

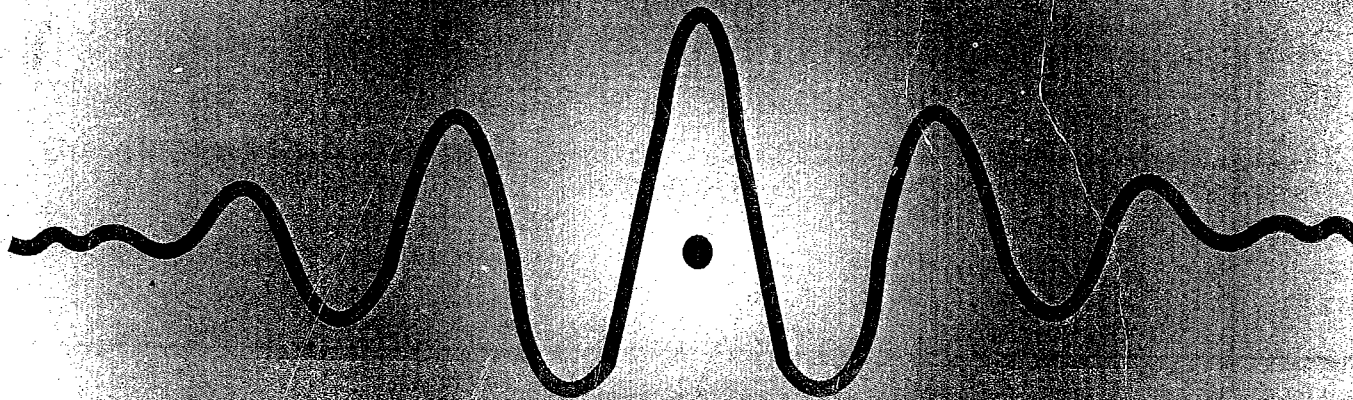
A Text Book Of

QUANTUM MECHANICS

T. Y. B. Sc. (PHYSICS)

Semester - III

Paper - IV (PH - 334)



V. K. WAGH
S. D. AGHAV

P. S. TAMBADE
B. M. LAWARE



NIRALI PRAKASHAN

This Text Book has been strictly written in accordance with the revised syllabus prescribed by the B. O. S. in Physics, University of Pune for T.Y.B.Sc. course (with effect from June 2004).

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T. Y. B. Sc.

Physics Paper - IV ; Semester - III
(PH - 334)

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NIRALI PRAKASHAN

"The Way to Excellence"

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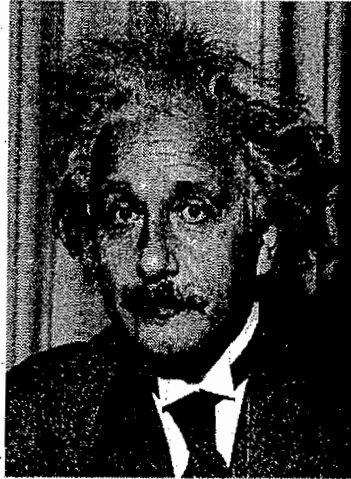
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Theoretical Physics is actual philosophy

- Albert Einstein



Let us not forget that knowledge and skills alone cannot lead human being happy and dignified society. I credit nothing, everything is determined, the beginning as well as end by forces over which we have no control. It is determined for the insect, as well as for the stars, human beings, vegetables or cosmic dust. We all dance to a mysterious fume intoned in the distances by an invariable priory.

$$\lambda = \frac{h}{p}$$

$$\omega = 2\pi\nu \quad \& \quad k = \frac{2\pi}{\lambda}$$

$$v_p = \frac{c\omega}{k}$$

$$v_g = \frac{d\omega}{dk}$$

$$E = h\nu \quad (\text{Einstein theory})$$

$$E = mc^2 \quad (\text{Relativity theory})$$

$$c = \nu\lambda$$

$$p = mc = m\nu\lambda$$

$$\psi = Ae^{i(kx - \omega t)}$$

$$\text{Schr time dep't eq'n} : i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

$$\text{Schr time indpt eq'n} : \nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

$$\text{time indpt Schr eq'n} : \psi(x, t) = \psi(x) e^{-\frac{iE}{\hbar}t}$$

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p \rangle}{m}$$

$$\frac{d\langle p \rangle}{dt} = \langle -\nabla V \rangle$$

$$\langle x \rangle = \int \psi^* x \psi d\tau$$

$$\langle p_x \rangle = \int \psi^* \left(i\hbar \frac{\partial \psi}{\partial x} \right) d\tau$$

$$[x, p_x] = i\hbar = [y, p_y] = [z, p_z] \quad [\text{scalar product } x \cdot x = 1 \text{ \& } x \cdot y = 0 = y \cdot x]$$

$$[x, p_y] = 0 = [y, p_x]$$

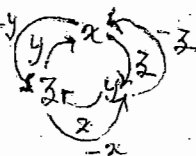
$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$[\hat{A}, \hat{B}] = [\hat{A}\hat{B} - \hat{B}\hat{A}]$$

$$[L_x, x] = 0 = [L_y, y] = [L_z, z]$$

$$[L_x, y] = i\hbar z$$

$$[\text{vector prod } \vec{r} \cdot \vec{r} = 0]$$



We feel great pleasure in bringing out this book of QUANTUM MECHANICS. It is for the revised syllabus of T. Y. B. Sc. (Physics) of Pune University with effect from June, 2004.

The main purpose of the book is to provide foundation as well as comprehensive background of Quantum Mechanics. The subject matter has been arranged systematically and methodically. The language used is very simple for the students to understand the subject easily. Throughout the book the mathematics has been kept as simple as possible.

A large number of solved problems of all types and grades have been included. Each chapter consists of an ample set of problems with detailed solutions, and a further set of problems with answer for practice.

Every attempt has been made to maintain accuracy in theory as well as numerical problems. In spite of great care some misprints and omissions might have occurred. All constructive suggestions by readers for improvement of the book will be greatly acknowledged.

We are thankful to Shri. Dineshbhai Furia, Mr. Jignesh Furia, Shri. M. P. Munde and the entire staff of Nirali Prakashan, for their kind co-operation in bringing the book in time.

June, 2004

Authors

Syllabus

Paper - IV : Semester - III : Quantum Mechanics

1. Historical background and initial development of Quantum Mechanics. Black body radiation and photoelectric effect (Discussion without derivation). Wave-particle duality. Wave packets. Phase-velocity and Group velocity. Discussion on the uncertainty principle with thought experiments. Different forms of the uncertainty relations. Problems. (7 Lectures)
2. Physical Interpretation of the wave function. Requirements of the wave function. The Schrodinger wave equation : Time-dependent and Time-independent versions. Schrodinger equation : Examples in one, two and three dimensions. Probability density and probability current density, equation of continuity. Operators in quantum mechanics. The Hamiltonian Operator. Energy Eigen values and Eigen functions. Expectation values. Ehrenfest's theorems. Problem. (15 Lectures)
3. Hermiticity of operators corresponding to observables in quantum mechanics. Position, linear momentum, Hamiltonian, angular momentum operators. Commutator brackets involving position, linear momentum and angular momentum operators. Raising and lowering operators L_+ and L_- . Parity and parity operator. Problems. (7 Lectures)
4. Applications of the time-independent Schrodinger wave equation to : A free particle, step potential, potential barrier, particle in a rigid box (one, two and three dimensions); Finite one-dimensional potential well. One-dimensional Harmonic Oscillator, Correspondence with the classical results for high degree of excitation. Problems. (11 Lectures)
5. Energy Eigen functions and Eigen values for a rigid rotator with a free axis and with fixed axis, separation of the solution to the Schrödinger equation for a spherically symmetric potential. Qualitative discussion on the radial and angular parts of the bound-state energy eigen functions for the hydrogen atom. Degeneracy. The quantum numbers n , l , m_l and m_s . Problems. (8 Lectures)

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4. APPLICATIONS OF SCHRODINGER'S EQUATION 4.1 – 4.52
5. SPHERICALLY SYMMETRIC POTENTIALS 5.1 – 5.20

CHAPTER 1

MATTER WAVES

INTRODUCTION

By the end of 19th century, many of the experimental results could not be explained on the basis of contemporary classical theories. For example, Rayleigh – Jeans law and Wien's law of black body radiation could not confirm the experimental energy distribution of radiation with respect to wavelength. Rayleigh Jeans law agreed only for long wavelengths but failed for short wavelengths while Wien's law agreed quite well with experimental results for small wavelengths, but failed for large wavelengths. In order to obtain correct distribution of black body radiations Max Planck in 1901 introduced the quantum concept of radiation and it eventually led to the conclusion that radiation is not emitted in continuous manner but in discrete packets of radiant energy, each one of energy $h\nu$, where ν is frequency and h is constant called Planck's constant. These packets are called photons or quanta of energy. Using this concept Planck was able to obtain correct energy distribution of black body radiations. Later Einstein used this concept to explain the specific heat of solids at low temperatures and also for the explanation of photoelectric effect.

1.1 HISTORICAL BACKGROUND

Let us take brief review of some theories that led to the foundation of quantum mechanics.

Black body radiation

A black body emits radiation when it is in thermal contact with surroundings. The radiations contain all the wavelengths ranging from 0 to ∞ . The energy density E_λ against the wavelength for different temperatures is shown in Fig. 1.1

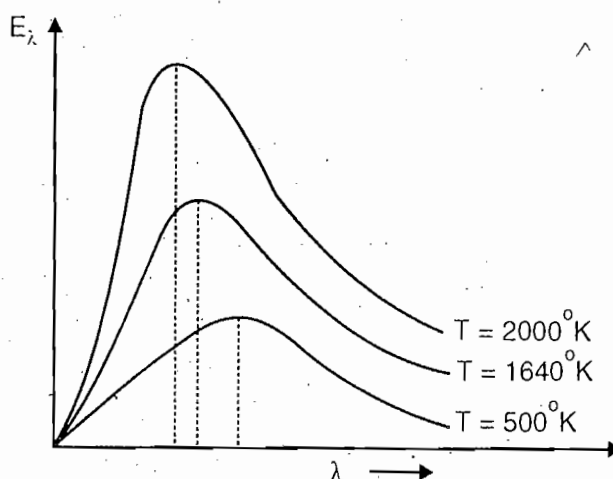


Fig. 1.1 : Black body distribution law

From general thermodynamic arguments, Kirchhoff showed that the distribution of black body radiation is independent of nature of the black body (*i.e.* materials of the wall of the black body) and depends only on its temperature T .

Using the idea of pressure exerted by radiations on the walls of the black body, Stefan and Boltzman (1884) showed that the total energy density was proportional to the 4th power of absolute temperature of the black body *i.e.* $E \propto T^4$ Stefan's law of Black body radiation is, thus, given by

$$E = \sigma T^4$$

where σ is Stefan's constant. Its value is $5.67 \times 10^{-8} \text{ W/m}^2 \text{ K}^4$.

The law was experimentally verified and found satisfactory. However this law does not tell anything about the energy distribution with respect to individual wavelengths.

Wien in 1893 established displacement laws which are

(1) $\lambda T = \text{constant}$ and (2) $E T^{-5} = \text{constant}$.

where λ is the wavelength corresponding to the temperature T and emissivity E of the black body.

Combining these laws and using Maxwell distribution, Wien obtained following law:

$$E_{\lambda} d\lambda = \frac{A}{\lambda^5} e^{-B/\lambda T} d\lambda \quad \dots(1.1)$$

where A and B are constants. It was observed that this law is valid only for the *short wavelength region*.

In 1900, Rayleigh and Jeans approached the energy distribution problem differently. They obtained following law,

$$E_{\lambda} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda \quad \dots(1.2)$$

where k is the Boltzman constant. This formula is in agreement with the experimental results in the *long wavelength region but fails totally in the short wavelength region*.

Thus, all attempts to obtain a *single* formula valid over the entire range of the wavelengths using classical ideas about radiation failed miserably.

Planck (1901) proposed a new formula for black body radiation. According to him each oscillator in the black body surface emits energy not continuously but in the discrete packets of energy

$$E = 0, \epsilon, 2\epsilon, 3\epsilon, 4\epsilon, \dots$$

with $\epsilon = h\nu$, h is called Planck's constant having value $6.625 \times 10^{-34} \text{ J-s}$. This is called quantisation of energy. With this idea, Planck successfully explained the black body radiation. He obtained formula for energy density as

$$(*) E_{\lambda} d\lambda = \frac{8\pi h c}{\lambda^5} \frac{1}{(e^{hc/\lambda kT} - 1)} d\lambda \quad \dots(1.3)$$

This is Planck's radiation formula. This is in exact agreement with the experimental results.

It is observed that for small wavelengths Planck's law reduces to Wien's formula and for longer wavelengths it reduces to Rayleigh and Jeans formula.

Photoelectric effect

It was observed by Lenard that when ultraviolet light was incident upon a metal surface like aluminium, electrons are ejected from the surface. The ejection of electrons from the metal surface when light is incident on it is called *photoelectric effect*. And the ejected electrons are called *photoelectrons*.

It was observed experimentally that

(1) When the frequency of incident radiation was changed, the energy of photoelectrons also changed.

(2) The energy of photoelectrons is independent of intensity of incident radiation.

- (3) Electrons are not emitted from the metal surface when frequency of incident radiation is less than certain frequency. This frequency, below which there is no emission of electrons, is called threshold frequency.

These are three major features of the photoelectric effect that could not be explained on the basis of classical wave theory of radiations. According to classical wave theory of light :

- (i) one could expect that if the intensity of the incident radiations is increased, the energy of the photoelectrons would increase and not their number. $I \uparrow \quad E \uparrow$
- (ii) the photoelectric effect should occur for any frequency provided that the light of sufficient intensity falls on the surface to eject electrons.
- (iii) if light of feeble intensity falls on the metal surface, there will be large time required to absorb sufficient light to eject electrons i.e. there should be time lag in the ejection of electrons. However, it is observed that the photoelectric effect is instantaneous and no time lag is observed.

In order to provide satisfactory explanation for Lenard's experimental observations, Einstein proposed a new revolutionary theory in 1905. According to him, the light (electromagnetic radiation) that is incident upon a metal surface consists of bundles (called quanta) of energy which later came to be called *photons*. He assumed that energy E of each bundle or photon is related to its frequency ν by the relation,

$$E = h\nu$$

where h is Planck's constant.

When such a photon is incident on the surface, all of its energy is absorbed by the surface. Part of the energy is used to eject the electron and remaining is given as kinetic energy to the electron. Kinetic energy of the ejected electron is given as

$$\text{K.E.} = h\nu - W \quad \dots(1.4)$$

where 'W' is called the work function and it is the energy required to remove the electron from the metal surface.

Theoretical prediction based on the Einstein's photon hypothesis satisfied all the experimental results.

