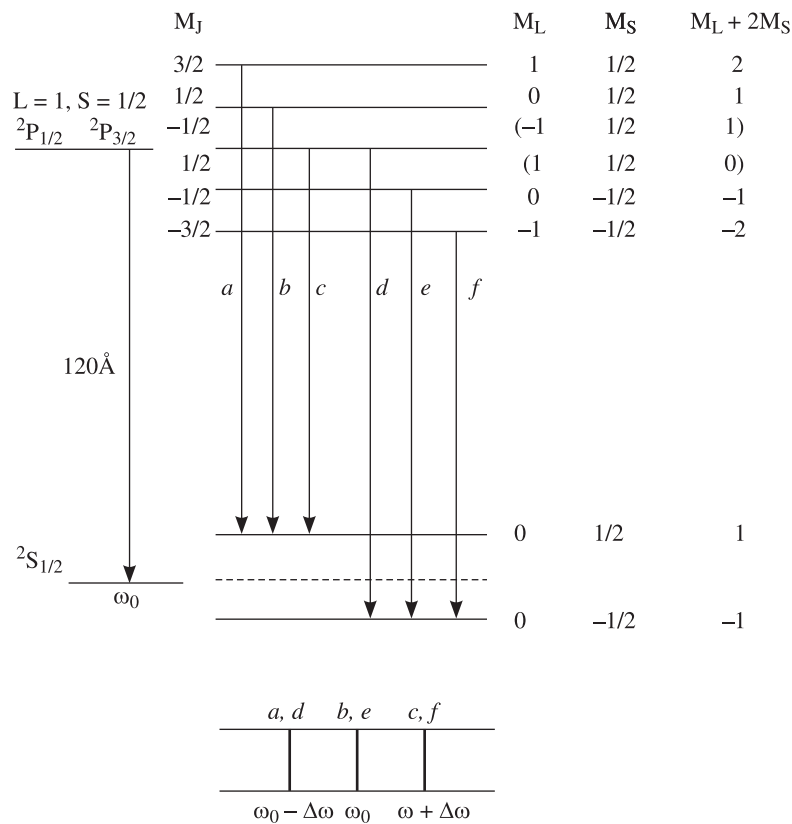


Fig. 4.3.3 Paschen-Back effect without L-S interaction

In the Fig. (4.3.3) the transition marked a, d correspond to $\Delta(m_l + 2m_s) = 1$ and hence have the same frequency $\omega_0 - \Delta\omega_0$, the transitions marked b, e correspond to $\Delta(m_l + 2m_s) = 0$ and have the frequency ω_0 and those marked c, f correspond to $\Delta(m_l + 2m_s) = -1$ and have the frequency $\omega_0 + \Delta\omega_0$. Thus, we have only three spectral lines in the strong magnetic field.

Let us calculate the Zeeman shift $d\lambda$ for the line $\lambda = 1210 \text{ \AA}$ (in hydrogen) emitted in the transition $2p \rightarrow 1s$ in a magnetic field of 5 Wb/m^2 . The frequency shift in normal Zeeman effect is

$$\Delta\omega_0 = \frac{\mu_\beta B}{\hbar}$$

The frequency shift, from Eqn. (4.3.5) is found to be

$$\Delta\omega = \Delta\omega_0 = \frac{\mu_\beta B}{\hbar} = \frac{eB}{2m}$$

The corresponding shift in wavelength

$$\Delta\lambda = \frac{eB\lambda^2}{4\pi mc} = 0.034 \text{ \AA}$$

The wavelengths of the Zeeman triplet are 1210.034 Å, 1210 Å and 1209.966 Å.

(ii) Two valence electron atom

All the arguments made in case of one-electron system are also valid for two-electron system. In two-electron system vectors $\mathbf{L}$ and $\mathbf{S}$ play the role of $\mathbf{l}$ and $\mathbf{s}$, the appropriate quantum numbers in this case are L, S, M_L and M_S . The total energy of atom in strong magnetic field is given by

$$\Delta E = \mu_B B (M_L + 2M_S) + A M_L M_S \quad \dots(4.3.6)$$

As an example we consider the splitting of triplet terms $^3S_1, ^3P_{0,1,2}$ in strong magnetic field. The computation of magnetic levels is shown the table given below. The Fig. (4.3.4) shows the splitting of terms and the transitions leading to the Paschen-Back pattern of the principal series triplet. The selection rules for the strong field are

$$\begin{aligned} \Delta M_L &= 0 \text{ for } \pi\text{-components} \\ &= \pm 1 \text{ for } \sigma\text{-components} \\ \Delta M_S &= 0 \end{aligned} \quad \dots(4.3.7)$$

It should be noted that if the small interaction between L and S viz., the term $a m_l m_s$ is omitted, the Paschen-Back pattern will transform into a normal triplet shown by thick lines in the figure.

Table 4.3.1: Computation of magnetic energies in strong magnetic field.

Terms	L	M_L	M_S	$M_L + 2M_S$	$M_L + 2M_S + A M_L M_S$
$^3P_2$	1	1	1	3	$3 + A$
	1	0	1	2	$2 + 0$
	1	-1	1	1	$1 + 0$
	1	1	0	1	$1 - A$
	1	0	0	0	$0 + 0$
	1	-1	0	-1	$-1 + 0$
$^3P_1$	1	1	-1	-1	$-1 - A$
	1	0	-1	-2	$-2 + 0$
	1	-1	-1	-3	$-3 + A$
$^3P_0$	1	-1	-1	-3	$-3 + A$

Paschen-Back effect has been observed only for very narrow multiplet. In Li, this multiplet (doublet) has a separation of 0.34 cm^{-1} and hence this effect can be observed. In sodium doublet separation is about 17 cm^{-1} . To observe Paschen-Back effect a very large magnetic field is required, which is a difficult task. In general, Paschen-Back effect can be observed if the magnetic splitting (Zeeman splitting) exceeds the fine structure splitting due to spin orbit interaction.

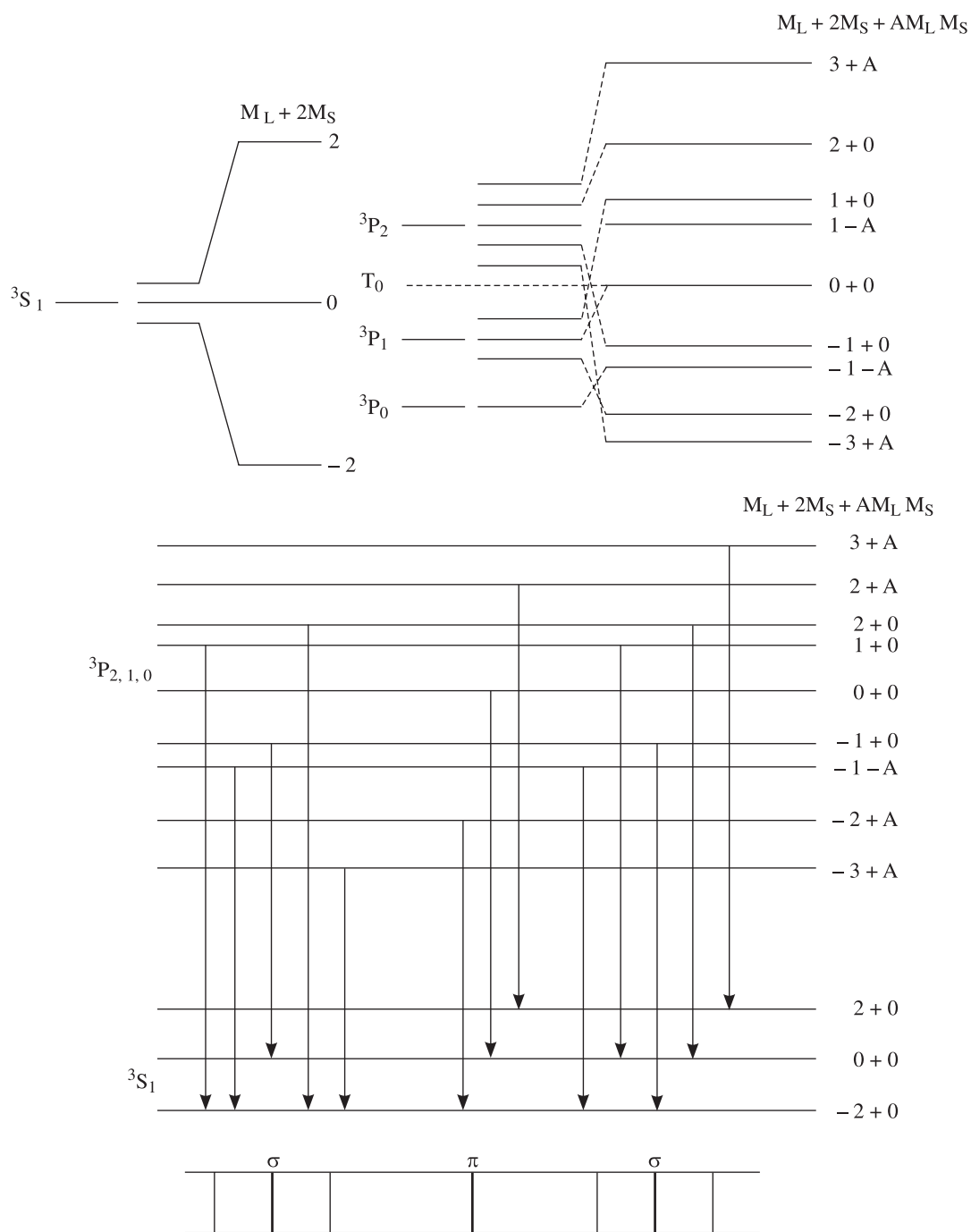


Fig. 4.3.4 Paschen-Back effect in a principal series triplet. Thick lines show the positions of normal triplet

Meaning of weak and strong magnetic field

A good Zeeman pattern is produced when the magnetic field of the order of 0.1 T is applied on the atom. A field is said to be weak when the total spread of Zeeman pattern of each line is small in comparison to the line separation cause by spin-orbit interaction. The line separation of D_1 and D_2 lines of sodium is about 17.2 cm^{-1} . A magnetic field of 3T produces Zeeman spread of 3.76 cm^{-1} in line D_1 and 4.70 cm^{-1} in D_2 line. The Zeeman spread is small compared with the line separation. Therefore, a magnetic field of 3T is weak in this case.

For Li, the doublet separation is about 0.34 cm^{-1} . A field of 3T produces a Zeeman pattern with spread of 1.4 cm^{-1} . In this case Zeeman spread is large compared with the line separation. Therefore, the magnetic field of 3T is a strong field in this case.

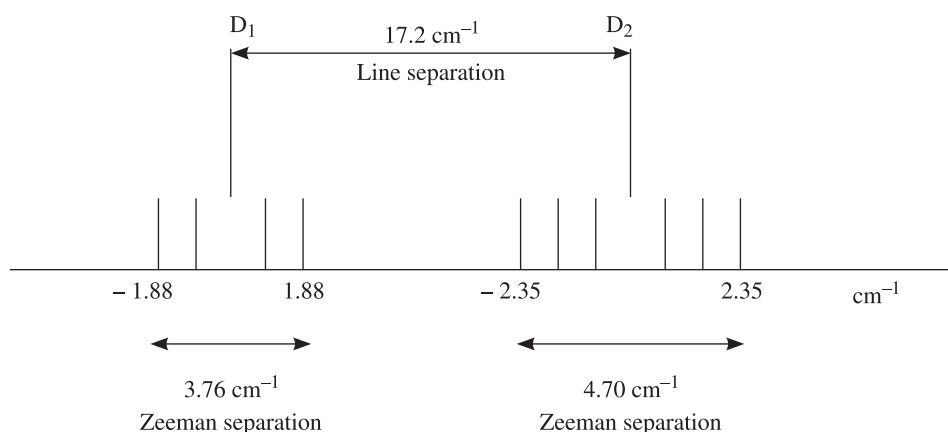


Fig. 4.3.5

4.4 STARK EFFECT

The splitting of spectral lines under the action of electric field is called Stark effect. It was Stark, who in 1913 demonstrated the splitting of Balmer lines of hydrogen atom in an electric field. A schematic diagram of the apparatus used for the study of transverse Stark effect is shown in the figure. A perforated cathode is placed at a distance of about 3 mm from the plate P. The pressure of the gas in the discharge tube is kept at a value such that the Crookes dark space is several cm long. Under this condition the energy is less than that required to produce ionization. A very high potential gradient is applied between the plate P and the cathode.

Under the action of applied electric field ξ , the initially degenerate level with quantum number n , splits into $2n - 1$ components with different energies. An important difference between the Zeeman and Stark effect is that each pair of levels with $M_J = +J$ and $M_J = -J$ arising from a given level has the exactly the same energy in electric field.

For a weak field ξ , the Stark effect in hydrogen lines produces a symmetrical pattern and the line separations are proportional to the strength of the applied electric field ξ . This effect is known as *linear or first order Stark Effect*.

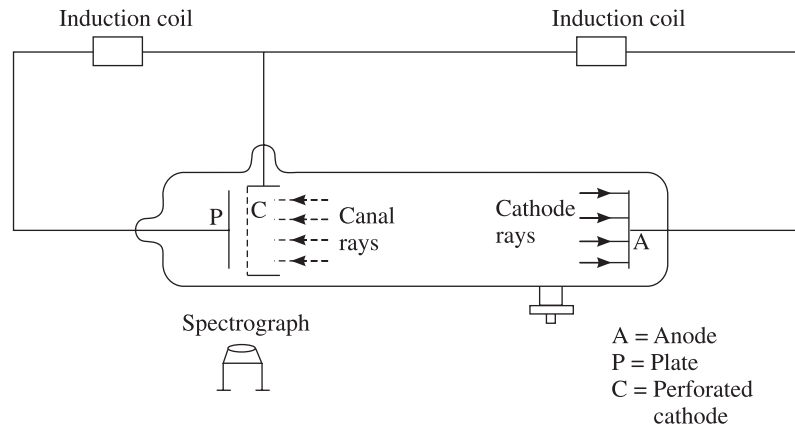


Fig. 4.4.1 Experimental set up to observe Stark effect

When ξ exceeds 10^7 V/m, the line separations are proportional to ξ^2 . This called *quadratic or second order Stark Effect*.

Let examine the linear Stark effect in Na D-lines, which are emitted in the transitions

$$3^2P_{1/2} - 3^2S_{1/2} \quad \text{and} \quad 3^2P_{3/2} - 3^2S_{1/2}$$

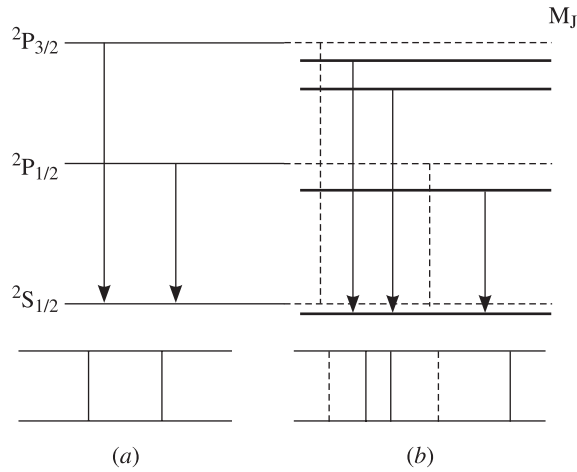


Fig. 4.4.2 (a) Field free transitions (b) Transitions in presence of field

The level with $J = 3/2$ splits into two sub-levels with $M_J = \pm 3/2$ and $M_J = \pm 1/2$. The levels $2P_{1/2}$ and $2S_{1/2}$ do not split. In presence of electric field three transitions will take place.

The quadratic Stark effect can be explained as follows. The electric field produces a relative shift of center of negative and positive charge in the atom. Thus, the electric field induces an electric dipole moment in the atom. This action of field is called electric polarization. The magnitude of

electric dipole moment is proportional to the strength of the field. The dipole moment interacts with the applied field ξ . The electric field exerts a torque, which makes the angular momentum $\mathbf{J}$ of the atom precess about the direction of the electric field such that the component of $\mathbf{J}$ along ξ is a constant. An increase in electric field ξ causes increase in precessional velocity. The energy shift is given by

$$\Delta E = \mu \xi, \quad \mu \text{ is dipole moment.}$$

Since μ is proportional to ξ , the splitting of energy level is proportional to the square of the electric field ξ . For potassium doublet, ($\lambda = 4044 \text{ \AA}$, $5^2P_{3/2} - 4^2S_{1/2}$ and $\lambda = 4047 \text{ \AA}$, $5^2P_{1/2} - 5^2S_{1/2}$) the wavelength shift $\Delta\lambda$ is plotted against ξ^2 , a straight line is observed.

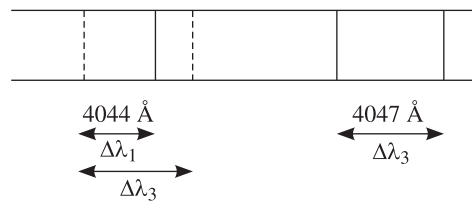


Fig. 4.4.3 Quadratic Stark effect in potassium doublet 4044 Å 4047 Å.

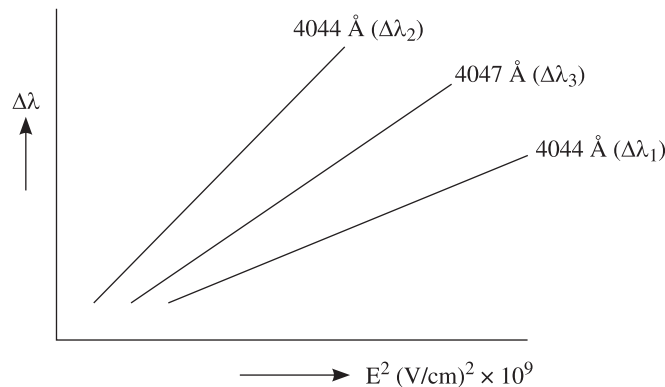


Fig. 4.4.4 Quadratic Stark effect

SOLVED EXAMPLES

Ex. 1. Calculate the normal Zeeman splitting of the line $6438 \text{ \AA}$ in a magnetic field of 0.5 T .

Sol. Zeeman shift
$$d\lambda = \frac{eB\lambda^2}{4\pi mc}.$$

Substituting $e = 1.6 \times 10^{-19}$ C, $B = 0.5$ T, $\lambda = 6438 \times 10^{-10}$ m, $m = 9.1 \times 10^{-31}$ kg, $c = 3 \times 10^8$ m/s, we find

$$d\lambda = 0.097 \times 10^{-10} \text{ m} = 0.097 \text{ \AA}.$$

Ex. 2. Compute the separation in Angstrom units of the outer two lines of a normal Zeeman pattern for spectral line of wavelength 612 nm in a magnetic field of 10 kg ($1 \text{ g} = 10^{-4}$ T).

Sol. Normal Zeeman shift

$$d\lambda = \frac{eB\lambda^2}{4\pi mc}$$

Substituting the given values we find

$$d\lambda = 0.175 \text{ \AA}$$

Separation of outer lines $= 2 d\lambda = 0.35 \text{ \AA}$.

Ex. 3. An atom in the state $^2P_{3/2}$ is located in an external magnetic field of 1.0 kg. In terms of vector model, find the angular velocity of precession of the total angular momentum of the atom.

Sol. Lande g -factor of the state $^2P_{3/2}$

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} = \frac{4}{3}$$

The angular velocity of precession

$$\omega = \frac{g\mu_B B}{\hbar} = \frac{4 \times (9.27 \times 10^{-24} \text{ J/T})(1 \times 10^{-1} \text{ T})}{3 \times (1.054 \times 10^{-34} \text{ Js})} = 1.2 \times 10^{10} \text{ rad/s}$$

Ex. 4. Into what number of sub-shells are the following terms split in a weak magnetic field?

(i) $^3P_0$ (ii) $^2F_{5/2}$ (iii) $^4D_{1/2}$.

Sol. (i) For the state $^3P_0$, $J = 0$, $M_J = 0$. This energy level does not split.

(ii) For the state $^2F_{5/2}$, $g \neq 0$, $J = 5/2$, M_J has $2J + 1 = 6$ values. Hence, it splits into six sub-levels.

(iii) For the state $^4D_{1/2}$, $g = 0$, it does not split at all.

Ex. 5. An atom is located in a magnetic field of 2.5 kg. Find the value of total splitting of the following terms (i) ^1D (ii) $^3F_4$.

Sol. (i) For the state ^1D , we have $S = 0$, $L = 2$, $J = 2$, $g = 1$. The total splitting is given by

$$\Delta E = 4 g \mu_B B$$

$$= 4 \times (5.79 \times 10^{-5} \text{ eV/T})(0.25 \text{ T})$$

$$= 57.9 \times 10^{-6} \text{ eV}.$$

(ii) For the state $^3F_4$, $S = 1$, $L = 3$, $J = 4$, $g = 5/4$. This level splits into 9 sub-levels. The total splitting is given by

$$\Delta E = 8 (g \mu_B B)$$

$$= 8 \times \frac{5}{4} \times 5.79 \times 10^{-5} \frac{\text{eV}}{\text{T}} \times 0.25 \text{ T}$$

$$= 144.85 \times 10^{-6} \text{ eV}.$$

Ex. 6. What kind of Zeeman effect, normal or anomalous is observed in a weak magnetic field in the case spectral lines caused by the following transitions:

(i) $^1P \rightarrow ^1S$ (ii) $^2D_{5/2} \rightarrow ^2P_{3/2}$ (iii) $^3D_1 \rightarrow ^3P_0$ (iv) $^5I_5 \rightarrow ^5H_4$.

Sol. (i) $^1P \rightarrow ^1S$. For the lower level $L = 0$, $S = 0$, $J = 0$, $g = 1$. It does not split.

For the upper level $L = 1$, $S = 0$, $J = 1$, $g = 1$, $M_J = -1, 0, 1$. It splits into three levels.

Normal Zeeman effect is observed.

(ii) $^2D_{5/2} \rightarrow ^2P_{3/2}$. For the lower level $L = 1$, $S = 1/2$, $J = 3/2$, $g = 4/3$. It splits into four sub-levels.

For the upper level $L = 2$, $S = 1/2$, $J = 5/2$, $g = 6/5$. It splits into six sub-levels.

Anomalous Zeeman pattern is observed.

(iii) $^3D_1 \rightarrow ^3P_0$. Lower level: $L = 1$, $S = 1$, $J = 0$, $g = 1$. It does not split.

Upper level: $L = 2$, $S = 1$, $J = 1$, $g = 1/2$. It splits into three sub-levels.

Normal Zeeman pattern is observed.

(iv) $^5I_5 \rightarrow ^5H_4$. Lower level: $L = 5$, $S = 2$, $J = 4$, $g = 19/20$. Upper level:

$L = 6$, $S = 2$, $J = 5$, $g = 19/20$. Since, the two levels have identical Lande g -factor, normal Zeeman pattern is observed.

Ex. 7. Draw the diagram of the permitted transitions between the terms $^2P_{3/2}$ and $^2S_{1/2}$ in a weak magnetic field. Find the displacements of the Zeeman components of that line in a magnetic field of $0.45 \mu\text{b/m}^2$.

Sol. Zeeman shift is given by

$$\Delta\omega = \frac{\mu_B B}{\hbar} (g' M_J' - g M_J)$$

State	L	S	J	g	M_J
$^2P_{3/2}$	1	1/2	3/2	4/3	3/2, 1/2, -1/2, -3/2
$^2S_{1/2}$	0	1/2	1/2	2	1/2, -1/2

Now $\frac{\mu_B B}{\hbar} = 3.95 \times 10^{11} \text{ rad/s}$ and

$$g' M_J' - g M_J = 5/3, 3/3, 1/3, -1/3, -3/3, -5/3.$$

Hence $\Delta\omega = \pm 6.59 \times 10^{10}, \pm 3.95 \times 10^{10}, \pm 1.31 \times 10^{10} \text{ rad/s}$.

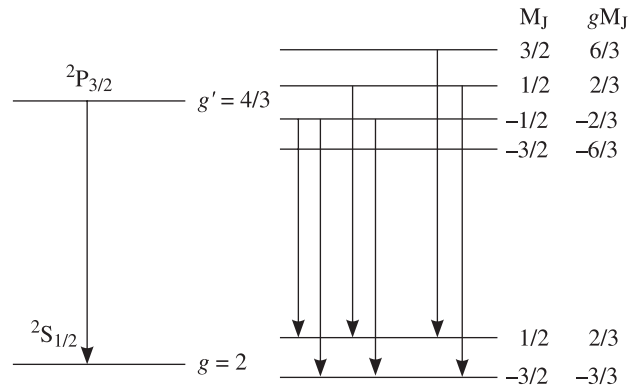


Fig. E-7

Ex. 8. A beam of electrons enters a uniform magnetic field of flux density $1.2 \mu\text{b/m}^2$. Find the energy difference in electron volts between electrons whose spins are parallel and anti-parallel to the field.

Sol. The energy difference

$$\Delta E = 2g_s\mu_\beta BJ$$

where

$$\mu_\beta = \frac{e\hbar}{2m} = 9.273 \times 10^{-24} \text{ J/T} = 5.79 \times 10^{-5} \text{ eV/T}$$

For a pure spin system $J = s = 1/2$ and $g = g_s = 2$.

$$\begin{aligned} \Delta E &= 2(2) \left(\frac{e\hbar}{2m} \right) \left(\frac{1}{2} \right) = 2(2)(5.79 \times 10^{-5} \text{ eV.s})(1.2 \text{ T}) \left(\frac{1}{2} \right) \\ &= 1.39 \times 10^{-4} \text{ eV.} \end{aligned}$$

Ex. 9. The spectral line resulting from the transition $2p \rightarrow 1s$ ($\lambda = 1210 \text{ \AA}$) in hydrogen atom is subjected to a huge magnetic field of 5T . Find the wavelengths of the spectral lines in the pattern.

Sol. In strong magnetic field B , the spin-orbit interaction is negligible. The orbital and spin angular momenta are separately quantized. The anomalous Zeeman pattern reverts to normal Zeeman pattern (Paschen-Back effect).

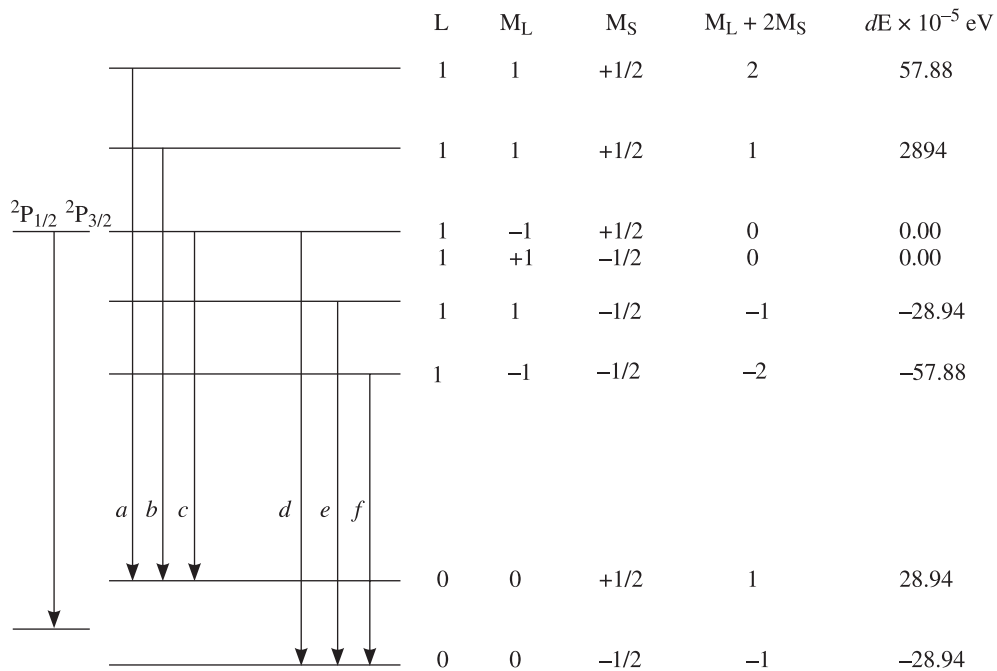


Fig. E-9

The change in magnetic energy of upper level due to interaction of magnetic moment of atom with applied magnetic field is given by

$$\begin{aligned} dE_{\text{upper}} &= \frac{e\hbar}{2m} B(M_L + 2M_S) \\ &= \left(5.79 \times 10^{-5} \frac{\text{eV}}{\text{T}} \right) (5\text{T})(M_L + 2M_S) \\ &= (28.94 \times 10^{-5} \text{eV})(M_L + 2M_S) \end{aligned}$$

The values of $M_L + 2M_S$ for upper levels are 2, 1, 0, 0, -1, -2. The states with the same values of $M_L + 2M_S$ coincide. Hence, the upper level splits in 5 sub-levels with energies shown in the figure. Similarly the lower energy level splits into two sub-levels.

The wavelength of a spectral line is given by

$$\frac{ch}{\lambda} = E_{\text{upper}} - E_{\text{lower}}$$

The change in wavelength due to change in energy is

$$\begin{aligned} -\frac{ch}{\lambda^2} d\lambda &= dE_{\text{upper}} - dE_{\text{lower}} \\ d\lambda &= -\frac{\lambda^2}{ch} (dE_{\text{upper}} - dE_{\text{lower}}) \\ &= -\frac{(1210 \text{ Å})^2}{12400 \text{ eV} \cdot \text{Å}} (dE_{\text{upper}} - dE_{\text{lower}}) \\ &= \left(-118 \frac{\text{Å}}{\text{eV}} \right) (dE_{\text{upper}} - dE_{\text{lower}}) \end{aligned}$$

The values of $(dE_{\text{upper}} - dE_{\text{lower}})$ for the transitions marked a, b, c, d, e, f in the figures are $(28.94, 0, -28.94, 28.94, 0, -28.94) \times 10^{-5} \text{ eV}$ respectively.

The transitions $(a, d), (b, e)$ and (c, f) coincide and hence, we get only three spectral lines.

For transitions marked a and d

$$\begin{aligned} d\lambda &= \left(-118 \frac{\text{Å}}{\text{eV}} \right) (dE_{\text{upper}} - dE_{\text{lower}}) \\ &= \left(-118 \frac{\text{Å}}{\text{eV}} \right) (57.88 - 28.94) \times 10^{-5} = -0.034 \text{ Å} \end{aligned}$$

Similarly for the transitions marked $b, e, d\lambda = 0$ and that for $c, f, d\lambda = 0.034 \text{ Å}$. The wavelengths of the lines in the pattern are 1210 Å and $1210 \pm 0.034 \text{ Å}$.

QUESTIONS AND PROBLEMS

1. What is Zeeman effect? Give the simple theory of normal Zeeman effect and obtain expression for the Zeeman effect. Explain the difference between a normal and anomalous Zeeman effects.

What should be the minimum value of the magnetic field to observe normal Zeeman effect?

Evaluate the magnetic field at which the Zeeman shift at 5400 Å spectral line is 0.1 Å.

2. Explain why does normal Zeeman effect occur only in atoms with even number of electrons? Differentiate between the normal Zeeman effect and anomalous Zeeman effect. Find an expression for Zeeman splitting for a two electron system.

Compute the Zeeman pattern for a diffuse series singlet-singlet transition.

3. What is anomalous Zeeman effect? Discuss the Zeeman splitting pattern of D_1 and D_2 lines of sodium.
4. Discuss the theory of Paschen-Back effect in one electron system and compute the pattern for the principal series doublet.
5. Distinguish between Zeeman and Paschen-Back effect. Outline the theory of Paschen-Back effect in one electron system and discuss the Paschen-Back pattern of ${}^2P \rightarrow {}^2S$ transition.
6. What is Lande g -factor? Calculate its value for the energy levels involved in the transitions ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ and ${}^1P_1 \rightarrow {}^1S_0$.

Can you get anomalous Zeeman pattern in both these transitions? Explain your answer.

7. Why Paschen-Back effect is called transition effect? Explain.

Obtain an expression for the change in energy in Paschen-Back effect.

Differentiate between normal Zeeman effect and Paschen-Back effect.

What will be the Zeeman shift for 6000 Å line in a magnetic field of 4 Tesla?

8. What is difference between normal Zeeman and Paschen-Back effect? Explain splitting of D-lines of sodium by Paschen-Back effect?
9. What is Stark effect? Discuss the weak-field Stark effect in H_α line of hydrogen. What are the main difference between Stark effect and Zeeman effect?
10. Calculate the g value for (i) ${}^2G_{9/2}$ (ii) ${}^3F_2$.

[Ans. (i) $L = 4, S = 1/2, J = 9/2, g = 10/9$

(ii) $L = 3, S = 1, J = 2, g = 2/3$]

11. Find the magnetic moment of an atom in state ${}^3P_2$.

[Ans. $\mu = g\mu_B\sqrt{J(J+1)}, g = 3/2, \mu = 3\sqrt{\frac{3}{2}}\mu_B$]

12. Find the magnetic moment of an atom in the state ${}^2P_{3/2}$. In how many sub-states will this state split in a weak magnetic field?

[Ans. $\mu = \frac{2}{3}\sqrt{15}\mu_B$. Number of sub-states = $2J + 1 = 4$]

13. An element emits light of wavelength 4500 Å. It is placed in a magnetic field of strength 0.3 Tesla. How far apart are the Zeeman components? $e/m = 1.76 \times 10^{11}$ C/kg, $c = 3 \times 10^8$ m/s.

[Ans. $\Delta\bar{\nu} = \frac{eB}{4\pi mc} = 14.0 \text{ m}^{-1}, \Delta\lambda = \lambda^2 \Delta\bar{\nu} = 283.5 \times 10^{-14} \text{ m} = 0.02835 \text{ Å}$]

X-RAYS AND X-RAY SPECTRA

5.1 INTRODUCTION

The German physicist Roentgen, while studying the properties of cathode rays in 1885 found that a very penetrating radiation was coming from the discharge tube. Since the nature of radiation was hitherto unknown, it was called X-rays. Subsequently, the properties of this radiation were thoroughly investigated and established but they are still known as X-rays. As we have already shown in the previous chapter that the characteristic spectrum in the visible region is correlated with the motion of electrons in atom, it is natural to seek a relationship between the structure of matter and characteristic X-ray spectrum. However, before turning to find such correlation, it is necessary to follow the experimental steps through which its basic nature was established.

The discovery of new and unknown radiation stimulated the imagination of many workers who made serious attempts to establish its nature. On the basis of several experiments, it was recognized that most of the properties of this radiation are similar to those of electromagnetic waves of very short wavelengths. Many attempts were made to observe the diffraction of X-rays by passing them through narrow slits. In 1906, Walter and Pohl carried out such an experiment and recorded the broadening of the image. Arnold Sommerfeld (1912) calculated the wavelength of X-rays and found that it is greater than $10 \text{ \AA}$. Later on, ruled gratings were used to observe X-ray diffraction and it was found that the wavelength of this radiation was of the order of $1 \text{ \AA}$.

5.2 LAUE PHOTOGRAPH

Although several methods of accurate measurements of the wavelength of X-rays were being developed, a German scientist, Von Laue made a remarkable discovery, which proved to be of tremendous importance for future development of physics, chemistry, metallurgy and medical science. Laue's ingenious suggestion was as follows. Since the wavelength of X-rays is of the order of $1 \text{ \AA}$, therefore, it is possible to observe the diffraction pattern if they are scattered by a crystal, which is a three-dimensional grating with inter atomic spacing of equal magnitude. On performing the experiment he actually observed a series of regularly spaced spots, called Laue's spots. Laue definitely established that these spots could only be due to diffraction of waves from atoms of the crystal. This experiment

proved two assumptions simultaneously, first: X-rays are electromagnetic waves of short wavelengths, second: atoms are regularly arranged in the crystal. Laue's experiment heralded a new era in physics by providing a very powerful tool for the determination crystal structure.

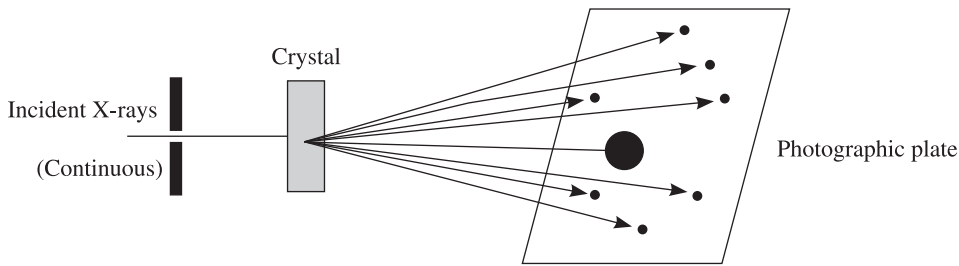


Fig. 5.2.1 Schematic diagram arrangement for getting Laue's photographs

5.3 CONTINUOUS AND CHARACTERISTIC X-RAYS

X-rays are produced when high-energy electrons, accelerated under high potential difference, strike a heavy metallic target. The distribution of X-rays intensity among various wavelengths at different accelerating potentials with molybdenum and tungsten as targets is shown in the Fig. (5.3.1). The important features of the curves may be stated as follows.

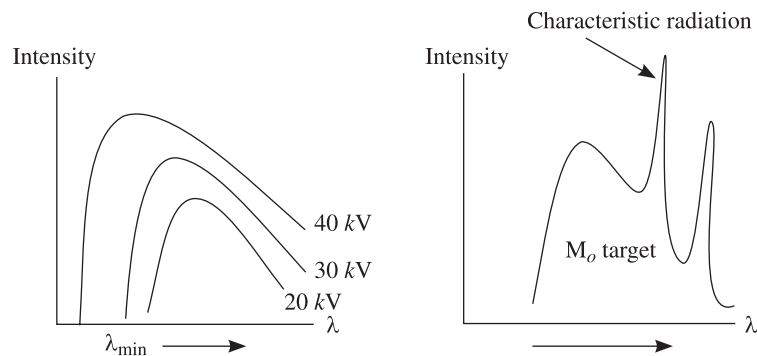


Fig. 5.3.1 Continuous and characteristic X-rays

- (i) For each accelerating potential there exists a short wavelength limit $\lambda_{\min}$ below which no radiation is produced. This short-wavelength limit depends only on the magnitude of the accelerating potential and not on the target material. Since the energy is continuously distributed among the various wavelengths like that in white radiation therefore the X-ray radiation is called *continuous* or *white radiation*. In 1915 Duane and Hunt observed that $\lambda_{\min}$ is proportional to the accelerating voltage.
- (ii) With increasing voltage the amount of radiation and intensity of radiation increases. For each target when the voltage is increased beyond a certain value, the intensity-wavelength

curve shows several peaks. In case of M_0 , peaks are observed at 35 kV. The wavelengths at which these peaks are observed are the characteristic of the target and are called *characteristic radiation*. The characteristic radiation is superposed on the continuous radiation.

Mechanism of Production of X-rays (Quantum Theory)

The classical theory provides no explanation for the existence of the short wavelength limit and the characteristic radiation. On the other hand, quantum theory provides straightforward explanation of both the experimental observations. As the highly energetic electron beam passes through the target material, it collides with the nuclei and the electrons of the target atoms. The electron-electron collisions, which are slow deceleration process, are not responsible for the production of X-rays.

X-rays are actually produced from less frequent but more catastrophic encounters of the incoming electrons with the target nuclei. In Fig. (5.3.2), an electron with initial kinetic energy T is shown passing nearby a nucleus. It interacts with the nucleus via Coulomb field, transferring momentum to the nucleus. In the process a part of energy of electron is converted into photon. The target nucleus is so heavy that it does not recoil. After encounter the electron moves with remaining energy T' . The frequency ν or the wavelength λ of the emitted radiation is given by

$$h\nu = ch/\lambda = T - T' \quad \dots(5.3.1)$$

The incoming electron suffers many encounters with target nuclei before coming to rest and loses different amount of energy in such collisions. The emitted radiation, therefore, forms a continuous spectrum.

The X-ray photon of shortest wavelength (highest frequency) is emitted when the incident electron loses all of its kinetic energy in a single encounter. In this case $T' = 0$ and hence

$$h\nu_{\max} = \frac{ch}{\lambda_{\min}} = T \quad \text{where } T = eV$$

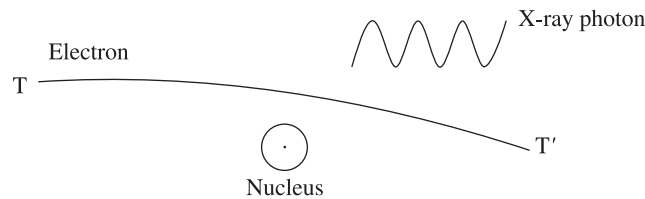


Fig. 5.3.2 Emission of continuous X-rays

V is the accelerating voltage. From above relation, we have

$$\frac{ch}{\lambda_{\min}} = eV$$

whence

$$\lambda_{\min} = \frac{ch}{eV} = \frac{12400}{V(\text{volt})} \text{ \AA} \quad \dots(5.3.2)$$

In expression (5.3.2) V represents the numerical value of applied voltage in volt. The above equation is known as Duane and Hunt law. Thus, we see that quantum theory provides an easy and convincing explanation for the existence of short wavelength limit. If we set $h = 0$ we get $\lambda_{\min} = 0$. This means that the existence of $\lambda_{\min}$ is a quantum mechanical phenomenon. The emission of X-ray from decelerating electron is called **Bremsstrahlung process**. This process is sometimes called **inverse photoelectric effect**. In a photoelectric process, photon is absorbed; its energy and momentum are transferred to electron. In *bremsstrahlung* process, a photon is created; its energy and momentum are derived from the electron-nuclear collision.

5.4 X-RAY ENERGY LEVELS AND CHARACTERISTIC X-RAYS

When a high-energetic electron of cathode ray strikes the target (anticathode) of the X-ray tube, it penetrates the target atom and knocks out one of the electron from the inner shell such as K or L shell. Thus, a vacancy or hole is created in the atom. If the vacancy or hole is created in K shell, it may be filled by electron from the L or M or N shell etc. If the vacancy is created in L shell, it may be filled by electron from L or M shell or higher shells. If the vacancy of K shell is filled up by electron from L shell, the vacancy moves from K to L shell. Thus, the electronic transition is opposite to the vacancy (*hole*) transition.

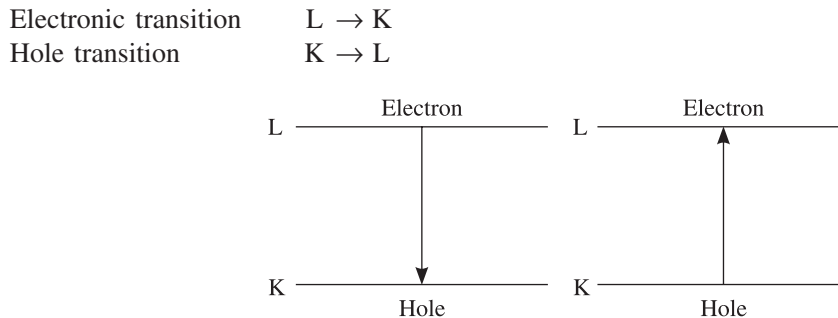


Fig. 5.4.1 Electron and hole transition

When the electrons make transition from L, M, N... shells to K shell, the spectral lines K series (K_{α} , K_{β} , ...) are emitted. Similarly, the electronic transitions from M, N, ... levels to L level give rise to spectral lines of L series (L_{α} , L_{β} , ...). The observations, made by high resolving power instruments, indicate that the individual lines of K series are not single but possess fine structure. This is true for the lines of L series too. Thus, the X-ray spectral lines show fine structure. The existence of fine structure can be explained as follows.

X-ray energy levels are specified by four quantum numbers: principal quantum number (n), orbital angular momentum quantum number (l) and total angular momentum quantum number (j) and magnetic quantum number m_j . For K shell, $n = 1$, $l = 0$ and $j = l \oplus s = 0 \oplus 1/2 = 1/2$. Thus we have a single K level, which can accommodate two electrons in the states corresponding to $m_j = -1/2$ and $1/2$. Similarly for L shell, $n = 2$, $l = 0, 1$, $j = 1 \oplus s = 0 \oplus 1/2$ and $1 \oplus 1/2$ i.e., $j = 1/2, 1/2, 3/2$. Thus, there are three levels in L shell designated by L_I , L_{II} , L_{III} . Of these the first level accommodates

two electrons corresponding to $m_j = -1/2, 1/2$, the second level two electrons corresponding to $m_j = -1/2, 1/2$, and the third level four electrons corresponding to $m_j = -3/2, -1/2, 1/2, 3/2$. Thus, the L shell can contain 8 electrons. Similarly for M shell, $n = 3$, we have five levels designated as $M_I, M_{II}, M_{III}, M_{IV}, M_V$. The N shell contains seven levels, which are denoted by $N_I, N_{II}, N_{III}, N_{IV}, N_V, N_{VI}, N_{VII}$. The spectral terms corresponding to these levels are:

K, $1^2S_{1/2}$,	L_I , $2^2S_{1/2}$,	L_{II} , $2^2P_{1/2}$,	L_{III} , $2^2P_{3/2}$,	M_I , $3^2S_{1/2}$,	M_{II} , $3^2P_{1/2}$,	M_{III} , $3^2P_{3/2}$,	M_{IV} , $3^2D_{3/2}$,	M_V , $3^2D_{5/2}$.
N_I , $4^2S_{1/2}$,	N_{II} , $4^2P_{1/2}$,	N_{III} , $4^2P_{3/2}$,	N_{IV} , $4^2D_{3/2}$,	N_V , $4^2D_{5/2}$,	N_{VI} , $4^2F_{5/2}$,	N_{VII} , $4^2F_{7/2}$		

The filling of electrons in these shells is shown in the table.

In X-ray spectroscopy a neutral atom in the ground state is assigned zero energy and that having vacancy (hole) in the inner level is assigned positive energy. For instance, if K electron is missing, it has a vacancy there and it is assumed to have positive energy equal to the energy required to remove the K electron from the atom. Obviously the energy of the atom having vacancy in K shell has highest energy. For tungsten ($_{74}\text{W}$) the energy levels are shown in the Fig. 5.4.2.

Table 5.4.1

Shell	l	j	m_j	Maximum no. of electrons	Level notation
K ($n = 1$)	0	1/2	1/2, -1/2	2	$K(1^2S_{1/2})$
L ($n = 2$)	0	1/2	1/2, -1/2	2	$L_I(2^2S_{1/2})$
	1	1/2	1/2, -1/2	2	$L_{II}(2^2P_{1/2})$
	1	3/2	3/2, 1/2, -1/2, -3/2	4	$L_{III}(2^2P_{3/2})$
M ($n = 3$)	0	1/2	1/2, -1/2	2	$M_I(3^2S_{1/2})$
	1	1/2	1/2, -1/2	2	$M_{II}(3^2P_{1/2})$
	1	3/2	3/2, 1/2, -1/2, -3/2	4	$M_{III}(3^2P_{3/2})$
	2	3/2	3/2, 1/2, -1/2, -3/2	4	$M_{IV}(3^2D_{3/2})$
	2	5/2	5/2, 3/2, 1/2, -1/2, -3/2, -5/2	6	$M_V(3^2D_{5/2})$
N $n = 4$	0	1/2	1/2, -1/2	2	$N_I(4^2S_{1/2})$
	1	1/2	1/2, -1/2	2	$N_{II}(4^2P_{1/2})$
	1	3/2	3/2, 1/2, -1/2, -3/2	4	$N_{III}(4^2P_{3/2})$
	2	3/2	3/2, 1/2, -1/2, -3/2	4	$N_{IV}(4^2D_{3/2})$
	2	5/2	5/2, 3/2, 1/2, -1/2, 3/2, 5/2	6	

The splitting of L level into three components (L_I , L_{II} , L_{III}), M level into five components (M_I , M_{II} , M_{III} , M_{IV} , M_V), N level into seven components (N_I , N_{II} , N_{III} , N_{IV} , N_V , N_{VI} , N_{VII}) etc., is called fine structure.

When a hole makes transition from K to L, M, N ... levels etc., the X-ray lines emitted are said to constitute K-series. Similarly, when a hole moves from L to M, N, ...etc., level, the lines of L series originate. The allowed transitions are those, which obey the selection rules

$$\Delta l = \pm 1, \Delta j = 0, \pm 1$$

A few lines emitted from tungsten are shown in the Fig. (5.4.2).

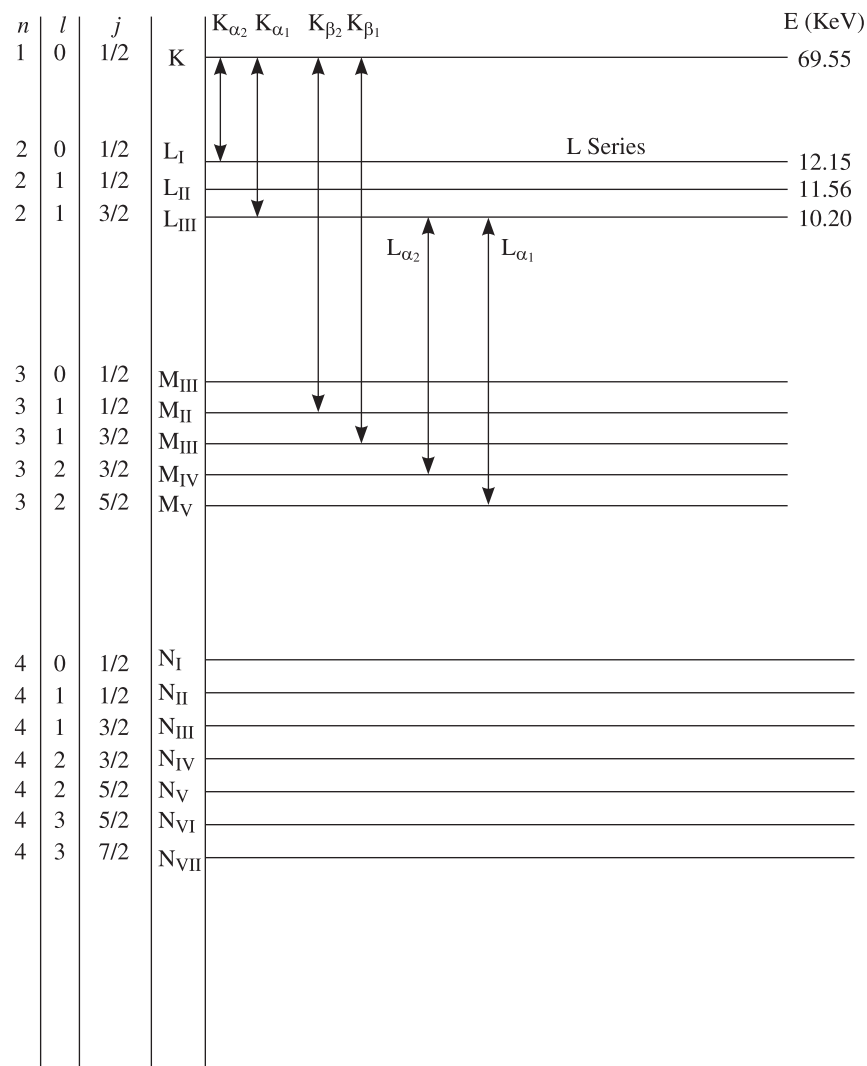


Fig. 5.4.2 X-ray energy levels of tungsten

In hydrogen atom the electron experiences the attractive force due to full nuclear charge of proton and the energy of electron is given by $E_n = -RchZ^2/n^2$ or the term value by $T_n = RZ^2/n^2$. In a heavy atom with filled K, L, M... shells, one of the K electron screens the nucleus as a result of which the other electron does not experience the full attractive force of the nucleus. In other words, each of the K electron 'sees' the nuclear charge reduced by one unit. This amounts to say that the screening constant σ of K electron is 1. Similarly, the each electron in L shell doesn't 'see' the full nuclear charge due to screening of K electrons (called internal screening) and due to the remaining electrons of L shell as well as, to some extent, due to outer electrons (called external screening). These two kinds of screening combine and reduce the nuclear charge for L electron. The screening constant L electron is nearly 2. For electrons of M shell, two K electrons and eight L electrons screen the nucleus and hence the screening constant for M shell is close to 10.

Taking spin-orbit interaction and relativity correction into consideration Dirac theory of electron gives the following expression for the term value of an energy level with principal quantum number n .

$$T_n = \frac{R(Z-\sigma)^2}{n^2} + \frac{R\alpha^2(Z-\sigma)^4}{n^4} \left\{ \frac{n}{j+\frac{1}{2}} - \frac{3}{4} \right\} + \frac{R\alpha^4(Z-\sigma)^6}{n^6} \left\{ \frac{1}{4} \left(\frac{n}{j+\frac{1}{2}} \right)^3 + \frac{3}{4} \left(\frac{n}{j+\frac{1}{2}} \right)^2 - \frac{3}{2} \left(\frac{n}{j+\frac{1}{2}} \right) + \frac{5}{8} \right\} \quad \dots(5.4.1)$$

5.5 MOSELEY'S LAW

In 1913, a young British physicist Henry Moseley (1887–1915) was undertaking a systematic study of the characteristic spectra of a large number of elements. During his investigation he found that the frequencies of the emitted lines were the characteristic properties of the elements. He established that square root of the frequencies of the spectral lines, for example K_α line, were proportional to the atomic number Z of the element.

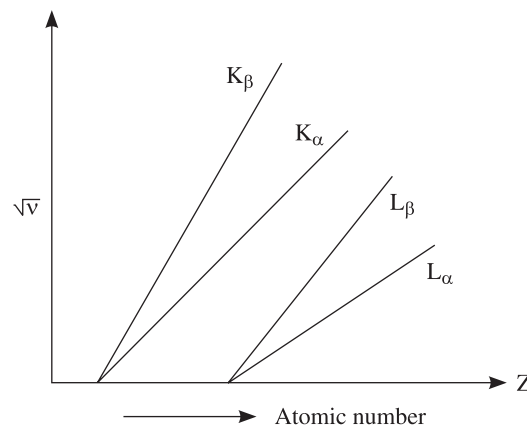


Fig. 5.5.1 Moseley's law

$$\sqrt{\nu} = a(Z - b) \quad \dots(5.5.1)$$

where a and b are constants for a given series.

Moseley's discovery is of extreme importance because it established that atomic number is more fundamental quantity than atomic weight. This fact formed the basis of deciding the correct order of elements in the periodic table.

Moseley discovery came after Bohr's theory of hydrogen atom was published. It is remarkable to note that Bohr's theory, although proposed for one electron atom, was capable of explaining the Moseley law. According to Bohr's theory the wavelength of a spectral line is given by

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

For K_α line $n_f = 1$, $n_i = 2$ and therefore

$$\frac{1}{\lambda_{K\alpha}} = \frac{3}{4} RZ^2 \quad \dots(5.5.2)$$

In Bohr's theory of one electron atom, the energy of electron in a shell is derived by assuming that the electron "sees" full nuclear charge. This assumption is valid for one electron only. In many electron atoms this assumption requires modification. In K shell there are two electrons; each electron *shields* or *screens* the nucleus for the other as a result of which an electron in the atom does not experience the attraction of the full nuclear charge. Similarly, an electron in the L shell is shielded by K electrons and to some extent by the other electrons of the L shell itself. Therefore each electron in the L shell does not see the full nuclear charge. This lessening effect of nuclear charge by surrounding electrons is known as *shielding effect* or *screening effect*. If the shielding effect is taken into account, the nuclear charge number Z in Eqn. (5.5.2) must be replaced by $(Z - b)$ where b is a measure of shielding effect. The formula (5.5.1) then becomes

$$\frac{1}{\lambda_{K\alpha}} = \frac{3}{4} R(Z - b)^2 \quad \dots(5.5.3)$$

For the lines of K series, $b = 1$ and those of L series, $b = 7.4$. Hence

$$\frac{1}{\lambda_{K\alpha}} = \frac{3}{4} R(Z - 1)^2 \quad \dots(5.5.4)$$

or

$$\nu_{K\alpha} = \frac{3cR}{4} (Z - 1)^2$$

5.6 SPIN-RELATIVITY DOUBLET OR REGULAR DOUBLET

A pair of energy levels having the same n , S , L values but different J values is called spin-relativity (regular) doublet. Such pairs are (L_{II}, L_{III}) , (M_{II}, M_{III}) , (M_{IV}, M_V) , (N_{II}, N_{III}) , (N_{IV}, N_V) ,

(N_{VI} , N_{VII}) or ($2^2P_{1/2}$, $2^2P_{3/2}$), ($3^2P_{1/2}$, $3^2P_{3/2}$), ($3^2D_{3/2}$, $3^2D_{5/2}$), ($4^2P_{1/2}$, $4^2P_{3/2}$), ($4^2D_{3/2}$, $4^2D_{5/2}$), ($4^2F_{5/2}$, $4^2F_{7/2}$).

It is observed that *the difference of wave numbers of spin relativity doublets is approximately proportional to the fourth power of effective atomic number*. This fact is known as **spin-relativity (regular) doublet law**. This law can be obtained from the Dirac result for the term value. Let us calculate the wave number separation for the screening doublet L_{II} and L_{III} .

For L_{II} , $n = 2$, $L = 1$, $S = 1/2$, $J = 1/2$, and for L_{III} , $n = 2$, $L = 2$, $S = 1/2$, $J = 3/2$. Thus

$$T_2(L_{II}) = \frac{R(Z-\sigma)^2}{2^2} + \frac{R\alpha^2(Z-\sigma)^4}{2^4} \left\{ 2 - \frac{3}{4} \right\} + \frac{R\alpha^4(Z-\sigma)^6}{2^6} \left\{ \frac{1}{4} \left(\frac{2}{1} \right)^3 + \frac{3}{4} \left(\frac{2}{1} \right)^2 - \frac{3}{2} \left(\frac{2}{1} \right) + \frac{5}{8} \right\} \quad \dots(5.6.1)$$

$$T_2(L_{III}) = \frac{R(Z-\sigma)^2}{2^2} + \frac{R\alpha^2(Z-\sigma)^4}{2^4} \left\{ 1 - \frac{3}{4} \right\} + \frac{R\alpha^4(Z-\sigma)^6}{2^6} \left\{ \frac{1}{4} + \frac{3}{4} - \frac{3}{2} + \frac{5}{8} \right\} \quad \dots(5.6.2)$$

$$T_2(L_{II}) - T_2(L_{III}) = \frac{R\alpha^2(Z-\sigma)^4}{16} \left\{ 1 + \frac{5}{8}(Z-\sigma)^2 \right\}$$

Neglecting the second term in the curly bracket we find that

$$\Delta\bar{\nu} = T_2(L_{II}) - T_2(L_{III}) = \frac{R\alpha^2(Z-\sigma)^4}{16}, \quad \sigma = 3.5$$

For a given value of L , $\sigma = \text{constant}$, hence $\Delta\bar{\nu} \propto (Z-\sigma)^4$.

Similarly, for M_{II} and M_{III} , we find

$$\Delta\bar{\nu}(M_{II}, M_{III}) = \frac{R\alpha^2(Z-\sigma)^4}{81} \left[\frac{3}{2} + \frac{31}{32} \alpha^2(Z-\sigma)^2 \right], \quad \sigma = 8.5 \quad \dots(5.6.3)$$

5.7 SCREENING (IRREGULAR) DOUBLET

A pair of levels having the same values of n , S and J but different values of L is called screening doublet. Examples of such pairs are:

(L_I , L_{II}), (M_I , M_{II}), (M_{III} , M_{IV}), (N_I , N_{II}), (N_{III} , N_{IV}), (N_V , N_{VI}) or ($2^2S_{1/2}$, $2^2P_{1/2}$), ($3^2S_{1/2}$, $3^2P_{1/2}$), ($3^2P_{3/2}$, $3^2D_{3/2}$), ($4^2S_{1/2}$, $4^2P_{1/2}$), ($4^2P_{3/2}$, $4^2D_{3/2}$), ($4^2D_{5/2}$, $4^2F_{5/2}$).

It is observed that *the difference in term values of pair of screening doublets is proportional to the difference in the values of screening constants of the two components of the doublet*. This law is known as the **screening (irregular) doublet law**.

Confining ourselves to the first term in the expression for term value, we have

$$T_n = \frac{R(Z - \sigma)^2}{n^2} \quad \dots(5.7.1)$$

$$\sqrt{T_n} = \frac{\sqrt{R}}{n} (Z - \sigma) \quad \dots(5.7.2)$$

For the screening doublet L_I and L_{II} , $n = 2$, we have

$$\sqrt{T_2}(L_I) = \frac{\sqrt{R}}{2} (Z - \sigma_I) \quad \dots(5.7.3)$$

$$\text{and} \quad \sqrt{T_2}(L_{II}) = \frac{\sqrt{R}}{2} (Z - \sigma_{II}) \quad \dots(5.7.4)$$

Therefore

$$\sqrt{T_2}(L_I) - \sqrt{T_2}(L_{II}) = \frac{\sqrt{R}}{2} [\sigma_{II} - \sigma_I] \quad \dots(5.7.5)$$

$$\text{or} \quad \Delta(\sqrt{T}) = \text{const.} (\sigma_{II} - \sigma_I)$$

which is independent of Z .

5.8 ABSORPTION OF X-RAYS

If a collimated beam of X-rays is made to pass through a medium, the intensity of beam decreases. Let I_0 be the intensity of incident beam, I the intensity after traversing a distance x , $-dI$ the reduction in intensity after traversing an infinitesimal distance dx . It is found that fractional loss of intensity is proportional to dx

$$\begin{aligned} -\frac{dI}{I} &\propto dx \\ -\frac{dI}{I} &= \mu dx \end{aligned} \quad \dots(5.8.1)$$

where μ is a constant called the *linear absorption coefficient* and has the dimensions of m^{-1} . The value of μ depends on the wavelength of X-rays and the absorbing material.

Integrating Eqn. (5.8.1), we have

$$\begin{aligned} \int_{I_0}^I \frac{dI}{I} &= -\mu \int_0^x dx \\ I &= I_0 e^{-\mu x} \end{aligned} \quad \dots(5.8.2)$$

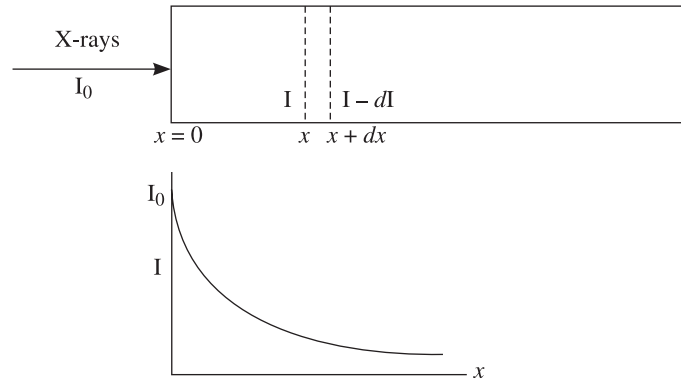


Fig. 5.8.1 Absorption of X-rays

Thus, the intensity of X-rays falls exponentially with the distance x traversed in the absorbing material. Eqn. (5.8.1) is usually expressed in terms of *mass absorption (attenuation) coefficient* μ_m which is defined by $\mu_m = \mu/\rho$, ρ being the density of the material. The linear absorption coefficient is a measure of the probability per unit length for removal of X-ray photons while passing through a material medium.

Mechanism of Absorption

The primary interaction processes responsible for the absorption of electromagnetic radiation are (i) photoelectric effect, (ii) Compton scattering and (iii) pair production. Because X-ray photons have energies in the range 1–100 KeV, they cannot produce pair production (for which threshold energy = 1.02 MeV). Therefore, the reduction in intensity of X-rays is caused by only the first two factors, the photoelectric effect being the dominant mechanism.

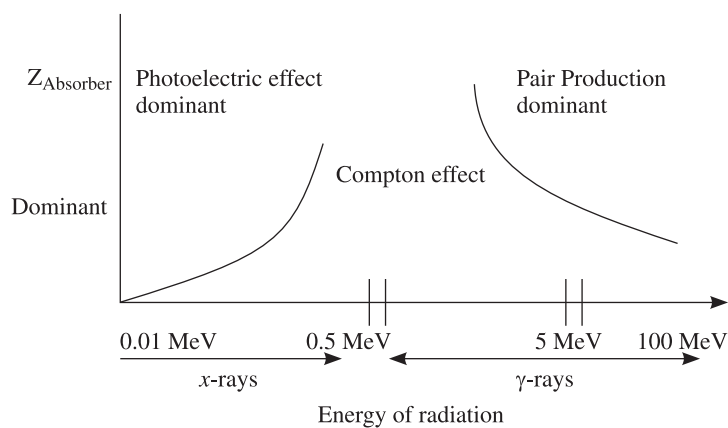


Fig. 5.8.2

Photoelectric Effect

The photoelectric effect is the term applied to a process in which an atom absorbs a photon and emits an electron. A peculiar characteristic of photoelectric effect is that a free electron cannot absorb or emit a photon because of the combined effect of the laws of conservation of energy and momentum. The probability of photoelectric effect is maximum if the energy of photon is comparable to the binding energies of electron. An increase in energy of photon should be accompanied by a drastic fall in the absorption coefficient because the atomic electrons become progressively more like free electrons. The binding energies of K electrons vary from 1.56 KeV for Al to 88.10 KeV for Pb, which lies in the X-ray range. Binding energies of L are less than those of K electrons. Hence photoelectric effect is more likely to take place with K and L electrons. Now we can explain the dependence of absorption coefficient on the energy (or wavelength) of X-ray photon. This dependence is shown in the Fig. (5.8.2). At very high energies (small wavelengths) of X-ray photons, the atomic electrons of the absorbing material behave like free electrons and hence the probability of photoelectric absorption is small. With decrease in energy (or increase in wavelength) of X-ray photons, the probability of photoelectric absorption increases and becomes maximum when the energy of photon becomes equal to the binding energy of K electrons. At this energy maximum number of K electrons are ejected from the absorbing material. The wavelength (λ_K) of the X-ray corresponding to maximum absorption is called **K absorption edge**. Obviously the wavelength λ_K of K absorption edge gives the binding energy E_K of K electron.

$$E_K = \frac{ch}{\lambda_K} \quad \dots(5.8.3)$$

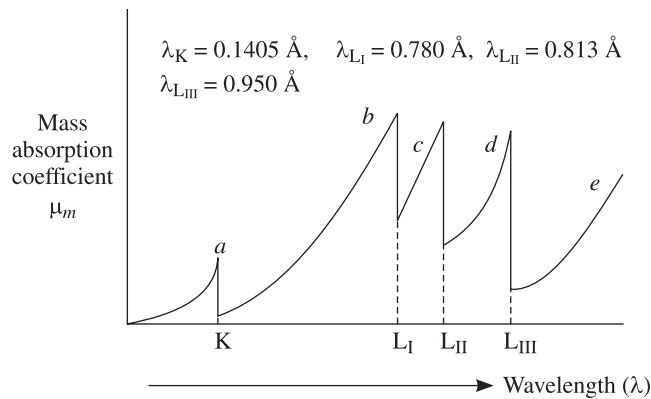


Fig. 5.8.3 K and L absorption edges of Pb

At energy lower than E_K or at wavelength greater than λ_K , the absorption suddenly drops because X-ray photons are unable to eject K electrons. Although this energy is sufficient to eject L electrons but probability of this ejection is small. With further decrease in energy (or increase in wavelength) the photoelectric absorption (associated with the ejection of L electrons) increases and again becomes maximum when the energy of photon is just equal to the binding energy of L electron. Since, there are three L levels, there are three absorption edges L_I , L_{II} and L_{III} . With further increase in energy we observe five absorption edges M_I , M_{II} , M_{III} , M_{IV} , M_V corresponding to five M levels.

Except at absorption edges, the dependence of photoelectric absorption on atomic number Z of the absorbing material and energy (E) of the photon is approximately described by the formula

$$\begin{aligned}\mu_{\text{photo}} &= CZ^4 E^{-3} \\ &= C'Z^4 \lambda^3\end{aligned}\quad \dots(5.8.4)$$

Absorption due to Compton Scattering

The scattering of X-ray photons by weakly bound atomic electrons is called the Compton effect. As a result of Compton scattering the X-ray photons are deflected from their original direction and hence don't reach the detector. The absorption coefficient corresponding to Compton effect is given by

$$\mu_{\text{Compton}} = C \frac{Z}{E}, \quad C = \text{constant} \quad \dots(5.8.5)$$

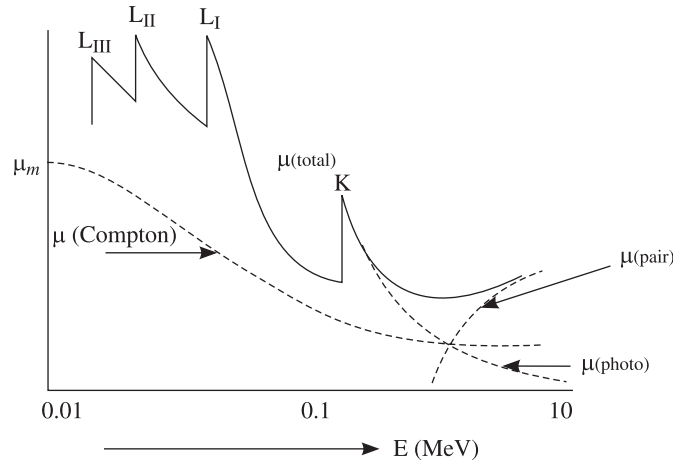


Fig. 5.8.4 Absorption coefficient vs energy of X-ray photon

In lead the Compton effect supersedes the photoelectric effect at energy $E > 0.5$ MeV. The contributions of photoelectric absorption, Compton scattering and pair production to the total absorption as function of energy is shown in the Fig. (5.8.4).

5.9 BRAGG'S LAW

A simplified way of looking at the process of X-ray diffraction by a crystal was proposed by W.L. Bragg. He suggested that through any crystal a set of equidistant parallel planes might be imagined through all the atoms of the crystal. In Fig. (5.9.1) some typical systems of planes with their spacing are shown. These planes are called *Bragg planes* and their spacing *Bragg spacing*.

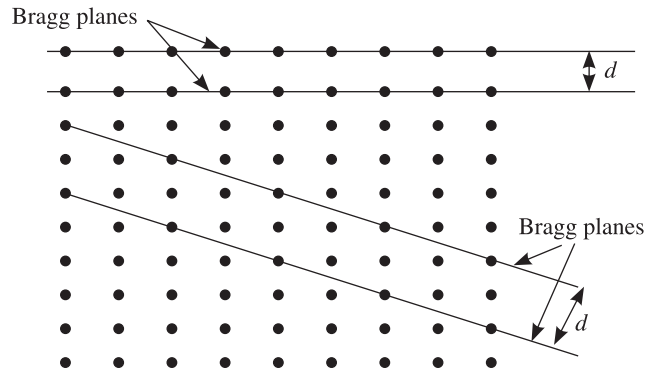


Fig. 5.9.1 Atoms in a crystal are arranged in a regular way in three dimensions. Here a hypothetical two-dimensional arrangement of atoms is shown. Atoms in a crystal are very close together. In the figure they are shown far apart. Some families of Bragg planes with their spacing are shown

Consider a set of parallel planes of atoms in a crystal, two of which are represented by the lines AA and BB. The actual planes are perpendicular to the plane of the paper. Suppose that a beam of monochromatic X-rays is incident at these planes. Let the incident rays make angle θ with the planes. This angle is called the *glancing angle*. The incident rays 1 and 2 will be scattered by atoms of the upper plane. These scattered waves reinforce in the direction $\theta' = \theta$, which is the condition of *specular reflection*. Thus, the atomic planes act as a mirror. Now consider the condition of reinforcement of waves reflected from successive planes that are parallel to AA. The requirement to be satisfied for the constructive interference is that the path difference for rays reflected from successive planes be equal to integral number of wavelength.