In 1921, Einstein received the Nobel Prize for predicting theoretically the law of photoelectric effect.

1.2 WAVE PARTICLE DUALITY

The nature of light is enigmatic since the days of Newton. Newton assumed that light consists of tiny particles called corpuscles, emitted by the luminous bodies. Using this theory, he could explain the phenomenon of reflection and refraction. But this theory failed to explain the phenomenon of interference of light. Huygen, Young and Fresnel, therefore, proposed wave theory of light. According to the wave theory, light propagates in the form of waves in a hypothetical medium called ether which is supposed to be present everywhere i.e. in vacuum also. This wave theory could explain not only phenomenon of reflection and refraction but also the interference, polarization and diffraction of light. In 1900, Maxwell showed that light waves are electromagnetic in nature and for their propagation no medium is necessary. Later, Hertz produced electromagnetic waves in laboratory and the wave nature of light was accepted widely. In 1887, Hallwachs discovered the phenomenon of photoelectric effect, but he could not explain it on the basis of wave theory of light.

In order to explain the phenomenon of photoelectric effect Einstein took into account particle nature of light. He assumed that light consists of packets of energy $h\nu$, where ν is the frequency

of light. These packets are called photons or quanta. In 1923, Compton used particle nature of electromagnetic radiations to explain scattering of X rays by electrons. This effect is called Compton effect.

The question thus arises, what is the true nature of light ? Here the term light is used to refer to electromagnetic radiations in general. Electromagnetic radiation has to be considered waves in some processes and as particles in some other processes. Both the natures are not observed in one process simultaneously. The processes in which path travelled by light is to be considered, the wave nature of light is to be applied. e.g. interference, diffraction. The processes in which there is interaction of light with matter, the particle nature of light needs to be applied. e.g. photoelectric effect, Compton scattering. Thus a dual nature (wave and particle) came to be associated with light.

1.3 DE BROGLIE HYPOTHESIS: MATTER WAVES

By 1924, it became evident that light has dual nature. The phenomena like interference, diffraction, polarization etc. are explained by using wave nature of light. The phenomena of photoelectric effect, Compton effect etc. are explained by using particle nature of light.

In 1924, Louis de Broglie put forward the suggestion that matter (like radiation) also has a dual nature, *i.e.* matter which is made up of discrete particles might exhibit wavelike properties under appropriate conditions. His argument was: if electromagnetic radiation can act like a wave sometimes and like a particle at other times, then things like electrons, protons etc. should also exhibit wave properties when they are in motion.

To put forth his theory, de Broglie made following arguments.

1. Nature loves symmetry.
2. Therefore, the two fundamental entities matter and energy must be mutually symmetrical as regards their properties.
3. Since radiant energy (light), earlier believed to have only wave nature, exhibited particle nature, the material particles must have wave nature when in motion.

The waves associated with a moving particle are called **matter waves**. *

Louis de Broglie suggested that certain basic physical concepts should apply to both the fundamental entities viz. waves and particles.

We know that the energy of photon of frequency ν is given as

$$E = h\nu \quad \dots(1.5)$$

The rest mass of photons is zero. If m is mass of photon in motion and c is its speed then according to theory of relativity the energy of photon is given by

$$E = mc^2 \quad \dots(1.6)$$

Therefore, from equations (1.5) and (1.6) we get

$$h\nu = mc^2 \quad \dots(1.7)$$

The photon travels with speed c in free space. Therefore, its momentum will be

$$p = mc$$

$$\therefore p = \frac{mc^2}{c} = \frac{E}{c}$$

or

$$p = \frac{h\nu}{c} \quad (\because E = h\nu)$$

Since, $c = \nu\lambda$, where λ is wavelength, we get

$$p = \frac{h}{\lambda} \quad \dots(1.8)$$

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$$\lambda = \frac{h}{p} \quad \dots(1.9)$$

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de Broglie put forward his hypothesis that equation (1.9) for photon can be applied to moving particles also. [If the particle of mass m moves with speed v , its momentum is $p=mv$.] Therefore, wavelength associated with moving particles is

$$\lambda = \frac{h}{mv} \quad \dots(1.10)$$

The wavelength of moving particles given by equation (1.10) is called de Broglie wavelength.

It is to be noted that the velocity of the de Broglie waves (matter waves) associated with a moving particle is not necessarily the velocity of the particle.

Let u be the velocity of matter wave associated with moving particle. Then,

$$u = v\lambda \quad \dots(1.11)$$

where v is frequency of waves. Using Eq.(1.10) in (1.11), we get

$$u = v \frac{h}{mv} = \frac{hv}{mv}$$

But $E = hv$ and $E = mc^2$, therefore,

$$u = \frac{mc^2}{mv}$$

$$u = \frac{c^2}{v}$$

$$\dots(1.12)$$

Thus, two different velocities are associated with a moving particle : one refers to the mechanical motion of the particle (v) and the other refers to the velocity of the associated matter wave (u). These two velocities are connected by the equation (1.12). Now the particle velocity $v < c$, hence the velocity of propagation of the matter wave $u > c$. Thus, the de Broglie waves are different from the electromagnetic waves, which travel with a constant speed.

Note : The relativistic energy of a particle is given as -

$$E = \sqrt{p^2 c^2 + m_0^2 c^4}$$

where m_0 is the rest mass of particle, p momentum of particle and c the speed of light.

Example 1: Calculate the wavelength associated with a particle of mass 2 g moving with velocity of 3.3125 km/s.

Solution : Here $m = 2 \text{ g} = 2 \times 10^{-3} \text{ kg}$. and $v = 3.3125 \text{ km/s} = 3312.5 \text{ m/s}$.

Therefore, momentum

$$\begin{aligned} p &= mv = 2 \times 10^{-3} \times 3312.5 \\ &= 6625 \times 10^{-3} \text{ kg-m/s} \\ &= 6.625 \text{ kg-m/s} \end{aligned}$$

The wavelength is

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{6.625 \times 10^{-34}}{6.625} \\ &= 10^{-34} \text{ m.} \end{aligned}$$

This associated wavelength is too small as compared to the dimensions of particle. In such cases, wavelength has no significance for macroscopic particles. However, the de Broglie wavelength has great significance for microscopic particles.

Example 2: Calculate the de Broglie wavelength of an electron moving with speed $1/10^{\text{th}}$ of the velocity of light.

Solution: Mass of electron, $m = 9.1 \times 10^{-31} \text{ kg}$.

Velocity of electron, $v = \frac{c}{10} = \frac{1}{10} \times 3 \times 10^8 \text{ m/s} = 3 \times 10^7 \text{ m/s}$.

Planck's constant, $h = 6.625 \times 10^{-34} \text{ J-s}$.

Momentum of electron, $p = mv = 9.1 \times 10^{-31} \times 3 \times 10^7 = 2.73 \times 10^{-23} \text{ kg-m/s}$

The wavelength of electron is given by

$$\lambda = \frac{h}{p} = \frac{6.625 \times 10^{-34}}{2.73 \times 10^{-23}} = 2.43 \times 10^{-11} \text{ m}$$

$$= 0.234 \times 10^{-10} \text{ m} = 0.234 \text{ \AA}$$

Example 3 : Obtain an expression for the de Broglie wavelength associated with an electron accelerated through V volts. Also find the wavelength for $100V$ and $54 V$.

Solution : The kinetic energy acquired by the electron accelerated through V volts is

$$\frac{1}{2} mv^2 = eV, \quad \text{where } e \text{ is charge on electron.}$$

$$\therefore mv^2 = 2eV \quad \text{and} \quad m^2 v^2 = 2meV$$

$$\therefore mv = \sqrt{2meV} \quad \text{or} \quad p = \sqrt{2meV}$$

$$\text{Therefore, wavelength associated with electron, } \lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}}$$

We have, $h = 6.625 \times 10^{-34} \text{ J-s}$, $m = 9.1 \times 10^{-31} \text{ kg}$, and $e = 1.6 \times 10^{-19} \text{ C}$

Using all these values we get,

$$\lambda = \frac{12.27 \times 10^{-10}}{\sqrt{V}} \text{ m}$$

$$\therefore \lambda = \frac{12.27}{\sqrt{V}} \text{ \AA} \quad \dots(1.13)$$

$$\text{For } V = 100 \text{ volts} \quad \lambda = \frac{12.27}{\sqrt{100}} \text{ \AA} = 1.227 \text{ \AA}$$

$$\text{For } V = 54 \text{ volts} \quad \lambda = \frac{12.27}{\sqrt{54}} \text{ \AA} = 1.67 \text{ \AA}$$

Example 4: Find the de Broglie wavelength of neutron whose energy is 1 eV ?

Given: Mass of neutron $= 1.676 \times 10^{-27} \text{ kg}$.

Solution: Kinetic energy of neutron $= 1 \text{ eV}$

$$= 1 \times 1.6 \times 10^{-19} \text{ J}$$

$$\therefore \frac{1}{2} mv^2 = 1.6 \times 10^{-19} \text{ J}$$

$$\therefore v^2 = \frac{2 \times 1.6 \times 10^{-19}}{m} = \frac{2 \times 1.6 \times 10^{-19}}{1.676 \times 10^{-27}} = 1.9093 \times 10^8$$

$$\therefore v = 1.38 \times 10^4 \text{ m/s.}$$

The de Broglie wavelength is given by

$$\lambda = \frac{h}{mv}$$

$$\begin{aligned}\lambda &= \frac{6.625 \times 10^{-34}}{1.676 \times 10^{-27} \times 1.38 \times 10^4} \\ &= 2.864 \times 10^{-11} \text{ m} = 0.286 \text{ \AA}\end{aligned}$$

1.4 EXPERIMENTAL EVIDENCE OF DE BROGLIE THEORY

Idea of de Broglie matter waves was totally new for the scientific world when it was put forth. Different scientists performed different experiments to check up the existence of matter waves. Soon direct evidence of the existence of de Broglie waves was furnished by experiments on the diffraction of electrons. We will consider here one such an experiment.

Davisson and Germer's Experiment

The Davisson and Germer's experiment is discussed below

Experimental arrangement: The experimental arrangement is shown below in Fig. 1.2. Electrons are produced by the filament (F), which is heated by low-tension battery (L.T.). These electrons are accelerated by a potential difference applied between filament F and grid G by means of high-tension battery (H.T.). These electrons pass through a series of apertures and emerge out in the form of collimated narrow beam, all having the same velocity. This assembly is called electron gun, since it shoots out electrons. These mono-energetic electrons fall on the target N, a single crystal of nickel. The electrons are scattered by the crystal in all directions. These scattered electrons can be collected by Faraday cylinder C called collector. The collector current is amplified and measured with a sensitive galvanometer G'. The collector can be moved along a graduated circular scale S to receive electrons at various angles between 20° and 90° . The collector consists of a double walled metallic cylinder having an entrance aperture. The two walls are insulated from each other. A retarding potential is applied between inner and outer walls of the collector such that only fast moving electrons having the minimum velocity as the velocity of emission from gun can enter the inner cylinder of the collector. The nickel crystal is face centered cubic type and it is so cut to present a smooth reflecting surface parallel to the lattice plane (111).

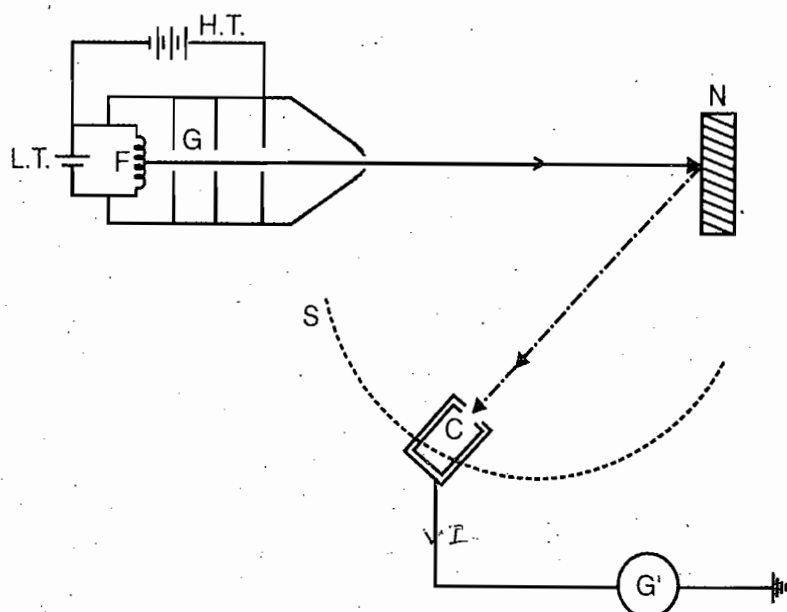


Figure 1.2 : Experimental arrangement

Experimental Procedure: (Normal incidence) The beam of electrons from electron gun falls normally on the surface of the crystal. The atomic planes of the crystal act like a plane diffraction grating. The electrons are diffracted in all directions. The diffracted electrons are collected by the collector moving through different angles on the scale S. For different angles the deflection in galvanometer is measured. The galvanometer deflection is plotted against the angle between the incident beam direction and the beam entering the collector (*co latitude*). The observations are repeated for different accelerating voltages and a number of curves are drawn which is shown in Fig. 1.3.

It is observed that a bump (spur) begins to appear in the curve for 44 volts. This bump moves upward as the voltage increases and attains maximum at 54 volts at an angle of 50° . With further increase in the accelerating voltage, the bump decreases in length and finally disappears at 68 volts.

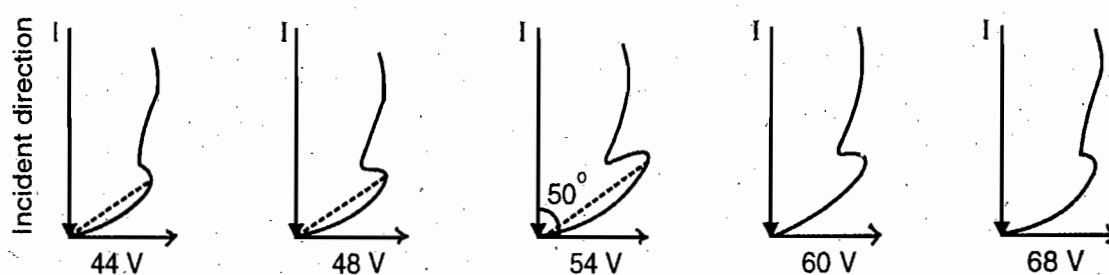


Fig. 1.3 : Variation of intensity I w. r. t. θ at various potentials

The occurrence of maximum bump at 54 volts can be taken as the proof of the existence of electron waves. At this voltage and 50° angle, the constructive interference takes place for the electron waves, scattered in this direction, from the regularly spaced atomic planes takes place.