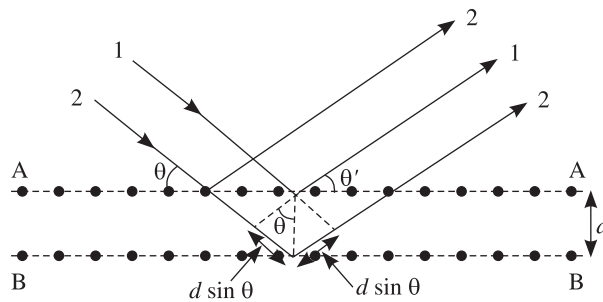


Fig. 5.9.2 Reflection of X-rays from Bragg planes

From the Fig. (5.9.2), we can see that the path difference between rays reflected from the successive planes having inter-planar distance d is $2d \sin \theta$. Hence the condition for constructive interference is

$$2d \sin \theta = n \lambda, \quad n = 1, 2, 3, \dots \quad \dots(5.9.1)$$

This equation is known as Bragg's law.

Bragg's Spectrometer

This spectrometer was designed by W. H. Bragg and his son W. L. Bragg to determine the wavelength of X-rays. It consists of (i) a crystal (usually of rock-salt or calcite or mica) mounted on a table, which can be rotated about a vertical axis (ii) a device for detecting reflected X-rays from the crystal. The detector, which is usually an ionization chamber, is mounted on a arm capable of rotating about the same vertical axis. Making use of slits, a narrow beam of X-rays is allowed to fall on the crystal at angle, say θ and the detector rotated to receive those rays, which are reflected at angle θ . From the very setting of the detector, it is clear that the X-rays reaching it obey the Bragg's condition. By varying the angle θ (by rotating the crystal and the detector both) reflections of different orders can be recorded. If $\theta_1, \theta_2, \theta_3, \dots$ are the Bragg's angles corresponding to the first, second, third orders then we have

$$2d \sin \theta_1 = \lambda$$

$$2d \sin \theta_2 = 2\lambda$$

If the Bragg's spacing d is known, the wavelength λ can be calculated.

From the following data let us calculate the inter-planar distance in sodium chloride crystal, which is a cubic lattice.

Molecular weight = 58.5 kg/k mol

Density = $2.16 \times 10^3 \text{ kg/m}^3$

Avogadro's number = $6.02 \times 10^{26} \text{ molecules/k mol}$

Molar volume $V_m = \frac{M}{\rho}$

Volume available to a single molecule = $\frac{V_m}{N_A} = \frac{M}{\rho N_A}$

Volume available to a single ion = $\frac{M}{2\rho N_A}$

If d is the inter-atomic distance then $d^3 = \frac{M}{2\rho N_A}$

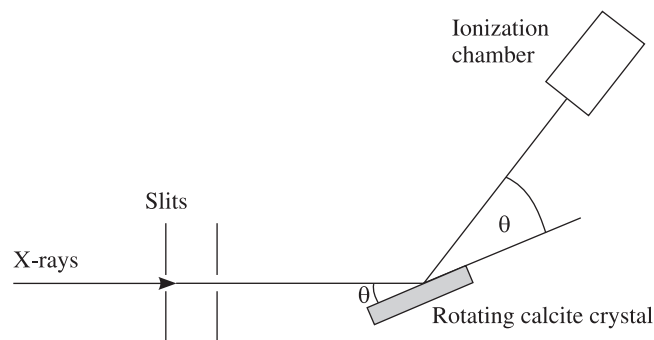


Fig. 5.9.3 Schematic diagram of Bragg's spectrometer

$$\therefore d = \left(\frac{M}{2\rho N_A} \right)^{1/3} = \left(\frac{58.5}{2 \times 2.16 \times 10^3 \times 6.02 \times 10^{26}} \right)^{1/3}$$

$$= 2.82 \times 10^{-10} \text{ m} = 2.82 \text{ \AA}.$$

SOLVED EXAMPLES

Ex. 1. What is the minimum voltage across an X-ray tube that will produce an X-ray having (i) the Compton wavelength, (ii) a wavelength of $1 \text{ \AA}$ and (iii) a wavelength to be capable of pair production.

Sol. (i) Compton wavelength $\lambda = \lambda_{\min} = 0.024 \text{ \AA}$

$$\lambda_{\min} = \frac{12400 \text{ eV} \cdot \text{\AA}}{x \text{ eV}} \text{ where } x \text{ is the numerical value of applied voltage in volt.}$$

$$x = \frac{12400 \text{ eV} \cdot \text{\AA}}{\lambda_{\min}} = \frac{12400 \text{ eV} \cdot \text{\AA}}{0.024 \text{ \AA}} = 511 \times 10^3 \text{ volt}$$

$$(ii) \quad x = \frac{12400 \text{ eV} \cdot \text{\AA}}{\lambda_{\min}} = \frac{12400 \text{ eV} \cdot \text{\AA}}{1 \text{ \AA}} = 12.4 \text{ KV}.$$

(iii) For pair production, the minimum energy of X-ray photon is 1.02 MeV . The electrons striking the target in X-ray tube must have at least this much energy. The tube, therefore, must be operated at 1.02 million volt.

Ex. 2. A voltage applied to an X-ray being increased n times, the short wave limit of X-ray continuous spectrum shifts by $d\lambda = 26 \text{ pm}$. If $n = 3/2$, find the initial voltage applied to the tube.

Sol. At initial voltage

$$\lambda_m = \frac{ch}{eV}$$

At the final voltage

$$\lambda'_m = \frac{ch}{eV'}$$

$$d\lambda = \lambda_m - \lambda'_m = \frac{ch}{e} \left(\frac{1}{V} - \frac{1}{V'} \right) = \frac{ch}{e} \left(\frac{1}{V} - \frac{1}{nV} \right)$$

$$V = \left(\frac{n-1}{n} \right) \frac{ch}{e \cdot d\lambda} = \left(\frac{1}{3} \right) \frac{12400 \text{ eV} \cdot \text{\AA}}{e \cdot (0.26 \text{ \AA})} = 15.9 \text{ KV}$$

Ex. 3. The wavelength of K_α line of an element is $1.54 \text{ \AA}$. Determine the atomic number of the target element.

Sol. For K_α line, $\frac{1}{\lambda} = \frac{3}{4} R(Z-1)^2$ whence $Z = 1 + \sqrt{\frac{4}{3\lambda R}}$

$$Z = 1 + 28.2 \approx 29.$$

Ex. 4. Find the wavelength of K_α line in Copper ($Z = 29$) if the wavelength of K_α line in iron is known to be 193 pm.

Sol. For copper the wavelength of K_α line is

$$\frac{1}{\lambda} = \frac{3}{4} R (Z_1 - 1)^2$$

and that for iron is

$$\frac{1}{\lambda'} = \frac{3}{4} R (Z_2 - 1)^2$$

$$\therefore \frac{\lambda'}{\lambda} = \frac{(Z_1 - 1)^2}{(Z_2 - 1)^2} = \left(\frac{28}{27} \right)^2$$

$$\lambda' = \left(\frac{28}{27} \right)^2 (193 \text{ pm}) = 154 \text{ pm}.$$

Ex. 5. Proceeding from Moseley's law find the wavelength of K_α line in Al and Co.

Sol. Moseley's law: $\frac{1}{\lambda} = \frac{3}{4} R (Z - 1)^2$

$$\therefore \lambda = \frac{4}{3R(Z-1)^2} = \frac{4}{3 \times 1.097 \times 10^7 (13-1)^2}$$

$$= 844 \times 10^{-12} \text{ m} = 844 \text{ pm}$$

For cobalt ($Z = 27$), $\lambda = 180 \text{ pm}$.

Ex. 6. How many elements are there in a row between those whose wavelengths of K_α line are equal to 250 pm and 179 pm?

Sol. For K_α line: $\frac{1}{\lambda} = \frac{3}{4} R (Z - 1)^2 \Rightarrow Z = 1 + \sqrt{\frac{4}{3\lambda R}}$

Putting $\lambda_1 = 250 \text{ pm}$ and $\lambda_2 = 179 \text{ pm}$ in above equation, we get

$$Z_1 = 23 \text{ and } Z_2 = 27$$

The required elements are: $Z = 24, 25$ and 26 .

Ex. 7. Calculate the binding energy of a K electron in vanadium ($Z = 23$) whose L absorption edge has a wavelength $\lambda_L = 2.4 \text{ nm}$.

Sol. Binding energy of L electron

$$E_L = \frac{ch}{\lambda_L}$$

$$= \frac{12400 \text{ eV} \cdot \text{\AA}}{24 \text{ \AA}} = 516 \text{ KeV}$$

Wavelength of K_α line is given by

$$E_K - E_L = \frac{ch}{\lambda_{K\alpha}} = \frac{3}{4} Rch(Z-1)^2, \quad (Rch = 13.6 \text{ eV})$$

$$= \frac{3 \times 13.6 \text{ eV} \times (23-1)^2}{4} = 4.937 \text{ KeV}$$

Binding energy of K electron $E_K = 0.516 \text{ KeV} + 4.937 \text{ KeV}$

$$= 5.55 \text{ KeV.}$$

Ex. 8. The K absorption edge of tungsten is $0.178 \text{ \AA}$ and the wavelength of K_α line is $0.210 \text{ \AA}$. Determine the wavelength of L absorption edge.

Sol. The wavelength of absorption edge is measure of the binding energy of the corresponding electron. The binding energy of K electron is

$$E_K = \frac{ch}{\lambda_K} = \frac{12.4 \text{ KeV} \cdot \text{\AA}}{0.178 \text{ \AA}} = 69.67 \text{ KeV}$$

The wavelength of K_α line is given by

$$E_K - E_L = \frac{ch}{\lambda_{K\alpha}}$$

$$= \frac{12.4 \text{ KeV} \cdot \text{\AA}}{0.210 \text{ \AA}} = 59.04 \text{ KeV}$$

$$\therefore E_L = (69.67 - 59.04) \text{ KeV} = 10.63 \text{ KeV}$$

The wavelength of L absorption edge is given by

$$E_L = \frac{ch}{\lambda_L} \Rightarrow \lambda_L = \frac{ch}{E_L} = \frac{12.4 \text{ KeV} \cdot \text{\AA}}{10.63 \text{ KeV}} = 1.17 \text{ \AA}.$$

Ex. 9. For tungsten the K absorption edge is $0.18 \text{ \AA}$. It is irradiated with X-rays of wavelength $0.10 \text{ \AA}$. What is the maximum kinetic energy of photoelectrons that are emitted from K shell?

Sol. Binding of K electron $E_K = \frac{ch}{\lambda_K} = \frac{12.4 \text{ KeV} \cdot \text{\AA}}{0.18 \text{ \AA}} = 68.89 \text{ KeV}$

Energy of incident photon $E = \frac{ch}{\lambda} = \frac{12.4 \text{ KeV} \cdot \text{\AA}}{0.10 \text{ \AA}} = 124 \text{ KeV}$

The maximum kinetic energy of ejected electron

$$K = (124 - 68.89) \text{ KeV} = 55.11 \text{ KeV.}$$

Ex. 10. Find the kinetic energy of the photoelectrons liberated by K_α radiation of zinc from the K shell of iron whose K band absorption edge wavelength $\lambda_K = 174 \text{ pm}$.

Sol. Binding energy of K electron in iron

$$E_K = \frac{ch}{\lambda_K} = \frac{12.4 \text{ KeV} \cdot \text{\AA}}{1.74 \text{ \AA}} = 7.126 \text{ KeV}$$

Energy of photon of K_α radiation

$$E = \frac{ch}{\lambda_{K\alpha}} = \frac{3}{4} Rch(Z-1)^2 = 8.578 \text{ KeV}$$

Kinetic energy of photoelectrons liberated from iron

$$K = E - E_K = (8.578 - 7.126) \text{ KeV} = 1.452 \text{ KeV}.$$

QUESTIONS AND PROBLEMS

1. What do you mean by continuous and characteristic X-rays? Describe the mechanism of their production.
2. What is Moseley's law? How can it be derived from Bohr's theory?
3. Derive Bragg's law. How is the wavelength of X-rays determined?
4. Giving energy level diagram, explain the origin of various series of characteristic X-rays.
5. The Duane-Hunt limit of a continuous spectrum, when an X-ray tube is operated at 50 kV is $0.249 \times 10^{-10} \text{ m}$. Calculate the value of the Planck's constant.
6. If X-rays of wavelength $0.5 \text{ \AA}$ are detected at an angle of 5° in the first order, what is the spacing between the adjacent planes of the crystal. At what angle will the second order maximum occur?
[Ans. $d = 2.86 \text{ \AA}$, $\theta = 18^\circ 3'$]
7. X-rays of wavelength $1.6 \text{ \AA}$ are diffracted by X-ray spectrograph at an angle of 30° in the second order. Calculate the interatomic spacing.
8. Calculate the longest wavelength that can be analyzed by a rock salt crystal of spacing $d = 2.82 \text{ \AA}$ (i) in the first order and (ii) in the second order.

[Ans. $5.64 \text{ \AA}$, $2.82 \text{ \AA}$]

UNIT

V

MOLECULAR SPECTRA OF DIATOMIC MOLECULES

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ROTATIONAL SPECTRA OF DIATOMIC MOLECULES

1.1 INTRODUCTION

We know that an atom has its own characteristic discrete energy levels. These energy levels arise due to different electronic configurations of the atom. When an electron in an atom makes transition from a higher energy state E_i to a lower energy state E_f , a photon of frequency $\nu = (E_i - E_f)/h$ is emitted. On the other hand, when an atom absorbs a photon of frequency ν , it is raised from a lower energy state to a higher energy state such that the difference of energy in the final and initial state is equal to the energy of photon $h\nu$. The electronic transitions from higher energy states to lower energy states give rise to emission spectra whereas those from lower energy states to higher energy states give rise to absorption spectra. The emission spectra consist of bright lines and absorption spectra consist of dark lines. A spectral line is characterized by its frequency and intensity. Like an atom, a molecule has also its own characteristic discrete energy levels. The total energy E of a molecule is made up of three parts: *electronic energy* E_e , *vibrational energy* E_v and *rotational energy* E_r .

$$E = E_e + E_v + E_r$$

The **electronic energy** of a molecule arises due to electronic configuration of electrons bonding the constituent atoms. Different electronic configurations give rise to different electronic energy levels. The difference between two electronic states of a molecule is of the order of 2–10 eV. An electronic transition with a change of energy 5 eV is accompanied by emission or absorption of radiation of wavelength λ given by

$$\lambda = \frac{ch}{\Delta E} = \frac{12400 \text{ eV}\cdot\text{\AA}}{5 \text{ eV}} = 2480 \text{ \AA}$$

The corresponding wave number is

$$\bar{\nu} = \frac{1}{\lambda} = 4.03 \times 10^6 \text{ m}^{-1}$$

This radiation lies in ultraviolet part of the electromagnetic spectrum. In general, electronic spectra of molecules lie in **visible and ultraviolet regions**.

The **vibrational energy** of a molecule is due to vibration of its constituent atoms. A simplest diatomic molecule (such as H_2 , O_2 , CO , HCl) may be considered as two point masses m_1 and m_2

connected by a spring-like force. Such a molecule can vibrate along the line joining the atoms and may be treated as a two-body oscillator whose frequency of vibration is given by

$$\omega = \sqrt{\frac{k}{\mu}} \quad \text{or} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

where k = force constant and $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass of the point masses. For O_2 molecule,

$k = 500 \text{ N/m}$ and $\mu = 1.4 \times 10^{-26} \text{ kg}$, the frequency of vibration comes out to be

$$\omega = 6 \times 10^{13} \text{ rad/s.}$$

The quantum mechanical treatment of harmonic oscillator with potential $V = \frac{1}{2} k\xi^2$, where ξ is displacement from equilibrium position, shows that the energy of oscillator is quantized and is given by

$$E = \left(\nu + \frac{1}{2}\right) \hbar \omega, \quad \nu = 0, 1, 2, 3, \dots$$

where ν is called vibrational quantum number. The separation of adjacent energy levels is $\hbar \omega$ i.e.,

$$\Delta E = \hbar \omega = (1.06 \times 10^{-34} \text{ Js})(6 \times 10^{13} \text{ s}) = 6 \times 10^{-21} \text{ J} = 0.014 \text{ eV.}$$

The transition between two adjacent energy levels gives rise to a spectral line of wavelength λ given by

$$\lambda = \frac{ch}{\Delta E} = \frac{12400 \text{ eV \AA}}{0.014 \text{ eV}} = 885714.28 \text{ \AA}$$

$$\bar{\nu} = 1.13 \times 10^4 \text{ m}^{-1}$$

The radiation of this wavelength lies in **infrared region**.

The **rotational energy** of a molecule arises due to its rotation about one of its axes. For example, a diatomic molecule can rotate about an axis passing through its center of mass and perpendicular to the line joining the atoms. Quantum—mechanical analysis rotational motion of this type of molecules shows that the energy of molecule is quantized and is given by

$$E_r = J(J+1) \frac{\hbar^2}{2I}, \quad J = 0, 1, 2, 3, \dots$$

where J is called angular momentum quantum number. I is moment of inertia of molecule and is given by $I = \mu r^2$, μ is reduced mass of molecule and r is distance between atoms.

The spacing of levels with $J = 0$ and $J = 1$ is

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{I}$$

For O_2 molecule, $I = 1.9 \times 10^{-46} \text{ kg m}^2$.

Therefore

$$\Delta E = \frac{(1.06 \times 10^{-34} \text{ Js})^2}{1.9 \times 10^{-46} \text{ kg m}^2} = 5.9 \times 10^{-23} \text{ J} = 3.69 \times 10^{-4} \text{ eV.}$$

The wavelength corresponding to this change in energy is

$$\lambda = \frac{ch}{\Delta E} = \frac{12400 \text{ eV}\text{\AA}}{3.69 \times 10^{-4} \text{ eV}} = 3.36 \times 10^7 \text{ \AA} = 3.36 \text{ mm}$$

$$\bar{\nu} = 2.98 \times 10^2 \text{ m}^{-1}$$

The radiation of this wavelength lies in **microwave region**.

The molecular spectra when observed by an instrument of medium resolving power are seen to consist of bands. When instruments of high resolving power are used the bands are seen to consist of a great number of closely spaced lines.

It is worth to notice that a molecule can interact with electromagnetic radiation only if it has permanent electric dipole moment. Homo-nuclear diatomic molecules, such as H_2 , O_2 , N_2 do not have electric dipole moment and hence give no absorption spectra. Hetero-nuclear molecules, such as HCl , CO , have permanent electric dipole moment and hence give absorption spectra. Vibrational spectra require a change in electric dipole moment during motion of constituent atoms in the molecule. Homo-nuclear diatomic molecules have no dipole moment and hence they do not interact with radiation. No absorption spectra result from these molecules. Hetero-nuclear diatomic molecules have permanent electric dipole moments and change in dipole moment always occurs during vibration and hence they give rise to absorption spectra. Electronic spectra are shown by all molecules because a change in electronic configuration in a molecule is always accompanied by a change in dipole moment.

The existence of three kinds of energy levels corresponding to three kinds of motion and coupling of these motions give rise to a very complicated energy level diagram of a molecule. To avoid the complication in analysis and interpretation of molecular spectra, we shall limit our discussion to simplest molecules: the diatomic molecules.

1.2 ROTATIONAL SPECTRA—MOLECULE AS RIGID ROTATOR

Pure rotation spectra of diatomic molecules are observed only when all other kinds of energy transitions do not occur. For free rotation, the substance must be in gaseous state. A sufficiently low temperature, the thermal energy is too small to alter vibrational and electronic energy of the molecule. At higher temperature, other forms of motion introduce additional energy levels and make the analysis of spectrum difficult.

A hetero-nuclear diatomic molecule may be thought of as a system of two point particles of masses m_1 and m_2 rigidly connected with a mass-less rod of length r . The molecule is capable of rotating about an axis passing through center of mass and perpendicular to the line joining the constituent atoms. Its moment of inertia I about the axis of rotation is

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2 \quad \dots(1.2.1)$$

where $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is reduced mass of the molecule. The rotational kinetic energy of molecule is

$$E = \frac{1}{2} I \omega^2 = \frac{|J|^2}{2I} \quad \dots(1.2.2)$$

where $\mathbf{J}$ is angular momentum of the molecule. According to quantum mechanics, the angular momentum of a microscopic system is quantized and its magnitude is given by

$$|\mathbf{J}| = \sqrt{J(J+1)} \hbar, \quad J = 0, 1, 2, 3, \dots \quad \dots(1.2.3)$$

where J is angular momentum quantum number. In view of Eqn. (1.2.3) the rotational kinetic energy can be expressed as

$$E = \frac{\hbar^2}{2I} J(J+1) = \left(\frac{h}{8\pi^2 I c} \right) h c J(J+1) \quad \dots(1.2.4)$$

It is customary to express the energy in terms of rotational constant B , defined by

$$B = \frac{h}{8\pi^2 I c} \quad \dots(1.2.5)$$

In terms of B , the energy E is expressed as

$$E(J) = B h J(J+1) \quad \dots(1.2.6)$$

To indicate that E depends on J we write E as $E(J)$, therefore

$$E(J) = B h J(J+1) \quad \dots(1.2.7)$$

The rotational energy levels are

$$E_0 = 0, E_1 = 2Bh, E_2 = 6Bh, E_3 = 12Bh, \dots$$

The rotational term values of a rigid rotator are

$$F(J) = \frac{E(J)}{ch} = BJ(J+1) \quad \dots(1.2.8)$$

In practice, rotational spectra are always observed as absorption. Such spectra result due to transitions of molecules from lower rotational energy states to higher energy states by absorbing photons from the radiation. It is usual practice to denote the rotational quantum number of higher energy level by J' and that of lower energy level by J'' . Not all transitions are permitted. Quantum mechanics permits only those transitions which obey the selection rules

$$\Delta J = J_f - J_i = \pm 1$$

+1 for absorption and -1 for emission. In absorption $J_i = J''$ and $J_f = J'$.

The wave number $\bar{\nu} \left(= \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\Delta E}{ch} \right)$ of the absorbed radiation corresponding to the transition

$J'' \rightarrow J'$ or $J'' \rightarrow J'' + 1$ is given by

$$\begin{aligned} \bar{\nu} &= F(J') - F(J'') = B[J'(J'+1) - J''(J''+1)] \\ \bar{\nu} &= B[(J''+1)(J''+2) - J''(J''+1)] \\ &= 2B(J''+1) \\ &= 2B(J+1), \quad J = 0, 1, 2, 3, \dots \quad \dots(1.2.9) \\ &= 2B, 4B, 6B, 8B, \dots \end{aligned}$$

where we have put $J'' = J$ = rotational quantum number of the lower energy level.

The frequency separation on wave number scale is

$$\Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 I c} \quad \dots(1.2.10)$$

Thus, the absorption spectrum consists of lines which on wave number scale are *equally spaced* with *constant separation* $2B$. Measuring the separation of lines, we can calculate the moment of inertia I and inter-nuclear distance r .

For HF molecule, $\Delta\bar{\nu} = 4050 \text{ m}^{-1}$, $B = 1/2$, $\Delta\bar{\nu} = 2025 \text{ m}^{-1}$. From Eqn. (1.2.10)

$$I = \frac{h}{8\pi^2 c \Delta\bar{\nu}} = \frac{6.6 \times 10^{-34} \text{ Js}}{8(3.14)^2 (3 \times 10^8 \text{ m/s})(2025 \text{ m}^{-1})}$$

$$I = 1.38 \times 10^{-47} \text{ kg m}^2$$

Since $I = \mu r^2$, $r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.38 \times 10^{-47} \text{ kg m}^2}{1.58 \times 10^{-27} \text{ kg}}} = 0.935 \times 10^{-10} \text{ m} = 0.94 \text{ \AA}.$

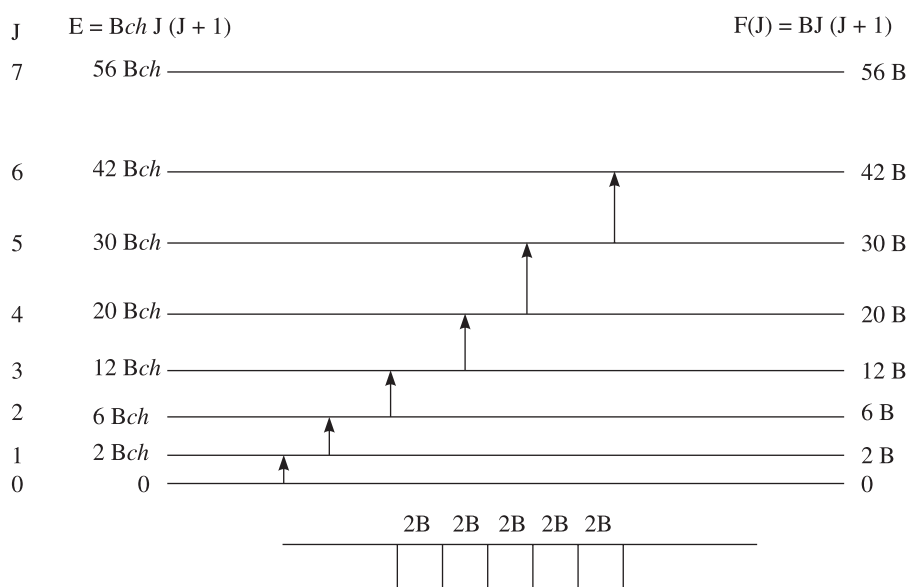


Fig. 1.2.1 Rotational absorption spectrum

The absorption spectrum of HCl contains wave numbers shown in the table given below. The difference of consecutive wave numbers is also given. These results show that wave-number separation is *nearly* constant. A closer look at the separation indicates that it slightly decreases with increasing J values.

$\bar{\nu} \text{ m}^{-1}$	$\Delta\bar{\nu} \text{ m}^{-1}$
8303	2070
10373	2057
12430	2073
14503	2048
16551	2035
18586	2052
20638	2012
22650	

Slightly decreasing trend in wave number separation at higher energies implies decrease in rotational constant B and hence increase in moment of inertia I . This means that our *rigid rotator* model for diatomic molecules needs correction. In fact, with increasing J values or energy the frequency of rotation of molecule increases. The centrifugal action stretches the bond and the atoms are, therefore, pulled apart. This increases the moment of inertia with increasing J values. When the effect of centrifugal distortion is taken into consideration, the energy of molecule comes out to be

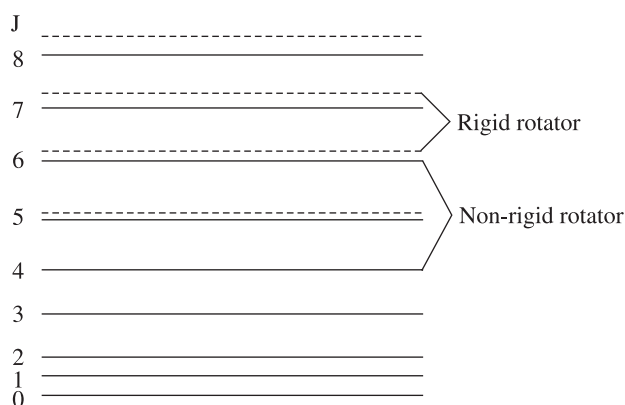


Fig. 1.2.2 Centrifugal stretching of bond causes decrease in wave number separation and convergence of lines at higher energies

$$E = BchJ(J+1) - DchJ^2(J+1)^2 \quad \dots(1.2.11)$$

$$F(J) = B J (J+1) - D J^2 (J+1)^2 \quad \dots(1.2.12)$$

where B and D are constants and are related to each other through the relation

$$D = \frac{4B^3}{\omega^2}, \quad \omega = \sqrt{\frac{k}{\mu}} \quad \dots(1.2.13)$$

K is force constant characterizing the elastic force between atoms. The effect of centrifugal distortion of the energy levels and wave number of spectral lines is shown in the Fig. (1.2.2).

The frequency of lines in wave numbers is given by

$$\begin{aligned}
 \bar{\nu} &= F(J') - F(J'') \\
 &= B[J'(J'+1) - DJ'^2(J'+1)^2] - B[J''(J''+1) - DJ''^2(J''+1)^2] \\
 &= 2B(J''+1) - 4D(J''+1)^3 \\
 &= 2B(J+1) - 4D(J+1)^3 \quad \dots(1.2.14)
 \end{aligned}$$

From this equation it is obvious that as J increases, the separation of lines $\Delta\bar{\nu}$ decreases. This is in agreement with the experimental observations.

1.3 ISOTOPIC SHIFT

The isotopic exchange of atoms in a diatomic molecule alters the moment of inertia but not the internuclear distance. As a result of this the wave number separation $\Delta\bar{\nu} = 2B = 2\left(\frac{h}{8\pi^2 I c}\right)$ slightly decreases with increasing I . If I_1 and I_2 are the moments of inertia of molecules corresponding to isotopic masses m_1 and m_2 , the wave numbers of the spectral lines of these molecules are given by

$$\bar{\nu}_{1,J \rightarrow J+1} = 2B_1(J+1) \quad \dots(1.3.1)$$

$$\bar{\nu}_{2,J \rightarrow J+1} = 2B_2(J+1) \quad \dots(1.3.2)$$

where B_1 and B_2 are the rotational constants of the two molecules. From Eqns. (1.3.1) and (1.3.2)

$$\Delta\bar{\nu} = \bar{\nu}_1 - \bar{\nu}_2 = 2(B_1 - B_2)(J+1) \quad \dots(1.3.3)$$

Therefore,
$$\frac{\Delta\bar{\nu}}{\bar{\nu}} = \left(1 - \frac{B_2}{B_1}\right) = \left(1 - \frac{I_1}{I_2}\right) = \left(1 - \frac{\mu_1}{\mu_2}\right) \quad \dots(1.3.4)$$

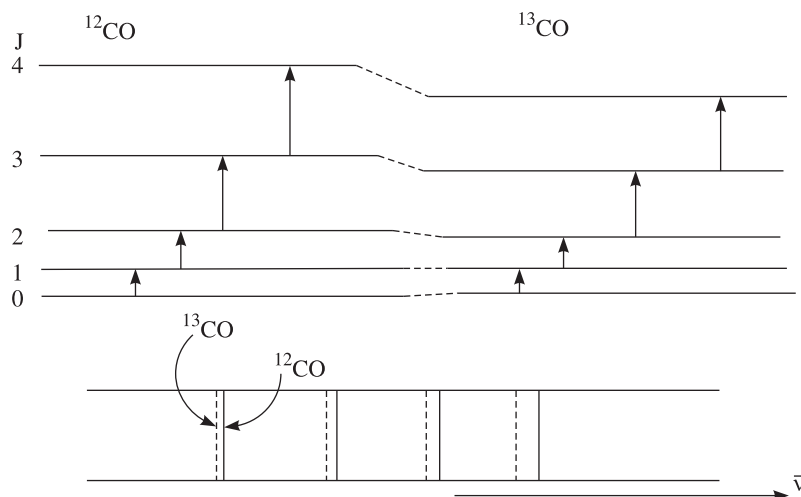


Fig. 1.3.1 Effect of isotopic exchange in CO molecule. Continuous lines represent absorption lines in ^{12}CO and dotted lines in ^{13}CO

From Eqn. (1.3.3), we see that isotopic shift $\Delta\bar{\nu}$ increases with increasing J values. Equation (1.3.4) may be used to determine the mass of one isotope if other is known. Effect of isotopic exchange on energy levels and wave number separation is shown in the Fig. (1.3.1).

1.4 INTENSITIES OF SPECTRAL LINES

The intensity of a spectral line is proportional to the number of molecules in the initial state. The number of molecules in the energy state E_J at temperature T is given by

$$N_J = N_0 \exp(-E_J/kT) \quad \dots(1.4.1)$$

where N_0 is the number of molecules in the state $J = 0$. The degeneracy of the state J is $(2J + 1)$. Taking degeneracy of the J th state into consideration, above formula for population of state J becomes

$$N_J = (2J + 1)N_0 \exp(-E_J/kT) \quad \dots(1.4.2)$$

The variation of N_J with J is shown in the Fig. (1.4.1). The number N_J is maximum for the value of J given by

$$J = \sqrt{\frac{kT}{2Bch}} - \frac{1}{2} \quad \dots(1.4.3)$$

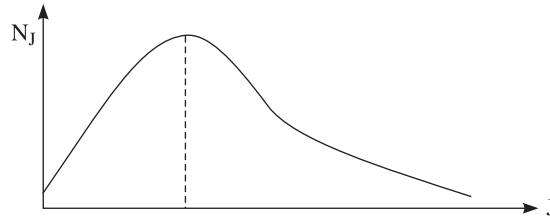


Fig. 1.4.1 Variation of population of an energy level with J

Hence, the intensity of spectral line is maximum for this value of J . For lower and higher values of J , the intensity is less.

VIBRATIONAL SPECTRA OF DIATOMIC MOLECULES

2.1 VIBRATIONAL SPECTRA—MOLECULE AS HARMONIC OSCILLATOR

Pure vibrational spectra are observable when other forms of molecular energies, except vibrational one, remain unchanged. Such spectra are obtained in liquid because molecular interaction between neighbouring molecules suppresses rotational motion. Hetero-nuclear diatomic molecules (HCl, CO, CN) have intrinsic electric dipole moment and are capable of interacting with electromagnetic radiation. Hence these molecules exhibit vibrational spectra. Homo-nuclear diatomic molecules do not have dipole moment and hence do not give vibrational spectra.

A diatomic molecule can vibrate along the inter-nuclear axis and may be regarded as a two-body oscillator. Its classical frequency of vibration is given by

$$\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad \bar{\omega} = \frac{\nu_{osc}}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots(2.1.1)$$

where k is force constant of the elastic force binding the atoms and μ is the reduced mass of the molecule. For CO molecule, $k = 1870$ N/m, $\mu = 1.14 \times 10^{-26}$ kg, the frequency of vibration is $\nu_{osc} = 2.04 \times 10^{13}$ Hz. For small amplitude or energy, the motion of atoms is pure harmonic and the potential energy of the molecule is $V = 1/2 k\xi^2$, ξ being the displacement of the oscillator. This potential energy is called harmonic or parabolic potential energy.

The quantum mechanical treatment of harmonic oscillator with potential $V = 1/2 k\xi^2$ shows that oscillator energy is quantized and is given by

$$E = \left(v + \frac{1}{2} \right) h\nu_{osc} = \left(v + \frac{1}{2} \right) hc\bar{\omega} \quad \dots(2.1.2)$$

The vibrational term value is

$$G(v) = \frac{E}{ch} = \left(v + \frac{1}{2} \right) \frac{\nu_{osc}}{c} = \bar{\omega} \left(v + \frac{1}{2} \right) \quad \dots(2.1.3)$$

where v is an integer ($v = 0, 1, 2, 3, \dots$), called vibration quantum number. $\bar{\omega}$ is frequency of classical oscillator in wave number units. It is also called vibrational constant. (Note that it is not the

angular frequency.) Minimum energy of oscillator is $E_{osc} = \frac{1}{2} h\nu_{osc}$ for $v = 0$. This energy E_{osc} is called zero-point energy. Eqn. (2.1.2 or 2.1.3) shows that the energy levels of a harmonic oscillator are equally spaced with constant separation $\Delta E = h\nu_{osc}$. When continuous electromagnetic radiation is passed through an assembly of polar molecules, which act as harmonic oscillator, they interact with radiation and go over to higher energy states by absorbing radiation. Such transitions give rise to absorption spectrum. The allowed vibration transitions are those which obey the selection rules

$$\Delta v = \pm 1 \quad \dots(2.1.4)$$

+ sign indicates absorption and – sign emission. The vibrational quantum numbers of the lower and upper states are denoted by v'' and v' respectively. The selection rule then becomes

$$v' - v'' = 1 \quad (\text{absorption})$$

The frequency of absorption line in wave number units when the molecule makes transition from $v'' (v) \rightarrow v' = (v + 1)$ is

$$\begin{aligned} \bar{\nu} &= G(v') - G(v'') = \bar{\omega}(v' + \frac{1}{2}) - \bar{\omega}(v'' + \frac{1}{2}) \\ &= \bar{\omega}(v + \frac{3}{2}) - \bar{\omega}(v + \frac{1}{2}) \\ &= \bar{\omega} = \bar{\omega}_{osc} \end{aligned}$$

Thus, all the allowed transitions leading to absorption lines have the same frequency equal to the frequency of the oscillator and the pure vibrational spectrum will consist of a single absorption line. This is in accordance with the classical electrodynamics.

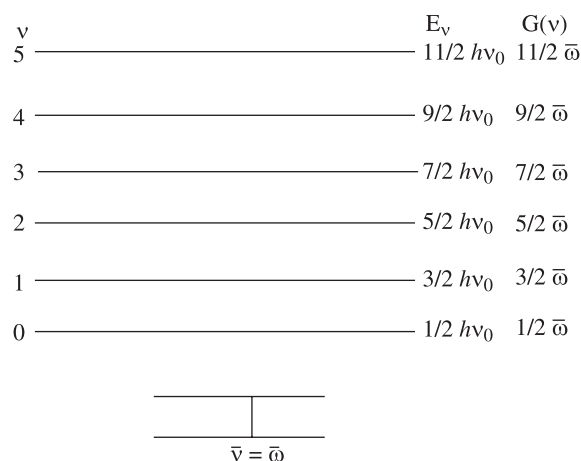


Fig. 2.1.1 Permitted vibrational transitions leading to a single spectral band

2.2 ANHARMONIC OSCILLATOR

Experimental investigations reveal that the vibration absorption spectrum of HCl shows, in addition to fundamental frequency $\bar{\nu}_1 = 2.886 \times 10^5 \text{ m}^{-1}$, lines at frequencies $\bar{\nu}_2 = 5.668 \times 10^5 \text{ m}^{-1}$ and

$\bar{\nu}_3 = 8.347 \times 10^5 \text{ m}^{-1}$. The frequencies $\bar{\nu}_2$ and $\bar{\nu}_3$ are called overtones or harmonics and are slightly less than twice and thrice of the fundamental frequency. The intensities of the overtones are much smaller than that of the fundamental line. The existence of overtones indicates that the selection rules $\Delta v = \pm 1$ are not valid.

At high energy the amplitude of vibration is so large, the oscillations are no longer pure harmonic and the harmonic potential $V = \frac{1}{2} k \xi^2$ does not accurately describe behaviour of the system. The large amplitude vibration is called *anharmonic vibration* and in such vibrations the potential energy is best approximated by following expression:

$$V = \frac{1}{2!} k_1 \xi^2 + \frac{1}{3!} k_2 \xi^3 + \frac{1}{4!} k_3 \xi^4 + \dots \quad \dots(2.2.1)$$

The task of finding *energy eigenvalues* and corresponding *eigen functions* by solving Schrodinger equation for oscillator with this form of potential is very complicated. P.M. Morse suggested a simple and more realistic potential function represented by

$$V = D_e [1 - \exp(a(r_e - r))]^2 \quad \dots(2.2.2)$$

where D_e is dissociation energy of the molecule (which is equal to the minimum energy that must be added to the molecule to bring the atoms at an infinite separation), r_e is equilibrium separation of atoms and r is separation of atoms.

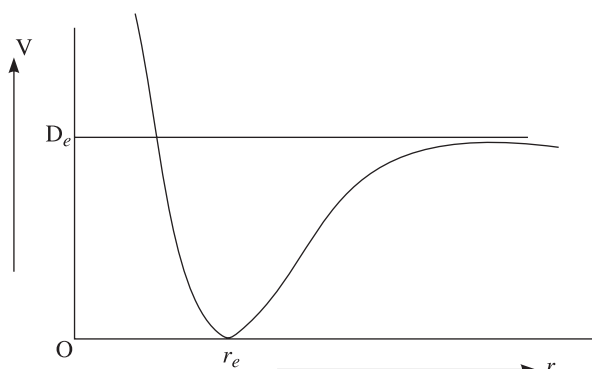


Fig. 2.2.1 Morse potential

Schrodinger equation for oscillator with Morse potential gives energy levels given by

$$E = \left(v + \frac{1}{2}\right) hc \bar{\omega}_e - \left(v + \frac{1}{2}\right)^2 hc x_e \bar{\omega}_e + \left(v + \frac{1}{2}\right)^3 hc y_e \bar{\omega}_e + \dots \quad \dots(2.2.3)$$

where

$$\bar{\omega}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots(2.2.4)$$

is the vibrational frequency in wave number units that the anharmonic oscillator would have classically for an infinitesimal amplitude, $x_e, y_e, \dots$ are *anharmonicity* constants. As an approximation the third

term can be omitted in Eqn. (2.2.3). With this approximation the energy of an *anharmonic* oscillator can be represented as follows:

$$E = \left(v + \frac{1}{2} \right) hc \bar{\omega}_e - \left(v + \frac{1}{2} \right)^2 hc x_e \bar{\omega}_e \quad \dots(2.2.5)$$

or term value

$$G(v) = \bar{\omega}_e \left(v + \frac{1}{2} \right) - x_e \bar{\omega}_e \left(v + \frac{1}{2} \right)^2 \quad \dots(2.2.6)$$

where $\bar{\omega}_e x_e \ll \bar{\omega}_e$.

The wave number of the absorption band arising from the transition $v'' \rightarrow v'$ is given by

$$\begin{aligned} \bar{\nu}_{v'' \rightarrow v'} &= G(v') - G(v'') = (v' - v'') \bar{\omega}_e - \left\{ \left(v' + \frac{1}{2} \right)^2 - \left(v'' + \frac{1}{2} \right)^2 \right\} x_e \bar{\omega}_e \\ &= (v' - v'') \bar{\omega}_e - \{ v'(v' + 1) - v''(v'' + 1) \} x_e \bar{\omega}_e \quad \dots(2.2.7) \end{aligned}$$

The selection rules for transitions between the energy levels of an *anharmonic* oscillator are found to be

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots$$

The wave numbers of the bands arising from the transitions $0 \rightarrow 1$, $0 \rightarrow 2$, and $0 \rightarrow 3$ can be found from Eqn. (2.2.7). These are:

$$\begin{aligned} \bar{\nu}_{0 \rightarrow 1} &= \bar{\nu}_1 = (1 - 2x_e) \bar{\omega}_e \\ \bar{\nu}_{0 \rightarrow 2} &= \bar{\nu}_2 = 2(1 - 3x_e) \bar{\omega}_e \\ \bar{\nu}_{0 \rightarrow 3} &= \bar{\nu}_3 = 3(1 - 4x_e) \bar{\omega}_e \\ \bar{\nu}_{0 \rightarrow 4} &= \bar{\nu}_4 = 4(1 - 5x_e) \bar{\omega}_e \quad \dots(2.2.8) \end{aligned}$$

The first band of wave number $\bar{\nu}_1$ arising from the transition $v'' = 0 \rightarrow v' = 1$, is called *fundamental band* and is most intense. The band corresponding to the transition $v'' = 0 \rightarrow v' = 2$, with $\Delta v = 2$ has small intensity and is called *first overtone*. The band corresponding to the transition $v'' = 0 \rightarrow v' = 3$ with $\Delta v = 3$, has much smaller intensity and is called *second overtone*. Only these three band have observable intensities.

The energy difference between the first excited state and the ground state is $\Delta E = h\nu_0$. For CO molecule this energy is $\Delta E = h\nu_0 = (6.62 \times 10^{-34} \text{ Js})(2.04 \times 10^{13}) = 13.5 \times 10^{-21} \text{ J} = 8.4 \times 10^{-2} \text{ eV} = 0.084 \text{ eV}$. At room temperature, thermal energy kT is about 0.026 eV. Thus, the thermal energy is not enough to raise the molecules from ground state to excited states. So the majority of the molecules lie in the ground state at normal temperature. This explains why the fundamental line is most intense. If the temperature of the sample is raised, the population of $v = 1$ state is increased and therefore, the probability of transition from higher states with selection rule $\Delta v = 1$ increases. The bands originating from such transitions constitute what we call *hot bands*.

From the measurements of frequency of fundamental band and of overtones, the frequency $\bar{\omega}_e$ and anharmonicity constant x_e can be calculated making use of Eqn. (2.2.8). The force constant k is found from the Eqn. (2.2.4) viz.,

$$k = 4\pi^2 c^2 \mu \bar{\omega}_e^2. \quad \dots(2.2.9)$$

2.3 ISOTOPIC SHIFT OF VIBRATIONAL LEVELS

The harmonic oscillator frequency $\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ depends on the reduced mass of the molecule. Since μ is different for different isotopes so is the oscillator frequency. Let $\bar{\omega}_e^i$ and $\bar{\omega}_e$ be the frequencies of the heavier and lighter isotope respectively. Let

$$\frac{\bar{\omega}_e^i}{\bar{\omega}_e} = \sqrt{\frac{\mu}{\mu^i}} = \rho(\text{say}) \quad \dots(2.3.1)$$

The vibrational terms for the two isotopes are

$$G(v) = \bar{\omega}_e \left(v + \frac{1}{2} \right) \quad \dots(2.3.2)$$

$$G^i(v) = \bar{\omega}_e^i \left(v + \frac{1}{2} \right) = \rho \bar{\omega}_e \left(v + \frac{1}{2} \right) \quad \dots(2.3.3)$$

The isotopic shift in term values of a vibrational level of quantum number v is

$$G^i(v) - G(v) = (\rho - 1) \bar{\omega}_e \left(v + \frac{1}{2} \right) \quad \dots(2.3.4)$$

Since $\rho < 1$, $G^i(v) < G(v)$.

Thus, the vibrational levels of heavier isotope lie a little deeper than the corresponding levels of lighter isotope.

If anharmonicity is taken into consideration, the vibrational term for lighter isotope is represented as

$$G(v) = \bar{\omega}_e \left(v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2$$

From theoretical analysis, the anharmonicity constant x_e^i is found to be related to x_e through the relation

$$x_e^i = \rho x_e$$

Making use of this relation and $\bar{\omega}_e^i = \rho \bar{\omega}_e$ we can find the vibrational term for heavier isotope

$$G^i(v) = \rho \bar{\omega}_e \left(v + \frac{1}{2} \right) - \rho^2 \bar{\omega}_e x_e \left(v + \frac{1}{2} \right)^2$$

The isotopic shift of a vibrational level in this case comes out to be

$$G^i(v) - G(v) = (\rho - 1)\bar{\omega}_e(v + \frac{1}{2}) - (\rho^2 - 1)\bar{\omega}_e x_e(v + \frac{1}{2})^2$$

Since ρ is only slightly different from 1, we can assume $\rho + 1 = 2$. With this approximation we have

$$G^i(v) - G(v) = (\rho - 1)(v + \frac{1}{2})\left[\bar{\omega}_e - 2\bar{\omega}_e x_e(v + \frac{1}{2})\right] \quad \dots(2.3.5)$$

Since $\rho < 1$, $G^i(v) - G(v)$ is negative. We come to the same conclusion that vibrational levels of heavier isotope lie deeper than those of lighter isotope. This is shown in the Fig. (2.3.1).

The isotopic shift of energy levels causes doubling of vibrational bands. The band shift is given by

$$\begin{aligned} \Delta\bar{v} &= \bar{v}^i - \bar{v} = \left[G^i(v') - G^i(v'')\right] - \left[G(v') - G(v'')\right] \\ &= (\rho - 1)\bar{\omega}_e(v' - v'')\left[1 - (\rho + 1)x_e(v' + v'' + 1)\right] \end{aligned}$$

For fundamental band

$$\Delta\bar{v}_{0 \rightarrow 1} = (\rho - 1)(1 - 4x_e)\bar{\omega}_e \quad \dots(2.3.6)$$

For first and second overtones

$$\Delta\bar{v}_{0 \rightarrow 2} = 2(\rho - 1)(1 - 6x_e)\bar{\omega}_e \quad \dots(2.3.7)$$

$$\Delta\bar{v}_{0 \rightarrow 3} = 3(\rho - 1)(1 - 8x_e)\bar{\omega}_e \quad \dots(2.3.8)$$

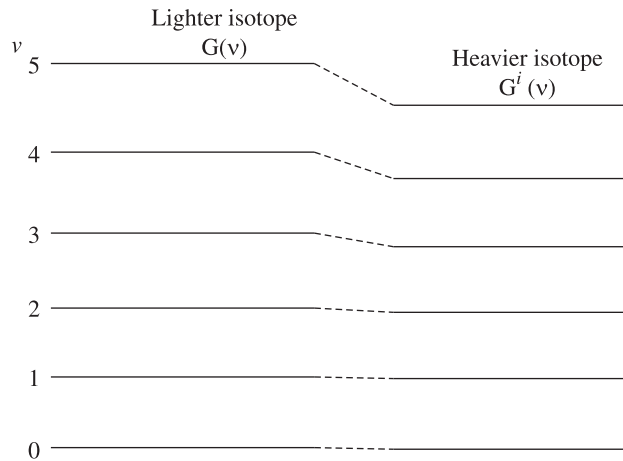


Fig. 2.3.1 Vibrational levels of two isotopes

VIBRATION-ROTATION SPECTRA OF DIATOMIC MOLECULES

3.1 ENERGY LEVELS OF A DIATOMIC MOLECULE AND VIBRATION-ROTATION SPECTRA

The spacing of electronic energy levels is nearly ten times that of vibrational energy levels and the spacing of vibrational levels is nearly hundred times that of rotational levels. Each electronic level has many equally spaced vibrational levels and each vibrational level has many closely spaced rotational levels. The energy level diagram of a molecule is schematically shown in the Fig. (3.1.1).

When an electromagnetic radiation of appropriate frequencies is passed through an assembly of molecules, the latter after absorbing some characteristic frequencies undergo transitions from lower energy states to higher energy states. In such transitions changes in rotational, vibrational and electronic energies of molecules occur. The resulting absorption spectrum consists of a large number of lines characteristic of molecules. We first consider the simple case in which the electronic energy states of molecules remain unchanged, only rotational and vibrational energies undergo change. To a first approximation, we assume that (i) vibrational and rotational energies do not interact, (ii) vibrations of molecules are pure harmonic and (iii) centrifugal distortion of molecule is negligibly small. Under this approximation the energy of a molecule is sum of its vibrational and rotational energies.

$$E = \left(v + \frac{1}{2} \right) hc \bar{\omega}_e + Bhc J(J+1) \quad \dots(3.1.1)$$

where
$$B = \frac{h}{8\pi^2 I c}$$

is the rotational constant and

$$\bar{\omega}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

is the wave number corresponding to classical frequency of harmonic oscillator.

The vibration-rotation term value is

$$T = G(v) + F(J) = \bar{\omega}_e \left(v + \frac{1}{2} \right) + BJ(J+1) \quad \dots(3.1.2)$$

The selection rules for vibrational transitions are $\Delta v = \pm 1$ and those for rotational transitions are $\Delta J = \pm 1$. The allowed transitions between the rotational and between the vibrational energy levels give rise to *vibrational-rotational spectra*. It is customary to denote the quantum numbers of rotational levels in the upper vibrational level v' and in the lower vibrational level v'' by J' and J'' respectively. It should be noted that energy of molecules in level with higher vibrational quantum number v' is always greater than that in level with lower quantum number v'' irrespective of the values of rotational quantum number J corresponding to these vibrational levels.

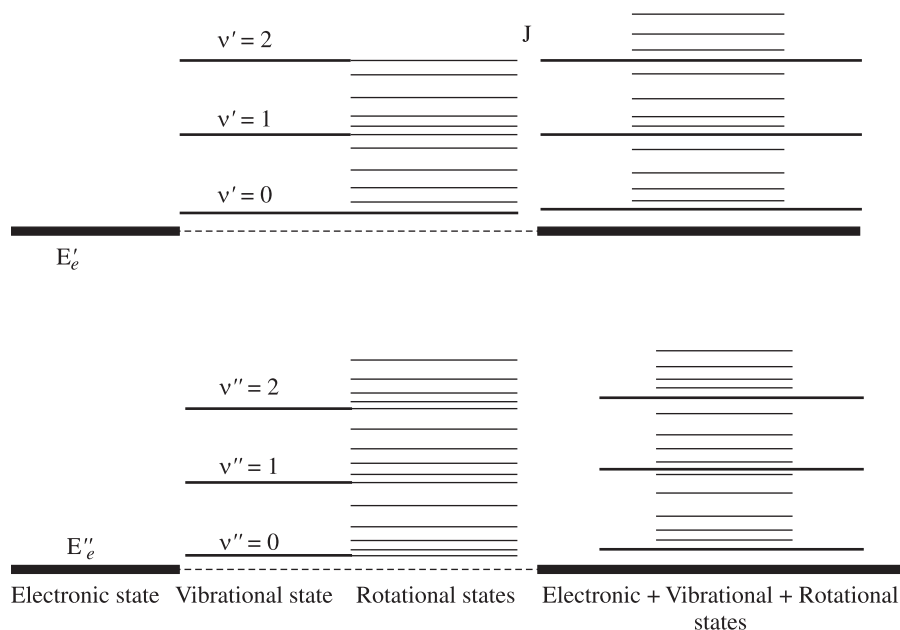


Fig. 3.1.1 Energy level diagram of a molecule

The wave number of the absorption band originating in the transition $v'' \rightarrow v'$ and $J'' \rightarrow J'$ is given by

$$\begin{aligned}\bar{\nu} &= [G(v') + BJ'(J' + 1)] - [G(v'') + BJ''(J'' + 1)] \\ &= (v' - v'')\bar{\omega}_e + B[J'(J' + 1) - J''(J'' + 1)]\end{aligned}\quad \dots(3.1.3)$$

For the vibrational transition $v'' = v \rightarrow v' = v' + 1$, this equation becomes

$$\bar{\nu} = \bar{\omega}_e + B[J'(J' + 1) - J''(J'' + 1)]\quad \dots(3.1.4)$$

These transitions fall in two groups. The collection of absorption lines obeying the selection rule $\Delta J = J' - J'' = -1$ constitute P-branch of the spectrum and the set of lines obeying the selection rule $\Delta J = J' - J'' = +1$ constitute R-branch of the spectrum. If we write $J'' = J$ for the quantum

number of the initial state (lower state) then the wave numbers of the lines of P-branch will be given by

$$\bar{\nu}_P = \bar{\omega}_e + B[(J'' - 1)J'' - J''(J'' + 1)] = \bar{\omega}_e - 2BJ, \quad J = 1, 2, 3, \dots \quad \dots(3.1.5)$$

Similarly, the wave numbers of the lines of R-branch will be given by

$$\bar{\nu}_R = \bar{\omega}_e + 2B(J + 1), \quad J = 0, 1, 2, 3, \dots \quad \dots(3.1.6)$$

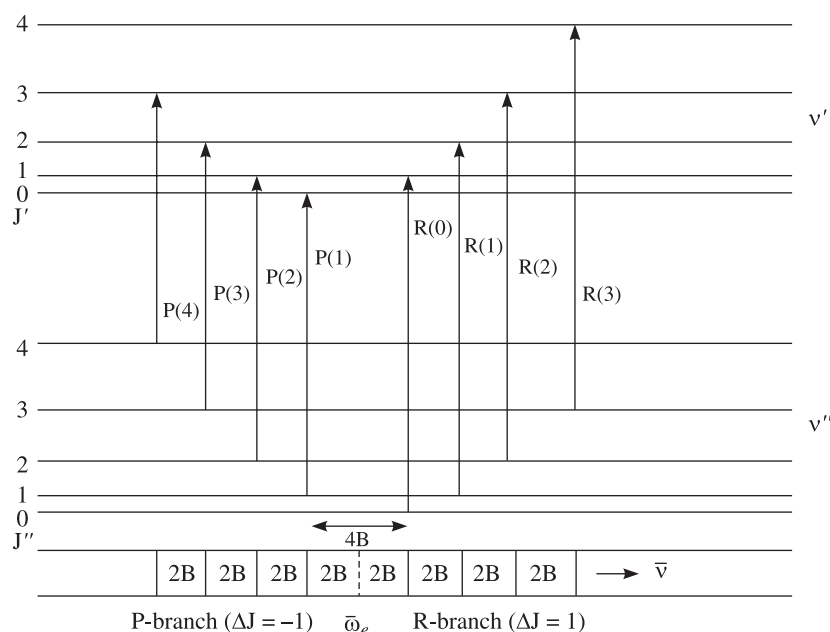


Fig. 3.1.2 Rotation-vibration spectrum of diatomic molecule

The wave number of spectral lines both P-and Q-branches can be expressed by a single formula as follows:

$$\bar{\nu} = \bar{\omega}_e \pm 2Bm, \quad m = 1, 2, 3, \dots \quad \dots(3.1.7)$$

In P-branch, $\bar{\nu}_P = \bar{\omega}_e$ requires that $J = J'' = 0$, this implies $J' = -1$, which is not possible because J cannot be negative. So the line at $\bar{\omega}_e$ does not appear in the spectrum. Similarly, in R-branch, appearance of line at $\bar{\omega}_e$ requires $J = J'' = -1$, which again not possible. The wave number separation of successive lines either in P-branch or in R-branch of the spectrum is $2B$. Thus, the rotation-vibration absorption spectrum of diatomic molecule consists of equally spaced lines on each side of the *band origin* $\bar{\omega}_e$ or the *center of the band*. The lines of P-branch have lower frequencies and those of R-branch have higher frequencies. The vibrational part of frequency $\bar{\omega}_e$ determines spectral region in which the band is located. The rotational part $\pm 2Bm$ determines the fine structure of the band. The region in which the vibration-rotation bands are found extends approximately from $8,000 \text{ \AA}$ to $50,000 \text{ \AA}$. That is these band lie in *infrared* portion of the spectrum.

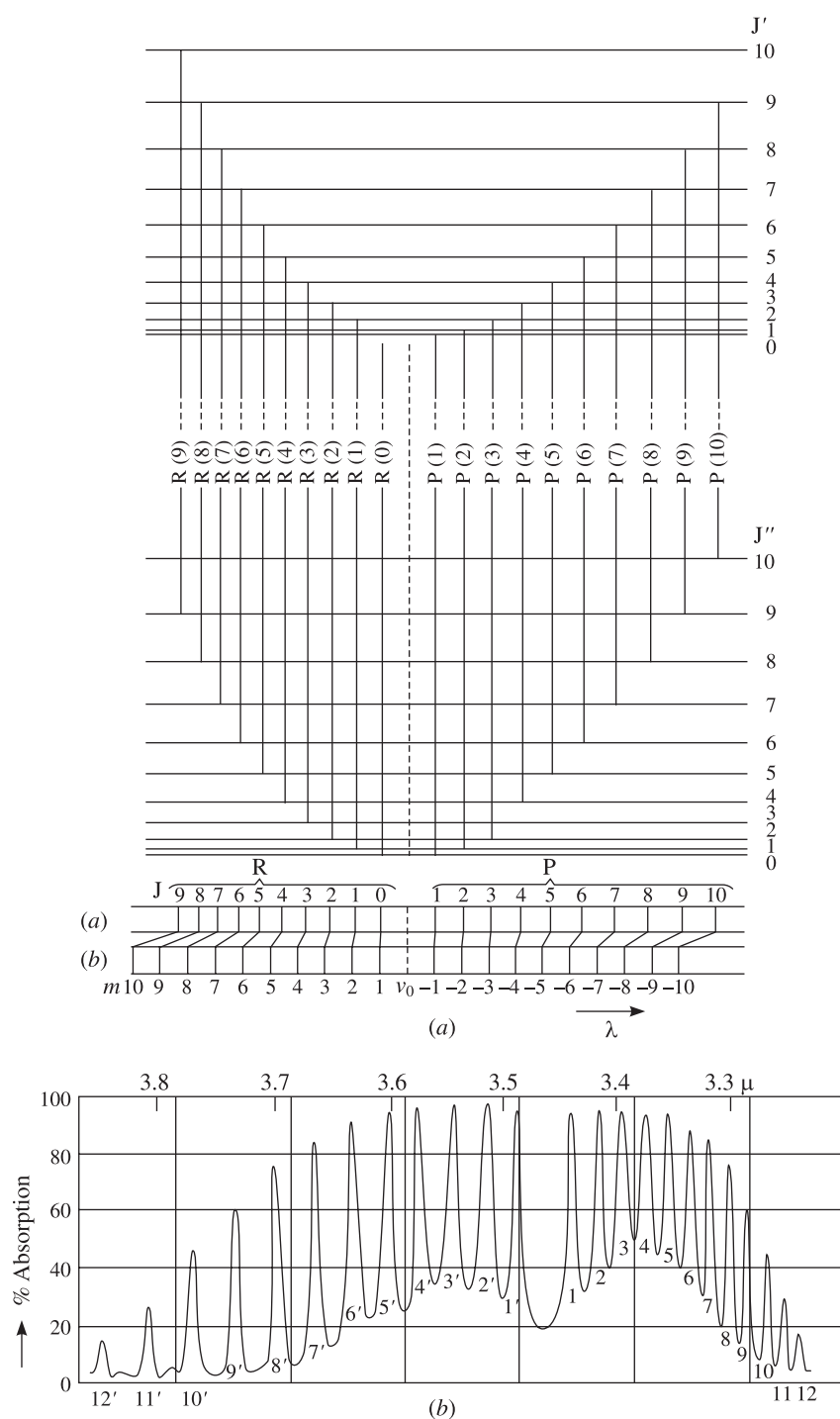


Fig. 3.1.3 (a) Energy level diagram of rotation-vibration band
(b) Absorption spectrum of HCl

3.2 EFFECT OF INTERACTION (COUPLING) OF VIBRATIONAL AND ROTATIONAL ENERGY ON VIBRATION-ROTATION SPECTRA

The assumption that vibrational and rotational energies of a diatomic molecule are independent of each other is far from reality. Certain features of vibration-rotation spectra indicate that there exists some kind of coupling between vibrational and rotational motion. As the vibrational energy of molecule increases, the average separation of constituent atom also increases. This causes increase in moment of inertia ($I = \mu r^2$). The rotational constant B is inversely proportional to moment of inertia, and hence it becomes function of vibrational quantum number v . B is smaller in state with high vibrational quantum number. We can represent the dependence of B on v in the form

$$B_v = B_e - \alpha \left(v + \frac{1}{2} \right) \quad \dots(3.2.1)$$

where B_v and B_e refer to the values of B in state with quantum number v and in equilibrium state respectively and α is a positive constant. Similarly, the constant D , which describes the non-rigidity of molecular bond, may be expressed as

$$D_v = D_e + \beta \left(v + \frac{1}{2} \right) \quad \dots(3.2.2)$$

where β is a constant and is very small compared to D_e . The correction term in D_v is very small and may be ignored.

Ignoring the centrifugal distortion, the energy of anharmonic oscillator is found to be

$$E_v + E_J = (v + \frac{1}{2})ch\bar{\omega}_e - (v + \frac{1}{2})^2 chx_e\bar{\omega}_e + B_v chJ(J+1)$$

Or term value

$$T(v, J) = G(v) + F(v, J) = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2 x_e\bar{\omega}_e + B_v J(J+1)$$

The wave number of the absorption lines of a particular band (v', v'') is given by

$$\begin{aligned} \bar{\nu} &= [G(v') + F(v', J')] - [G(v'') + F(v'', J'')] \\ &= [G(v') - G(v'')] + [F(v', J') - F(v'', J'')] \\ &= \bar{\nu}_0 + B'_v J'(J'+1) - B''_v J''(J''+1) \end{aligned} \quad \dots(3.2.3)$$

where $\bar{\nu}_0$ is the wave number corresponding to pure vibrational transition between two vibrational levels with both J' and J'' equal to zero. This wave number is the **center of the band** or **band origin**. Most of the diatomic molecules have no angular momentum about the inter-nuclear axis and the selection rules $\Delta J = \pm 1$ are valid. The selection rule $\Delta J = -1$ gives a series of lines called *P-branch* and $\Delta J = +1$ gives the series of lines called *R-branch*. For such molecules the transitions with $\Delta J = 0$ are forbidden.

For a molecule possessing electronic angular momentum $\Lambda\hbar$ about the inter-nuclear axis, selection rule is $\Delta J = 0, \pm 1$. Here Λ is quantum number for resultant electronic angular momentum. *Nitric*

oxide has an unpaired electron and hence has electronic angular momentum ($\Lambda \neq 0$). In this molecule the transition with $\Delta J = 0$ is allowed. The transitions obeying the selection rule $\Delta J = 0$ give rise to *Q-branch* of spectrum.

The wave numbers of lines of *P-branch* are obtained making use of the selection rule $\Delta J = -1$ i.e., $J' - J'' = -1$ or by replacing J' by $J'' - 1$ in Eqn.(3.2.3).

$$\bar{\nu}_P = \bar{\nu}_0 - (B'_{v'} + B''_{v''})J'' + (B'_{v'} - B''_{v''})J''^2, \quad J'' = 1, 2, 3, \dots$$

Writing J for J'' we have

$$\bar{\nu}_P = \bar{\nu}_0 - (B'_{v'} + B''_{v''})J + (B'_{v'} - B''_{v''})J^2, \quad J = 1, 2, 3, \dots \quad \dots(3.2.4)$$

The lines of *P-branch* are denoted by $P(1), P(2), P(3), \dots$

Since $B'_v < B''_v$ (B_v decreases slightly with increasing v . $B \propto 1/\mu r^2$, r increases with increasing value of v), the difference $B'_v - B''_v$ is negative. Thus, both the linear and quadratic terms in J are of the same sign (negative) and hence the lines of *P-branch* get farther apart as J values go increasing.

Similarly, the wave numbers of lines of *R-branch* making use of selection rule $\Delta J = +1$ i.e., by replacing J' by $J'' + 1$ in Eqn. (3.2.3).

$$\bar{\nu}_R = \bar{\nu}_0 + 2B'_{v'} + (3B'_{v'} - B''_{v''})J'' + (B'_{v'} - B''_{v''})J''^2 \quad J'' = 0, 1, 2, \dots$$

Writing J for J'' , we obtain

$$\begin{aligned} \bar{\nu}_R &= \bar{\nu}_0 + 2B'_{v'} + (3B'_{v'} - B''_{v''})J + (B'_{v'} - B''_{v''})J^2, \\ J &= 0, 1, 2, \dots \end{aligned} \quad \dots(3.2.5)$$

The lines of *R-branch* are denoted by $R(0), R(1), R(2), \dots$

Since $B'_v < B''_v$, the term $B'_v - B''_v$ is negative but has very small value. Therefore, the term $3B'_{v'} - B''_{v''}$ is positive. The linear and quadratic terms in J are of opposite sign. As a consequence of this, the line spacing in *R-branch* decreases very slowly and the lines ultimately converge and the point where lines converge is called **band head**.

For *Q-branch* $J' = J''$ and we obtain

$$\bar{\nu}_Q = \bar{\nu}_0 + (B'_{v'} - B''_{v''})J'' + (B'_{v'} - B''_{v''})J''^2 \quad J'' = 0, 1, 2, \dots$$

Writing J for J'' , we get

$$\bar{\nu}_Q = \bar{\nu}_0 + (B'_{v'} - B''_{v''})J + (B'_{v'} - B''_{v''})J^2 \quad J = 0, 1, 2, \dots \quad \dots(3.2.6)$$

It is possible to represent the wave numbers of lines of *P*- and *R*-branch by means of a single formula

$$\bar{\nu}_{P,R} = \bar{\nu}_0 + (B'_{v'} + B''_{v''})m + (B'_{v'} - B''_{v''})m^2 \quad \dots(3.2.7)$$

where m takes the values $-1, -2, -3, \dots$ for *P-branch* and $1, 2, 3, \dots$ for *R-branch*.

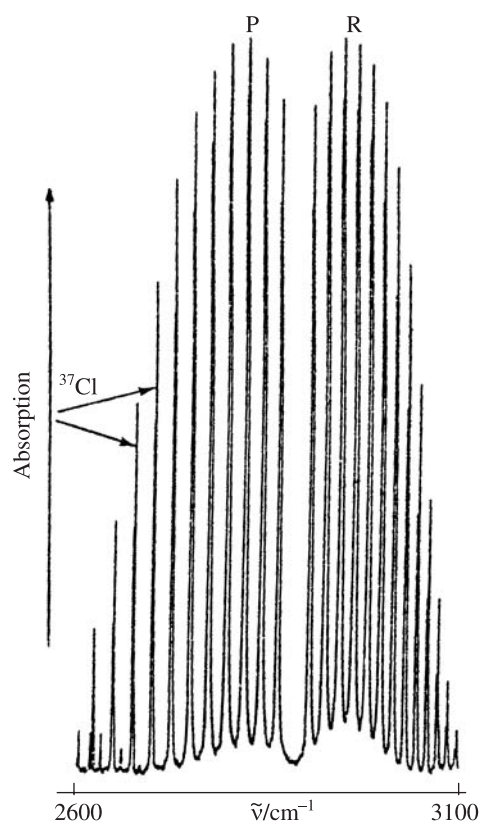


Fig 3.2.1 Absorption curves for fundamental transitions $0 \rightarrow 1$ in HCl

The absorption curve for the fundamental transition ($v'' = 0 \rightarrow v' = 1$) for HCl is shown in the Fig. (3.2.1). The lines of *P-branch* and *R-branch* can be seen in the curve. No line is observed at the center of the *P-* and *R-branches*. In fact, this is the position of *Q-branch*, which is not observed in HCl. In the case $B'_v = B''_v$, a single line is observed in *Q-branch*. Actually B'_v slightly differs from B''_v and hence *Q-branch* consists of a number of lines which are very closely spaced. It is observed only in those molecules having $\Lambda \neq 0$.

The average inter-nuclear distance r_e increases with increase in vibrational energy and hence

the rotational constant $B \left(= \frac{h}{8\pi^2 I c}, I = \mu r_e^2 \right)$ is smaller in the upper vibrational state than that in the

lower state. Thus, $B'_v < B''_v$, from Eqn. (3.2.4) it is evident that the separation of lines in *P-branch* increases as one moves towards the lower frequency side of band origin. This means band head (where the lines converge) appears on higher frequency side of band origin *i.e.*, band head is formed in *R-branch*. Such a band is said to be degraded (shaded) towards the red. In vibration-rotation spectra bands are always degraded towards the red only.

Measuring the values of B_v for two or three vibrational levels, B_e can be calculated. From this value of B_e , we can calculate moment of inertia and hence inter-nuclear distance.

ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

4.1 ELECTRONIC SPECTRA OF DIATOMIC MOLECULES

When atoms combine to form a molecule, the inner electrons in each of the participating atom may be regarded as constituent part of the parent atom while the outer electrons belong to the molecule as a whole. A molecule in ground state has a definite electronic configuration and the energy of its electrons is called ground state electronic energy. The energy of molecule due to its electrons depends upon the relative positions of the nuclei *i.e.*, electronic energy includes the electrostatic energy of nuclei of the molecule. The variation electronic energy of a diatomic molecule with inter-nuclear distance in ground state is shown in the Fig. (4.1.1). In excited states the dependence of electronic energies may be represented by similar curves.