According to de Broglie theory, the wavelength of electrons accelerated through potential V is given by

$$\lambda = \frac{12.27}{\sqrt{V}} \text{ \AA}$$

Therefore, for $V = 54 \text{ V}$, we get,

$$\lambda = \frac{12.27}{\sqrt{54}} \text{ \AA} = 1.67 \text{ \AA} \quad \dots(1.14)$$

For the nickel crystal, for the (1 1 1) reflecting plane, the separation between atomic planes is $d = 2.15 \text{ \AA}$. Applying the law of reflection grating

$$n\lambda = d \sin \theta \quad \dots(1.15)$$

For first order $n = 1$. Also, $\theta = 50^\circ$.

$$\therefore \lambda = 2.15 \sin 50^\circ$$

$$\therefore \lambda = 1.65 \text{ \AA}$$

Thus, the experimental value is in close agreement with theoretical value. This shows that electrons behave like waves. \square

Thus, the Davisson and Germer's experiment confirmed the wave nature of moving electrons.

1.5 WAVE GROUP OR WAVE PACKET

We have seen that the matter has dual nature. Sometimes it behaves like a particle and sometimes as a wave. The amplitude of de Broglie wave corresponding to the moving particle represents the probability with which the particle can be found at a particular place at a particular time. de Broglie wave associated with a particle is a pilot wave which controls the motion of particle in space. Therefore, it is necessary that the amplitude of the de Broglie wave must be modulated in such a way that it is non-zero only over the finite region of space in the vicinity of the particle at an instant. According to de Broglie's view, a group of waves or wave packet is associated with each material particle in motion. A wave packet is a group of waves, each having slightly different wavelength and velocity. This is also called wave group. Their phases and amplitudes are such that they interfere constructively over a small region; over which the particle is located and outside the region they interfere destructively. As time passes, the wave group must surely move along the direction of motion of particle with the same velocity as the particle. Such a wave packet is shown in the Fig.1.4 below.



Fig.1.4 : Wave group

To understand the nature of the wave packet or wave group and how the amplitude is modulated, let us assume that a moving particle is associated with a number of plane waves having slightly different wavelengths and velocities and propagating along positive x-direction. For mathematical simplicity, consider only two such waves. They are represented as

$$\left. \begin{aligned} \psi_1 &= A \sin(\omega t - kx) \\ \text{and} \quad \psi_2 &= A \sin\{(\omega + d\omega)t - (k + dk)x\} \end{aligned} \right\} \quad \dots (1.16)$$

where $\omega = 2\pi\nu$ and $k = \frac{2\pi}{\lambda}$ (propagation constant) and wave velocity or phase velocity $v_p = \frac{\omega}{k}$

Phase velocity is the velocity with which the wave propagates.

According to the principle of superposition, the resultant displacement is given by

$$\psi = \psi_1 + \psi_2$$

$$\psi = A[\sin(\omega t - kx) + \sin\{(\omega + d\omega)t - (k + dk)x\}]$$

$$\therefore \psi = 2A \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \sin\left\{\left(\omega + \frac{d\omega}{2}\right)t - \left(k + \frac{dk}{2}\right)x\right\} \quad \dots (1.17)$$

$d\omega$ and dk are very small. Therefore, above equation can be written as

$$\begin{aligned} \sin A + \sin B & \quad \psi = 2A \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \sin(\omega t - kx) \quad \dots (1.18) \\ = 2 \cos\left(\frac{A-B}{2}\right) \sin\left(\frac{A+B}{2}\right) & = B \sin(\omega t - kx) \end{aligned}$$

The above equation represents a wave traveling with wave or phase velocity $v_p = \frac{\omega}{k}$ whose amplitude 'B' is

$$B = 2A \cos\left(\frac{d\omega}{2}t - \frac{dk}{2}x\right) \quad \dots(1.19)$$

This amplitude B itself represents another wave traveling with velocity v_g called *group velocity* and it is given by

$$v_g = \frac{\text{coefficient of } t}{\text{coefficient of } x} = \frac{d\omega/2}{dk/2} = \frac{d\omega}{dk}$$

$$\therefore \text{group velocity} \quad \boxed{v_g = \frac{d\omega}{dk}} \quad \dots(1.20)$$

It can be shown that, for an infinitely large number of propagating waves with slightly different wave lengths that combine to form a group, the dependence of phase velocity v_p and the group velocity v_g , on ω , k and $d\omega$ and dk is exactly the same as considered in the above simple case of combination of only two waves.

Depending upon how the phase velocity varies with ω and k in a particular situation the group velocity may be less or more than the phase velocities of the member waves of a wave group.

Since $\omega = 2\pi\nu$ and $k = \frac{2\pi}{\lambda}$, we get $d\omega = 2\pi d\nu$ and $dk = -\frac{2\pi}{\lambda^2} d\lambda$.

Therefore, equation (1.20) can also be written as

$$v_g = -\frac{1}{\lambda^2} \frac{\partial \nu}{\partial \lambda} = -\lambda^2 \frac{\partial \nu}{\partial \lambda} \quad \dots(1.21)$$

The two waves of slightly different frequencies and their resultant superposition wave (i.e. the wave group) are shown in the Fig 1.5.

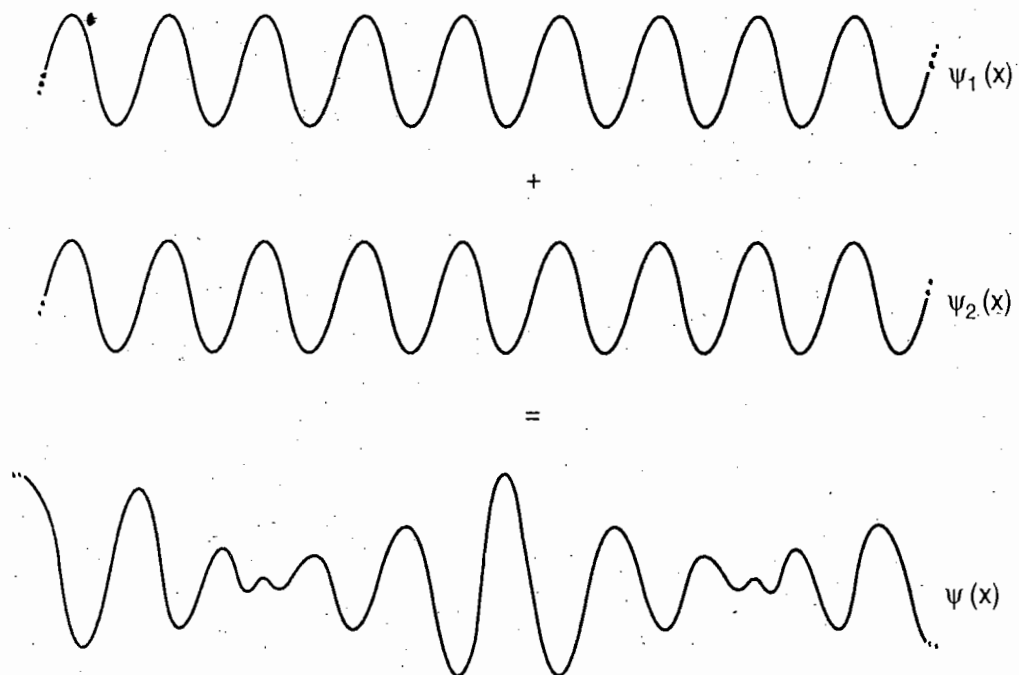


Fig. 1.5 : Superposition of two waves with slightly different frequencies.

Since $v_p = \frac{\omega}{k}$, we can write $\omega = kv_p$. Using in equation (1.20), we get

$$v_g = \frac{d\omega}{dk}$$

$$v_g = \frac{d(kv_p)}{dk}$$

$$\therefore v_g = v_p + k \frac{dv_p}{dk} \quad \dots(1.22)$$

Equation (1.22) represents the relation between group velocity v_g , phase or wave velocity v_p and propagation constant k .

Since $k = \frac{2\pi}{\lambda}$

$$v_g = v_p + \left(\frac{2\pi}{\lambda} \right) \left(\frac{dv_p}{d\lambda} \cdot \frac{d\lambda}{dk} \right) = v_p - \lambda \frac{dv_p}{d\lambda}$$

$$\therefore dk = -\frac{2\pi}{\lambda^2} d\lambda$$

Using in equation (1.22), we get

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda} \quad \dots(1.23)$$

Equation (1.23) represents the relation between group velocity v_g , phase or wave velocity v_p and wavelength λ .

To show that the particle velocity (v) is the same as the group velocity (v_g). Imp.

If E and V are the total energy and potential energy of a particle moving with velocity v , then its kinetic energy is given by

$$\frac{1}{2}mv^2 = E - V$$

$$[T.E = E = \frac{1}{2}mv^2 + V = K.E + P.E] \quad \dots(1.24)$$

But the total energy $E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \frac{h}{2\pi} \omega = \hbar\omega$

where $\hbar = \frac{h}{2\pi}$

and momentum $p = mv = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k$

$$\left(\lambda = \frac{h}{p} \right)$$

With these values equation (1.24) can be written as

$$\frac{1}{2} \frac{m^2 v^2}{m} = E - V \Rightarrow \frac{1}{2} \frac{\hbar^2 k^2}{m} = \hbar\omega - V$$

$$\therefore \omega = \frac{1}{2} \frac{\hbar k^2}{m} + \frac{V}{\hbar} \quad d.\omega \propto d.k$$

Differentiating with respect to k , we get

$$v_g = \frac{d\omega}{dk} = \frac{\hbar k}{m} = p = mv = v$$

But $v_g = \frac{d\omega}{dk}$ and $p = mv = \hbar k$. Therefore,

$$v_g = \frac{mv}{m} = v$$

$$\therefore v_g = v \quad \dots(1.25)$$

Thus, we see that velocity of particle is equal to the group velocity or the velocity of wave packet. Hence, we conclude that the wave group propagates with the particle.

Example 5 : The velocity of ocean waves is given by $\sqrt{\frac{g\lambda}{2\pi}}$. Find the group velocity.

Solution : The group velocity v_g is given by

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda}$$

The velocity of ocean waves is $v_p = \sqrt{\frac{g\lambda}{2\pi}} = \sqrt{\frac{g}{2\pi}} \lambda^{1/2}$ $\frac{dv_p}{d\lambda} = \sqrt{\frac{g}{2\pi}} \lambda^{-1/2} \times \frac{1}{2}$

$$v_g = \sqrt{\frac{g\lambda}{2\pi}} - \frac{\lambda}{2} \sqrt{\frac{g}{2\pi\lambda}}$$

$$= \sqrt{\frac{g\lambda}{2\pi}} - \frac{1}{2} \sqrt{\frac{g\lambda^2}{2\pi\lambda}}$$

$$v_g = \sqrt{\frac{g\lambda}{2\pi}} - \lambda \sqrt{\frac{g}{2\pi}} \times \frac{1}{2} \lambda^{-1/2} = \frac{1}{2} \sqrt{\frac{g}{2\pi}} \lambda^{-1/2}$$

$$= \frac{1}{2} \sqrt{\frac{g}{2\pi\lambda}}$$

$$v_g = \sqrt{\frac{g\lambda}{2\pi}} - \frac{1}{2} \sqrt{\frac{g\lambda}{2\pi}}$$

$$v_g = \frac{1}{2} \sqrt{\frac{g\lambda}{2\pi}} = \frac{1}{2} v_p$$

i.e., the group velocity is half the phase or wave velocity.

Example 6 : The velocity of waves (v_p) through the medium of refractive index n is $\sqrt{n/k}$. Find the group velocity in the medium.

Solution : The velocity of wave or phase velocity $v_p = \sqrt{\frac{n}{k}}$

But refractive index $n = \frac{c}{v_p}$, where c is velocity of waves in vacuum.

$$\therefore v_p = \sqrt{\frac{c}{k v_p}}$$

$$\text{or } v_p^2 = \frac{c}{k v_p}$$

$$\therefore v_p^3 = \frac{c}{k}$$

$$\text{or } v_p = \left(\frac{c}{k}\right)^{1/3}$$

The relation between the group velocity and the phase velocity is given as

$$v_g = v_p + k \frac{dv_p}{dk}$$

$$v_g = v_p + k \frac{d}{dk} \left(\frac{c}{k}\right)^{1/3} = v_p + kc^{1/3} \frac{d(k^{-1/3})}{dk}$$

$$= v_p - \frac{1}{3} kc^{1/3} \times k^{-4/3} = v_p - \frac{1}{3} \left(\frac{c}{k}\right)^{1/3}$$

$$v_g = v_p - \frac{1}{3} v_p = \frac{2}{3} v_p$$

Example 7: Show that the phase velocity of the de Broglie waves associated with a particle of rest mass m_0 and wavelength λ is given by

$$v_p = c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2} \text{ where } c \text{ is velocity of light.}$$

Solution: The phase velocity is given by $v_p = \frac{\omega}{k} = \frac{2\pi\nu}{2\pi/\lambda} = \nu\lambda$

We have energy $E = h\nu$

The relativistic energy is given by

$$E = \sqrt{p^2 c^2 + m_0^2 c^4}$$

$$\therefore E = pc \sqrt{1 + \frac{m_0^2 c^4}{p^2 c^2}}$$

$$= pc \sqrt{1 + \frac{m_0^2 c^2}{p^2}}$$

Since $p = \frac{h}{\lambda}$, we get,

$$E = \frac{h}{\lambda} c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2}$$

$$\therefore \frac{E\lambda}{h} = c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2}$$

or

$$\frac{h\nu\lambda}{h} = c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2}$$

\therefore

$$\nu\lambda = c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2}$$

$$v_p = c \sqrt{1 + \left(\frac{m_0 c \lambda}{h}\right)^2}$$

or

I *Imp*

Example 8: Velocity of the ripple waves produced on the surface of a liquid is equal to $\sqrt{\frac{2\pi T}{\rho\lambda}}$, where T is the surface tension and ρ is the density of liquid. Find the group velocity.

Solution: We have

$$v_p = \sqrt{\frac{2\pi T}{\rho\lambda}}$$

\therefore

$$\frac{dv_p}{d\lambda} = -\frac{1}{2\lambda} \sqrt{\frac{2\pi T}{\rho\lambda}} = -\frac{1}{2\lambda} v_p$$

\therefore

$$\lambda \frac{dv_p}{d\lambda} = -\frac{1}{2} v_p$$

Now,

$$v_g = v_p - \lambda \frac{dv_p}{d\lambda}$$

\therefore

$$v_g = v_p - \left(-\frac{1}{2}v_p\right)$$

\therefore

$$v_g = \frac{3}{2}v_p$$

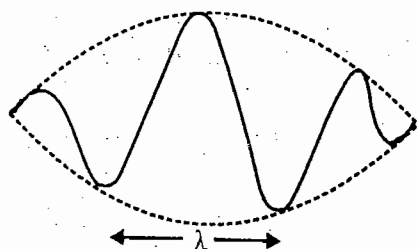
1.6 HEISENBERG'S UNCERTAINTY PRINCIPLE

In classical Physics, the dynamical variables like position, components of linear momenta, components of angular momenta etc. are assumed to be measured with precise accuracy at a given instant of time *i.e.* the basic laws in physics (such as Newton's laws) have *deterministic nature*.