Any change in electron configuration is accompanied by a change in electronic energy. The electronic energy levels of a molecule are much more complicated than that in atoms. The outer electron levels of a molecule have energies with absolute value in the range electron volt. According to Born-Openheimer approximation the total energy of a molecule can be written as sum of three parts: electronic energy E_e , vibration energy E_v and rotational energy E_r .

$$E = E_e + E_v + E_r$$

or in terms of term values

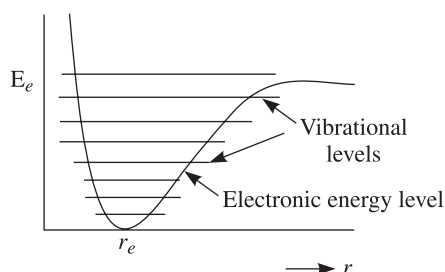


Fig. 4.1.1

$$T = T_e + G(v) + F(J)$$

The vibration energy is expressed as

$$E_v = (v + \frac{1}{2})ch\bar{\omega}_e - (v + \frac{1}{2})^2 chx_e\bar{\omega}_e + \dots \quad \dots(4.1.1)$$

or vibration term is

$$G(v) = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2 x_e\bar{\omega}_e + \dots \quad (4.1.2)$$

where $\bar{\omega}_e$ is the equilibrium frequency and x_e anharmonicity constant in a particular electronic state and has different values in different electronic state. The inclusion of x_e takes into account the interaction between electronic and vibrational energy states.

The rotational energy is expressed as

$$E_r = B_v J(J+1)ch + D_v J^2(J+1)^2 ch + \dots \quad \dots(4.1.3)$$

The corresponding term value is

$$F(J) = B_v J(J+1) + D_v J^2(J+1)^2 + \dots \quad \dots(4.1.4)$$

The values of rotational constant B_v and centrifugal distortion constant D_v are different in different vibrational and electronic states.

A change in electronic energy involves change in all the three kinds of energy. It is worth to observe that there is always a change in electronic dipole moment in an electronic transition whether the molecule is non-polar or polar and therefore all kinds of molecule exhibit electronic band spectra. The wave numbers of spectroscopic lines originating from the transitions between two electronic states are given by

$$\begin{aligned} \bar{\nu} &= (T'_e - T''_e) + [G'(v') - G''(v'')] + [F'(J') - F''(J'')] \\ &= \bar{\nu}_e + \bar{\nu}_v + \bar{\nu}_r \end{aligned} \quad \dots(4.1.5)$$

Single prime refers to higher state and double prime to lower state. The frequency $\bar{\nu}_e = T'_e - T''_e$ is constant for a given pair of electronic levels. The terms $G'(v')$ and $G''(v'')$ belong to different electronic states with different $\bar{\omega}_e$ and $x_e\bar{\omega}_e$ and it is also possible that $G'(v') < G''(v'')$. Similarly, $F'(J')$ and $F''(J'')$ also belong to different electronic levels, possibility of $F'(J') < F''(J'')$ is always there.

Vibrational (Course) Structure of Electronic Spectra

In order to have a general picture of electronic spectra, we shall, for the time being, ignore the rotational transitions and shall concentrate on the possible transitions between the different vibrational levels belonging to different electronic levels. The wave numbers of the lines are given by

$$\begin{aligned} \bar{\nu} &= \bar{\nu}_e + \bar{\nu}_v \\ &= \bar{\nu}_e + [G'(v') - G''(v'')] \end{aligned}$$

$$= \bar{\nu}_e + \left[\bar{\omega}'_e \left(v' + \frac{1}{2} \right) - \bar{\omega}'_e x'_e \left(v' + \frac{1}{2} \right)^2 + \bar{\omega}'_e y'_e \left(v' + \frac{1}{2} \right)^3 \right] - \left[\bar{\omega}''_e \left(v'' + \frac{1}{2} \right) - \bar{\omega}''_e x''_e \left(v'' + \frac{1}{2} \right)^2 + \bar{\omega}''_e y''_e \left(v'' + \frac{1}{2} \right)^3 \right] \quad \dots(4.1.6)$$

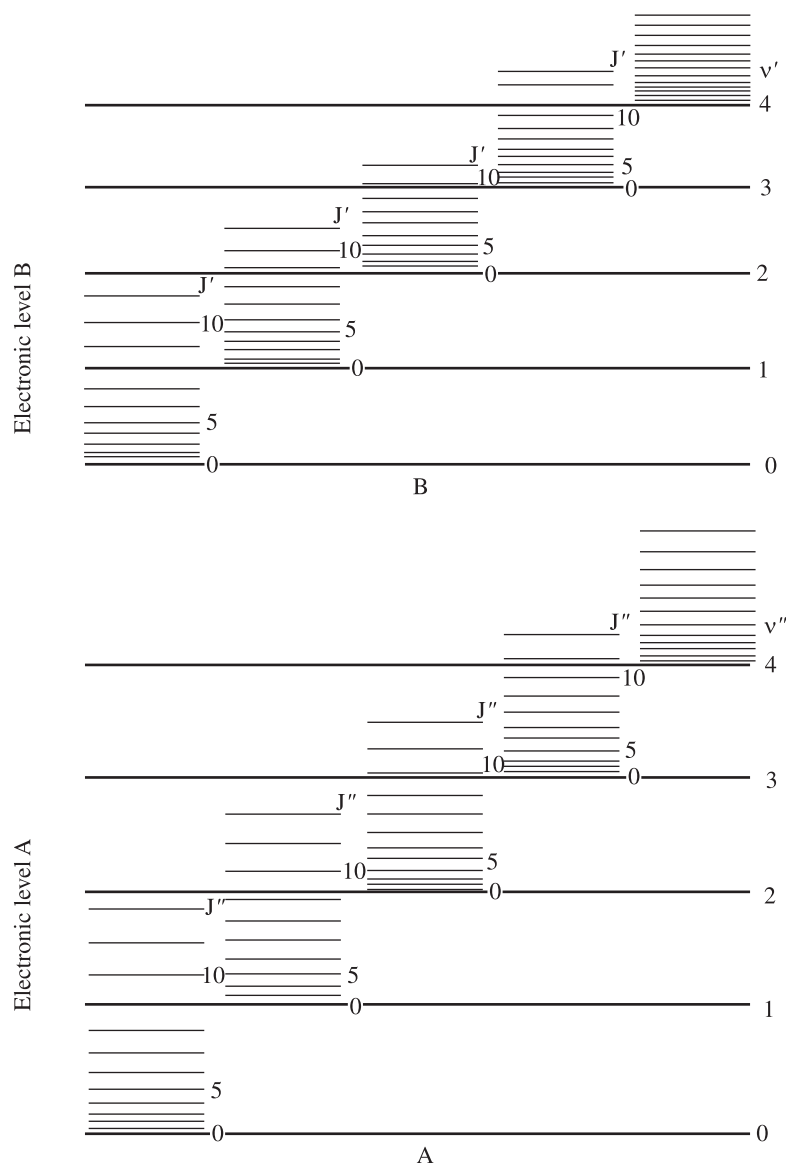


Fig. 4.1.2 Vibrational and rotational levels of two electronic states A and B of a molecule (schematic)

For a given pair of electronic levels, Eqn. (4.1.6) gives all possible transitions between different vibrational levels of the two electronic levels. For electronic transitions, there is no strict selection rule for the vibration quantum number v . Each vibration state of upper electronic level may combine with each vibration state of lower electronic level. These transitions create numerous lines in the vibration spectrum. When observed with an instrument of high resolving power, each of these lines is found to be composed of many closely spaced lines, called fine structure. So each line resulting from vibrational transition is in fact a group of lines and hence called a **band**. The lines of fine structure of each band result from rotational transitions which we have ignored for a while. *All the bands due transitions between a given pair of electronic states, for all possible values of v' and v'' are said to form a **band system**.*

*If we consider all possible transitions between all electronic levels, the electronic spectrum of a molecule consists of **many band system**.*

The intensity of band drops rapidly with increasing value of $|\Delta v|$. At room temperature, most molecules occupy the ground state $v'' = 0$ and therefore most intense band is $0 \rightarrow 1$ and is called fundamental band. The bands $0 \rightarrow 2$, $0 \rightarrow 3$ etc. are called overtones. The lines resulting from all the possible transitions are shown in the Deslandre table.

The set of bands having constant value of $v' - v''$ is called a **sequence**. The main sequence lies along the diagonal from upper left corner to the lower right corner. Other sequences consist of frequencies lying along the lines parallel to the above diagonal.

The set of bands arising from the transitions $v'' \rightarrow v'$ (or $v' v''$) having a definite value of either v' or v'' while the other increases by unity constitute a **progression**. The set of bands with $v'' = 0$ and $v' = 1, 2, 3, \dots$ is called v' -progression with $v'' = 0$. This progression consists of bands $\bar{\nu}_{00}, \bar{\nu}_{10}, \bar{\nu}_{20}, \bar{\nu}_{30}, \dots$. The bands of this progression lie in the first vertical column of Deslandre table. The set of bands with $v' = 0$ and $v'' = 0, 1, 2, 3, \dots$ is called v'' -progression with $v' = 0$. These bands with frequencies $\bar{\nu}_{00}, \bar{\nu}_{01}, \bar{\nu}_{02}, \dots$ lie along the horizontal row of the Deslandre table.

Eqn. (4.1.6) giving the frequency of bands can be written as

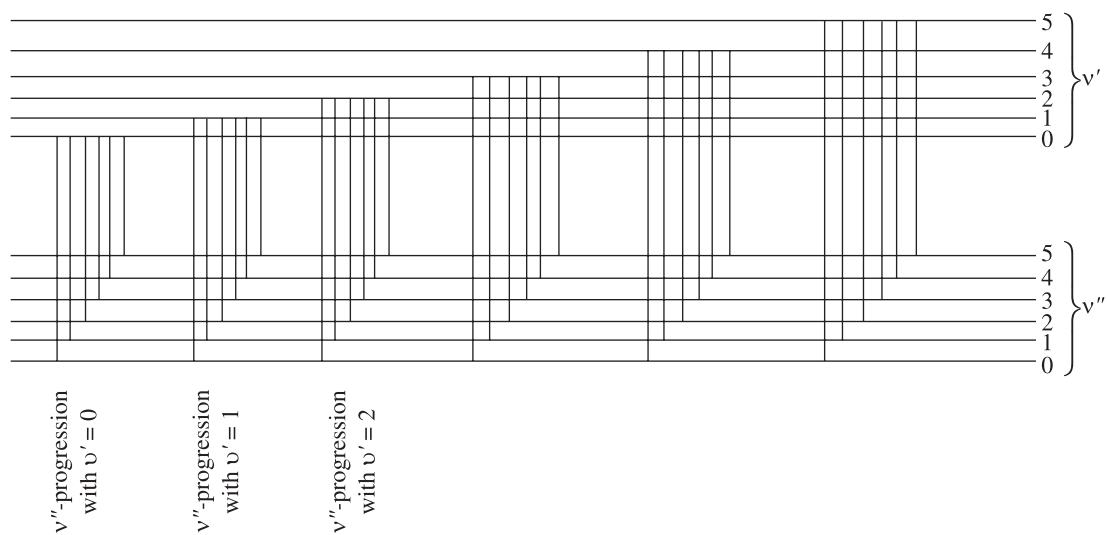
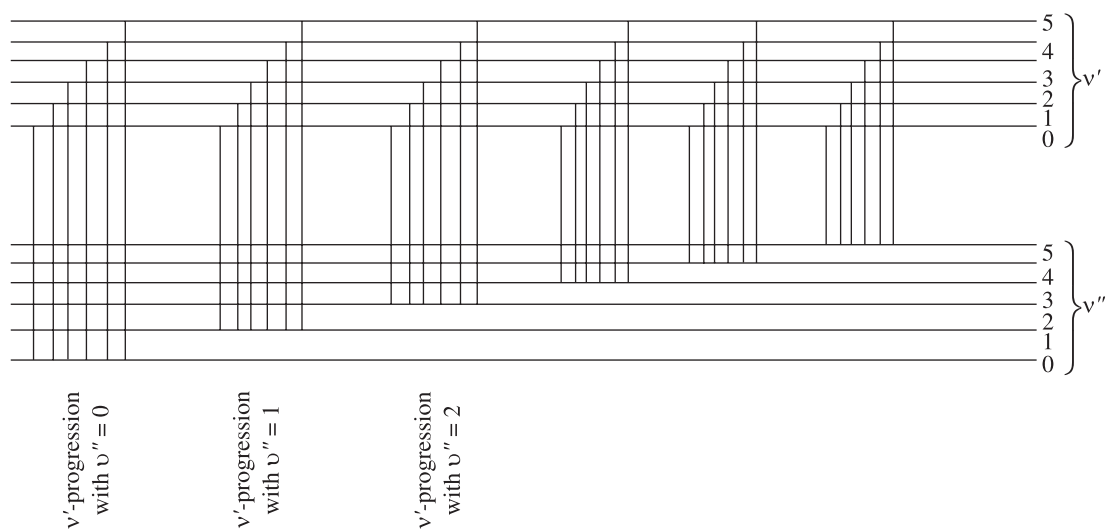
$$\bar{\nu} = \bar{\nu}_{00} + (\omega'_0 v' - \omega'_0 x'_0 v'^2 + \omega'_0 y'_0 v'^3 + \dots) - (\omega''_0 v'' - \omega''_0 x''_0 v''^2 + \omega''_0 y''_0 v''^3 + \dots) \quad \dots(4.1.7)$$

$$\text{where } \bar{\nu}_{00} = \bar{\nu}_e + \frac{1}{2}(\bar{\omega}'_e - \bar{\omega}''_e) - \frac{1}{4}(\bar{\omega}'_e x'_e - \bar{\omega}''_e x''_e) + \frac{1}{8}(\bar{\omega}'_e y'_e - \bar{\omega}''_e y''_e) \quad \dots(4.1.8)$$

is the term independent of v' and v'' i.e., it is the frequency of transition $v'' = 0 \rightarrow v' = 0$ (0-0 band).

$$\text{or } \bar{\nu}_{00} = \bar{\nu}_e + \left(\frac{1}{2} \bar{\omega}'_e - \frac{1}{4} \bar{\omega}'_e x'_e + \frac{1}{8} \bar{\omega}'_e y'_e + \dots \right) - \left(\frac{1}{2} \bar{\omega}''_e - \frac{1}{4} \bar{\omega}''_e x''_e + \frac{1}{8} \bar{\omega}''_e y''_e + \dots \right) \quad \dots(4.1.9)$$

and $\omega_0 = \bar{\omega}_e - \bar{\omega}_e x_e + \frac{3}{4} \bar{\omega}_e y_e \dots$ coefficient of v' .

Fig. 4.1.3 v'' -progressions with $v' = \text{constant}$ Fig. 4.1.4 v' -progressions with $v'' = \text{constant}$

$v' \backslash v''$	0	1	2	3	4	5	6	
0	$\bar{\nu}_{00}$	$\bar{\nu}_{01}$	$\bar{\nu}_{02}$	$\bar{\nu}_{03}$	$\bar{\nu}_{04}$	$\bar{\nu}_{05}$	$\bar{\nu}_{06}$	v'' -progression with $v' = 0$
1	$\bar{\nu}_{10}$	$\bar{\nu}_{11}$	$\bar{\nu}_{12}$	$\bar{\nu}_{13}$	$\bar{\nu}_{14}$	$\bar{\nu}_{15}$	$\bar{\nu}_{16}$	v'' -progression with $v' = 1$
2	$\bar{\nu}_{20}$	$\bar{\nu}_{21}$	$\bar{\nu}_{22}$	$\bar{\nu}_{23}$	$\bar{\nu}_{24}$	$\bar{\nu}_{25}$	$\bar{\nu}_{26}$	v'' -progression with $v' = 2$
3	$\bar{\nu}_{30}$	$\bar{\nu}_{31}$	$\bar{\nu}_{32}$	$\bar{\nu}_{33}$	$\bar{\nu}_{34}$	$\bar{\nu}_{35}$	$\bar{\nu}_{36}$	
4	$\bar{\nu}_{40}$	$\bar{\nu}_{41}$	$\bar{\nu}_{42}$	$\bar{\nu}_{43}$	$\bar{\nu}_{44}$	$\bar{\nu}_{45}$	$\bar{\nu}_{46}$	
5	$\bar{\nu}_{50}$	$\bar{\nu}_{51}$	$\bar{\nu}_{52}$	$\bar{\nu}_{53}$	$\bar{\nu}_{54}$	$\bar{\nu}_{55}$	$\bar{\nu}_{56}$	
6	$\bar{\nu}_{60}$	$\bar{\nu}_{61}$	$\bar{\nu}_{62}$	$\bar{\nu}_{63}$	$\bar{\nu}_{64}$	$\bar{\nu}_{65}$	$\bar{\nu}_{66}$	

v' -progression with $v'' = 0$ v' -progression with $v'' = 4$

Sequence $v' - v'' = -1$
 Sequence $v' - v'' = 0$
 Sequence $v' - v'' = 1$

Fig. 4.1.5 Deslandre Table

It is interesting to observe that electronic absorption spectrum consists of a single progression only with $v'' = 0$. This can be explained as follows. At room temperature, most molecules are in the lowest vibrational state ($v'' = 0$). After absorbing energy from surrounding radiation they are raised to higher electronic state. Since the molecules can jump to any quantum state of higher quantum number without restriction, the most probable vibrational transitions are $0 \rightarrow 1, 0 \rightarrow 2, 0 \rightarrow 3, \dots$ etc. Obviously, these constitute a single progression with $v'' = 0$. If the temperature is raised, an appreciable number of molecules are excited to $v' = 1$ state. Then the probability of transitions $1 \rightarrow 0, 1 \rightarrow 1, 1 \rightarrow 2, 1 \rightarrow 3, 1 \rightarrow 4, \dots$ etc. is enhanced and the progression $v' = 1$ appears in the absorption spectrum.

Rotational Structure (Fine Structure) of Electronic Bands

So far in the analysis of structure of electronic bands we considered the transitions between vibrational states of different electronic levels and ignored the rotational states associated with each vibrational state. Now we shall consider the role of rotational states in determining the structure of electronic bands. Examination of electronic spectrum of molecules with instruments of high resolving power reveals that each vibrational band is composed of a large number of closely spaced lines, called

fine structure of band. These lines originate from transitions between rotational states of different electronic levels.

For a given vibrational transition, the wave numbers of lines resulting from rotational transitions are given by

$$\begin{aligned}\bar{\nu} &= \bar{\nu}_e + [G'(v') - G''(v'')] + [F'(v', J') - F''(v'', J'')] \\ &= \bar{\nu}_0 + [F'(v', J') - F''(v'', J'')] \end{aligned} \quad \dots(4.1.10)$$

where $\bar{\nu}_0 = \bar{\nu}_e + [G'(v') - G''(v'')]$ is the wave number of band origin. F' and F'' are the rotational terms belonging to upper and lower electronic states respectively. In terms of rotational constants B'_v and B''_v of upper and lower electronic states we can express $\bar{\nu}$ as

$$\bar{\nu} = \bar{\nu}_0 + B'_v J'(J' + 1) - B''_v J''(J'' + 1) \quad \dots(4.1.11)$$

If the total electronic angular momentum Λ of the molecule is zero in both upper and lower electronic states *i.e.*, both are Σ states, the selection rule is

$$\Delta J = \pm 1$$

The set of lines obeying the selection rule $\Delta J = J' - J'' = -1$ is called P-branch and the set of lines obeying the selection rule $\Delta J = J' - J'' = +1$ is called R-branch. Putting $J' = J'' - 1$ in Eqn. (4.1.11) we get the wave numbers of lines of P-branch.

$$\bar{\nu}_P = \bar{\nu}_0 - (B'_v + B''_v)J'' + (B'_v - B''_v)J''^2, \quad J'' = 1, 2, 3, \dots \quad \dots(4.1.12)$$

Similarly, putting $J' = J'' + 1$ in Eqn. (4.1.11), we get the wave numbers of lines of R-branch.

$$\bar{\nu}_R = \bar{\nu}_0 + 2B'_v + (3B'_v - B''_v)J'' + (B'_v - B''_v)J''^2, \quad J'' = 0, 1, 2, 3, \dots \quad \dots(4.1.13)$$

If the total orbital angular momentum in any of the two electronic states (upper or lower) is not zero, the selection rule for J is $\Delta J = J' - J'' = 0, \pm 1$. In this case lines of Q-branch make their appearance and the wave number of lines of Q-branch are given by

$$\bar{\nu}_Q = \bar{\nu}_0 + (B'_v - B''_v)J'' + (B'_v - B''_v)J''^2, \quad \dots(4.1.14)$$

The wave numbers of lines of *P*- and *R*-branches can be represented by a single formula given by

$$\bar{\nu}_{PR} = \bar{\nu}_0 + (B'_v + B''_v)m + (B'_v - B''_v)m^2 \quad \dots(4.1.15)$$

where
and

$$\begin{aligned}m &= -J'' = -1, -2, -3, \dots \text{for } P\text{-branch} \\ m &= J'' + 1 = 1, 2, 3, \dots \text{for } R\text{-branch}\end{aligned}$$

Since $m \neq 0$ either in *P*-branch or in *R*-branch, a line is missing for $m = 0$. This missing line of frequency $\bar{\nu} = \bar{\nu}_0$ is the center of the band and corresponds to the transition $J'' = 0 \rightarrow J'' = 0$.

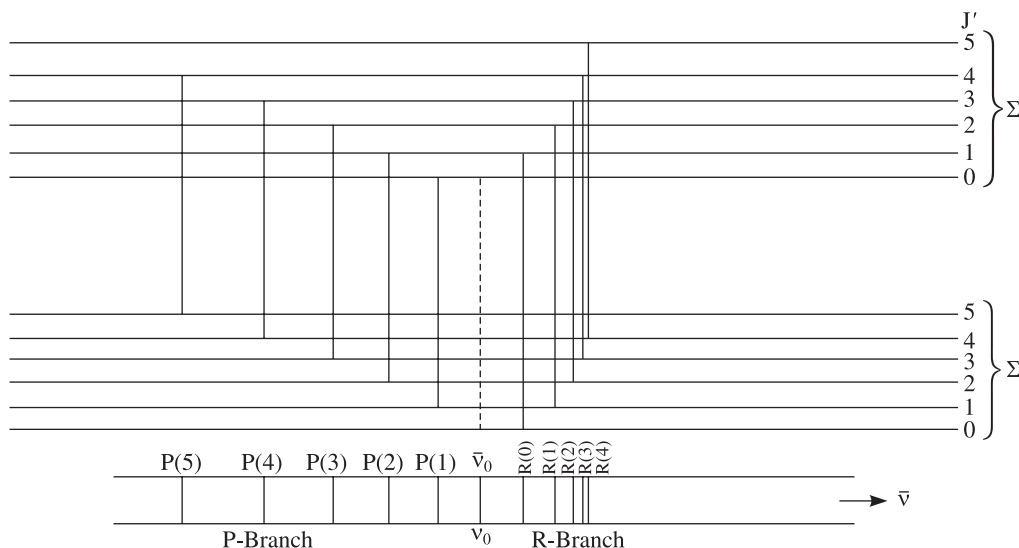


Fig. 4.1.6 P-branch consists of lines P(1), P(2), P(3),....etc. and R-branch consists of lines R(0), R(1), R(2), R(3),.....etc.

Formation of Band Head

The rotational constants B'_v and B''_v belong to different electronic states as well as, in general, different vibrational states and therefore they differ considerably. Also the difference $B'_v - B''_v$ may be negative or positive. [In case of vibration-rotation spectrum, which lies in infrared region, B'_v and B''_v belong to the vibrational states of the same electronic states, so their difference is quite small.]

Now let us consider the case, $B'_v - B''_v = \text{negative i.e., } B'_v < B''_v$. The wave numbers of lines of R-branch is given by

$$\bar{\nu}_R = \bar{\nu}_0 + (B'_v + B''_v) m + (B'_v - B''_v) m^2, \quad m = 1, 2, 3, \dots \quad \dots(4.1.16)$$

Since $B'_v < B''_v$, the last term containing m^2 is negative. Substituting $m = 1, 2, 3, \dots$ in eqn. (4.1.16), we find that $\bar{\nu}$ increases first and after attaining a maximum value it begins to decrease with further increase in the value of m . This happens because for the smaller values of m , the change in the term containing m dominates over the change in the term containing m^2 . After the frequency $\bar{\nu}$ attains maximum value, this trend is reversed. Before $\bar{\nu}_{\text{max}}$, the separation between successive lines gradually decreases and therefore the lines begins to crowd. The frequency at which the separation of lines becomes zero is called **band head**. A further increase in the value of m , causes decrease in frequency but increase in separation between consecutive lines. In other words, the successive lines begin to turn back upon themselves and this trend continues toward the lower frequency side. The band head is point where the reversal of frequency change takes place. [In electronic band there is a strong tendency of head formation whereas in vibration-rotation band the tendency of head formation is almost negligible and band head is not observed.]

In *P-branch* the wave number of lines is given by

$$\bar{\nu}_P = \bar{\nu}_0 + (B'_V + B''_V) m + (B'_V - B''_V) m^2, \quad m = -1, -2, -3, \dots \quad \dots(4.1.17)$$

The terms containing m and m^2 both are negative. As the value of m increases numerically, the frequencies of lines gradually decreases but the separations of consecutive lines increases *i.e.*, the lines get more and more widely separated. At the same time the intensity of lines diminishes with increasing value of $|m|$. This results in gradual *shading off* the band on the lower frequency side of band origin.

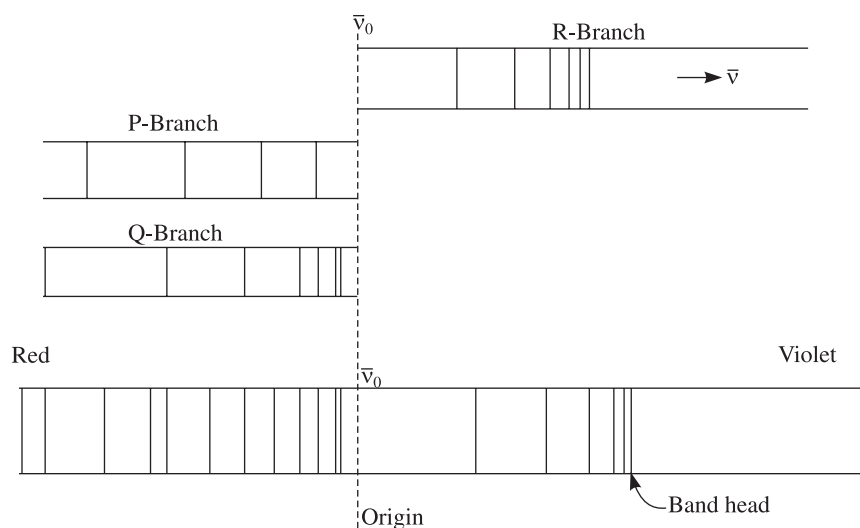


Fig. 4.1.7 Rotational fine structure of vibration-electronic transition

Thus, if $B'_V < B''_V$, the band will be *degraded* (*shaded*) toward the *red* end (lower frequency side or higher wavelength side) of the spectrum. The *band head* is *formed in R-branch* *i.e.*, on the higher frequency side of zero or null line.

If $B'_V > B''_V$, arguments made above are reversed. The band is formed in P-branch and it is degraded (*shaded*) toward violet end.

[In electronic spectrum both red and violet degraded bands are observed whereas in vibration-rotation bands only red degraded bands are observed.]

If $B'_V = B''_V$, *i.e.*, vibration-rotation interaction is zero, both the branches consist of equally spaced lines and band would be headless.

All the bands resulting from transitions between a given pair of electronic states, for all possible values of v' and v'' are said to form a band system.

There are many electronic states of a molecule, therefore, all possible transitions between various electronic states give rise to many band system in the electronic spectrum of a molecule.

Fortrat Diagram

The dependence of frequency $\bar{\nu}$ of line in electronic spectra on m (or J) is represented by Fortrat diagram. In this diagram $\bar{\nu}$ is plotted on abscissa and m (or J) on ordinate. The points $(\bar{\nu}, m)$ are represented by small circles. The curve joining these points is a parabola. The vertex of the parabola corresponds to the band head. The value of m corresponding to band head is obtained by solving the equation

$$\frac{d\bar{\nu}}{dm} = 0$$

$$(B'_v + B''_v) + 2(B'_v - B''_v)m = 0$$

$$m_{head} = -\frac{B'_v + B''_v}{2(B'_v - B''_v)} \quad \dots(4.1.18)$$

If m comes out to be fraction, the nearest whole number will be the value of m .

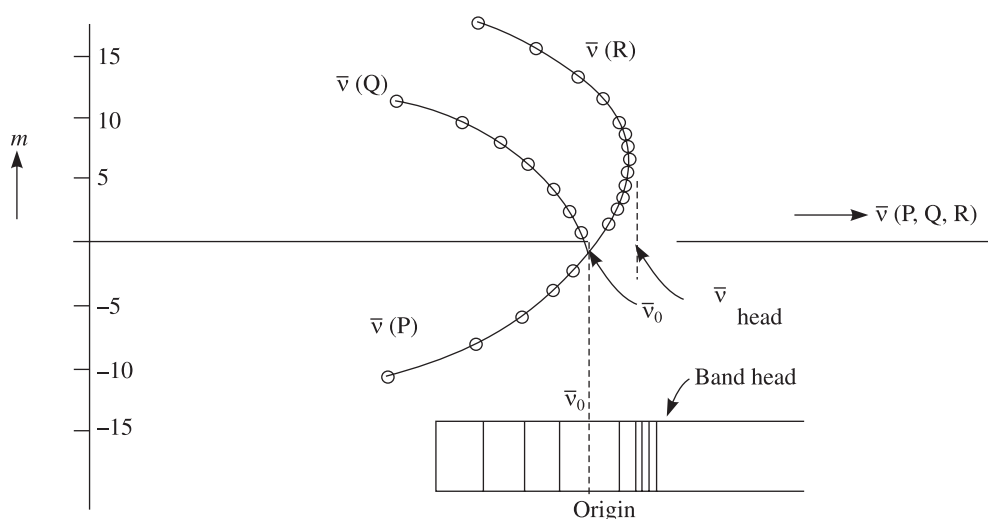


Fig. 4.1.8 Fortrat diagram

The separation of band head from the band origin is given by

$$\bar{\nu}_{head} - \bar{\nu}_0 = (B'_v + B''_v)m_{head} + (B'_v - B''_v)m_{head}^2$$

Substituting the value of m_{head} from Eqn. (4.1.18) in above equation, we find

$$\bar{\nu}_{head} - \bar{\nu}_0 = -\frac{(B'_v + B''_v)^2}{4(B'_v - B''_v)} \quad \dots(4.1.19)$$

For a band degraded toward red, $(\bar{\nu}_{head} - \bar{\nu}_0)$ is positive and for that degraded toward violet this difference is negative. Since B'_v and B''_v have different values in different vibrational states, the distance of different bands in a band system are different.

The value of J'' corresponding to Q-head is obtained by setting $\frac{d\bar{\nu}_Q}{dJ''} = 0$. From Eqn. (4.1.14), we have

$$(B'_v - B''_v) + 2(B'_v - B''_v) = 0$$

$$J'' = -\frac{1}{2}$$

Thus, the position of Q-band head does not depend on the values of B'_v and B''_v .

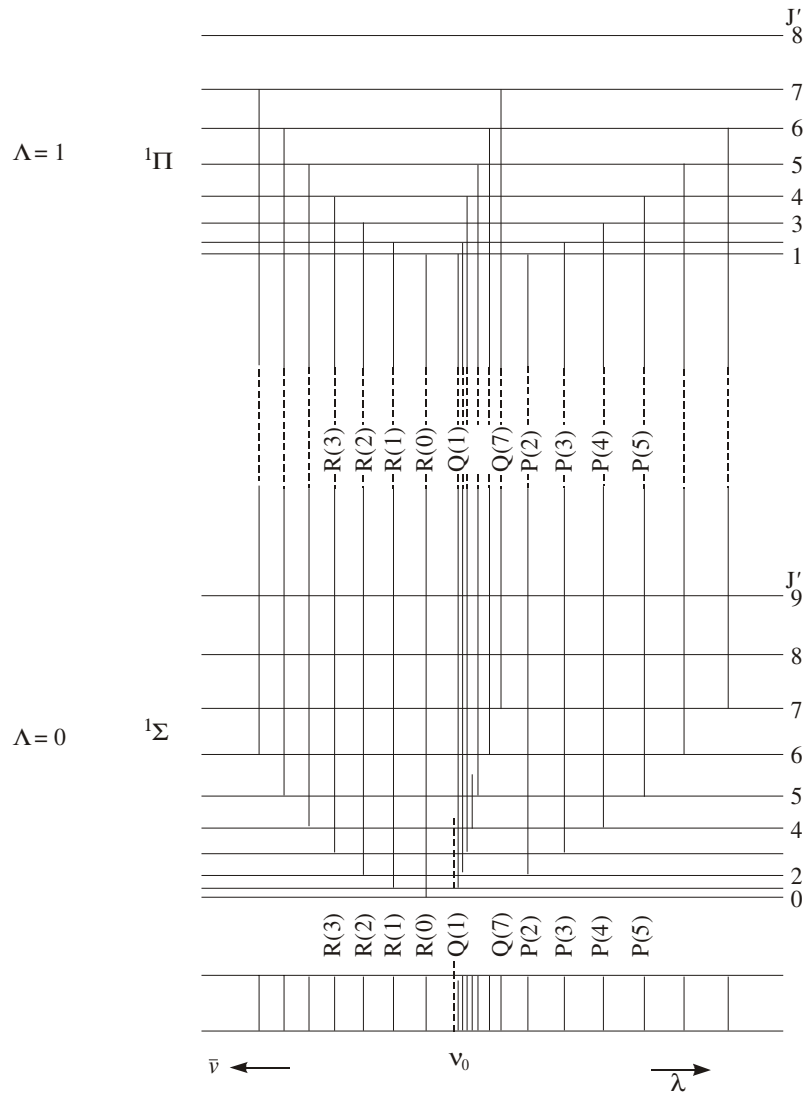


Fig. 4.1.9 Energy level diagram for a band with P, Q, and R-branches

4.2 FRANCK-CONDON PRINCIPLE: ABSORPTION

Examination of electronic spectra reveals that in some spectra (0, 0) band is most intense, in others intensity of bands rises up to certain value of v' and then diminishes for higher values of v' ; yet in others intensity of band increases with increasing value of v' and finally a continuum is observed. Three typical cases of intensity distribution in absorption band series are shown schematically.

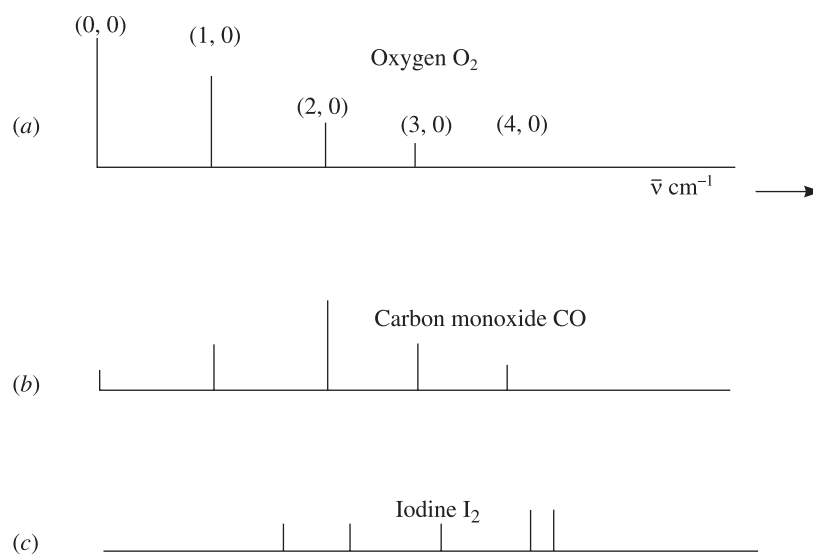


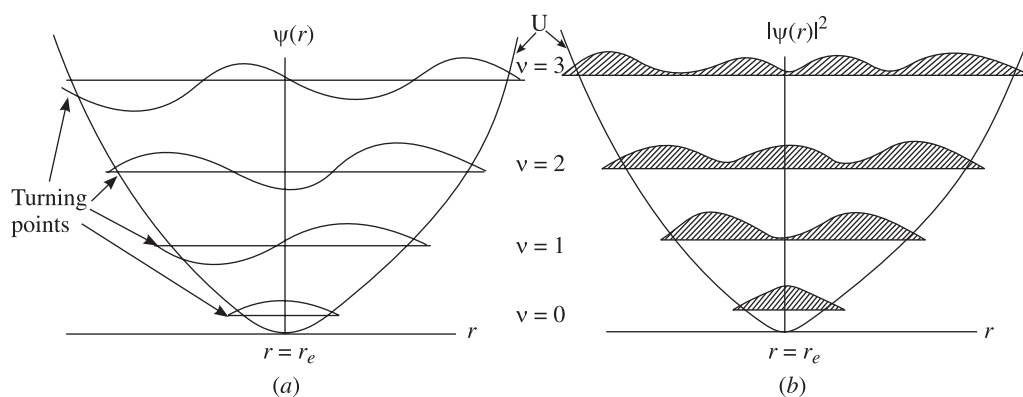
Fig. 4.2.1 Intensity distribution in a band (v'' -progression with $v'' = 0$)

The intensity distribution in different bands of a band system can be understood in terms of *Franck-Condon principle*. According to this principle, *the transition from one vibrational level of lower electronic state to a vibrational level of upper electronic state takes place so rapidly (10^{-15} s) in comparison to the vibrational motion of nuclei that nuclei before and after the transition have very nearly the same inter-nuclear distance and velocity*. This means that the electronic transitions leading to the appearance of absorption bands must be represented by vertical lines. Except the transitions starting from lowest electronic state, the most probable transitions will be those which start from the extreme positions (turning points) of the nuclei for any given vibrational level. The most probable transition will be attended with most intense band.

Case I: $r'_e = r''_e$: To explain the intensity distribution shown in Fig. (4.2.1a), we consider the potential energy curves of the two electronic states as sketched in Fig. (4.2.2a). The curves are so drawn that the minima of two curves lie one above the other. Inter-nuclear distance in the two states has the same value. Before absorption the molecule is in the lowest energy level $v'' = 0$. The most probable position of finding the vibrating nuclei in this level is the central point of the classical limits and the kinetic energy of the nuclei (which is equal to the vertical distance from minima of the curve to the lowest energy level) is minimum compared with those in the higher levels. It can easily be seen that the transition AB satisfies the requirements Franck-Condon principle *i.e.*, the position

and velocity be almost unaltered in the transition. Obviously, the (0, 0) transition is most probable and hence the corresponding band will be the most intense band.

Transitions from $v'' = 0$ to higher values of v' is accompanied by an appreciable amount of change in inter-nuclear distance and velocity. The change in inter-nuclear distance and velocity increases progressively with increasing value of v' and hence the probabilities of such transitions go on diminishing and hence the intensities of corresponding bands.

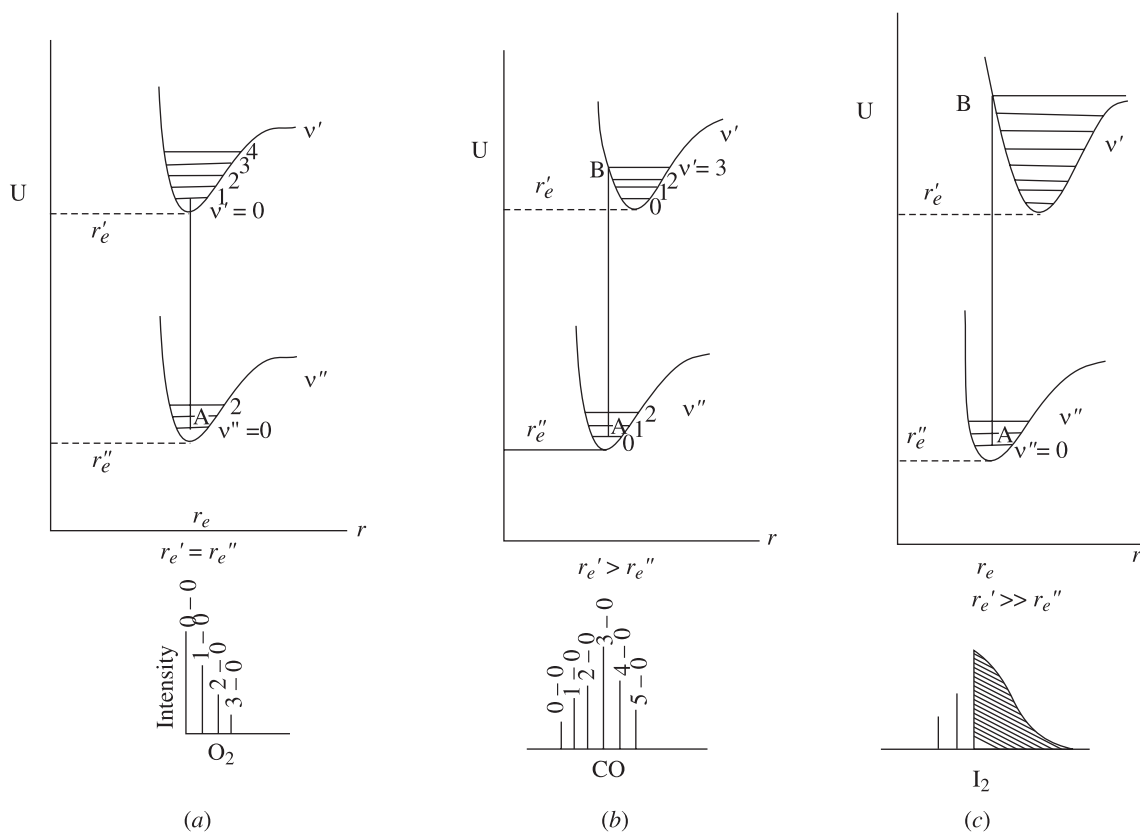


(a) Vibrational wave functions of harmonic oscillator.

(b) Variation of probability $|\psi(r)|^2$. In the ground state ($v = 0$), the probability density is maximum at $r = r_e$ (mid-point of turning points). In this state ($v = 0$), kinetic energy is minimum. In the excited states ($v > 0$), the probability density $|\psi(r)|^2$ is maximum near the turning points. The nuclei are most likely to be found at this value of internuclear distance. Obviously, kinetic energies of nuclei will be minimum near the turning points.

Fig. 4.2.2

Case II: $r'_e > r''_e$: To explain the intensity distribution shown in Fig. (4.2.3b), we consider two potential energy curves sketched for the lower and upper electronic states. The curves are so drawn that the minimum of the upper electronic state is somewhat displaced towards the right ($r'_e > r''_e$). According to the Frank-Condon principle, the most probable transition is AB, where B is vertically above A and near the turning point of the vibrational level corresponding to some higher value of v' . Obviously, the (0, 0) transition is not the most probable one hence the corresponding line will be less intense. For the transition AB, the internuclear distance has the same value before and after transition, the kinetic energy has nearly the same value at A and B, the probability of finding the nuclei at inter-nuclear distance corresponding to these points is maximum. Thus, vibrational level in the upper electronic state in the neighbourhood of B, will be the upper vibrational level of the most probable transition hence the corresponding band will be the most intense band. The probability of transition starting from $v'' = 0$ to still higher values of v' will go on diminishing. This explains the intensity distribution of Fig. (4.2.1b). Similar intensity distribution is obtained when the minimum of the upper curve is somewhat displaced towards the left of the minimum of the lower curve.



- (a) For vertical transition AB (i) $r_e' = r_e''$ (ii) Velocities of nuclei in the initial and final states are equal. The $(0-0)$ band is most intense.
- (b) For vertical transition AB (which corresponds to $3-0$ band) (i) r_e internuclear distance has the same value and (ii) velocities of nuclei have the same value in the initial and final states.
- (c) The vertical transition AB meets the requirements of Frank-Condon principle.

Fig. 4.2.3

Case III: $r_e' \gg r_e''$: Let us explain the intensity distribution of Fig. (4.2.1c). The potential energy curves needed for this case are shown in Fig. (4.2.3c). In this case the minimum of the curve for upper state is displaced by a greater distance than that in Fig. (4.2.3b). The vertical transition AB strictly fulfills the requirement of Franck-Condon principle. Notice that the point B lies at the level of the continuous region of the vibrational term spectrum of the upper state. After such an electronic transition, the atoms will get themselves at infinite distance apart and the molecule will be dissociated. The discrete absorption lines will be observed if the points in the upper state to which transitions

takes place lies some what below B and continuum is observed when the end point of transition lies some what above B.

Thus, in v' -progression with $v'' = 0$, the most intense absorption band will always correspond to the vertically upward transition which starts from the minimum of the lower potential energy curve, if we disregard the zero point energy of vibration of nuclei. The transitions, which do not originate from $v'' = 0$, are most probable when they start from the extreme positions (turning points) of nuclei.

Franck-Condon Principle: Emission

For the explanation of intensity distribution in emission bands within a band system of electronic spectrum, refer to the potential energy curves for upper and lower electronic states of Fig. (4.2.4). In the upper state, during vibrational motion represented by horizontal line AB, the molecule spends maximum time at the turning points A and B and minimum time at the intermediate positions. So the electronic transition starts either from A or from B. When the molecule starts from B, it finds itself at point C, vertically below B, after transition. The point C becomes the new turning point of the vibrational motion CD. When the molecule starts from A, it will be at point F, vertically below A, after transition. The point F will be the new turning point, in this case, of the vibrational motion FE.

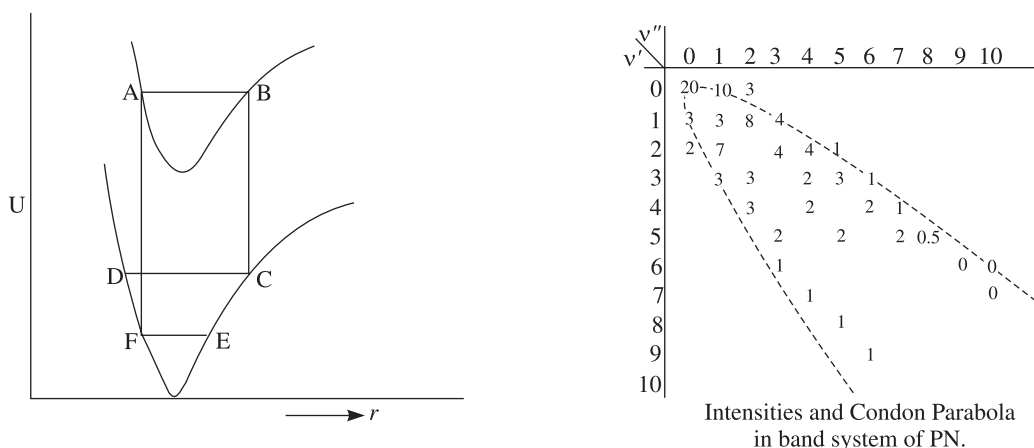


Fig. 4.2.4

It is evident that there are two values of v'' for which probability of the transition from a given value of v' , according to Franck-Condon principle, is maximum and hence there will be two intensity maxima in v'' -progression with $v' = \text{constant}$.

In Fig. 4.2.4, the intensities of PN band are arranged in array. The horizontal rows represent v'' -progression with $v' = \text{constant}$. Each row contains two intensity maxima (except $v' = 0$). As v' increases, both the turning points C and F move upward but this upward shift of C is more rapid than that of F. Meaning thereby, the two intensity maxima get more and more separated with increasing v' . Of course, the value of v'' corresponding to intensity maxima also increases. The curve joining

the intensity maxima is a parabola with principal diagonal as its axis. This parabola is known as *Condon parabola*.

If the minima of the potential energy curves have the same value of r , the intensity maxima in each progression ($v' = \text{constant}$) merge together and the Condon parabola degenerates into a straight line, which is coincident with the principal diagonal. In this case, the most intense bands are those for which $v' = v''$.

Quantum Mechanical Treatment

The probability of transition between two energy levels characterized by total wave function ψ' and ψ'' is proportional to the square of matrix element R of electric dipole moment (also called transition moment)

$$R = \int \psi'^* \mu \psi'' d\tau \quad \dots(4.2.1)$$

The Cartesian components of vector μ are $\sum e_i x_i$, $\sum e_i y_i$ and $\sum e_i z_i$.

To a first approximation, the total eigen function ψ may be assumed to be the product of the electronic ψ_e , vibrational ψ_v and rotational ψ_r eigen functions respectively and the reciprocal of internuclear distance r .

$$\psi = \psi_e \frac{1}{r} \psi_v \psi_r \quad \dots(4.2.2)$$

To a good approximation, the rotational motion may be neglected and under this approximation the wave function becomes

$$\psi = \psi_e \psi_v \quad \dots(4.2.3)$$

The electric moment μ may be resolved into two parts: electronic part μ_e and nuclear part μ_n .

$$\mu = \mu_e + \mu_n \quad \dots(4.2.4)$$

Thus

$$R = \int \mu_e \psi_e'^* \psi_v' \psi_e'' \psi_v'' d\tau + \int \mu_n \psi_e'^* \psi_v' \psi_e'' \psi_v'' d\tau \quad \dots(4.2.5)$$

where the volume element $d\tau$ is product of $d\tau_e$ the volume element of electronic coordinates and $d\tau_n$ the volume element of nuclear coordinates. Keeping in mind that vibration wave functions are real, Eqn. (4.2.5) may be written as

$$R = \int \psi_v' \psi_v'' d\tau_n \int \mu_e \psi_e'^* \psi_e'' d\tau_e + \int \mu_n \psi_v' \psi_v'' d\tau_n \int \psi_e'^* \psi_e'' d\tau_e \quad \dots(4.2.6)$$

The electronic wave functions $\psi_e'^*$ and ψ_e'' belong to different electronic states and therefore they are orthogonal

$$\int \psi_e'^* \psi_e'' d\tau_e = 0 \quad \dots(4.2.7)$$

Equation (4.2.6) then simplifies to

$$R = \int \psi_v' \psi_v'' d\tau_n \int \mu_e \psi_e'^* \psi_e'' d\tau_e \quad \dots(4.2.8)$$

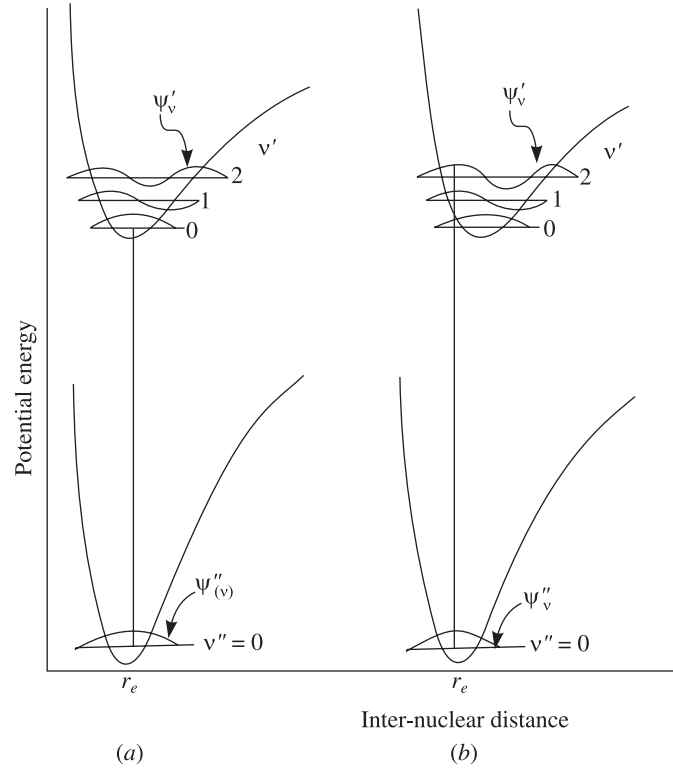


Fig. 4.2.5 Electronic transitions: (a) $r''_e = r'_e$. Maximum value of overlap integral is for $0 \rightarrow 0$ transition, (b) $r''_e < r'_e$. Maximum value of overlap integral is for $0 \rightarrow 2$ transition

Since the vibrational wave function depends only on internuclear distance r , we can replace $d\tau_n$ by dr ,

$$\text{Therefore} \quad R = \int \psi'_v \psi''_v dr \int \mu_e \psi_e^* \psi_e'' d\tau_e \quad \dots(4.2.9)$$

The electronic transition probability is proportional to the square of matrix element

$$R_e = \int \mu_e \psi_e^* \psi_e'' d\tau_e \quad \dots(4.2.10)$$

The electronic wave function ψ_e depends to some extent on the internuclear distance r but it varies very slowly. If we disregard the slow variation of ψ_e on r , we can replace R_e by an average value $\bar{R}_e$. Thus, the matrix element for the electronic transition between the vibrational levels v' and v'' can be expressed as

$$R^{v'v''} = \bar{R}_e \int \psi'_v \psi''_v dr \quad \dots(4.2.11)$$

The integral appearing in Eqn. (4.2.11) is called *overlap integral*.

The transition probability and hence the emission and absorption intensities of bands is proportional to the square of overlap integral.

Refer to the potential energy curves of lower and upper electronic states of Fig. (4.2.5a). The minima of the potential energy curves lie one above the other. Also shown are the wave functions over the vibrational levels. The value of the overlap integral is maximum for the transition $0 \rightarrow 0$ and hence, according to Franck-Condon principle, (0, 0) band will be most intense. The potential energy curves of Fig. (4.2.5b) are such that their minima are displaced relative to one another. The overlap integral is maximum for transition $0 \rightarrow 2$ and therefore this band (2, 0) will be most intense.

4.3 MOLECULAR STATES

Like atomic states, molecular states are defined by certain quantum numbers, which are defined as described below:

Orbital Angular Momentum Quantum Number Λ

When atoms combine to form a molecule, the inner electrons in each atom can be regarded as remaining associated with their parent nucleus, but the outer electrons come to belong to the molecule as a whole rather than to any individual nucleus. In a diatomic molecule, there exists a strong electric field in the direction of inter-nuclear axis. As a consequence of this field the resultant orbital angular momentum $\mathbf{L}$ of all electrons undergo a precession about the direction of the electric field. The space quantization of vector $\mathbf{L}$ permits only discrete values for the component of $\mathbf{L}$ along the field direction. The component of $\mathbf{L}$ along field direction is represented by vector $\mathbf{\Lambda}$ whose magnitude is given by $\Lambda\hbar$, where Λ is quantum number specifying the magnitude of vector $\mathbf{\Lambda}$. The allowed values of Λ are

$$\Lambda = 0, 1, 2, 3, \dots, L \quad \dots(4.3.1)$$

where L is quantum number of the resultant orbital angular momentum $\mathbf{L}$ for all electrons in the molecule. The vector $\mathbf{L}$ is not defined, so L cannot be specified at all. For each value of L , there are $L + 1$ values of Λ . Each value of Λ corresponds to a distinct energy state. The negative values of Λ are not considered because $\Lambda = +L$ and $\Lambda = -L$ represent the same state with identical energies. Therefore, for each value of L , there are $L + 1$ molecular energy states. Thus, all the states (except $\Lambda = 0$) are doubly degenerate. Molecular states are represented by symbols $\Sigma, \Pi, \Delta, \Phi, \dots$ according to following scheme:

Λ	0	1	2	3	4.....
states	Σ	Π	Δ	Φ	

Spin Quantum Number Σ

The appearance of fine structure of electronic bands necessitates the introduction of spin quantum number. The spin of electrons in a molecule outside the closed shells, add up to form a resultant spin angular momentum $\mathbf{S}$. The quantum number associated with $\mathbf{S}$ is represented by S . The quantum number S is obtained by adding spins of various electrons outside the closed shells. If the total number of electrons is even, S is zero or integer. If the total number of electrons is odd, S is odd number of half integer. The orbital motion of electron in states other than $\Lambda = 0$, produces magnetic field in the

direction of inter-nuclear axis. This field causes precession of vector $\mathbf{S}$ about the direction of the field. The permitted components of $\mathbf{S}$ along the inter-nuclear axis is given by quantum number Σ whose allowed values are

$$\Sigma = S, S - 1, S - 2, \dots, 0, \dots, -(S - 1), -S. \quad \dots(4.3.2)$$

Thus, there are $2S + 1$ different values of Σ for every value of S . The quantum number Σ is not defined for the state $\Lambda = 0$ (*i.e.*, Σ -state). The quantity $2S + 1$ is referred to as the multiplicity of the state characterized by quantum number S .

Total Angular Momentum Quantum Number Ω

In atom, the orbital angular momenta of electrons strongly couple to form a resultant $\mathbf{L}$ and so do the spin momenta to form a resultant $\mathbf{S}$. The two resultant vectors then combine to give total electronic angular momentum $\mathbf{J}$. Similar phenomena takes place in molecule too. The components of orbital angular momentum Λ and spin angular momentum Σ in the direction of inter-nuclear axis combine to form a resultant angular momentum Ω . The quantum number associated with Ω is represented by Ω . The allowed values of Ω are obtained by taking magnitude of algebraic sum of quantum numbers Λ and Σ .

$$\Omega = |\Lambda + \Sigma| \quad \dots(4.3.3)$$

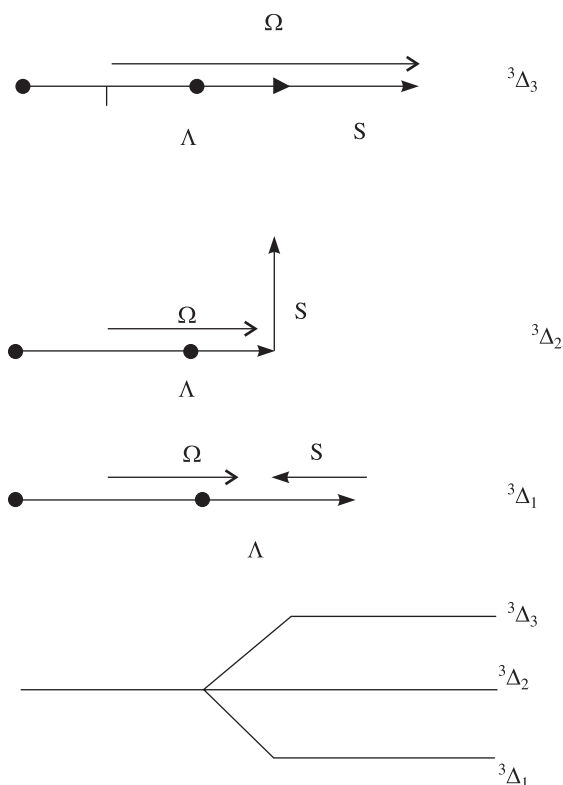


Fig. 4.3.1 Addition of Λ and S ($\Lambda = 2$, $S = 1$). Energy level diagram for ${}^3\Delta$ state

Only the positive values of Ω have significance. For $\Lambda \neq 0$, there are $2S + 1$ possible values of Σ , hence for a given value of Λ , other than zero, there are $2S + 1$ different values of Ω . These correspond to somewhat different energies of the state. Thus, a molecular term with a given value of Λ ($\Lambda \neq 0$) splits into a multiplet of $2S + 1$ components. If $\Lambda = 0$, there is no magnetic field in the direction of inter-nuclear axis, quantum number Σ is not defined, and consequently, the Σ -state does not split. So long as the molecule performs no rotation about the inter-nuclear axis, the state Σ' remains single. Nevertheless, $2S + 1$ is called the multiplicity of a state.

To determine the molecular state, we consider an example in which $\Lambda = 2$ and $S = 1$. The relative orientation of vectors $\mathbf{\Lambda}$, $\mathbf{S}$ and $\mathbf{\Omega}$ are shown in the Fig. 4.3.1.

The multiplicity $2S + 1$ is added to the symbol as a left superscript and the value of $\Lambda + \Sigma$ as subscript. The components of ${}^3\Delta$ are designated as ${}^3\Delta_3$, ${}^3\Delta_2$, ${}^3\Delta_1$.

EXAMPLES

(a) Components of ${}^1\Pi$:

$$S = 0, \Sigma = 0, \Lambda = 1, \Omega = |\Lambda + \Sigma| = 1. \text{ State is } {}^1\Pi_1.$$

(b) Components of ${}^2\Pi$:

$$\Lambda = 1, S = 1/2, \Sigma = +1/2, -1/2, \Omega = |\Lambda + \Sigma| = 1/2, 3/2. \text{ States are } {}^2\Pi_{1/2}, {}^2\Pi_{3/2}.$$

(c) Components of ${}^3\Pi$:

$$\Lambda = 1, S = 1, \Sigma = -1, 0, 1, \Omega = |\Lambda + \Sigma| = 2, 1, 0. \text{ States are } {}^3\Pi_2, {}^3\Pi_1, {}^3\Pi_0.$$

(d) Components of ${}^4\Pi$:

$$\Lambda = 1, S = 3/2, \Sigma = -3/2, -1/2, 1/2, 3/2. \Omega = |\Lambda + \Sigma| = -1/2, 1/2, 3/2, 5/2.$$

In this case four values of Σ correspond to four different equidistant energy levels even though two of them have the same Ω values ($\Omega = |\Lambda + \Sigma| = 1/2$). Hence $\Lambda + \Sigma$, rather than Ω is used to distinguish the multiplet components.

The states are ${}^4\Pi_{5/2}, {}^4\Pi_{3/2}, {}^4\Pi_{1/2}, {}^4\Pi_{-1/2}$.

(e) Components of ${}^4\Delta$:

$$\Lambda = 2, S = 3/2, \Sigma = -3/2, -1/2, 1/2, 3/2. \Omega = |\Lambda + \Sigma| = 1/2, 3/2, 5/2, 7/2.$$

The states are ${}^4\Delta_{7/2}, {}^4\Delta_{5/2}, {}^4\Delta_{3/2}, {}^4\Delta_{1/2}$.

(f) Components of ${}^4\Phi$:

$$\Lambda = 3, S = 3/2, \Sigma = -3/2, -1/2, 1/2, 3/2. \Omega = |\Lambda + \Sigma| = 3/2, 5/2, 7/2, 9/2.$$

The states are ${}^4\Phi_{9/2}, {}^4\Phi_{7/2}, {}^4\Phi_{5/2}, {}^4\Phi_{3/2}$.

RAMAN SPECTRA

5.1 INTRODUCTION

When a monochromatic light of frequency ν_0 is made to pass through a cell containing a transparent substance, most of the light passes through the substance without suffering any changes. Only a very small fraction (0.1%) of light is scattered by the molecules of the sample in all directions. A large part of the scattered light has frequency ν_0 , which is the same as that of the incident light. This type of scattering is called Rayleigh (or elastic) scattering. In addition to Rayleigh scattering, the scattered light is observed to have both lower and higher frequencies than the incident one. Although this change in frequency due to scattering of light by molecules, was predicted theoretically by Smekal in 1923 but was experimentally discovered by Sir C.V. Raman and his collaborators in 1928. For this discovery Raman was awarded Nobel Prize in 1930. The Raman scattered light constitutes a very small fraction of incident light and hence is very weak. The lines of lower frequencies are called Stokes lines and those of higher frequencies are called Anti-stokes lines.

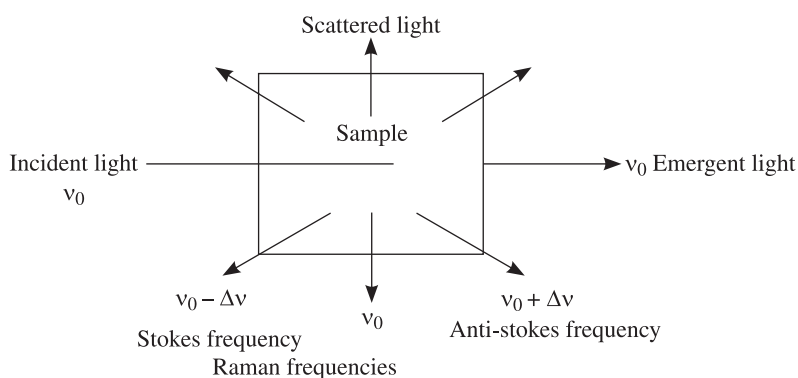


Fig. 5.1.1 Raman effect

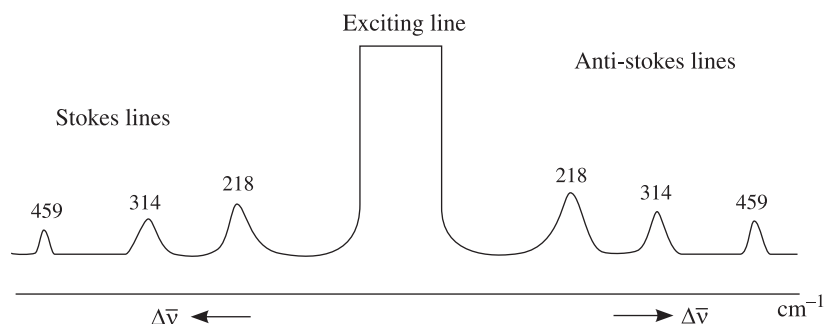


Fig. 5.1.2 Vibrational spectrum of CCl_4 . Raman lines are displaced from the frequency of any exciting line by 218, 314 and 459 cm^{-1}

To observe Raman spectrum, an intense highly monochromatic radiation in the visible region is employed as an exciting (incident) radiation. Before 1960, the radiation of wavelength $4358\text{\AA}$ emitted from mercury Toronto arc was used but now a days laser sources are extensively used because they are capable of producing highly coherent, monochromatic, and very intense narrow beam of light. With laser sources, multistage photomultipliers are used as detectors for recording of Raman spectrum.

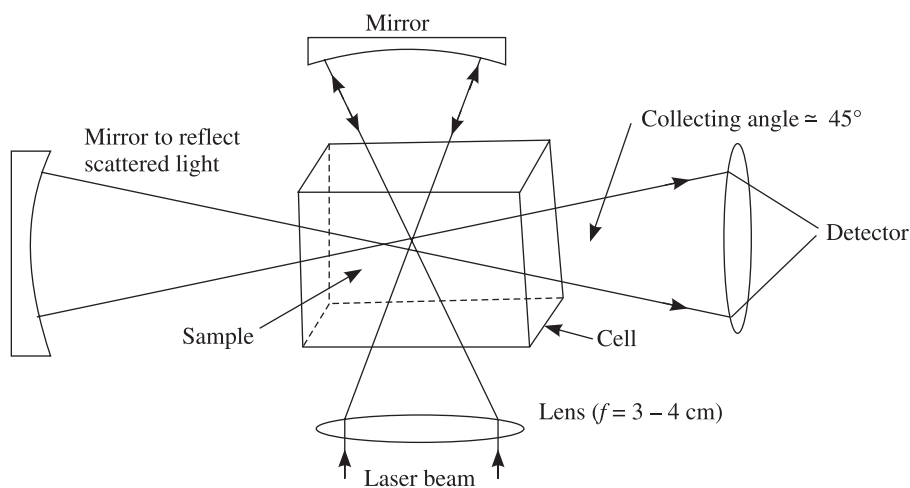


Fig. 5.1.3 (a) Experimental set up for observing Raman spectrum

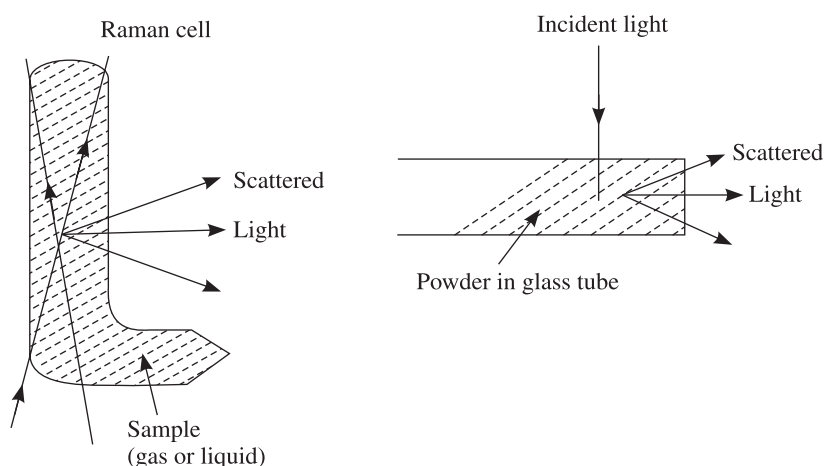


Fig. 5.1.3 (b) Raman cells

Laser sources : He-Ne 6328 Å Red
 Ar 5145 Å Green
 Kr 6471 Å Red

5.2 CLASSICAL THEORY OF RAMAN EFFECT

When a molecule is placed in an electric field $\mathbf{E}$, a dipole moment $\mathbf{P}$ is induced in it. The ease with which the molecule gets polarized is measured by a quantity α , called *polarizability* and the relation between $\mathbf{P}$ and $\mathbf{E}$ is written as

$$|\mathbf{P}| = \alpha |\mathbf{E}|$$

For an isotropic molecule, the induced dipole moment is in the direction of the electric field and the polarizability α is a scalar. In non-isotropic molecule, $\mathbf{P}$ is not in the direction of $\mathbf{E}$, the electric field in one direction produces dipole moment in different directions and α is a tensor. In such molecules the relation between $\mathbf{P}$ (P_x, P_y, P_z) and $\mathbf{E}$ (E_x, E_y, E_z) is expressed as

$$P_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$

$$P_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$

$$P_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

The polarizability tensor α is defined by nine coefficients $\alpha_{xx}, \alpha_{xy}, \dots, \alpha_{zz}$. Since $\alpha_{xy} = \alpha_{yx}, \alpha_{yz} = \alpha_{zy}, \alpha_{zx} = \alpha_{xz}$, the quantity α is defined by six coefficients. From above equations it is evident that x -component of electric field E_x produces dipole moment in molecule not only in x -direction but also in y - and z -directions. This act of electric field also holds for y and z components. The relation between the six polarizability coefficients and coordinates x, y and z is

$$\alpha_{xx}x^2 + \alpha_{yy}y^2 + \alpha_{zz}z^2 + 2\alpha_{xy}xy + 2\alpha_{yz}yz + 2\alpha_{zx}zx = 1$$

This equation represents an ellipsoid.

When a non-isotropic molecule is subjected to an electromagnetic radiation, the oscillating electric field induces time varying dipole moment and the polarizability also becomes a time varying function. For a molecule to exhibit Raman scattering, any component of its polarizability must change in the course of rotation or vibration. Therefore, it is necessary for the molecule to be polarizable to different extents in different directions. For a diatomic molecule whether homonuclear or not, the polarizability ellipsoid is not spherical and it will also change its dimensions in the course of vibration, hence all such molecules exhibit both rotational and vibrational Raman spectra.

If x represents the displacement during the oscillation of molecule, the variation of polarizability may be expressed as

$$\alpha = \alpha_0 + \beta \frac{x}{A}$$

where α_0 = equilibrium polarizability, β = rate of variation of polarizability with displacement, A = amplitude of oscillation of molecule. Assuming the molecule as a harmonic oscillator, the displacement x can be represented as

$$x = A \cos 2\pi\nu_v t$$

where ν_v is the frequency of oscillation.

The polarizability may now be written as

$$\alpha = \alpha_0 + \beta \cos 2\pi\nu_v t$$

If $E = E_0 \cos 2\pi\nu_0 t$ represents the oscillating electric field of the incident radiation, the dipole moment induced in the molecule can be expressed as

$$\begin{aligned} P &= \alpha E = \alpha_0 E_0 \cos 2\pi\nu_0 t + \beta E_0 \cos 2\pi\nu_v t \cos 2\pi\nu_0 t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \beta E_0 \{ \cos 2\pi(\nu_0 + \nu_v)t + \cos 2\pi(\nu_0 - \nu_v)t \} \end{aligned}$$

It is evident from this equation that the dipole moment of molecule oscillates not only with frequency ν_0 of the incident radiation but also with frequencies $\nu_0 - \nu_v$ and $\nu_0 + \nu_v$. The first frequency ν_0 of the oscillating dipole is interpreted in terms of Rayleigh scattering. The frequencies $\nu_0 - \nu_v$ and $\nu_0 + \nu_v$ are interpreted as the vibrational Raman (Stokes and anti-Stokes) frequencies.