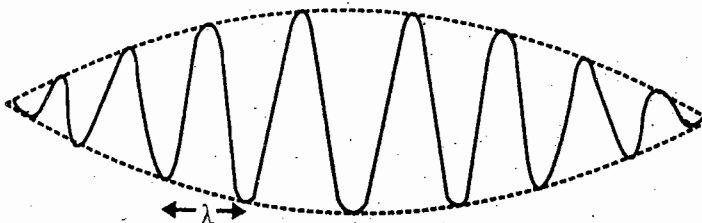
According to Bohr and Heisenberg, the probabilistic nature is a fundamental one in quantum physics which dominates the micro world and the deterministic nature is discarded. A careful analysis of motion of microphysical system shows that there is a fundamental limit to the accuracy to which variables like position, momentum, angular momentum etc. are measured.

[We have seen that the moving material particle has dual nature *i.e.*, it behaves like a particle in some processes and wave in some other processes. To study the motion of a particle, its position and momentum need to be simultaneously measured. Werner Heisenberg in 1927 proposed a very far reaching principle called *uncertainty principle*. According to this principle, if we measure accurately the position of particle, its momentum become uncertain and vice versa. The moving particle considered to have wave packet associated with it. The particle may be anywhere in the wave packet and if the packet is small *i.e.* wave group is narrow its position can be found more accurately. But when the wave packet is small the spread of wavelength, associated with it is more *i.e.* wavelength and consequently the momentum of the particle becomes uncertain. On the other hand, if the wave packet is long the momentum of the particle becomes more certain but the position becomes uncertain.

Heisenberg's uncertainty principle states that it is impossible to determine precisely and simultaneously the momentum and position of a moving particle. The short wave group is shown in Fig. 1.6(a) and long wave group is shown in Fig. 1.6 (b).



(a) short wave group



(b) long wave group

Fig 1.6

In mathematical form the uncertainty principle is given as: If Δx is uncertainty in the measurement of position and Δp_x is uncertainty in the measurement of momentum, then the product of two uncertainties is at least of the order of Planck's constant. It is given as

$$\Delta x \cdot \Delta p_x \approx \hbar \quad \dots(1.26)$$

If Δx is small, Δp_x will be large and *vice versa*. It means that if one quantity is measured more accurately, the other quantity becomes less accurate. More precise relation of uncertainty principle is

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

where momentum p_x is known to within accuracy of Δp_x and the position x at the same time to within accuracy Δx . Here \hbar (read as h-bar) is taken as $h/2\pi$. The symbol appears often in quantum mechanics as the basic unit of angular momentum because it has dimensions of angular momentum.

The uncertainty relations for the remaining components of linear momentum are given as

$$\Delta y \cdot \Delta p_y \geq \frac{\hbar}{2}$$

and

$$\Delta z \cdot \Delta p_z \geq \frac{\hbar}{2}$$

The above uncertainty relations represent the law of nature. The uncertainties are not due to any defects in the measuring instrument. The principle says that even with ideal instruments we never get the uncertainty product $\Delta x \cdot \Delta p_x$ less than $\hbar/2$.

Heisenberg's principle of uncertainty can be illustrated with the help of a few thought experiments. A thought experiment may not be performed in actual practice but in its consideration no physical laws are violated.

1. γ -ray microscope :

We shall consider here the famous argument by Bohr with the so called ' γ -ray microscope'. This is a thought experiment and cannot be performed experimentally.

The experimental arrangement is shown in Fig. 1.7 (a).

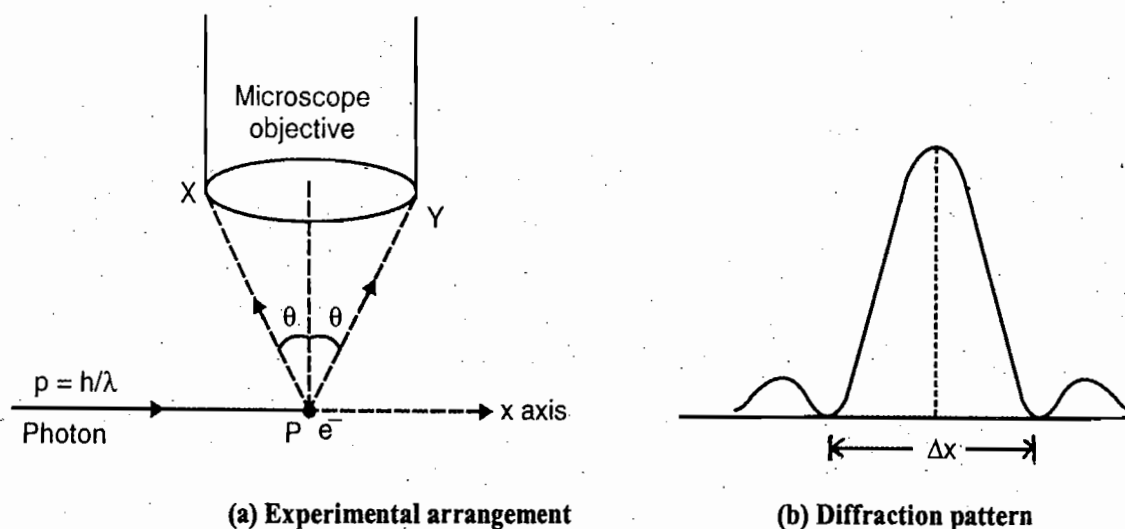


Fig. 1.7 : γ ray microscope

Suppose we try to measure the position (x) and corresponding linear momentum (p_x) of an electron using an imaginary microscope of high resolution. The electron can be observed when at least one photon scattered from electron enters in the aperture of the microscope. The resolving power of microscope is given by the relation,

$$\Delta x = \frac{\lambda}{2 \sin \theta} \quad \dots(1.28)$$

where Δx is the smallest distance between two points which can be just resolved by the microscope, λ is the wavelength of light used for illumination and θ is the semi-vertical angle of the cone of rays entering in the objective of the microscope as shown in Fig 1.7 (a). The corresponding diffraction pattern is shown in Fig. 1.7 (b). To increase the resolving power i.e. to make the uncertainty in position Δx small from equation (1.28) we see that λ must be made small, because $\sin \theta$ could not be increased above unity. Therefore, the radiations of smaller wavelength i.e. γ radiations need to be used to illuminate the electron at P.

The incoming photon (γ -ray) along x-direction will interact with the electron and get scattered in all directions. In order to see the electron, the scattered photon should enter the microscope within the angle 2θ . The momentum imparted by the photon to the electron will be of the order of h/λ .

The component of momentum of scattered photon along PX is $\sim -\frac{h}{\lambda} \sin \theta$

The component of momentum of scattered photon along PY is $\sim \frac{h}{\lambda} \sin \theta$.

The momentum imparted by the photon to the electron is, therefore, anything between the above two limits. Hence uncertainty in the momentum measurement in the x-direction is

$$\Delta p = \frac{h}{\lambda} \sin \theta - \left(-\frac{h}{\lambda} \sin \theta \right) = \frac{2h}{\lambda} \sin \theta$$

$$\therefore \Delta x \cdot \Delta p = \frac{\lambda}{2 \sin \theta} \times \frac{2h}{\lambda} \sin \theta = h$$

$$\text{i.e.} \quad \Delta x \cdot \Delta p = h$$

There are various other factors which contribute to uncertainties. Therefore, more sophisticated approach will show that $\Delta x \cdot \Delta p \geq \hbar$ \square

Imp. 2. Electron diffraction Experiment:

Consider a beam of electrons falling on a narrow slit of width ' d ' as shown in Fig. 1.8. The beam spreads out after passing through the slit due to diffraction and the diffraction pattern is observed on the photographic plate P kept at a distance from the slit. Every electron registered on the photographic plate must have passed through the slit, but cannot specify its exact location in the slit as the electron crosses it. Hence, the uncertainty in specifying the position of electron is equal to the slit width i.e. $\Delta x = d$.

From the wave theory of light we know that for first order diffraction

$$2 d \sin \theta = \lambda$$

$$\Delta x = \frac{\lambda}{2 \sin \theta} \quad \dots(1.29)$$

where λ be the wavelength and θ be the angle of diffraction for first order.

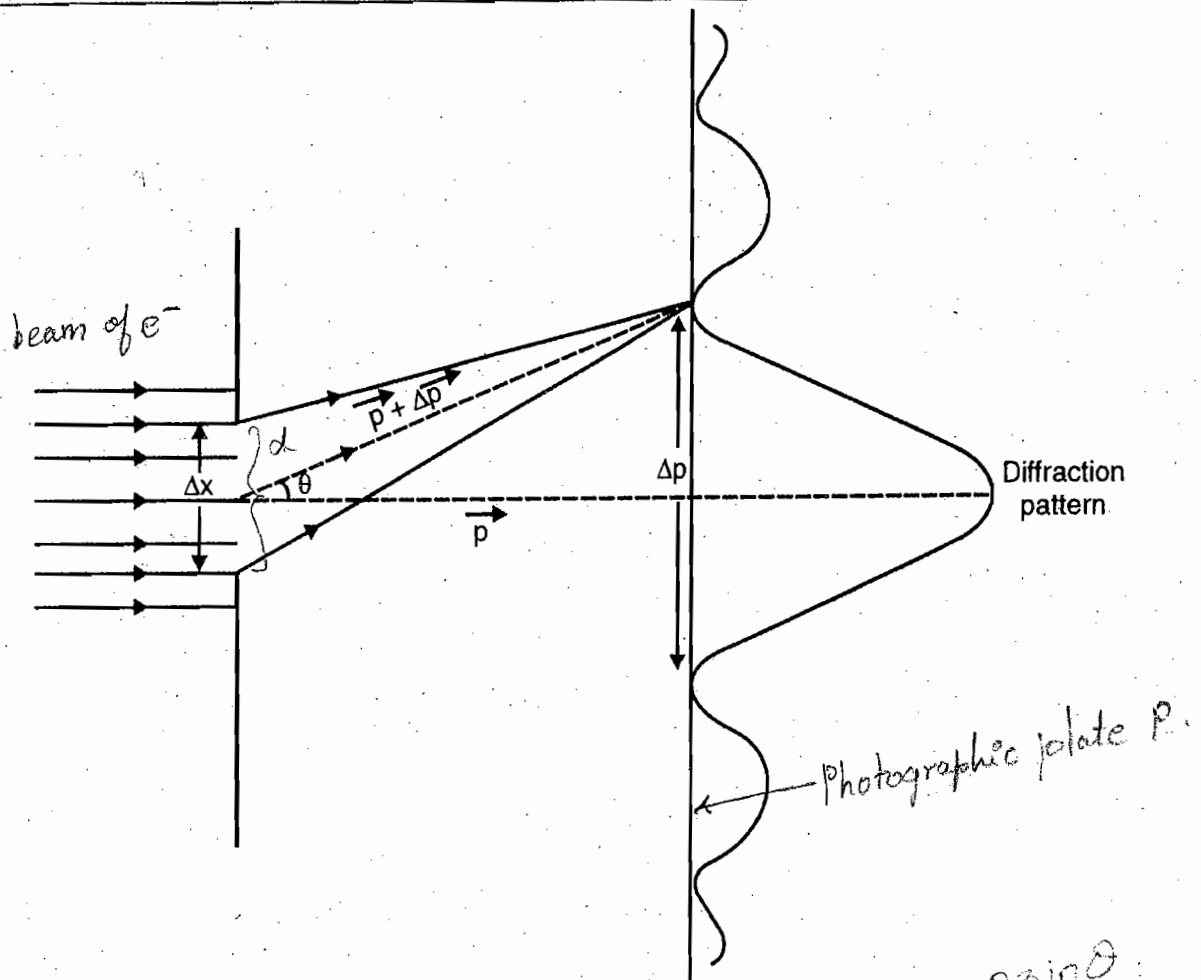


Fig 1.8 : Electron diffraction experiment

Let p be the momentum of electron along the incident direction. When the electron is deflected at the slit, it acquires an additional momentum $p \sin \theta$ in the direction perpendicular to the original direction. As the electron may be anywhere within the pattern from angle $-\theta$ to $+\theta$, the component of momentum of the electron may have any value between $-p \sin \theta$ to $p \sin \theta$. Therefore, uncertainty in the component of momentum is

$$\Delta p = p \sin \theta - (-p \sin \theta) = 2p \sin \theta.$$

From de Broglie hypothesis $p = \frac{h}{\lambda}$

$$\therefore \Delta p = \frac{2h}{\lambda} \sin \theta \quad \dots(1.30)$$

From equations (1.29) and (1.30), we get

$$\Delta x \cdot \Delta p = \frac{\lambda}{2 \sin \theta} \times \frac{2h}{\lambda} \sin \theta$$

$$\therefore \Delta x \cdot \Delta p \sim h$$

This is the uncertainty relation.

1.7 DIFFERENT FORMS OF UNCERTAINTY RELATION Imp

1. Time energy uncertainty relation:

Consider the kinetic energy of the particle

$$E = \frac{1}{2} m v^2 = \frac{p^2}{2m}$$

The uncertainty in E is ΔE and it is given by $\frac{mv}{m} \Delta p$

$$\Delta E = \frac{p}{m} \Delta p = v \Delta p \quad (\text{since } p = mv)$$

If v is taken as the recoil velocity of the particle due to incident light, the uncertainty in the position is related to the uncertainty of the time of the observation

$$\Delta x = v \Delta t$$

$$\therefore \Delta E \Delta t = v \Delta p \times \frac{\Delta x}{v} = \Delta p \times \Delta x$$

$$\therefore \boxed{\Delta E \Delta t = \hbar/2} \quad \dots(1.31)$$

2. Angular momentum-angular displacement uncertainty relation: $\int mp$

In order to obtain uncertainty relation between the uncertainty ΔL in angular momentum and corresponding uncertainty $\Delta \theta$ in angular displacement, consider a particle of mass m moving with speed v along the arc of radius r as shown in Fig. 1.9.

The angular momentum at an instant is given by

$$\boxed{L = mvr = pr}$$

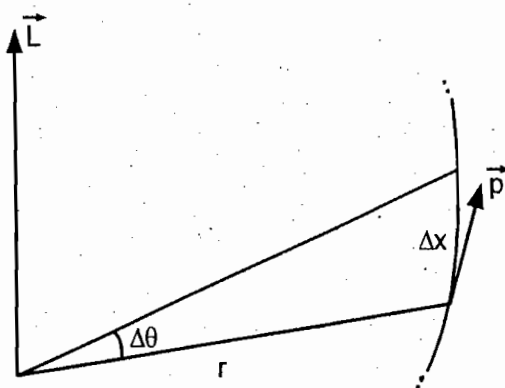


Fig. 1.9

If Δx is the uncertainty in the position along the arc and $\Delta \theta$ is the uncertainty in the angular position, then

$$\Delta x = r \Delta \theta$$

If the uncertainty in the momentum is Δp , then the uncertainty in the angular momentum is $\Delta L = r \Delta p$

Hence

$$\Delta p = \frac{\Delta L}{r}$$

\therefore

$$\Delta p \Delta x = \frac{\Delta L}{r} r \Delta \theta = \Delta L \Delta \theta$$

But $\Delta p \Delta x \geq \hbar/2$

\therefore

$$\Delta L \Delta \theta \geq \hbar/2 \quad \dots(1.32)$$

This is the required result.

Example 9: What is the smallest possible uncertainty in the position of an electron moving with velocity 10^6 m/s ?

Solution: Let Δx be the minimum uncertainty in the determination of position of the electron, then according to uncertainty principle

$$\Delta x \cdot \Delta p = \hbar/2 \quad \text{where } \hbar = \frac{h}{2\pi} = 1.055 \times 10^{-34} \text{ J-s.}$$

Taking the maximum uncertainty in the momentum $\Delta p = p = mv$, assuming that the direction of motion which completely uncertain.

Mass of electron $m = 9.1 \times 10^{-31}$ kg and velocity $v = 10^6$ m/s.

$$\therefore \Delta p = 9.1 \times 10^{-31} \times 10^6 \text{ kg-m/s} = 9.1 \times 10^{-25} \text{ kg-m/s}$$

$$\therefore \Delta x = \frac{\hbar}{2\Delta p}$$

$$= \frac{1.055 \times 10^{-34}}{2 \times 9.1 \times 10^{-25}} = 0.5795 \times 10^{-10} \text{ m} = 0.5795 \text{ \AA}.$$

$$\therefore \Delta x = 0.5795 \text{ \AA}.$$

Example 10: An electron has speed of 6000 m/s with an accuracy of 0.05%. Calculate the uncertainty with which the position of electron can be located.

Solution: Mass of the electron $m = 9.1 \times 10^{-31}$ kg.

Velocity of electron $v = 6000$ m/s.

The momentum of electron $p = mv = 9.1 \times 10^{-31} \times 6000 = 54.6 \times 10^{-28}$ kg-m/s

$$\begin{aligned} \text{Uncertainty in momentum } \Delta p &= 0.05\% \text{ of } p = \frac{0.05}{100} \times 54.6 \times 10^{-28} \\ &= 5 \times 54.6 \times 10^{-32} \text{ kg-m/s} \end{aligned}$$

$$\therefore \Delta p = 2.83 \times 10^{-29} \text{ kg-m/s}$$

$$\begin{aligned} \text{Uncertainty in position is given by } \Delta x &= \frac{\hbar}{2\Delta p} = \frac{1.055 \times 10^{-34}}{2 \times 2.83 \times 10^{-29}} = 0.189 \times 10^{-5} \text{ m} \\ \therefore \Delta x &= 1.89 \times 10^{-6} \text{ m} \end{aligned}$$

Example 11 : Show that for a free particle the uncertainty relation can also be written as

$$\Delta \lambda \Delta x \geq \lambda^2/4\pi$$

where Δx is uncertainty in the position and $\Delta \lambda$ is simultaneous uncertainty in the wavelength.

Solution : We have uncertainty relation

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2} \quad \dots(i)$$

According to de Broglie hypothesis

$$p = \frac{h}{\lambda}$$

On differentiation we get

$$dp = -\frac{h}{\lambda^2} d\lambda$$

Uncertainty relation involves the product of only the magnitude of uncertainties.

$$\Delta p = \frac{h}{\lambda^2} \Delta \lambda \quad \dots(ii)$$

Using (ii) in (i), we get

$$\Delta x \frac{h}{\lambda^2} \Delta \lambda \geq \frac{h}{2}$$

$$\therefore \Delta x \Delta \lambda \geq \frac{h}{2} \frac{\lambda^2}{h}$$

$$\text{or} \quad \Delta x \Delta \lambda \geq \frac{h}{4\pi} \frac{\lambda^2}{h}$$

$$\therefore \Delta x \Delta \lambda \geq \frac{\lambda^2}{4\pi}$$

Example 12 : A typical atomic nucleus has diameter 0.5×10^{-14} m. Using the uncertainty principle, show that an electron cannot exist inside the nucleus.

Solution : The diameter of the nucleus is $d = 2 \times 0.5 \times 10^{-14}$ m. So for an electron to be confined within the nucleus, the uncertainty in position must not exceed d .

$$\therefore \Delta x = 1 \times 10^{-14} \text{ m}$$

$$\text{We have uncertainty relation } \Delta x \cdot \Delta p \geq \frac{h}{2}$$

$$\therefore \Delta p = \frac{h}{2\Delta x} = \frac{1.055 \times 10^{-34}}{2 \times 10^{-14}} \\ = 0.5275 \times 10^{-20} \text{ kg m/s.}$$

If this is uncertainty in the momentum of electron in the nucleus, the momentum itself must be at least comparable to in magnitude i.e. $p \sim \Delta p$.

$$E = \frac{p^2}{2m} = \frac{(0.5275 \times 10^{-20})^2}{2 \times 9.1 \times 10^{-31}} \\ = 1.5285 \times 10^{-12} \text{ J}$$

$$\therefore E = 1.5825 \times 10^{-12} \text{ J}$$

$$\therefore E = \frac{1.5825 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV} = 0.9890 \times 10^7 \text{ eV} \\ = 9.89 \times 10^6 \text{ eV} = 9.89 \text{ MeV}$$

$$\text{or} \quad E \approx 10 \text{ MeV}$$

This shows that if the electron exists in the nucleus, its energy must be at least 10 MeV. Experiments show that the electron in an atom never has more than a very small fraction of this energy. Thus, the electron cannot be present in the nucleus.

QUESTIONS

1. Give an informative account of dual nature of matter and radiation.
2. What are matter waves? Obtain an expression for their wavelength.
3. Write short notes on wave velocity and group velocity.
4. Obtain the expression for group velocity?
5. Show that the group velocity is equal to the particle velocity.
6. Write a note on de Broglie hypothesis.
7. Write a note on Heisenberg's uncertainty principle. Give different forms of uncertainty relations.

8. Show that $\Delta L \Delta \theta \geq \hbar/2$ and $\Delta E \Delta t \geq \hbar/2$.
9. Discuss the γ ray microscope experiment to illustrate the uncertainty relation.
10. Discuss the electron diffraction experiment to illustrate the uncertainty relation.
11. Show that $v_g = v_p + k \frac{dv_p}{dk}$.
12. Show that $v_g = v_p - \lambda \frac{dv_p}{d\lambda}$.

Interp

PROBLEMS

1. For surface tension waves in shallow water, the relation between frequency and wavelength is given by

$$v = \sqrt{\frac{2\pi T}{\rho \lambda^3}}$$

where T is surface tension and ρ density of water. Find phase velocity and group velocity.

2. What is the energy uncertainty of states with life time of 2.8×10^{-10} s.
(Ans. : 1.178 MeV)
3. A particle moving with kinetic energy equal to its 50 eV has wavelength 2.8 \AA . If the kinetic energy is doubled what would be its wavelength?
(Ans. : 1.97 \AA)
4. Find the de Broglie wavelength of 50 eV electron.
(Ans. : 1.54 \AA)

5. Show that the de Broglie wavelength of a particle of charge 'e', rest mass m_0 , moving with relativistic speeds is given by

$$\lambda = \frac{h}{\sqrt{2m_0 eV}} \sqrt{1 + \frac{eV}{2m_0 c^2}}$$

(Hint: Use relativistic energy $E = \sqrt{p^2 c^2 + m_0^2 c^4}$ and $p = h/\lambda$).

6. An electron has speed of 2×10^4 cm/s accurate to 0.01%. What is uncertainties in the position of electron?
(Ans. : 0.29 cm)
7. The average life time for which electron stays in a given excited state before it jumps to lower energy states is about 10^{-8} seconds. What is the uncertainty in the frequency of emitted spectral lines?
(Ans. : 10^8 Hz)
8. Calculate the de Broglie wavelength of an electron traveling at 1% of the speed of light.
(Ans. : 2.43 \AA)
9. What is the de Broglie wave of neutron whose energy is 1 eV?
(Ans. : 0.286 \AA)

CHAPTER 2

SCHRÖDINGER'S WAVE EQUATION

INTRODUCTION

In classical physics, the motion of a body is governed by the Newton's laws of motion. The position, momentum, angular momentum etc. can be measured precisely at any instant of time. But in quantum mechanics the precise simultaneous measurement of certain pairs of dynamical variables is discarded and we talk in terms of probability.

We have seen in the first chapter that the moving particle has wave nature and the motion of a particle is guided by the wave group. The mathematical function which describes the wave group is the wave function $\Psi(x, y, z, t)$. As the particle moves under the action of external forces, the wave function changes with time. The motion of a particle is described by the wave function $\Psi(x, y, z, t)$. So scientists tried to build up a mathematical formulation based on $\Psi(x, y, z, t)$. In 1926, Erwin Schrödinger developed an equation in terms of $\Psi(x, y, z, t)$. The equation is now called Schrödinger's equation. In subsequent sections we will see the solutions of quantum mechanical problems that can be solved by using this equation.

2.1 PHYSICAL INTERPRETATION OF WAVE FUNCTION

We know that the moving particle has a wave nature. The mathematical function, which describes motion, is the wave function $\Psi(x, y, z, t)$. The wave function contains all the information of associated particle, which is allowed by the uncertainty principle. But the wave function Ψ itself has no physical interpretation, as it may be positive, negative or complex. The basic connection between the properties of the particle and its associated wave function is expressed in terms of the probability density. The square of absolute magnitude of wave function $|\Psi|^2$ (called probability density) evaluated at a particular place at a particular instant of time is proportional to the probability of finding the particle there at that time. As the wave functions are usually complex with real and imaginary parts, the probability density $|\Psi|^2$ is taken as the product $\Psi\Psi^*$, where Ψ^* is a complex conjugate of Ψ . This interpretation was given by Max Born in 1926. According to Born's postulate,

"If, at an instant t , a measurement is made to locate a particle having the wave-function $\Psi(x, t)$, then the probability $P(x, t)$ of finding the particle in a range x and $x + dx$ will be equal to $\Psi(x, t)\Psi^*(x, t) dx$."

Since $|\Psi|^2$ or $\Psi\Psi^*$ represents the probability density, the integral of $|\Psi|^2$ over all space representing the total probability must be finite because the particle is certainly present somewhere. Because of the way of definition of Ψ , $|\Psi|^2$ cannot be negative or complex. Thus, there is only one possibility that the integral of $|\Psi|^2$ or $\Psi\Psi^*$ be a finite quantity. Since the particle under consideration will always be found somewhere, total probability always equal to unity i.e.

$$\int |\Psi|^2 dV = 1$$

or

$$\boxed{\int \Psi\Psi^* dV = 1} \quad \text{normalizing cond}$$

Ψ can be -ve, +ve or complex

Physical interpretation of wave func says that it is a measure of probability of finding a particle in a certain region of space.

Relaⁿ betⁿ wave func & particle \Rightarrow prob^y dens^{ity}

$|\Psi|^2 \Rightarrow$ |wave func|² \propto prob^y of finding particle at that time

The integral in the above equation is carried out over the entire space. The above condition on Ψ is called the *normalisation condition*. The wave function that satisfies the above condition is called normalised wave function.

If $\int \Psi \Psi^* dV$ is finite quantity but not equal unity, the wave function is not normalised.

However, it can be normalised. The normalisation procedure is as follows,

If Ψ is not normalised, multiply it by some constant A . Then evaluate the integral over the entire space and equate it to unity and calculate the constant A called normalisation constant. Thus,

$$\int A \Psi (A \Psi)^* dV = 1$$

$$\text{or } A A^* \int \Psi \Psi^* dV = 1$$

As A is real constant, we get

$$|A|^2 \int \Psi \Psi^* dV = 1$$

This gives normalisation constant as

$$|A|^2 = \frac{1}{\int \Psi \Psi^* dV}$$

The normalisation constant A can be taken as positive square root of the above result.

2.2 SCHRÖDINGER TIME DEPENDENT WAVE EQUATION

In order to obtain Schrödinger wave equation, we will start with an equation of a wave propagating along $+X$ axis. The general equation for the wave motion of a particle is given by

$$y = A e^{i(kx - \omega t)}$$

In quantum mechanics, the wave function Ψ corresponds to the variable y of general wave motion. However, Ψ itself is not a measurable quantity, and may, therefore, be complex. For this reason, we assume that Ψ for a particle moving freely along $+x$ axis is specified by

$$\Psi = A e^{i(kx - \omega t)} \quad \dots(2.1)$$

The de Broglie – Einstein postulates are

$$\lambda = \frac{h}{p} \quad \text{and} \quad E = h\nu$$

We can write above equations as

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k \quad (\because k = 2\pi/\lambda)$$

and

$$E = h\nu = \frac{h}{2\pi} 2\pi\nu = \hbar\omega \quad (\because \omega = 2\pi\nu)$$

Therefore,

$$k = \frac{p}{\hbar} \quad \text{and} \quad \omega = \frac{E}{\hbar}$$

Using these in equation (2.1), we get

$$\Psi = A e^{i\left(\frac{p}{\hbar}x - \frac{E}{\hbar}t\right)}$$

or

$$\Psi = Ae^{\frac{i}{\hbar}(px - Et)} \quad \begin{matrix} (1) \text{ d.w.r.t. } x \text{ (twice)} \\ (2) \text{ d.w.r.t. } t \end{matrix} \quad \dots(2.2)$$

Equation (2.2) represents the wave equivalent of a free particle of total energy E and momentum p moving in the $+x$ direction. Equation (2.2) is true only for the particles moving freely. But we are interested in situations where the motion of particle is constrained by some restrictions. We wish to obtain differential equation for the wave function Ψ , which can be solved in specific situations. This equation is called Schrödinger's equation.