Now, we shall show that rotation of molecule will also give Raman scattering. During the rotation of molecule, its orientation with respect to electric field of incident radiation undergoes continuous change. If the molecule has different polarizabilities in different directions, its polarization will vary with time. The time variation of polarizability can be expressed as

$$\alpha = \alpha_0 + \beta' \cos 2\pi(2\nu_r)t$$

where ν_r represents the frequency of rotation of molecule. The presence of multiplication factor 2 before ν_r accounts for the fact that the rotation of molecule through angle π brings it into an orientation in which its polarizability has the same value as that in the initial state. Thus, the polarizability varies at a rate that is twice as great as the rotation. The dipole moment of the molecule is given by

$$P = \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \beta' E_0 \{ \cos 2\pi(\nu_0 - 2\nu_r)t + \cos 2\pi(\nu_0 + 2\nu_r)t \}$$

This equation states that the scattered radiation should consist of three frequencies ν_0 , $\nu_0 - 2\nu_r$ and $\nu_0 + 2\nu_r$. The frequency ν_0 is the frequency of incident radiation, $\nu_0 - 2\nu_r$ and $\nu_0 + 2\nu_r$ are the Stokes and Anti-stokes frequencies.

5.3 QUANTUM THEORY OF RAMAN EFFECT

The quantum model of radiation treats a monochromatic radiation of frequency $\bar{\nu}$ as a stream of particles (photons) of energy $hc\bar{\nu}$. When a radiation of frequency $\bar{\nu}_i$ passes through matter, the possible events that may occur with incident photon are as follows:

- (i) The incident photon collides elastically with the molecule of the scattering substance and is scattered without any change in its frequency. This is called Rayleigh scattering ($\bar{\nu}_s = \bar{\nu}_i$).
- (ii) The incident photon collides inelastically with a molecule lying initially in a lower energy state E'' causing the latter to go over to higher energy state E' . In this process the incident photon transfers some of its energy to the molecule and is scattered with diminished frequency $\bar{\nu}_s$. Applying the law of conservation of energy to the collision process, we have

$$\begin{aligned} hc\bar{\nu}_i + E'' &= hc\bar{\nu}_s + E' \\ \bar{\nu}_i - \bar{\nu}_s &= \frac{E' - E''}{hc} \end{aligned} \quad \dots(5.3.1)$$

Since $E' > E''$, the Raman displacement $\Delta\bar{\nu} = \bar{\nu}_i - \bar{\nu}_s$ is positive, $\bar{\nu}_s < \bar{\nu}_i$. The frequency $\bar{\nu}_s$ of scattered light, in this case, is called *Stokes frequency*.

- (iii) The incident photon collides inelastically with a molecule, which is already in excited state E' , and acquires energy from the molecule causing it to go over to lower state E'' . In this case the scattered photon has frequency $\bar{\nu}_s$ greater than that of the incident photon $\bar{\nu}_i$. The law of conservation of energy is

$$\begin{aligned} hc\bar{\nu}_i + E' &= hc\bar{\nu}_s + E'' \\ \bar{\nu}_i - \bar{\nu}_s &= -\frac{E' - E''}{hc} \end{aligned} \quad \dots(5.3.2)$$

The Raman displacement $\Delta\bar{\nu} = \bar{\nu}_i - \bar{\nu}_s$ is negative, *i.e.*, $\bar{\nu}_s > \bar{\nu}_i$. The scattered radiation of higher frequency is called *anti-Stokes frequency*. It is evident from equations (5.3.1) and (5.3.2) that the Raman displacement is characteristic of scattering substance and is independent of exciting frequency ($\bar{\nu}_i$). A schematic diagram showing stokes and anti-stokes transitions is given below. It is worth to notice that the broken horizontal lines do not correspond to any energy level. Actual transitions are shown by heavy line.

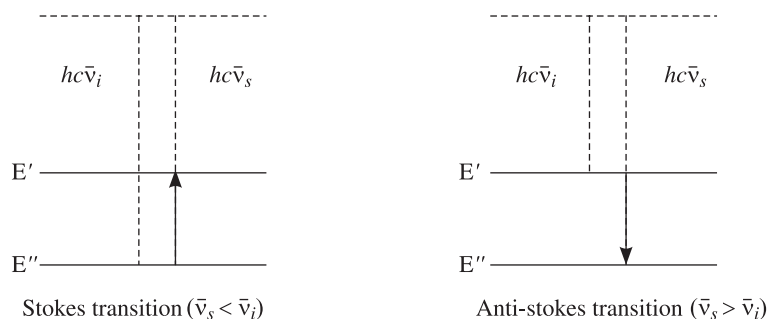


Fig. 5.3.1 Stokes and Anti-stokes transitions

Raman displacement $\Delta\bar{\nu}$ lies within the range of 100 cm^{-1} to 3000 cm^{-1} , which falls in the infrared region. This indicates that the origin of Raman lines can be traced in the transitions between rotational and vibrational levels of molecules of the scattering substance.

Vibrational Raman Scattering

Vibrational Raman effect is observed when the energy levels E' and E'' involved in Raman transition correspond to the vibrational energy levels. The vibrational energy levels of a diatomic molecule are given by

$$E = (v + \frac{1}{2})hc\bar{\omega}_e - (v + \frac{1}{2})^2 hc x_e \bar{\omega}_e$$

The corresponding term value is

$$G = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2 x_e \bar{\omega}_e$$

The allowed transitions are subject to the selection rules $\Delta v = \pm 1$. Vibrational Raman shift for Stokes line, which corresponds to transition $v'' = 0 \rightarrow v' = 1$, is given by

$$\begin{aligned}\Delta\bar{\nu} &= G'(v') - G''(v'') \\ &= (1 - 2x_e)\bar{\omega}_e\end{aligned}$$

The frequency $(1 - 2x_e)\bar{\omega}_e$ is the center of the fundamental band in the infrared spectrum of the molecule. The intensity of a line is proportional to the population of molecules in the initial state. Since a majority of molecules are in the ground state ($v'' = 0$) at room temperature, the Stokes lines are obviously more intense. Since a very small number of molecules are in the state with $v' = 1$, the anti-Stokes lines, which correspond to the transition $v' = 1 \rightarrow v'' = 0$, are so weak that they are to observe.

It is worth to note that the presence of permanent dipole moment is not a condition for the occurrence of Raman spectrum. The necessary condition for the Raman line to appear is that the polarizability of dipole moment of molecule should change during the vibration or rotation. Symmetric molecules such as H_2 , N_2 , O_2 , F_2 , Cl_2 , which do not give infrared spectrum, give Raman spectra. Thus, valuable information about a symmetric molecule can be obtained from the analysis of Raman spectra which is not possible from infrared spectra.

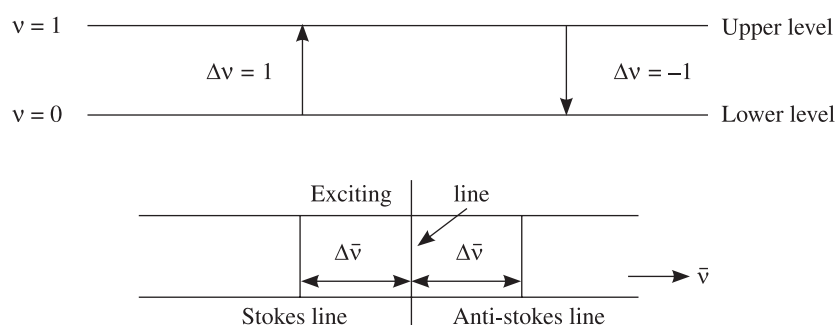


Fig. 5.3.2 Raman spectrum of HCl molecule

When vibration Raman spectrum of a diatomic molecule is observed with a spectrograph of small dispersive power, only one Stokes line and one Anti-stokes line for each exciting line with relatively large Raman displacement is found. This is because even if molecules with different v values were present, the vibrational levels of harmonic oscillator are equidistant. The Raman shift for some molecules is given below:

HCl	HBr	HI	NO	H ₂	N ₂	O ₂
2886	2558	2233	1877	4160	2330	1554.7 cm ⁻¹

Rotational Raman Spectrum

The rotational energy levels of a diatomic molecule are given by

$$E = B h_c J(J+1)$$

The corresponding term values are

$$F = B J(J+1)$$

The selection rules for rotational Raman transitions for diatomic molecules in Σ state (*i.e.*, $\Lambda = 0$) are

$$\Delta J = 0, \pm 2.$$

+ sign for Stokes lines and – for anti-Stokes lines. [For diatomic molecule in other than Σ state (*i.e.*, $\Lambda \neq 0$), the selection rules are $\Delta J = 0, \pm 1, \pm 2$]

The Raman shift of Stokes lines ($\Delta J = 2$, *i.e.*, $J' = J'' + 2$) is given by

$$\begin{aligned}
 \Delta \bar{\nu} &= B J'(J' + 1) - B J''(J'' + 1) \\
 &= B(J'' + 2)(J'' + 3) - J''(J'' + 1) \\
 &= 2B(2J'' + 3) \\
 &= 2B(2J + 3) \quad J = 0, 1, 2, 3, \dots, \\
 &= 4B(J + 3/2) = 6B, 10B, 14B, \dots
 \end{aligned}$$

The Raman shift of Anti-stokes lines ($\Delta J = -2$, *i.e.*, $J' = J'' - 2$) is

$$\begin{aligned}\Delta\bar{\nu} &= -2B(2J+3), \quad J = 0, 1, 2, 3, \dots \\ &= -4B(J+3/2) = -6B, -10B, -14B, \dots\end{aligned}$$

Notice that the first line ($J = 0$) is displaced by a frequency of $6B$ on both sides of the exciting line. The subsequent lines are separated by a frequency of $4B$. Thus, the rotational Raman spectrum consists of two sets of lines, one on the lower frequency side (Stokes lines) and the other on the higher frequency side of the exciting line. [In ordinary rotational spectrum, the successive lines are separated by $2B$. This difference is due to change in selection rule *i.e.*, change in J by two units in Raman effect.]

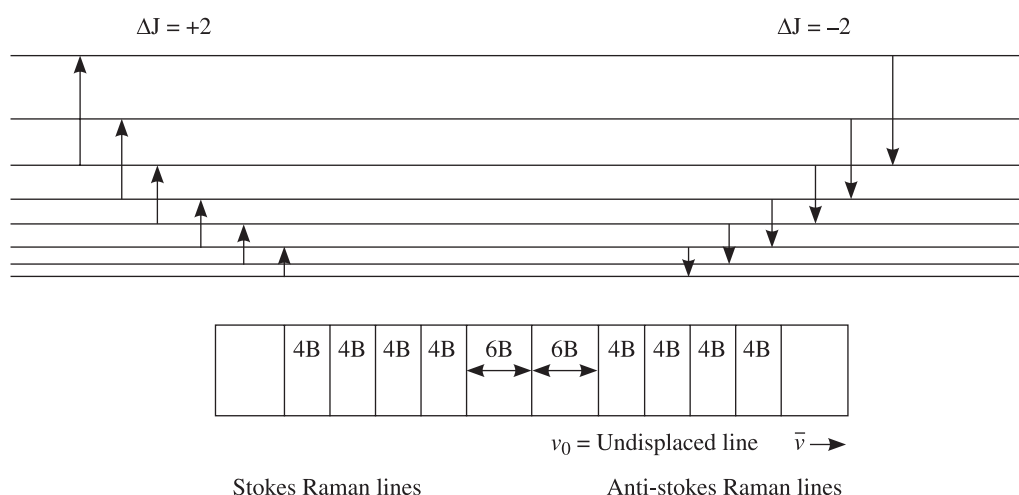


Fig. 5.3.3 Rotational Raman spectrum

Since the rotational energy of diatomic molecule is small, a considerable number of molecules occupy the higher rotational energy levels at room temperature because of the thermal motion. For this reason Stokes and anti-Stokes lines appear with nearly equal intensity.

Homo-nuclear diatomic molecules do not give infrared spectrum but they do give Raman spectrum. Therefore, rotational and vibrational constants can be calculated from the analysis of Raman spectra of such molecules.

The rotational Raman displacements [$\Delta\bar{\nu} = \pm 4B(J+3/2)$] are much smaller than the vibrational Raman displacements [$\Delta\bar{\nu} = (1-2x_e)\bar{\omega}_e$]. Therefore, the Raman spectrum will consist of a very intense line representing the exciting line. On either side of this line, there will be Stokes and anti-Stokes lines of almost equal intensity corresponding to rotational transitions. At a greater distance from the exciting line, on the low frequency side there will be a strong Stokes line for the Q-branch ($\Delta J = 0$). Close to it there may be weaker lines of O and S branches for $\Delta J = -2$ and $+2$.

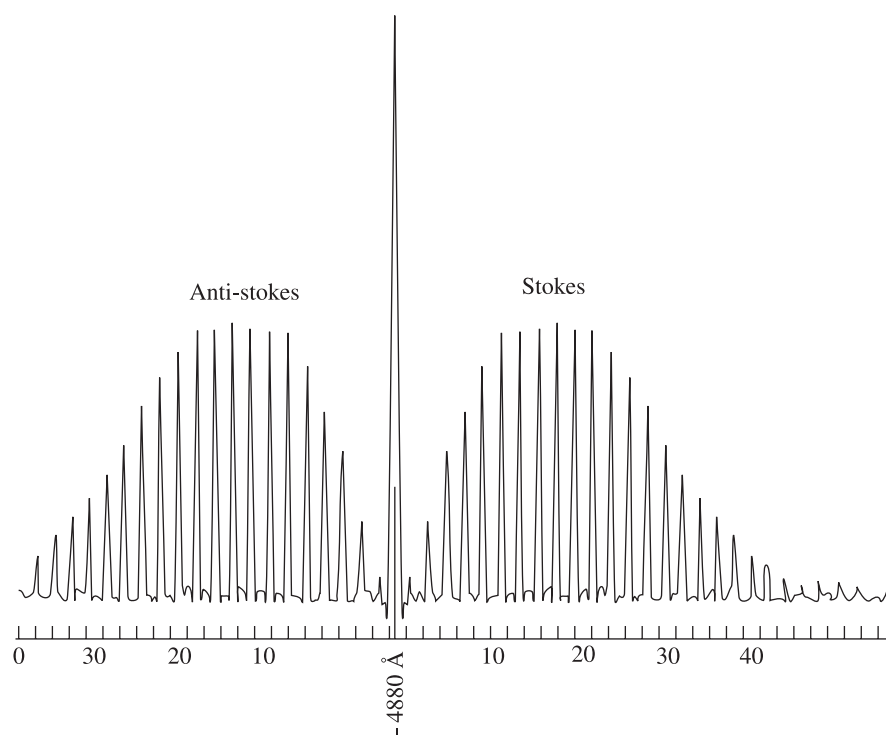


Fig. 5.3.4 Pure rotational Raman spectrum of CO_2

Vibration-rotation Raman Spectrum

The vibration-rotation energy of a diatomic molecule is given by

$$E = (v + \frac{1}{2})hc\bar{\omega}_e - (v + \frac{1}{2})^2 hc x_e \bar{\omega}_e + BhcJ(J+1)$$

or the term value is given by

$$T = (v + \frac{1}{2})\bar{\omega}_e - (v + \frac{1}{2})^2 x_e \bar{\omega}_e + BJ(J+1)$$

The Raman shift corresponding to the transition $v'' \rightarrow v'$, $J'' \rightarrow J'$ is

$$\Delta\bar{\nu} = [(v' + \frac{1}{2})\bar{\omega}_e - (v' + \frac{1}{2})^2 x_e \bar{\omega}_e + BJ'(J'+1)] - [(v'' + \frac{1}{2})\bar{\omega}_e - (v'' + \frac{1}{2})^2 x_e \bar{\omega}_e + BJ''(J''+1)]$$

The transitions are subject to the selection rules

$$\Delta v = \pm 1 \quad \text{and} \quad \Delta J = 0, \pm 2$$

Designation of branches are made according to the following scheme:

Branch	<i>O</i>	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
ΔJ	-2	-1	0	1	2

The vibrational transition $1 \leftarrow 0$, $v' = v'' + 1$ and $J' = J''$, which corresponds to Q-branch, gives the Raman shift

$$\Delta\bar{\nu}_Q = (1 - 2x_e)\bar{\omega}_e = \bar{\nu}_0 \quad \text{for all } J \text{ values.}$$

Notice that Q-branch makes its appearance in Raman spectrum whereas it is absent in infrared spectrum.

The selection rules $\Delta v = 1$ and $\Delta J = 2$ with $v' = 1 \leftarrow v'' = 0$ give the wave number of the lines of S branch with Raman shift

$$\Delta\bar{\nu}_S = \bar{\nu}_0 + [BJ'(J' + 1) - BJ''(J'' + 1)]$$

Substituting $J' = J'' + 2$, we have

$$\begin{aligned}\Delta\bar{\nu}_S &= \bar{\nu}_0 + B[(J'' + 2)(J'' + 3) - J''(J'' + 1)] \\ &= \bar{\nu}_0 + B[4J'' + 6] \\ &= \bar{\nu}_0 + B[4J + 6] \quad J = 0, 1, 2, 3, \dots \\ &= \bar{\nu}_0 + 4B(J + 3/2)\end{aligned}$$

The selection rules $\Delta v = 1$ and $\Delta J = -2$ i.e., $J' = J'' - 2$, with $J'' = 2, 3, 4, \dots$ give the lines of O branch with Raman shift

$$\begin{aligned}\Delta\bar{\nu}_O &= \bar{\nu}_0 + B[(J'' - 2)(J'' - 1) - J''(J'' + 1)] \\ &= \bar{\nu}_0 - B[4J'' - 2], \quad J'' = 2, 3, 4, \dots \\ &= \bar{\nu}_0 - B[4J'' + 6], \quad J'' = 0, 1, 2, \dots \\ &= \bar{\nu}_0 - B[4J + 6] \quad J = 0, 1, 2, 3, \dots \\ &= \bar{\nu}_0 - 4B[J + 3/2]\end{aligned}$$

From the analysis of O and S branches of Raman spectrum it is possible to determine B from which moment of inertia and inter-nuclear distance can be determined.

The Anti-stokes lines are observed at high frequency side at the same distance from the exciting line.

Raman Effect and Fluorescence

- (1) **Raman effect** is a light scattering phenomenon. It can occur for any frequency of incident radiation. The frequency of Raman lines (Stokes and Anti-stokes) depends on the frequency of the exciting line. The Raman displacement depends on the nature of scattering substance.

Fluorescence is a phenomenon in which incident light quantum is completely absorbed by the molecule and it is raised to an excited state from which it makes transition to the lower energy levels after a certain time. The downward transition may take place in several steps with emission of radiation at each step. The frequency of emitted radiation is always less than that of the incident radiation i.e., only Stokes frequencies are observed. It occurs

only for the absorbed frequency. The frequency of the Stokes line does not depend on the frequency of the incident radiation but depends on the nature of the fluorescent material.

- (2) **Raman lines** are strongly polarized whereas **fluorescent lines** are not.
 (3) **Raman lines** are weak in intensity whereas **fluorescent lines** have considerable intensity.

SOLVED EXAMPLES

Ex. 1. For oxygen molecule, the internuclear distance is 1.21×10^{-10} m, mass of oxygen atom is 2.7×10^{-26} kg. Calculate moment of inertia I , rotational constant B , separation of energy levels in m^{-1} and the wave number of the line corresponding to the transition $J = 0 \rightarrow J = 1$ in absorption spectrum.

Sol. Moment of inertia of molecule

$$I = \mu r^2 \quad \text{where } \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{m}{2} = \frac{2.7 \times 10^{-26}}{2} \text{ kg} = 1.35 \times 10^{-26} \text{ kg}$$

$$I = (1.35 \times 10^{-26} \text{ kg})(1.21 \times 10^{-10} \text{ m})^2 = 1.976 \times 10^{-46} \text{ kg m}^2$$

$$\begin{aligned} \text{Rotational constant} \quad B &= \frac{h}{8\pi^2 I c} = \frac{6.626 \times 10^{-34} \text{ Js}}{8 \times 9.86 \times (1.976 \times 10^{-46} \text{ kg}) \times (3 \times 10^8 \text{ ms}^{-1})} \\ &= 141.5 \text{ m}^{-1} \end{aligned}$$

Energy in m^{-1} or rotational term value is given by

$$F(J) = B J(J+1), \quad J = 0, 1, 2, \dots$$

Separation of two consecutive rotational terms is

$$\Delta F = F(J+1) - F(J) = B[(J+1)(J+2) - J(J+1)] = 2B(J+1)$$

Frequency of line corresponding to the transition $J = 0 \rightarrow J = 1$ is

$$\bar{\nu} = F(1) - F(0) = 2B = 2 \times 141.5 = 283.0 \text{ m}^{-1}$$

Ex. 2. For hydrogen molecule the internuclear distance is $0.74 \text{ \AA}$, mass of hydrogen atom is $1.6738 \times 10^{-27} \text{ kg}$, calculate the rotational energy levels in electron volts.

Sol. Moment of inertia of molecule

$$\begin{aligned} I &= \mu r^2 = \frac{1}{2} m r^2 = \frac{1}{2} (1.6738 \times 10^{-27} \text{ kg})(0.74 \times 10^{-10})^2 \text{ kg m}^2 \\ &= 4.60 \times 10^{-48} \text{ kg m}^2 \end{aligned}$$

Rotational energy of molecule

$$E(J) = \frac{\hbar^2}{2I} J(J+1) = \frac{(1.054 \times 10^{-34} \text{ Js})^2}{2(4.60 \times 10^{-48} \text{ kg m}^2)} J(J+1)$$

$$E(J) = (7.54 \times 10^{-3} \text{ eV}) J(J+1)$$

This gives $E_0 = 0$, $E_1 = 1.51 \times 10^{-2} \text{ eV}$, $E_2 = 4.54 \times 10^{-2} \text{ eV}$, $E_3 = 9.05 \times 10^{-2} \text{ eV}$.

Ex. 3. The OH-radical has a moment of inertia of $1.48 \times 10^{-47} \text{ kg m}^2$. Calculate its internuclear distance. What are its angular momentum and angular velocity in the state $J = 5$. Determine the energy absorbed in the transition $J = 6 \leftarrow J = 5$ and corresponding wave number of the absorption line.

Sol. Reduced mass of the molecule $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{16 \times 1}{16 + 1} u = \frac{16}{17} u = \frac{16}{17} \times 1.68 \times 10^{-27} \text{ kg}$
 $= 1.563 \times 10^{-27} \text{ kg}$

Moment of inertia of molecule $I = \mu r^2 \quad \therefore r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.48 \times 10^{-47}}{1.563 \times 10^{-27}}}$

$$r = 9.73 \times 10^{-11} \text{ m} = 0.973 \text{ \AA}$$

Magnitude of angular momentum $|J| = \sqrt{J(J+1)} \hbar$

In the state with $J = 5$, we have $|J| = \sqrt{5(5+1)} (1.054 \times 10^{-34}) = 5.77 \times 10^{-34} \text{ Js}$

Angular velocity $\omega = \frac{|J|}{I} = \frac{5.77 \times 10^{-34}}{1.48 \times 10^{-47}} = 3.90 \times 10^{13} \text{ rad/s}$

Wave number of line corresponding to transition $J = 5 \rightarrow J = 6$ is

$$\begin{aligned} \bar{\nu}_{5 \rightarrow 6} &= 2B(J+1), J=5 \\ &= 12B = 12 \left(\frac{h}{8\pi^2 I c} \right) = \frac{12 \times 6.63 \times 10^{-34} \text{ Js}}{8 \times 9.86 \times (1.48 \times 10^{-47} \text{ kg m}^2) \times (3 \times 10^8 \text{ ms}^{-1})} \\ &= 2.27 \times 10^4 \text{ m}^{-1} \end{aligned}$$

Energy of corresponding photon $E = ch\bar{\nu} = 4.5 \times 10^{-21} \text{ J}$.

Ex. 4. Rotational spectrum of CO shows a strong absorption line at frequency $1.153 \times 10^{11} \text{ Hz}$. Calculate the internuclear distance.

Sol. Rotational term $F(J) = B J(J+1)$

Wave number of absorption line

$$\bar{\nu}_{0 \rightarrow 1} = F(1) - F(0) = 2B$$

Since $\bar{\nu} = \frac{\nu}{c}$, therefore, $\frac{\nu}{c} = 2B$ or $B = \frac{\nu}{2c}$ or $\frac{h}{8\pi^2 I c} = \frac{\nu}{2c}$

This gives $I = \frac{h}{4\pi^2 \nu} = \frac{6.63 \times 10^{-34} \text{ Js}}{4 \times 9.86 \times 1.153 \times 10^{11} \text{ s}^{-1}} = 1.46 \times 10^{-46} \text{ kg m}^2$

$$\text{Internuclear distance } r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.46 \times 10^{-46}}{11.38 \times 10^{-27}}} = 1.13 \times 10^{-10} \text{ m} = 1.13 \text{ \AA}.$$

Ex. 5. The experimental values of wave number of line of P and R branches in absorption spectrum of HCl are given below. Find equilibrium internuclear distance and force constant of the molecule.

$\bar{\nu} (P) \text{ cm}^{-1}$	$\bar{\nu} (R) \text{ cm}^{-1}$
2906.3	3012.2
2927.5	3033.4
2948.7	3054.6
2969.9	3078.8

Sol. The separation of successive line of P-branch or R-branch is $2B$. From the given data,

$$\Delta \bar{\nu} = 2B = 21.2 \text{ cm}^{-1}.$$

$$B = 10.6 \text{ cm}^{-1}$$

$$\mu = 1.62 \times 10^{-27} \text{ kg}$$

$$\begin{aligned} \text{Moment of inertia } I &= \frac{h}{8\pi^2 Bc} = \frac{6.62 \times 10^{-34} \text{ Js}}{8 \times 9.86 \times (1060 \text{ m}^{-1})(3 \times 10^8 \text{ m/s})} \\ &= 2.64 \times 10^{-47} \text{ kg m}^2 \end{aligned}$$

$$r_e = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.64 \times 10^{-47} \text{ kg m}^2}{1.62 \times 10^{-27} \text{ kg}}} = 1.276 \times 10^{-10} \text{ m} = 1.27 \text{ \AA}$$

$$\text{Equilibrium frequency in wave number unit } \bar{\nu}_0 = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\text{Therefore, } k = 4\pi^2 \mu c^2 \bar{\nu}_0^2 \quad \text{where } \bar{\nu}_0 = \frac{2969.9 + 3010.2}{2} = 2991 \text{ cm}^{-1}$$

From these values, we find

$$k = 530 \text{ N/m}.$$

Ex. 6. The ground state vibrational energy of hydrogen molecule is 0.0273 eV. Find the force constant of the molecule.

Sol. Ground state energy of molecule corresponds to $v = 0$, therefore,

$$E_0 = \frac{1}{2} \hbar \omega, \text{ where } \omega = \sqrt{\frac{k}{\mu}}$$

Therefore,

$$k = \mu \left(\frac{2E_0}{\hbar} \right)^2 = (8.37 \times 10^{-28} \text{ kg}) \left(\frac{2 \times 0.273 \text{ eV}}{6.58 \times 10^{-16} \text{ eVs}} \right)^2$$

$$= 576 \text{ N/m.}$$

Ex. 7. In the near infrared spectrum of HCl molecule, there is a single intense band at 2885.9 cm^{-1} . Assuming that this band is due to the transition between vibrational levels, find the force constant of the molecule.

Sol. Reduced mass of the molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1 \times 35}{1 + 35} u = \frac{35}{36} \times 1.66 \times 10^{-27} \text{ kg}$$

$$= 1.63 \times 10^{-27} \text{ kg}$$

Wave number of line $\bar{\nu} = 288590 \text{ m}^{-1}$

Force constant of molecule

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

$$= 4 \times 9.86 \times (3 \times 10^8 \text{ m/s})^2 (288590 \text{ m}^{-1})^2 (1.63 \times 10^{-27} \text{ kg})$$

$$= 481.86 \text{ N/m.}$$

Ex. 8. Determine the vibrational energy levels of CO molecule in eV and cm^{-1} . $k_{\text{CO}} = 1870 \text{ N/m}$.

Sol. Reduced mass of CO molecule $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 16}{12 + 16} u = \frac{48}{7} u$

$$\mu = 1.14 \times 10^{-26} \text{ kg}$$

Frequency of vibration of molecule $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.14} \sqrt{\frac{1870 \text{ N/m}}{1.145 \times 10^{-26} \text{ kg}}}$

$$= 6.45 \times 10^{13} \text{ Hz}$$

Energy of molecule $E = (v + \frac{1}{2}) h\nu, \quad v = 0, 1, 2, \dots$

$$E = (v + \frac{1}{2}) (6.6 \times 10^{-34} \text{ Js} \times 6.45 \times 10^{13} \text{ Hz}) = (4.25 \times 10^{-20} \text{ J}) (v + \frac{1}{2})$$

$$= (0.265 \text{ eV}) (v + \frac{1}{2})$$

$$= 0.132 \text{ eV}, 0.396 \text{ eV}, 0.660 \text{ eV}, \dots$$

$$= 1064.5, 3193.7, 5322.5 \text{ cm}^{-1} \quad (1 \text{ eV} = 8065 \text{ cm}^{-1}).$$

Ex. 9. HCl molecule absorbs strongly infrared radiation of wavelength 3.465μ . Calculate the force constant of the molecule.

Sol. Reduced mass of HCl $\mu = 1.61 \times 10^{-27} \text{ kg}$

Frequency of radiation $\nu = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{3.465 \times 10^{-6} \text{ m}} = 8.658 \times 10^{13} \text{ s}^{-1}$

This is the frequency of molecule. Therefore,

$$k = 4\pi^2 \nu^2 \mu = 4 \times 9.86 \times (8.658 \times 10^{13} \text{ s}^{-1})^2 (1.61 \times 10^{-27} \text{ kg}) \\ = 475.9 \text{ N/m.}$$

Ex. 10. *HCl shows a strong absorption line in infrared spectrum at $2.886 \times 10^5 \text{ m}^{-1}$. Find the amplitude of vibration in the ground state.*

Sol. Force constant of molecule $k = 4\pi^2 c^2 \mu \bar{\nu}^2$

$$k = 4 \times 9.86 \times (3 \times 10^8 \text{ m/s})^2 (1.62 \times 10^{-27} \text{ kg}) (2.886 \times 10^5 \text{ m}^{-1})^2 = 480.7 \text{ N/m}$$

The amplitude of vibration ξ in the ground state $E_0 = \frac{1}{2} h c \bar{\nu} = \frac{1}{2} k \xi^2$

$$\xi = \sqrt{\frac{h c \bar{\nu}}{k}} = \sqrt{\frac{(6.6 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s})(2.886 \times 10^5 \text{ m}^{-1})}{480.7 \text{ N/m}}} \\ = 0.11 \times 10^{-10} \text{ m} = 0.11 \text{ \AA.}$$

Ex. 11. *The fundamental band for CO molecule is centered at 2143.3 cm^{-1} , and the first overtone at 4259.7 cm^{-1} . Calculate $\bar{\omega}_e$ and $x_e \bar{\omega}_e$.*

Sol. The wave numbers of fundamental and first overtone are given by

$$\bar{\nu}_1 = (1 - 2x_e) \bar{\omega}_e = 214330 \text{ m}^{-1}$$

$$\bar{\nu}_2 = (1 - 3x_e) 2\bar{\omega}_e = 425970 \text{ m}^{-1}$$

From these equations, we find $x_e = 0.006$, $\bar{\omega}_e = 217020 \text{ m}^{-1}$, $x_e \bar{\omega}_e = 1302 \text{ m}^{-1}$.

Ex. 12. *The spectrum HCl shows a very intense absorption at 2886 cm^{-1} and a weaker at 5668 cm^{-1} and a very weak one at 8347 cm^{-1} . Find the equilibrium frequency $\bar{\omega}_e$, anharmonicity constant and force constant.*

$$\text{Sol.} \quad \bar{\nu}_1 = \bar{\omega}_e (1 - 2x_e) = 2886 \quad \dots(1)$$

$$\bar{\nu}_2 = 2\bar{\omega}_e (1 - 3x_e) = 5668 \quad \dots(2)$$

$$\bar{\nu}_3 = 3\bar{\omega}_e (1 - 4x_e) = 8347 \quad \dots(3)$$

From the first two equations, we get

$$\frac{\bar{\nu}_1}{\bar{\nu}_2} = \frac{1 - 2x_e}{2(1 - 3x_e)} = \frac{2886}{5668}$$

$$\therefore x_e = 0.0174$$

From (1) $\bar{\omega}_e = 2990 \text{ cm}^{-1}$, $x_e \bar{\omega}_e = 52 \text{ cm}^{-1}$

Force constant $k = 4\pi^2 c^2 \mu \bar{\omega}_e^2$

$$k = 4 \times 9.86 (3 \times 10^8 \text{ m/s})^2 (1.61 \times 10^{-27} \text{ kg}) (299000 \text{ m}^{-1})^2$$

$$= 510.9 \text{ N/m.}$$

Ex. 13. The vibration-rotation absorption spectrum of CH molecule shows two peaks at $8.657 \times 10^{13} \text{ Hz}$ and $8.483 \times 10^{13} \text{ Hz}$ on either side of the central frequency. Calculate the equilibrium separation and force constant of the molecule.

Sol. Wave numbers of the absorption lines in vibration-rotation spectrum is given by

$$\bar{\nu}_{\pm} = \bar{\nu}_0 \pm 2Bm, \quad m = 1, 2, \dots$$

$$\nu_+ = \nu_0 + 2Bc \quad \text{and} \quad \nu_- = \nu_0 - 2Bc, \quad \text{for } m = 1$$

Therefore, $B = \frac{\nu_+ - \nu_-}{4c}$

$$\frac{h}{8\pi^2 Ic} = \frac{\Delta\nu}{4c}, \quad \Delta\nu = 0.174 \times 10^{13} \text{ s}^{-1}$$

$$I = \frac{h}{2\pi^2 \Delta\nu} = \frac{6.6 \times 10^{-34} \text{ Js}}{2 \times 9.86 \times (0.174 \times 10^{13} \text{ s}^{-1})}$$

$$= 1.929 \times 10^{-47} \text{ kg m}^2$$

Equilibrium internuclear distance

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.929 \times 10^{-47} \text{ kg m}^2}{1.544 \times 10^{-27} \text{ kg}}} = 1.12 \times 10^{-10} \text{ m}$$

Central frequency ν_0 is given by $\nu_0 = \frac{\nu_+ + \nu_-}{2} = 8.570 \times 10^{13} \text{ s}^{-1}$

Since $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

$$\Rightarrow k = 4\pi^2 \mu \nu_0^2 = 4 \times 9.86 \times (1.544 \times 10^{-27} \text{ kg}) (8.570 \times 10^{13} \text{ s}^{-1})^2$$

$$= 448 \text{ N/m.}$$

Ex. 14. Find the frequencies corresponding to the two peaks on either side of the central frequency in the absorption spectrum of a gas of CH molecules if the carbon is ^{12}C and hydrogen is ^1H . Mass of C atom is $12u$ and of H atom is $1.008u$. For CH molecule $r = 0.112 \text{ nm}$, $\mu = 4.002 \times 10^{-27} \text{ kg}$ and $k = 448 \text{ N/m}$. $1 u = 1.66 \times 10^{-27} \text{ kg}$.