Differentiating equation (2.2) w. r. t. x we get

$$\left(\frac{\partial \Psi}{\partial x}\right) = \frac{ip}{\hbar} Ae^{\frac{i}{\hbar}(px - Et)} \quad \dots(2.3)$$

Again differentiating above equation with respect to x , we get

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x^2} &= -\frac{p^2}{\hbar^2} Ae^{\frac{i}{\hbar}(px - Et)} \\ \therefore \left(\frac{\partial^2 \Psi}{\partial x^2}\right) &= -\frac{p^2}{\hbar^2} \Psi \quad \dots(2.4) \end{aligned}$$

Therefore, from the above equation, we get

$$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \quad \dots(2.5)$$

Differentiating equation (2.2) with respect to t , we get

$$\begin{aligned} \left(\frac{\partial \Psi}{\partial t}\right) &= -\frac{iE}{\hbar} Ae^{\frac{i}{\hbar}(px - Et)} \\ \text{or } \left(\frac{\partial \Psi}{\partial t}\right) &= -\frac{iE}{\hbar} \Psi \end{aligned}$$

Above equation can be written as

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = E\Psi \quad \left(-\frac{1}{i} = i\right)$$

or

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad \dots(2.6)$$

When speed of the particle is small compared to the velocity of light, the total energy E of a particle is the sum of kinetic energy $p^2/2m$ and potential energy $V(x)$. $T.E = K.E + P.E$

$$\frac{1}{2} m v^2 = \frac{1}{2} \frac{m^2 v^2}{m} \quad E = \frac{p^2}{2m} + V \quad \dots(2.7)$$

Multiplying equation (2.7) on both sides by Ψ , we get

$$E\Psi = \frac{p^2 \Psi}{2m} + V\Psi \quad \dots(2.8)$$

Substituting $p^2 \Psi$ and $E\Psi$ from equations (2.5) and (2.6) in equation (2.8), we get

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad \dots(2.9)$$

Equation (2.9) was first obtained by Schrödinger in 1926 and, therefore, called Schrödinger's wave equation. This is Schrödinger's *time dependent equation*. Equation (2.9) is a one-dimensional equation, since it is for motion along X -direction.

In two dimensions, the equation (2.9) can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} \right) + V\Psi \quad \dots(2.10)$$

where $\Psi = \Psi(x, y, t)$

In three dimensions, the equation (2.9) can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + V\Psi$$

or

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad \dots(2.11)$$

where

$$\Psi = \Psi(x, y, z, t)$$

and

$$\nabla^2 \Psi = \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2}$$

2.3 SCHRÖDINGER'S TIME INDEPENDENT EQUATION

In number of situations the potential energy of a particle is independent of the time explicitly and depends on the position only. In such situations Schrödinger's equation is simplified by removing the time dependent part.

□ We have one-dimensional Schrödinger's equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad \dots(2.12)$$

where $\Psi = \Psi(x, t)$

This equation can be solved by separation of variables method.

Let

$$\Psi(x, t) = \psi(x) \phi(t)$$

$$\Psi = \psi \phi \quad \dots(2.13)$$

Using equation (2.13) in (2.12), we get

$$i\hbar \frac{\partial (\psi \phi)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 (\psi \phi)}{\partial x^2} + V(\psi \phi)$$

$$i\hbar \psi \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2m} \phi \frac{\partial^2 \psi}{\partial x^2} + V\psi \phi$$

Dividing above equation throughout by $\psi \phi$, we get

$$\text{L.H.S } \frac{PE}{\psi \phi} \text{ only } i\hbar \frac{1}{\phi} \frac{\partial \phi}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V \text{ } \frac{K.E}{\psi \phi} \text{ only R.H.S} \quad \dots(2.14)$$

The right side of above equation is function of x only and the left side is function of t only. This is possible only when both sides are equal to some constant, say E . We denote this constant as energy E because first term on RHS is kinetic energy and second term is potential energy. Therefore,

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V = E \quad \dots(2.15)$$

and

$$i\hbar \frac{1}{\phi} \frac{\partial \phi}{\partial t} = E \quad \dots(2.16)$$

Equation (2.15) can be written as

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0} \quad \dots(2.17)$$

This is Schrödinger's *one dimensional time independent equation*. Since the differential equation does not involve the time variable 't', the solution ψ also does not depend upon time t. Hence the equation is also called steady state equation or indpt of time.

In three dimensions (x, y, z), Schrödinger's time independent equation is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

or $\boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0} \quad \dots(2.18)$

where $\psi = \psi(x, y, z)$ and $\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$

Solution of time part equation:

Equation (2.16) can be written as

$$\frac{1}{\phi} \frac{\partial\phi}{\partial t} = \frac{1}{i\hbar} E$$

Since ϕ depends only on 't', we have

$$\frac{1}{\phi} \frac{d\phi}{dt} = -\frac{i}{\hbar} E$$

$$\therefore \int \frac{d\phi}{\phi} = -\left(\frac{i}{\hbar} E\right) dt$$

On integration we get,

$$\ln(\phi) = -\frac{i}{\hbar} E t + \ln A \quad \text{where } A \text{ is a constant.}$$

$$\therefore \phi = A e^{-\frac{iE}{\hbar} t}$$

Ignoring the multiplicative constant A, we write

$$\Psi(x, t) = \psi(x) e^{-\frac{iE}{\hbar} t} \quad \dots(2.19)$$

Equation (2.17) is called the time-independent Schrödinger equation, because the time variable does not enter the equation. The solution $\psi(x)$ of equation (2.17) determines the space dependence of the solutions $\Psi(x, t)$ to the Schrödinger's equation. The solutions $\psi(x)$ of equation (2.17) are called *eigen functions*.

In three dimensions, the wave function is given by

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-\frac{iE}{\hbar} t}$$

One should keep clearly in mind the difference between Schrödinger's equation and time-independent Schrödinger equation, and also the difference between eigen function $\psi(x)$ and the wave function $\Psi(x, t)$. In the above wave function is always represented by a capital letter Ψ , and the eigen function by small letter ψ . Eigen function $\psi(x)$ is the solution of time-independent Schrödinger equation, while $\Psi(x, t)$ is the solution of Schrödinger's equation itself and is given by equation (2.19).

2.4 REQUIREMENTS ON WAVE FUNCTION

In the next chapter we will consider some problems of finding solutions of the time-independent Schrödinger's equation. These problems will show that the energy quantisation appears quite naturally when particle moves under certain force field. This is very significant property because it is observed that the acceptable solutions of Schrödinger's time-independent equation can be found only for certain values of the total energy E .

To be an acceptable solution of Schrödinger's time-independent equation, the wave function $\psi(x, y, z)$ and its first order derivative $d\psi/dx$ should satisfy certain requirements. These requirements are :

ψ must be continuous everywhere i.e. at each and every point in the space

ψ must be finite everywhere

ψ must be single valued everywhere

Similarly, the first order derivative must be continuous, finite and single valued every where. These requirements come from the fact that probability of finding the particle at any point in the space is decided by $|\Psi|^2$ and the probability has to be single valued and finite (and less than 1). The probability function has to be continuous because it must have some value (≤ 1) at each and every point in the region of the space over it likely to be found.

In order that $d\psi/dx$ be finite, the wave function must be continuous. If the wave function $\psi(x)$ is discontinuous, the first order derivative $d\psi/dx$ will be infinite at the discontinuity and the second order derivative will also be infinite. We have Schrödinger's time-independent equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

For finite values of E , V and $\psi(x)$, the second order derivative $\frac{d^2\psi}{dx^2}$ must be finite. This requires that $d\psi/dx$ must be finite and hence the wave function should be continuous.

Thus it is necessary that the wave function must be mathematically 'well behaved' and satisfies the above requirements. In Fig. 2.1 the wave functions in (a), (b), (c) and (d) are not acceptable. Wave function in (e) is well behaved and hence acceptable.

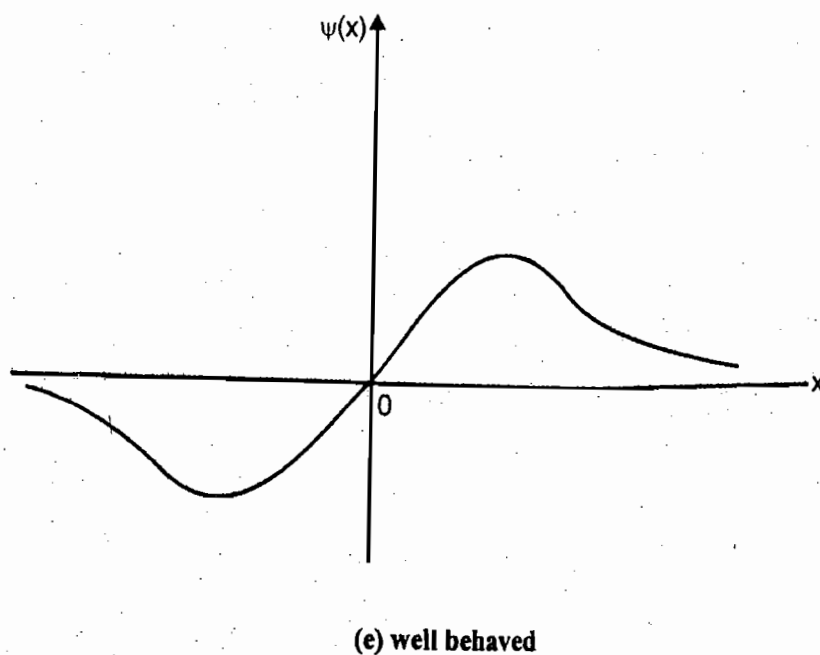
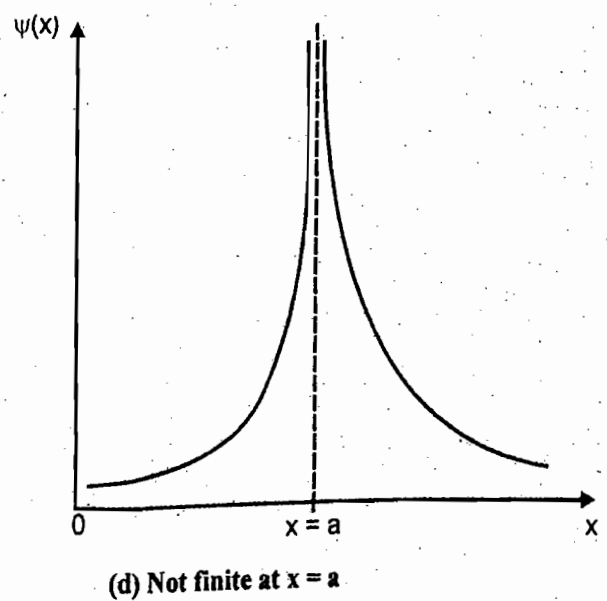
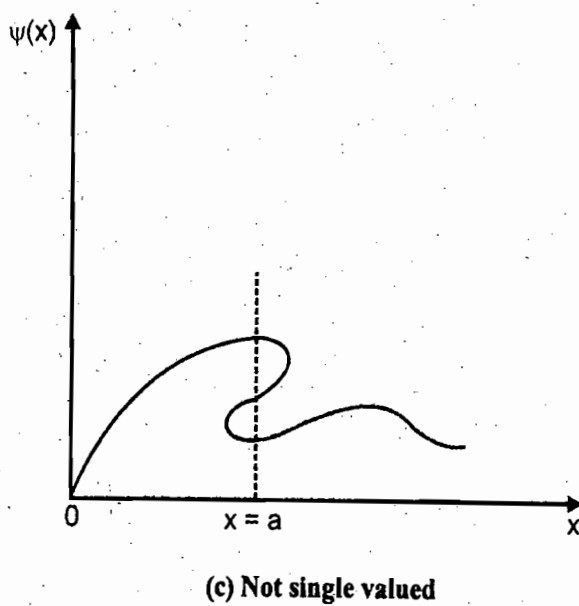
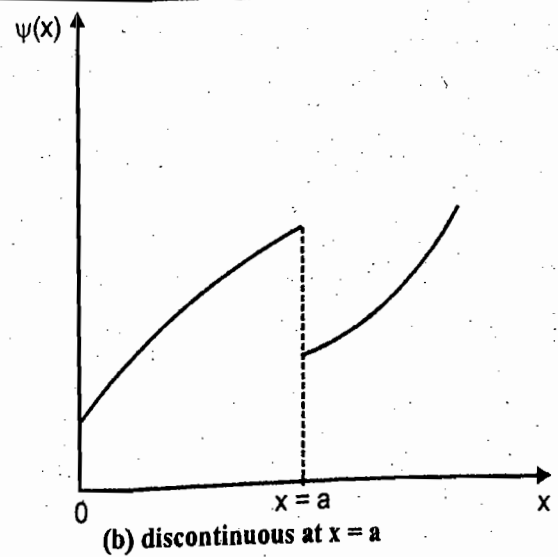
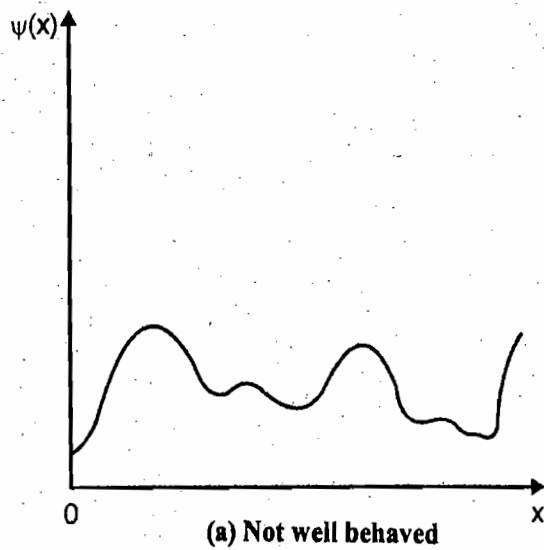


Fig. 2.1 : Different types of wave functions

2.5 PROBABILITY CURRENT DENSITY

Physical interpretation of wave function says that it is a measure of probability of finding a particle in a certain region of space. In general the wave function Ψ may be expressed as $\Psi(\vec{r}, t)$. Depending upon the variables used, it may be denoted as $\Psi(x, y, z, t)$ or $\Psi(r, \theta, \phi)$. The probability density is given as $\rho = \Psi\Psi^*$, where Ψ^* is complex conjugate of Ψ . Since the particle is certainly to be found somewhere in space, the total probability must be equal to unity i.e. $\int \Psi\Psi^* d\tau = 1$, where $d\tau$ is volume element. In other words, the wave function must be normalised

to unity. Now this statement must be true at all times during motion, since the particle will always be found somewhere in a whole region of space. Therefore, total probability must always be conserved i.e. $\Psi\Psi^*$ must be independent of time. This gives

$$\text{indep. } t. \quad - \frac{\partial}{\partial t} \left(\int \Psi\Psi^* d\tau \right) = 0$$

or

$$\int \frac{\partial}{\partial t} (\Psi\Psi^*) d\tau = 0 \quad \dots(2.20)$$

Let us consider the integral $\int \frac{\partial}{\partial t} (\Psi\Psi^*) d\tau$ over an arbitrary volume element τ . We have

$$\int \frac{\partial}{\partial t} (\Psi\Psi^*) d\tau = \int \left[\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t} \right] d\tau \quad \dots(2.21)$$

We have Schrödinger's time dependent equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \quad \dots(2.22)$$

$$\therefore \left(\frac{\partial \Psi}{\partial t} \right) = \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) \text{ complex conjugate}$$

Complex conjugate of equation (2.22) is

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \quad \dots(2.23)$$

$$\therefore \left(\frac{\partial \Psi^*}{\partial t} \right) = -\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right)$$

Using $\frac{\partial \Psi^*}{\partial t}$ and $\frac{\partial \Psi}{\partial t}$ in equation (2.21), we get

$$\begin{aligned} \int \frac{\partial}{\partial t} (\Psi\Psi^*) d\tau &= \int \left[\Psi^* \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) - \Psi \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) \right] d\tau \\ &= \frac{1}{i\hbar} \int \left[\Psi^* \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) - \Psi \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) \right] d\tau \end{aligned}$$

$$= \frac{1}{i\hbar} \int_{\tau} \left[-\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] + \underbrace{\nabla \Psi \Psi^* - \nabla \Psi^* \Psi}_{=0} \right] d\tau$$

Since $\nabla \Psi^* \Psi = \nabla \Psi \Psi^*$, we get

$$\begin{aligned} \int_{\tau} \frac{\partial}{\partial t} (\Psi \Psi^*) d\tau &= \frac{1}{i\hbar} \int_{\tau} \left[-\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] \right] d\tau \\ \int_{\tau} \frac{\partial}{\partial t} (\Psi \Psi^*) d\tau &= -\frac{\hbar}{2mi} \int_{\tau} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] d\tau \quad \dots(2.24) \end{aligned}$$

Using Green's theorem, the volume integral can be converted into surface integral. Therefore,

$$\int_{\tau} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] d\tau = \int_S [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \cdot d\vec{S},$$

where 'S' is the surface which encloses volume τ .