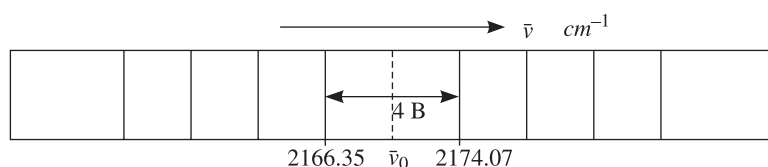
Sol. Central frequency $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = 5.325 \times 10^{13} \text{ s}^{-1}$

Moment of inertia of molecule $I = \mu r^2 = 5.02 \times 10^{-47} \text{ kg m}^2$

Frequencies of the lines on either side of central line are given by

$$\begin{aligned} \nu &= \nu_0 \pm 2cB = \nu_0 \pm 2c \left(\frac{h}{8\pi^2 I c} \right) = (5.325 \pm 0.033) \times 10^{13} \text{ s}^{-1} \\ &= 5.358 \times 10^{13} \text{ Hz}, 5.292 \times 10^{13} \text{ Hz}. \end{aligned}$$

Ex. 15. The vibration-rotation spectrum of CO molecule is shown in the figure. Calculate the equilibrium internuclear distance, central frequency and force constant of the molecule.



Sol. From the spectrum $4B = 7.72 \text{ cm}^{-1} \quad \therefore \quad B = 1.93 \text{ cm}^{-1}$

Central frequency $\bar{\nu}_0 = \frac{\bar{\nu}_+ + \bar{\nu}_-}{2} = \frac{2174.07 + 2166.35}{2} = 2170.21 \text{ cm}^{-1}$

From the relation $B = \frac{h}{8\pi^2 I c}, \quad I = \frac{h}{8\pi^2 B c} = 1.4567 \times 10^{-46} \text{ kg m}^2.$

Internuclear distance $r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{1.4567 \times 10^{-46} \text{ kg m}^2}{1.145 \times 10^{-26} \text{ kg}}} = 1.13 \text{ Å}$

Force constant $k = 4\pi^2 \mu c^2 \bar{\nu}_0^2 = 1910 \text{ N/m}.$

Ex. 16. The fundamental band for DCl^{35} is centered at 2011.00 cm^{-1} . Assuming the internuclear distance to constant at 1.288 Å , calculate the wave number of the first two lines of each of the P and R branches.

Sol. Reduced mass of molecule $\mu = 3.142 \times 10^{-27} \text{ kg}.$

Rotational constant $B = \frac{h}{8\pi^2 I c} = 536 \text{ m}^{-1}$

$$\bar{\nu}_{R(0)} = \bar{\nu}_0 + 2B = (201100 + 1072) \text{ m}^{-1} = 202172 \text{ m}^{-1}$$

$$\bar{\nu}_{R(1)} = \bar{\nu}_0 + 4B = 203244 \text{ m}^{-1}$$

$$\bar{\nu}_{P(1)} = \bar{\nu}_0 - 2B = 200028 \text{ m}^{-1}$$

$$\bar{\nu}_{P(2)} = \bar{\nu}_0 - 4B = 199056 \text{ m}^{-1}$$

Ex. 17. Assuming that there is no interaction between vibration and rotation, calculate the separation of the lines $R(0)$ and $P(1)$ of the fundamental band of HCl^{35} . The mean internuclear distance for HCl^{35} in the $v = 0$ and $v = 1$ level is $1.293 \text{ \AA}$.

Sol. Since r is the same in the two states, B also has the same value in the two states.

$$\mu = 1.62 \times 10^{-27} \text{ kg.}$$

$$B = \frac{h}{8\pi^2 I_c} = 1033 \text{ m}^{-1}$$

$$\bar{\nu}_{R(0)} = \bar{\nu}_0 + 2B \text{ and } \bar{\nu}_{P(1)} = \bar{\nu}_0 - 2B$$

Separation between the two lines

$$\Delta\bar{\nu} = 4B = 4132 \text{ m}^{-1}.$$

Ex. 18. For I_2 molecule $\bar{\omega}_e = 214.6 \text{ cm}^{-1}$ and $\bar{\omega}_e x_e = 0.6 \text{ cm}^{-1}$, calculate the temperature at which the number of molecules in the state $v = 1$ is $1/e$ of that in the state ground state. At what temperature the number of molecules in the state $v = 1$ state will be 10% of that in the ground state. Assume that the molecule behaves like anharmonic oscillator.

Sol.

$$\begin{aligned} \Delta E &= E_{v=1} - E_{v=0} \\ (i) \quad &= hc \left[\left\{ 1 + \frac{1}{2} \right\} \bar{\omega}_e - \left(1 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \right] - \left\{ \left(0 + \frac{1}{2} \right) \bar{\omega}_e - \left(0 + \frac{1}{2} \right)^2 \bar{\omega}_e x_e \right\} \\ &= hc [\bar{\omega}_e - 2\bar{\omega}_e x_e] \\ &= 1.986 \times 10^{-25} \text{ Jm} [21460 - 120] \text{ m}^{-1} = 4.238 \times 10^{-21} \text{ J} \end{aligned}$$

The fraction of molecules in the state $v = 1$ is given by

$$\frac{N_1}{N_0} = \exp \left(-\frac{\Delta E}{kT} \right)$$

$$\exp(-1) = \exp \left(-\frac{4.238 \times 10^{-21} \text{ J}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times T} \right)$$

$$\therefore T = 300 \text{ K}$$

$$(ii) \quad \frac{1}{10} = \exp \left(-\frac{\Delta E}{kT} \right) \Rightarrow T = \frac{\Delta E}{2.30k} = \frac{4.238 \times 10^{-21} \text{ J}}{2.30 \times 1.38 \times 10^{-23} \text{ JK}^{-1}} = 133.5 \text{ K.}$$

Ex. 19. With exciting line $4358 \text{ \AA}$ the pure rotation Raman spectrum of a sample gives Stokes line at $4458 \text{ \AA}$. Deduce the wavelength of Anti-stokes line.

$$\text{Sol.} \quad \bar{\nu}_{\text{exciting}} = \frac{1}{4358 \times 10^{-10} \text{ m}} = 2.2946 \times 10^6 \text{ m}^{-1}$$

$$\bar{\nu}_{\text{stokes}} = \frac{1}{4458 \times 10^{-10} \text{ m}} = 2.2431 \times 10^6 \text{ m}^{-1}$$

Raman shift $\Delta\bar{\nu} = 0.0515 \times 10^6 \text{ m}^{-1}$

$$\bar{\nu}_{\text{anti-stokes}} = \bar{\nu}_{\text{exc}} + \Delta\bar{\nu} = 2.3461 \times 10^6 \text{ m}^{-1}$$

$$\lambda_{\text{anti-stokes}} = 4262.6 \times 10^{-10} \text{ m} = 4262.6 \text{ \AA}.$$

Ex. 20. In the rotational Raman spectrum of HCl, the displacements from the exciting line are given by $\Delta\bar{\nu} = \pm(62.4 + 41.6J) \text{ cm}^{-1}$. Calculate the moment of inertia of molecule.

Sol. Rotational Raman shift is given by

$$\Delta\bar{\nu} = \pm 2B(2J + 3)$$

Given that $\Delta\bar{\nu} = \pm(62.4 + 41.6J) \text{ cm}^{-1}$

Therefore $4B = 41.6 \Rightarrow B = 10.4 \text{ cm}^{-1}$

$$\begin{aligned} I &= \frac{h}{8\pi^2 B c} = \frac{6.62 \times 10^{-34} \text{ Js}}{8 \times 9.86 \times 1040 \text{ m}^{-1} \times 3 \times 10^8 \text{ ms}^{-1}} \\ &= 2.7 \times 10^{-47} \text{ kg m}^2. \end{aligned}$$

Ex. 21. For the ground state of O_2 molecule the values of $\bar{\omega}_e$ and $\bar{\omega}_e x_e$ are 1580.36 and 12.07 cm^{-1} respectively. Calculate the zero point energy and the expected vibrational Raman shift.

Sol. The vibrational energy of molecule is

$$E_v = (v + \frac{1}{2})hc\bar{\omega}_e - (v + \frac{1}{2})^2 hc\bar{\omega}_e x_e, \quad v = 0, 1, 2,$$

Zero point energy $E_{v=0} = (\frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e)hc$

$$\begin{aligned} E_0 &= \left(\frac{158036}{2} - \frac{1207}{4} \right) \times 6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1} \\ &= 1.563 \times 10^{-20} \text{ J} \end{aligned}$$

Majority of the molecules will be in the ground state ($v = 0$). Vibrational Raman shift is

$$\Delta\bar{\nu}_{1 \leftarrow 0} = \frac{E_1 - E_0}{hc} \quad (\Delta v = \pm 1)$$

$$\begin{aligned} \Delta\bar{\nu} &= \left(\frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e \right) - \left(\frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e \right) = \bar{\omega}_e - 2x_e\bar{\omega}_e \\ &= (1580.36 - 24.14) \text{ cm}^{-1} \\ &= 1556.22 \text{ cm}^{-1}. \end{aligned}$$

QUESTIONS AND PROBLEMS

1. (a) Explain the origin of far infrared (rotational) absorption spectrum of diatomic molecules.
 (b) Why far infrared spectrum is not obtained for homonuclear diatomic molecules?
 (c) What information can be obtained from the analysis of pure rotation spectra.
 (d) Discuss the effect of centrifugal stretching of bond on the spectrum.
2. Describe the characteristics of far infrared absorption spectrum of diatomic molecules. What changes occur in the spectrum when
 (a) the molecule is assumed to be non-rigid rotator.
 (b) one of the atom is replaced by its heavier isotope.
 Discuss the variation of intensity of rotational lines with temperature.
3. Describe the salient features of infrared (vibration) spectrum of diatomic molecules. Explain the nature of spectrum assuming the molecule to be an anharmonic oscillator.
 (a) What information about the molecule can one obtain from the analysis of infrared absorption spectrum?
 (b) Explain the variation of intensity of infrared bands.
 (c) Why is infrared spectrum not obtained for homonuclear diatomic molecule?
4. How does a diatomic molecule as rotating-vibrator explain the main features of near infrared absorption spectrum? Why is infrared spectrum not obtained for homonuclear diatomic molecule?
5. Discuss the effect of interaction (coupling) of vibrational and rotational motion of molecule on vibration-rotation spectrum.
6. Describe the coarse structure and fine structure of electronic spectra of diatomic molecules. Explain the terms progressions and sequence.
7. (a) In the electronic spectrum of a diatomic molecule the bands are degraded either towards red or towards violet. On the basis of the shading of the bands what information will be obtained about the internuclear distance of the molecule in both of the electronic states?
 (b) Write down the components of the $^3\pi$ and $^3\Delta$ molecular states.
8. On the basis of Franck-Condon principle discuss the intensity distribution within a band system obtained in the process of emission and absorption.
9. What is Raman effect? Give quantum theory of Raman scattering.
10. Describe and explain the main features of
 (a) Vibrational Raman scattering.
 (b) Rotational Raman scattering.
 (c) Vibration-rotation Raman scattering.
11. Give the quantum mechanical theory of Franck-Condon principle.

12. Write notes on the following:
- (a) Isotopic shift in vibrational spectrum of diatomic molecule.
 - (b) Formation of band head in electronic spectra of diatomic molecule.
 - (c) Shading or degradation of bands in electronic spectra of diatomic molecule.
 - (d) Raman effect and fluorescence.
13. Calculate the rotational energy levels of oxygen molecules in electron volt. Mass of oxygen atom is 2.7×10^{-26} kg, internuclear distance is $1.2 \text{ \AA}$. Compare these energy levels with thermal at room temperature 27°C . What conclusions do you draw regarding the occupation of higher rotational energy levels? [Ans. $E_J = (6.0 \times 10^{-5} \text{ eV}) J(J+1)$ and $kT = 0.0258 \text{ eV}$]
14. Calculate the rotational energy levels of HCl molecule, given that: reduced mass of the molecule $\mu = 1.62 \times 10^{-27}$ kg, internuclear distance $r = 1.30 \text{ \AA}$. [Ans. $E_J = (1.25 \times 10^{-3} \text{ eV}) J(J+1)$]

LASERS AND MASERS

6.1 INTRODUCTION

The words MASER and LASER are acronyms for Microwave Amplification by Stimulated Emission of Radiation and Light Amplification by Stimulated Emission of Radiation respectively. The working of these devices is based on the phenomenon of *stimulated emission*, which was first suggested by Einstein in 1917. In this process an assembly of atoms or molecules, initially in the excited state, are *stimulated (induced)* by radiation of appropriate frequency to drop to lower energy state thereby emitting radiation of the same frequency as that of the stimulating radiation. In 1953, Soviet scientists N. Basov and A. Prokhorov and American scientists C. Townes and J. Weber independently developed MASERS. In 1964 Basov, Prokhorov and Townes were awarded Nobel Prize for this work. In 1955 Gordon, Zeiger and Townes fabricated *ammonia maser*. Soon after this discovery the principle of *maser* was extended to optical range and in 1960 T. Meiman (USA) developed the first *maser* in the optical range called LASER. In 1961 A. Javan operated the first gas laser, *helium-neon gas laser*. Since then a large number of masers and lasers have been developed. This chapter is devoted to an elementary account of basic principles of these devices.

6.2 STIMULATED EMISSION

The Einstein's Coefficients

Consider an assembly of identical atoms in equilibrium with radiation at temperature T . Let E_1 and E_2 be two energy levels of the atoms. The frequency ω of radiation is such that

$$\omega = \frac{E_2 - E_1}{\hbar} \quad \dots(6.2.1)$$

Prior to 1917, it was supposed that the thermal equilibrium of atomic system and radiation was determined by only two processes.

- (i) *stimulated (induced) absorption* in which atoms are raised under the action of radiation from the lower energy level to the higher one.

- (ii) *spontaneous emission* in which the atoms return of their own from higher energy level to the lower one.

In 1917, Einstein while investigating this problem realized that two processes mentioned earlier viz stimulated absorption and spontaneous emission alone are not sufficient to maintain the equilibrium of the atomic system and the radiation. He introduced the concept of *stimulated (induced) emission* in which the external radiation persuades the excited atoms to jump from the higher energy level to the lower one by giving up energy. Thus, according to Einstein the equilibrium of matter and radiation governed by three processes:

- (i) stimulated (induced) absorption.
- (ii) spontaneous emission.
- (iii) stimulated (induced) emission.

Let N_1 and N_2 be the number of atoms in the energy levels E_1 and E_2 respectively and $u(\omega)$ be the density of external radiation. The number of stimulated absorption per unit time per unit volume is proportional to the number of atoms in the initial state and the energy density of the radiation *i.e.*,

$$R_{12} = B_{12} N_1 u(\omega) \quad \dots(6.2.2)$$

where B_{12} is proportionality constant.

The number of spontaneous emission per unit time/volume depends only on the number of atoms in the excited state *i.e.*

$$R_{21} = A_{21} N_2 \quad \dots(6.2.3)$$

where A_{21} is a constant.

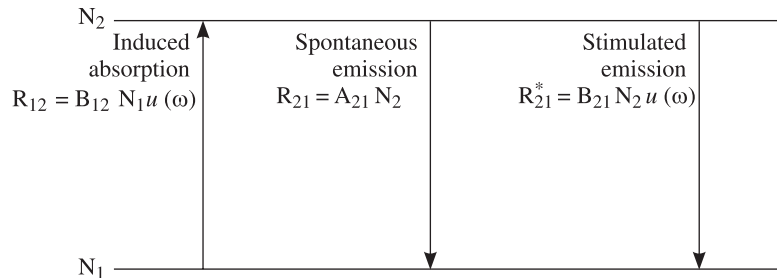


Fig. 6.1.1 Induced, spontaneous and stimulated transitions

The number of stimulated emission per unit time/volume is proportional to the number of atoms in the excited state and the density of stimulating radiation *i.e.*

$$R_{21}^* = B_{21} N_2 u(\omega) \quad \dots(6.2.4)$$

The coefficients A and B 's are called the Einstein's coefficients.

In thermal equilibrium the number of upward transitions must be equal to the number of downward transitions *i.e.*

$$R_{12} = R_{21} + R_{21}^*$$

$$B_{12} N_1 u(\omega) = A_{21} N_2 + B_{21} N_2 u(\omega)$$

Whence

$$u(\omega) = \frac{A_{21}}{B_{21}} \frac{1}{\left(\frac{B_{12}}{B_{21}} \frac{N_1}{N_2} - 1 \right)} \quad \dots(6.2.5)$$

According to Boltzmann equation

$$N_1 = c.e^{-E_1/kT}$$

$$N_2 = c.e^{-E_2/kT}$$

where c is a constant. From these equations, we find

$$\frac{N_1}{N_2} = e^{(E_2 - E_1)/kT} = e^{\hbar\omega/kT} \quad \dots(6.2.6)$$

Making use of this result we can write eqn. (6.2.5) as

$$u(\omega) = \frac{A_{21}}{B_{21}} \frac{1}{\frac{B_{12}}{B_{21}} e^{\hbar\omega/kT} - 1} \quad \dots(6.2.7)$$

According to Planck's radiation law the energy density of a radiation, which is in equilibrium with matter, is given by

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} \quad \dots(6.2.8)$$

Comparison of (6.2.7) and (6.2.8) gives

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega^3}{\pi^2 c^3} \quad \dots(6.2.9)$$

and

$$B_{12} = B_{21} \quad \dots(6.2.10)$$

The Einstein's coefficients represent the transition probabilities per unit time. Eqn.(6.2.10) states that the stimulated absorption and stimulated emission are equally probable. The ratio of number of spontaneous transitions to that of stimulated emissions is given by

$$\begin{aligned} \frac{R_{21}}{R_{21}^*} &= \frac{A_{21}}{B_{21}u(\omega)} \\ &= \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{u(\omega)} \\ &= e^{\hbar\omega/kT} - 1 \end{aligned} \quad \dots(6.2.11)$$

In microwave region ($\lambda = 0.1\text{m}$) at room temperature $T = 300\text{ K}$

$$\frac{\hbar\omega}{kT} = \frac{ch}{\lambda kT} = \frac{12400\text{eV}\cdot\text{\AA}}{(10^9\text{\AA})(0.025\text{eV})} = 4.96 \times 10^{-4} \approx 5 \times 10^{-4}$$

$$e^{\hbar\omega/kT} \approx 1$$

whence

$$\frac{R_{21}}{R_{21}^*} \approx 0$$

This means that in the microwave region the rate of stimulated emission is much higher than the spontaneous emission. Also

$$\frac{N_2}{N_1} = e^{-\hbar\omega/kT} \approx 1$$

i.e., the energy levels E_1 and E_2 are nearly equally populated.

In the optical region ($\lambda = 5000\text{ \AA}$), we have

$$\frac{\hbar\omega}{kT} = \frac{ch}{\lambda kT} = \frac{12400\text{eV}\cdot\text{\AA}}{(5000\text{\AA})(0.025\text{eV})} \approx 100$$

$$\therefore \frac{R_{21}}{R_{21}^*} = e^{100} - 1 \approx \text{a very large number}$$

That is, the spontaneous emission is more predominant in the optical region.

The photons or the wave trains emitted in spontaneous emission move in random directions and have no definite phase relationship with each other. In other words, the radiation is incoherent. On the other hand, *the photons or the wave trains emitted in stimulated emission have the same frequency, the same direction of propagation, the same phase and the same state of polarization i.e., the stimulating and stimulated radiation are strictly coherent.* This feature of stimulated emission underlies the action of a *laser – a device in which the number of stimulated emissions predominate the spontaneous emission.* Since, the number of stimulated emissions is proportional to the number of atoms in the upper level, it is essential to increase the number of atoms in the upper level.

6.3 POPULATION INVERSION

When an atomic system is in thermodynamic equilibrium, Boltzmann's law determines the distribution of atoms in different energy states

$$N_i = C \cdot e^{-E_i/kT} \quad \dots(6.3.1)$$

where N_i is the number of atoms in energy state E_i and T is the temperature of the system. It is evident from the above formula that the population in a state diminishes with increase in energy of

that state. If an atomic system has two characteristic energy states E_1 and $E_2 (> E_1)$ with populations N_1 and N_2 respectively then

$$\frac{N_1}{N_2} = e^{-(E_1 - E_2)/kT} \quad \dots(6.3.2)$$

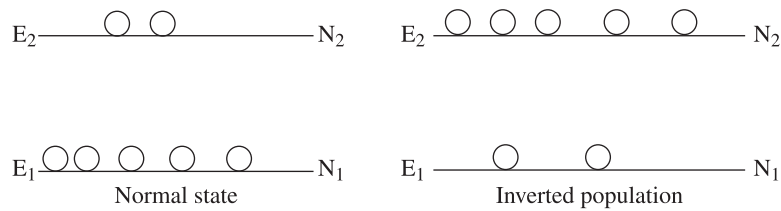


Fig. 6.3.1 Population inversion

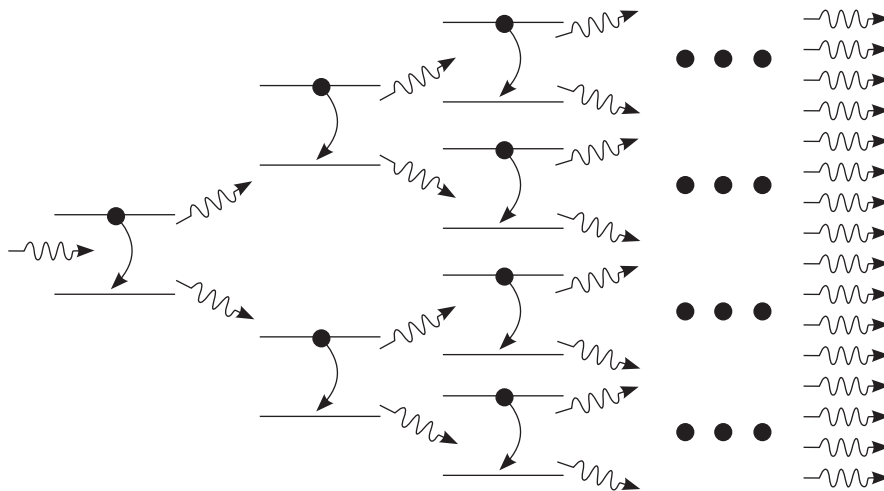


Fig. 6.3.2 A photon stimulates an excited atom causing it to emit a photon. The incident and the emitted photons induce other excited atoms to emit photons. This process rapidly multiplies and an intense laser beam builds up

At equilibrium, the lower energy state will be more populated than the upper state. Consequently in such system the absorption of radiation will predominate over the stimulated emission. A light beam while passing through such medium will get attenuated. A medium having this property is said to have positive absorption coefficient. To obtain amplification of incident light, a condition has to be created in which stimulated emission predominates over the stimulated absorption. Obviously this can be achieved if we can bring the system in a state with greater number of atoms in the upper state

than that in the lower state. A system having $N_2 > N_1$ is said to have **inverse population**. From equation (6.3.2), we can see that the states of population inversion ($N_2 > N_1$, $E_2 > E_1$) correspond to negative value of temperature T and therefore such states are called states with negative temperature. The population inversion is obtained by what is called **optical pumping**, which is a process of imparting energy to the working substance of a laser to transfer the atoms to excited states. In a substance with inverse population the stimulated emission may exceed the absorption of light and hence a light beam while passing through the medium will be amplified. Such a medium is called **active medium**. Allowing the light beam to traverse the same active medium many times before it emerges may further enhance its amplification.

6.4 THREE LEVEL LASER

In case of two levels laser, the method of pumping fails to produce the desired population inversion because the excited atoms residing in the excited state for a very short time interval lose their energy through spontaneous emission and through collision with electrons and drop to the lower level. To overcome this difficulty a three levels scheme was suggested by Basov, Prokhorov and Townes in 1955 and the ruby laser was developed in 1960 by T. Meiman. In order to understand the working principle of three-levels laser let us consider the energy level diagram of atom participating in lasing action. Such an atom has three energy levels shown in the figure. By means flash light of appropriate frequency the atoms are lifted from the ground state E_1 to excited state E_2 where their life time is extremely small (10^{-8} sec). Some of the atoms spontaneously revert to the ground state whose probability is small. But most of the atoms rapidly pass through *non-radiative* transition to the *metastable* state (E_3) where their life time is considerable long ($\approx 10^5$ times) and stay there for long.

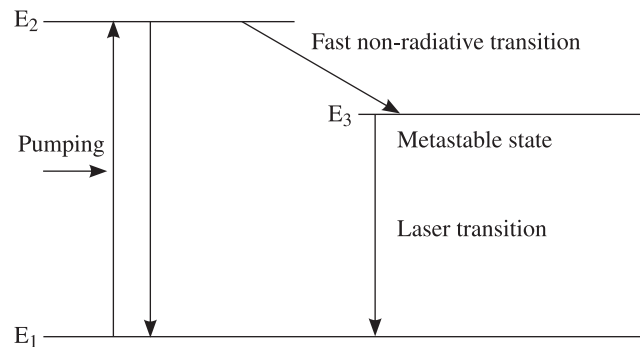


Fig. 6.4.1 Three level laser

In this way the population in the level E_3 increases and that in E_1 decreases. The state of population inversion is thus achieved. The photon emitted in the spontaneous transition ($E_3 \rightarrow E_1$) although its probability is small but not zero, induces the atoms in the *metastable* state to drop to the ground state. The photon emitted in this way further induces other excited atoms. The stimulated emission builds up rapidly.

6.5 THE RUBY LASER

A ruby is aluminium oxide (Al_2O_3) crystal in which some of the aluminium atoms are substituted by chromium ions (Cr^{3+}). In such a crystal, stimulated transitions occur in the chromium ions. The chromium ion has two wide energy bands E_2 and E_3 very close to the ground level E_1 and also a double level E_4 and E_5 . Light tube, which produces light with a broad band of frequencies, is used to illuminate the chromium ions. Under the action of this light the chromium ions are raised from the ground state to E_2 and E_3 , which is a group of closely spaced energy levels. In these energy states the life-time of ions is very small ($\approx 10^{-8}$ sec.). During this time some of the ions pass to the ground state (spontaneous emission). Most of the ions, however, pass to the *metastable* state E_4 and E_5 . The probabilities of these transitions are much greater than the spontaneous transitions ($E_2 \rightarrow E_1$, $E_3 \rightarrow E_1$). The energy of non-radiative transitions ($E_2 \rightarrow E_4$, $E_3 \rightarrow E_5$) is transferred to the crystal lattice. In the *metastable* states the life-times of ions is about 10^{-3} sec. which is about 10^5 times greater than the life-time in ordinary excited state. In this way the population of *metastable* state may exceed that of the ground state E_1 . In other words, the population of these two states will be inverted. The population inversion is promoted still more by the low probability of the spontaneous transition of ions from *metastable* states to the ground state.

The probability of spontaneous emission from the *metastable* states to the ground state is small but not zero. A photon emitted in spontaneous transition. ($E_4 \rightarrow E_1$, $E_5 \rightarrow E_1$) may cause stimulated emission producing additional photons of wavelengths $6927 \text{ \AA}$ and $6943 \text{ \AA}$, which subsequently further stimulate other excited ions to jump to the ground state. This process repeats again and again and a cascade of photons is formed. The photons whose direction is parallel to the axis of the ruby rod suffer multiple reflections at its ends. In their way, these photons stimulate the excited ions to return to the ground state by emitting photons. The process of formation of cascade results in increase in intensity of the beam.

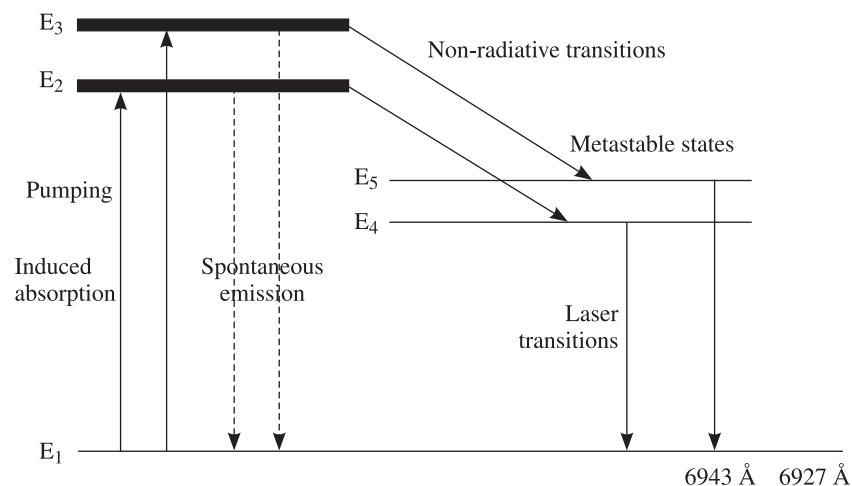


Fig. 6.5.1 Action of Ruby laser

6.6 HELIUM-NEON LASER

The Helium-Neon gas laser consists of a mixture Helium and Neon in the ratio of 7: 1. The gaseous is kept at low pressure (1 mm of Hg) in a discharge tube of about 1m long. At the both ends of the tube parallel mirrors are placed one of which is partly transparent. The spacing of mirrors is equal to integral multiple of half-wavelength of the laser radiation. An electric discharge is produced in the gas by connecting the electrodes to a high frequency a.c. source. The electrons from the discharge collide with helium atoms and the latter are excited to *metastable* states of energies 19.81 eV and 20.5 eV. These excited states of helium are very close to the excited states of neon. When excited helium atoms collide with neon atoms in the ground state, a resonant energy transfer takes place and the neon atoms are raised from their ground states to excited states. If the rate of upward transitions is greater than the radiative decay of the excited atoms, the population in the excited state exceeds that in the ground state. In this way, population inversion is achieved. Thus, the purpose of helium atoms is to create population inversion in neon atoms. The important LASER transitions in neon atoms are:

$$\begin{array}{lll} E_4 \rightarrow E_6 & 3s \rightarrow 3p & \lambda = 3.39 \mu\text{m} \\ E_4 \rightarrow E_5 & 3s \rightarrow 2p & \lambda = 6328 \text{ \AA} \\ E_3 \rightarrow E_5 & 2s \rightarrow 2p & \lambda = 1.15 \mu\text{m} \end{array}$$

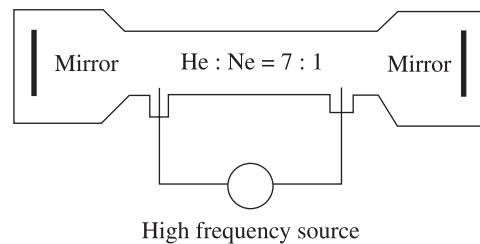


Fig. 6.6.1 Helium-Neon laser

The wavelengths 3.39 μm and 1.15 μm are not in visible region.

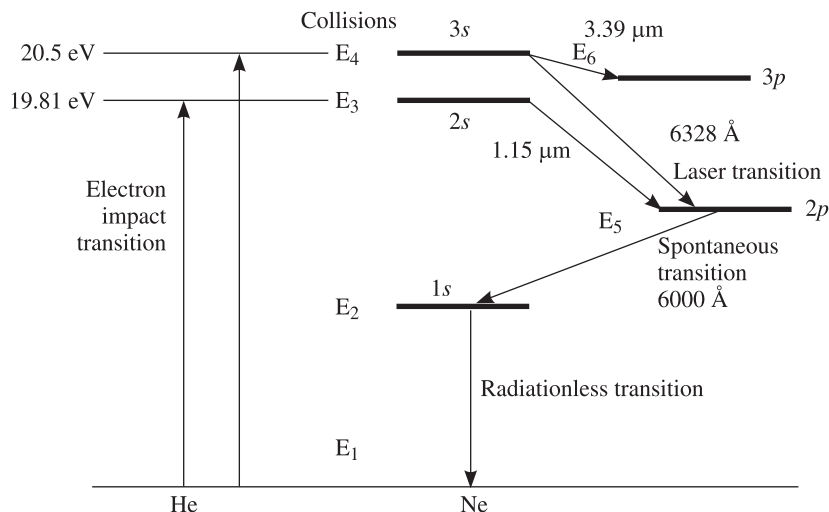


Fig. 6.6.2 Transitions in He-Ne Laser

6.7 AMMONIA MASER

In 1955 Gordon, Zeiger and Townes first developed the ammonia maser. The vibrational energy levels of ammonia molecule consist of pairs of energy levels with small separation compared to the separation of one pair from the other. The lowest pair of energy levels, which has a separation of 10^{-4} eV, is used in the fabrication of ammonia maser. This energy difference corresponds to frequency 23870 MHz or wavelength 1.25 cm.

By heating the ammonia molecules in an oven a collimated beam of molecules is obtained. The beam consists of molecules in the upper and the lower excited states. In order to separate these two kinds of molecules, the beam is passed through an inhomogeneous electric field produced by four metallic rods placed symmetrically around the beam and connected to a *d.c.* source of 15 kV. This arrangement acts as a focuser and separator both. Due to different electric properties (polarizabilities) the two kinds of molecules behave differently in the inhomogeneous electric field. The polarizabilities of molecules in the lower and the upper states are opposite in sign. Therefore, the molecules in the upper state are repelled away and those in the lower state are attracted towards the electrodes. Thus the molecules in the lower state are dispersed and those in the upper state proceed undeviated along the axis and enter a cavity. All the molecules in the cavity are in the upper state. A signal of frequency 23870 MHz is fed to the cavity that triggers the stimulated emission. The amplified radiation comes from another aperture of the cavity.

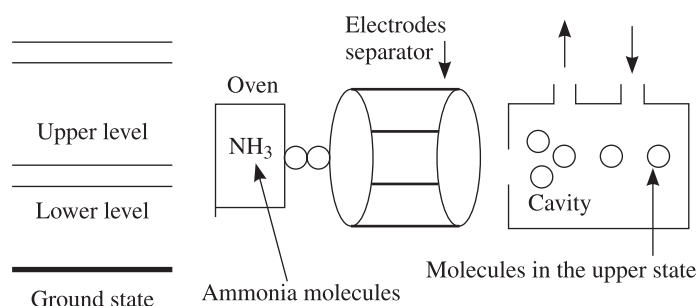


Fig. 6.7.1 Ammonia maser

6.8 CHARACTERISTICS OF LASER

The most striking features in which laser differs from conventional sources are following:

1. **Directionality:** The light from a conventional source spreads in all direction whereas the radiation from a laser travels in one direction only. Owing to this property the light from a laser can be transmitted over a very long distance without appreciable spread.
2. **Intensity:** Due to diverging nature of ordinary light, its intensity falls rapidly with distance whereas the intensity of laser radiation remains almost unaltered after traversing a very long distance.

3. **Monochromatic nature of radiation:** The photons emitted in stimulated emission have essentially the same frequency and is therefore strictly monochromatic.
4. The wave trains emitted during stimulated emission possesses definite phase relationship with each other and hence the laser light is highly coherent.

Applications

The directional and the coherence properties of laser light allows it to be used where tremendous spatial concentration of power is required. The extremely concentrated power may be used in constructive and destructive both ways. In constructive way, it may be used in cutting hard material, drilling metal plates, producing high temperature for nuclear fusion reaction, etc. In destructive ways it may be used to destroy enemy installations, planes, war-heads missiles, etc.

In medicine laser light is used as a very useful surgical tool.

In communication it is used to transmit information more conveniently than radio and microwaves. In fact laser has revolutionized the field of communication.

In scientific research it offers as an extraordinary light source for investigating molecular structure (Raman effect).

QUESTIONS AND PROBLEMS

1. Explain the terms: *induced absorption*, *spontaneous emission* and *stimulated emission*. Obtain expressions for Einstein's A and B coefficients and discuss their physical significance.
2. Distinguish between spontaneous and stimulated emission of radiation. Obtain a relation between the transition probabilities of two emissions.
3. Explain *population inversion* and *optical pumping* with suitable examples.
4. Explain what do you understand by meta-stable states and population inversion? How is the population inversion achieved and why is it necessary for producing laser beam? Describe briefly the characteristics of Laser.
5. What is the principle of three level laser? Describe the principle, construction and working of three level Ruby laser.
6. Describe the principle and working of Helium-Neon laser with suitable diagrams.
7. Describe the principle and working of ammonia maser giving appropriate diagrams.

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