With this equation (2.24) becomes

$$\int_{\tau} \frac{\partial}{\partial t} (\Psi \Psi^*) d\tau = -\frac{\hbar}{2mi} \int_S [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \cdot d\vec{S}$$

or

$$\int_{\tau} \frac{\partial}{\partial t} (\Psi \Psi^*) d\tau = - \int_S \frac{\hbar}{2mi} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \cdot d\vec{S}$$

Let

$$\vec{J} = \frac{\hbar}{2mi} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \quad \dots(2.25)$$

$$\therefore \frac{\partial}{\partial t} \left(\int_{\tau} \Psi \Psi^* d\tau \right) = - \int_S \vec{J} \cdot d\vec{S}$$

$$\therefore \int_{\tau} \frac{\partial \rho}{\partial t} d\tau = - \int_S \vec{J} \cdot d\vec{S} \quad \dots(2.26)$$

According to Gauss divergence theorem, $\int_S \vec{J} \cdot d\vec{S} = \int_{\tau} \nabla \cdot \vec{J} d\tau$

Using in equation (2.26), we get

$$\int_{\tau} \frac{\partial \rho}{\partial t} d\tau = - \int_{\tau} \nabla \cdot \vec{J} d\tau$$

$$\therefore \int_{\tau} \left(\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} \right) d\tau = 0$$

This is true for any arbitrary volume. Therefore,

$$\nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0 \quad \dots(2.27)$$

Equation (2.27) is called equation of continuity. The form of the equation is the same as the equation of continuity in fluid mechanics. We have

$$\vec{J} = \frac{\hbar}{2mi} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*] \quad (2.24)$$

\vec{J} is called probability current density.

fore, It can also be written as

$$\vec{J} = \text{Re} \left[\Psi^* \frac{\hbar}{im} \nabla \Psi \right]$$

Here Re stands for real part of the quantity inside the bracket.

Physical significance of equation of continuity

(1) Equation (2.26) may be written as

$$\nabla \cdot \vec{J} = - \frac{\partial \rho}{\partial t}$$

If $\frac{\partial \rho}{\partial t}$ is positive, $\nabla \cdot \vec{J}$ is negative, then there is net inward flow of the probability current states

and there is increase in total probability inside a given region. If there is increase in probability density in a given volume, there is decrease in density somewhere else.

If $\frac{\partial \rho}{\partial t}$ is negative, $\nabla \cdot \vec{J}$ is positive, then there is net outward flow of the probability current and there is decrease in total probability in a given region. If there is decrease in probability density in a given volume, there is increase in density somewhere else.

(2) If for any states ρ is independent of time, then $\frac{\partial \rho}{\partial t} = 0$. Thus, $\nabla \cdot \vec{J} = 0$. These states are called stationary states.

2.6 DEFINITION OF AN OPERATOR

The mathematical operation like differentiation, integration, multiplication, division, addition, subtraction etc. can be represented by certain symbols known as operators. In other words an operator \hat{O} is a mathematical operation which may be applied to function $f(x)$, which changes the function $f(x)$ to another function say $g(x)$. This can be represented as

$$\hat{O} f(x) = g(x)$$

For example,

$$\hat{O} \left(\frac{d}{dx} (4x^2 + 2x) \right) = 8x + 2$$

$f(x) \quad g(x)$

In operator language $\hat{O} = \frac{d}{dx}$ operates on the function $f(x) = 4x^2 + 2x$ and changes the function $f(x)$ to function $g(x) = 8x + 2$.

Operators in Quantum mechanics

The wave function for one-dimensional motion of a free particle along x-axis is given as

$$\Psi(x, t) = A e^{\frac{i}{\hbar}(px - Et)}$$

Differentiating equation (2.2) with respect to x we get

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} A e^{\frac{i}{\hbar}(px - Et)}$$

or

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} \Psi$$

\therefore

$$p\Psi = \hbar \frac{\partial \Psi}{\partial x}$$

or

$$p\Psi = -i\hbar \frac{\partial \Psi}{\partial x} \text{ momentum operator} \quad \dots(2.28)$$

Differentiating $\Psi(x, t)$ with respect to t , we get

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} A e^{\frac{i}{\hbar}(px - Et)}$$

or

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$$

\therefore

$$-i\hbar \frac{\partial \Psi}{\partial t} = E\Psi$$

or

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad \dots(2.29)$$

Equation (2.28) indicates that there is an association between the dynamical quantity p and the differential operator $-i\hbar \frac{\partial}{\partial x}$. That is the effect of multiplying $\Psi(x, t)$ by p is the same as the operating the differential operator $-i\hbar \frac{\partial}{\partial x}$ on $\Psi(x, t)$. This differential operator $\left(-i\hbar \frac{\partial}{\partial x}\right)$ is called momentum operator. It can be written as

$$\hat{p} = -i\hbar \frac{\partial}{\partial x} \quad \dots(2.30)$$

As it is related to variable x , we have

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

Corresponding components of momentum operators for y and z variables are

$$\hat{p}_y = -i\hbar \frac{\partial}{\partial y}$$

and

$$\hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

In three dimensions, the momentum operator is

$$\hat{\vec{p}} = -i\hbar \nabla$$

From equation (2.29), a similar association can be found between dynamical variable E and the differential operator $i\hbar \frac{\partial}{\partial t}$. Thus,

$$E = i\hbar \frac{\partial}{\partial t} \quad \dots(2.31)$$

We have Schrödinger's time independent equation

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

$$\text{or} \quad -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

$$\text{or} \quad \left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = E\psi \quad \dots(2.32)$$

$$\text{or} \quad H\psi = E\psi$$

where $H = -\frac{\hbar^2}{2m} \nabla^2 + V$ is called as *Hamiltonian operator*, since $H = K.E. + P.E. = T + V$ is the Hamiltonian of the system.]

2.7 EIGEN FUNCTIONS AND EIGEN VALUES

[Let ψ be a well behaved function of the state of the system and an operator \hat{A} operates on this function such that it satisfies the equation

$$\hat{A} \psi(x) = a \psi(x) \quad \dots(2.33)$$

eigenvalue *eigen function*

where a is a scalar. Then we say that a is an eigen value of the operator \hat{A} and the operand $\psi(x)$ is called the eigen function of \hat{A} . Eigen is the german word meaning characteristic or proper.

For example,

$$\frac{d^2}{dx^2} e^{4x} = 16 e^{4x}$$

We say that $\frac{d^2}{dx^2}$ is the operator operating on function e^{4x} giving result $16 e^{4x}$. The operand e^{4x} is called eigen function of operator $\frac{d^2}{dx^2}$ and 16 is the eigen value.

The total energy operator E of equation (2.31) is usually written as

$$E = -\frac{\hbar^2}{2m} \nabla^2 + V$$

and is usually called the Hamiltonian operator. If the Hamiltonian operator $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$ operates on a wave function ψ_n , we get

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi_n = E_n \psi_n$$

$$\text{or} \quad H \psi_n = E_n \psi_n$$

The wave function ψ_n is called eigen function and E_n is the corresponding energy eigen value of the Hamiltonian operator H .

2.8 EXPECTATION VALUES

□ The minimum uncertainty with which two conjugate pairs of physical quantities can be measured is given by

$$\Delta x, \Delta p_x \geq \frac{\hbar}{2} \quad \text{or} \quad \Delta E, \Delta t \geq \frac{\hbar}{2}$$

position & momentum *energy & time*

When Schrödinger's wave equation is solved for a particle with necessary boundary conditions, the solution $\Psi(x, y, z, t)$ gives all information as regards position, momentum, energy etc. as permitted by the Heisenberg's uncertainty principle. This information is in terms of probability and not in terms of exact values.

Consider a wave function $\Psi(x, t)$ associated with a particle. In measurement of position of a particle in a system described by wave function, there is certain finite probability however small that a particle be found at any the position x within the range x and $x + dx$ as long as the wave function is not zero in this range. Generally, wave function is non-zero over the extended range of x -axis. Thus, in general, we are not able to state that x co-ordinate has a definite value. We, therefore, calculate average of x of the position of the particle. If $P(x, t) dx = \Psi(x, t) \Psi^*(x, t) dx$ be the probability of finding the particle in a range x and $x + dx$. Then the expectation value of x over whole range is given by

$$\langle x \rangle = \frac{\int x P(x, t) dx}{\int P(x, t) dx}$$

$$\text{or} \quad \langle x \rangle = \frac{\int \Psi^* x \Psi dx}{\int \Psi^* \Psi dx} \quad \dots(2.34)$$

If the wave function is normalised, we have $\int \Psi^* \Psi dx = 1$ for whole region, then

$$\langle x \rangle = \int \Psi^* x \Psi dx \quad \dots(2.35)$$

Thus, in general, the expectation value of any dynamical variable f which is a scalar function of (x, t) obtained as follows

$$\langle f \rangle = \frac{\int \Psi^* f \Psi dx}{\int \Psi^* \Psi dx}$$

For normalised wave function,

$$\langle f \rangle = \int \Psi^* f \Psi dx$$

The expectation value of momentum and energy cannot be found in the same way.

In order to obtain expectation value of p_x and E corresponding operators are used in integrand. Thus,

$$\langle p \rangle = \int \Psi^* \hat{p} \Psi dx$$

$$= \int \Psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi dx$$

$$\langle p \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx \quad \dots(2.36)$$

Similarly,

$$\langle E \rangle = \int \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi dx$$

or

$$\langle E \rangle = i\hbar \int \Psi^* \frac{\partial \Psi}{\partial t} dx \quad \dots(2.37)$$

Thus, if a dynamical variable 'a' is expressed in terms of its operator \hat{A} , the expectation value is obtained by using the following relation

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi dx$$

In general

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi d\tau$$

where $d\tau$ represents the typical volume element of the entire space.

2.9 EHRENFEST'S THEOREM

We know that momentum \vec{p} of a particle is mass m multiplied by velocity \vec{v} i.e. $\vec{p} = m\vec{v}$

In case of one-dimensional motion $p_x = m \frac{dx}{dt}$ or $\frac{dx}{dt} = \frac{p_x}{m}$. According to Heisenberg's uncertainty principle x and p_x cannot be determined simultaneously with arbitrary accuracy. So x is uncertain to the extent the overall size of the wave group. Accordingly p_x is also uncertain. Question then

arise: what is the relation corresponding to $\frac{dx}{dt} = \frac{p_x}{m}$ or $\frac{d\vec{r}}{dt} = \frac{\vec{p}}{m}$ in quantum mechanics? The answer is provided by Ehrenfest Theorem. The classical relations between the variables associated with the moving particles hold provided the physical quantities are replaced by their respective expectation values. In other words the theorem states that the average motion of wave packet agrees with the motion of the corresponding classical motion of particle. This is, in fact, the Ehrenfest theorem.

Thus for one-dimensional motion along x-axis:

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}$$

For motion in any direction

$$\frac{d\langle \vec{r} \rangle}{dt} = \frac{\langle \vec{p} \rangle}{m}$$

The above relation is often called 'Ehrenfest's first theorem'

For motion of a particle along x-axis in a conservative force field

$$\frac{d\langle p_x \rangle}{dt} = \left\langle -\frac{dV}{dx} \right\rangle$$

In general,

$$\frac{d\langle \vec{p} \rangle}{dt} = \langle -\nabla V \rangle \quad \text{second thm}$$

Proof of first theorem:

The expectation value of x is given as

$$\frac{d}{dt} \langle \bar{x} \rangle = \frac{\langle p \rangle}{m}$$

$$\langle x \rangle = \int \Psi^* x \Psi d\tau \quad \frac{d}{dt} \Psi^* (x \Psi) = \frac{d\Psi^*}{dt} x \Psi + \Psi^* \frac{d(x\Psi)}{dt}$$

$$\therefore \frac{d\langle x \rangle}{dt} = \int \left(\frac{d\Psi^*}{dt} x \Psi + \Psi^* x \frac{d\Psi}{dt} \right) d\tau \quad \dots(2.38)$$

We have Schrödinger's time dependent equation

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

$$\therefore \frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right)$$

Complex conjugate of above equation is

$$\frac{\partial \Psi^*}{\partial t} = -\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right)$$

In the above we have used $V = V^*$, since V is real.

Using $\frac{\partial \Psi^*}{\partial t}$ and $\frac{\partial \Psi}{\partial t}$ in equation (2.38), we get

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \int \left[\left(-\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \right) \right) x \Psi + \Psi^* x \left(\frac{1}{i\hbar} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi \right) \right) \right] d\tau \\ &= \frac{\hbar}{2mi} \int_{\tau} [(\nabla^2 \Psi^*) x \Psi - \Psi^* x (\nabla^2 \Psi)] d\tau \\ &= \frac{\hbar}{2mi} \left[\int_{\tau} (\nabla^2 \Psi^*) x \Psi d\tau - \int_{\tau} \Psi^* x (\nabla^2 \Psi) d\tau \right] \quad \dots(2.39) \end{aligned}$$

Green's second theorem is given as $vol \rightarrow surf$

$$\int_{\tau} [\Psi_1 (\nabla^2 \Psi_2) - \Psi_2 (\nabla^2 \Psi_1)] d\tau = \int_S [\Psi_1 \nabla \Psi_2 - \Psi_2 \nabla \Psi_1] \cdot \vec{dS}$$

where S is the surface which encloses the volume τ .

Let $\Psi_1 = \Psi^*$ and $\Psi_2 = x\Psi$

Then using the above theorem, we get

$$\int_{\tau} [\Psi^* \nabla^2 (x\Psi) - (x\Psi) \nabla^2 \Psi^*] d\tau = \int_S [\Psi^* \nabla (x\Psi) - (x\Psi) \nabla \Psi^*] \cdot \vec{dS} \quad \dots(2.40)$$

Since the volume integral is over the entire space, the surface ' S ' which encloses the entire volume will be at infinity. But $\Psi \rightarrow 0$ and $\nabla \Psi \rightarrow 0$ at infinity. Hence the surface integral in the above case vanishes at infinity. Therefore, from equation (2.40), we get

$$\int_{\tau} [\Psi^* \nabla^2 (x\Psi) - (x\Psi) \nabla^2 \Psi^*] d\tau = 0$$

$$\text{or} \quad \int_{\tau} \Psi^* \nabla^2 (x\Psi) d\tau - \int_{\tau} (x\Psi) \nabla^2 \Psi^* d\tau = 0$$

$$\text{This gives} \quad \int_{\tau} (x\Psi) \nabla^2 \Psi^* d\tau = \int_{\tau} \Psi^* \nabla^2 (x\Psi) d\tau \quad \dots(2.41)$$

Using equation (2.41) in the first term on RHS of equation (2.39), we get

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= \frac{\hbar}{2mi} \left[\int_{\tau} \Psi^* \nabla^2 (x\Psi) d\tau - \int_{\tau} \Psi^* x (\nabla^2 \Psi) d\tau \right] \\ \frac{d\langle x \rangle}{dt} &= -\frac{i\hbar}{2m} \left[\int_{\tau} \Psi^* \nabla^2 (x\Psi) d\tau - \int_{\tau} \Psi^* x (\nabla^2 \Psi) d\tau \right] \quad \dots(2.42) \end{aligned}$$

Now consider the term $\nabla^2 (x\Psi)$

$$\begin{aligned} \text{We have} \quad \nabla^2 (x\Psi) &= \frac{\partial^2 (x\Psi)}{\partial x^2} + \frac{\partial^2 (x\Psi)}{\partial y^2} + \frac{\partial^2 (x\Psi)}{\partial z^2} \\ &= \frac{\partial}{\partial x} \frac{\partial (x\Psi)}{\partial x} + \frac{\partial^2 (x\Psi)}{\partial y^2} + \frac{\partial^2 (x\Psi)}{\partial z^2} \\ &= \frac{\partial}{\partial x} \left(\Psi + x \frac{\partial \Psi}{\partial x} \right) + x \frac{\partial^2 \Psi}{\partial y^2} + x \frac{\partial^2 \Psi}{\partial z^2} \\ &= \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi}{\partial x} + x \frac{\partial^2 \Psi}{\partial x^2} + x \frac{\partial^2 \Psi}{\partial y^2} + x \frac{\partial^2 \Psi}{\partial z^2} \\ &= 2 \frac{\partial \Psi}{\partial x} + x \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) \\ \therefore \quad \nabla^2 (x\Psi) &= 2 \frac{\partial \Psi}{\partial x} + x \nabla^2 \Psi \end{aligned}$$

Using this in equation (2.42), we get

$$\begin{aligned} \frac{d\langle x \rangle}{dt} &= -\frac{i\hbar}{2m} \left[\int_{\tau} \Psi^* \left(2 \frac{\partial \Psi}{\partial x} + x \nabla^2 \Psi \right) d\tau - \int_{\tau} \Psi^* x (\nabla^2 \Psi) d\tau \right] \\ &= -\frac{i\hbar}{2m} \left[\int_{\tau} \Psi^* \left(2 \frac{\partial \Psi}{\partial x} \right) + \int_{\tau} \Psi^* x \nabla^2 \Psi d\tau - \int_{\tau} \Psi^* x (\nabla^2 \Psi) d\tau \right] \\ &= -\frac{i\hbar}{2m} \int_{\tau} \Psi^* \left(2 \frac{\partial \Psi}{\partial x} \right) d\tau \\ &= -\frac{i\hbar}{m} \int_{\tau} \Psi^* \left(\frac{\partial \Psi}{\partial x} \right) d\tau \end{aligned}$$

$$\therefore \frac{d\langle x \rangle}{dt} = \frac{1}{m} \left[-i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \right]$$

But from equation (2.36), $\langle p_x \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx$

$$\therefore \frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m} \quad \dots(2.43)$$

This is the required result, corresponding to the classical relation between position and velocity. Similarly,

$$\frac{d\langle y \rangle}{dt} = \frac{\langle p_y \rangle}{m} \text{ and } \frac{d\langle z \rangle}{dt} = \frac{\langle p_z \rangle}{m}$$

Therefore, in general,

$$\frac{d\langle \vec{r} \rangle}{dt} = \frac{\langle \vec{p} \rangle}{m}$$

Proof of second theorem:

We have expectation value of momentum

$$\langle p_x \rangle = -i\hbar \int \Psi^* \frac{\partial \Psi}{\partial x} dx$$

Differentiating with respect to t, we get

$$\frac{d\langle p_x \rangle}{dt} = -i\hbar \frac{\partial}{\partial t} \int \Psi^* \frac{\partial \Psi}{\partial x} dx$$

$$= -i\hbar \int \left(\frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t} \right) dx$$

$$= -i\hbar \int \left(\frac{\partial \Psi^*}{\partial t} \frac{\partial \Psi}{\partial x} + \Psi^* \frac{\partial}{\partial x} \frac{\partial \Psi}{\partial t} \right) dx$$

$$\therefore \frac{d\langle p_x \rangle}{dt} = \int_{-\infty}^{\infty} \left[\left(-i\hbar \frac{\partial \Psi^*}{\partial t} \right) \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} \left(i\hbar \frac{\partial \Psi}{\partial t} \right) \right] dx \quad \dots(2.44)$$

We have Schrödinger's time dependent equation.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

Complex conjugate of above equation is

$$-i\hbar \frac{\partial \Psi^*}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V\Psi^* \quad (\because V = V^* \text{ being real})$$

Using above two equations in equation (2.44), we get

$$\begin{aligned}\frac{d\langle p_x \rangle}{dt} &= \int_{\tau} \left[\left(-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V \Psi^* \right) \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial}{\partial x} \left(-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \right) \right] d\tau \\ &= \int_{\tau} \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} + V \Psi^* \frac{\partial \Psi}{\partial x} + \frac{\hbar^2}{2m} \Psi^* \frac{\partial}{\partial x} (\nabla^2 \Psi) - \Psi^* \frac{\partial V \Psi}{\partial x} \right] d\tau \\ &= \int_{\tau} \left[-\frac{\hbar^2}{2m} \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} + V \Psi^* \frac{\partial \Psi}{\partial x} + \frac{\hbar^2}{2m} \Psi^* \nabla^2 \left(\frac{\partial \Psi}{\partial x} \right) - \Psi^* \frac{\partial V \Psi}{\partial x} \right] d\tau\end{aligned}$$

Rearranging the terms on RHS we get

$$\frac{d\langle p_x \rangle}{dt} = \frac{\hbar^2}{2m} \int_{\tau} \left[\Psi^* \nabla^2 \left(\frac{\partial \Psi}{\partial x} \right) - \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} \right] d\tau + \int_{\tau} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial V \Psi}{\partial x} \right] d\tau \quad \dots(2.45)$$

Consider the integral of the first term $\int_{\tau} \left[\Psi^* \nabla^2 \left(\frac{\partial \Psi}{\partial x} \right) - \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} \right] d\tau$. Using Green's second theorem, we can convert this integral into surface integral i.e.

$$\int_{\tau} \left[\Psi^* \nabla^2 \left(\frac{\partial \Psi}{\partial x} \right) - \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} \right] d\tau = \int_S \left[\Psi^* \nabla \left(\frac{\partial \Psi}{\partial x} \right) - \nabla \Psi^* \frac{\partial \Psi}{\partial x} \right] \cdot d\vec{S}$$

But the surface S encloses the entire volume. The surface is at infinity, but at infinity Ψ and its first order derivative tends to zero. Therefore, the surface integral is zero. Thus, we get

$$\int_{\tau} \left[\Psi^* \nabla^2 \left(\frac{\partial \Psi}{\partial x} \right) - \nabla^2 \Psi^* \frac{\partial \Psi}{\partial x} \right] d\tau = 0$$

Using in equation (2.45), we get

$$\begin{aligned}\frac{d\langle p_x \rangle}{dt} &= \int_{\tau} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial V \Psi}{\partial x} \right] d\tau \\ &= \int_{\tau} \left[V \Psi^* \frac{\partial \Psi}{\partial x} - \Psi^* \frac{\partial V}{\partial x} \Psi - \Psi^* V \frac{\partial \Psi}{\partial x} \right] d\tau \\ &= \int_{\tau} \left[-\Psi^* \frac{\partial V}{\partial x} \Psi \right] d\tau\end{aligned}$$

$$\therefore \frac{d\langle p_x \rangle}{dt} = \int_{\tau} \Psi^* \left(-\frac{\partial V}{\partial x} \right) \Psi d\tau$$

The RHS of the above equation represents the expectation value of $-\frac{\partial V}{\partial x}$

$$\therefore \frac{d\langle p_x \rangle}{dt} = \left\langle -\frac{dV}{dx} \right\rangle$$

Similarly, $\frac{d\langle p_y \rangle}{dt} = \left\langle -\frac{dV}{dy} \right\rangle$ and $\frac{d\langle p_z \rangle}{dt} = \left\langle -\frac{dV}{dz} \right\rangle$. Therefore, $\frac{d\langle \vec{p} \rangle}{dt} = \langle -\nabla V \rangle$.

Thus there exists a relation among expectation values which is exactly parallel to Newton's second law expressed in terms of potential energy.

ILLUSTRATIVE EXAMPLES

Example 1 : A wave function of a particle moving in the range $-\infty$ to $+\infty$ is given by

$$\psi(x) = e^{-\alpha x^2/2}$$

Normalise the wave function and find the expectation value of x and p_x .

Solution : In order to normalise the wave function, multiply the rhs by constant A.

$$\therefore \psi(x) = A e^{-\alpha x^2/2}$$

Condition for normalisation is

$$\int |\Psi|^2 dx = 1 \quad \text{or} \quad \int \Psi \Psi^* dx = 1$$

$$\therefore \int_{-\infty}^{\infty} A e^{-\alpha x^2/2} A^* e^{-\alpha x^2/2} dx = 1$$

$$\therefore AA^* \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$

$$\text{or} \quad |A|^2 \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = 1$$

We have the general integral $\int_{-\infty}^{\infty} e^{-\beta x^2} dx = \sqrt{\frac{\pi}{\beta}}$

$$\therefore |A|^2 \sqrt{\frac{\pi}{\alpha}} = 1$$

$$\therefore |A|^2 = \sqrt{\frac{\alpha}{\pi}}$$

$$\text{or} \quad A = \left(\frac{\alpha}{\pi} \right)^{1/4}$$

$$\therefore \psi(x) = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2}$$

Expectation value of x is given as

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \Psi x \Psi^* dx = \int_{-\infty}^{\infty} x |\Psi|^2 dx$$

$$\begin{aligned} \therefore \langle x \rangle &= \int_{-\infty}^{\infty} x \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} dx \\ &= \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx \end{aligned}$$

The integral on RHS is odd integral and its value over the entire range $(-\infty, \infty)$ is zero.

$$\therefore \langle x \rangle = 0$$

The expectation value of $\langle p_x \rangle$ is given as

$$\langle p_x \rangle = -i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx$$

$$= -i\hbar \int_{-\infty}^{\infty} \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \frac{\partial}{\partial x} \left(\left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha x^2/2} \right) dx$$

$$= -i\hbar \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \frac{\partial}{\partial x} (e^{-\alpha x^2/2}) dx$$

$$= -i\hbar \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} (-\alpha x) e^{-\alpha x^2/2} dx$$

$$= i\hbar \alpha \left(\frac{\alpha}{\pi} \right)^{1/2} \int_{-\infty}^{\infty} x e^{-\alpha x^2} dx$$

The integral on RHS is odd integral and its value is zero.

$$\therefore \langle p_x \rangle = 0$$

Example 2 : Normalise the wave function $\psi(x) = \frac{1+ix}{1+ix^2}$. The range of x is from $-\infty$ to $+\infty$.

Solution : Let $\psi(x) = A \frac{1+ix}{1+ix^2}$, where A is the normalisation constant.

$$\psi^* \psi = A^* \frac{1-ix}{1-ix^2} A \frac{1+ix}{1+ix^2} = |A|^2 \frac{1+x^2}{1+x^4}$$

Condition for normalisation is

$$\int |\Psi|^2 dx = 1 \quad \text{or} \quad \int \Psi \Psi^* dx = 1$$

$$\therefore |A|^2 \int_{-\infty}^{\infty} \frac{1+x^2}{1+x^4} dx = 1 \quad \text{both N\&D} \quad \text{Let, } t = x - \frac{1}{x} \quad \dots(i)$$

In the integrand of equation (i), dividing each term in the numerator and denominator by x^2 , we get,

$$\int_{-\infty}^{\infty} \frac{1+x^2}{1+x^4} dx = \int_{-\infty}^{\infty} \frac{1+1/x^2}{x^2+1/x^2} dx \quad \dots(ii)$$

Let $x - \frac{1}{x} = t$ (i) sq (ii) d.w.r.t ... (iii)

Squaring on both sides, we get

$$x^2 - 2 + \frac{1}{x^2} = t^2$$

$$\therefore x^2 + \frac{1}{x^2} = t^2 + 2$$

Differentiating equation (iii) above we get,

$$\left(1 + \frac{1}{x^2}\right) dx = dt$$

Using these in equation (ii) above, we get,

$$\int_{-\infty}^{\infty} \frac{1+x^2}{1+x^4} dx = \int_{-\infty}^{\infty} \frac{1}{t^2+2} dt$$

From equation (iii) it is easily observed that as $x \rightarrow \infty$, $t \rightarrow \infty$ and as $x \rightarrow -\infty$, $t \rightarrow -\infty$.

Therefore, equation (i) becomes

$$\therefore |A|^2 \int_{-\infty}^{\infty} \frac{1}{t^2+2} dt = 1 \quad \text{Handwritten: } \int_{-\infty}^{\infty} \frac{1}{x^2+a^2} dx = \frac{1}{a} \tan^{-1}\left(\frac{x}{a}\right)$$

$$\therefore |A|^2 \left[\frac{1}{\sqrt{2}} \tan^{-1}\left(\frac{t}{\sqrt{2}}\right) \right]_{-\infty}^{\infty} = 1$$

$$|A|^2 \frac{1}{\sqrt{2}} \left[\frac{\pi}{2} - \left(-\frac{\pi}{2}\right) \right] = 1$$

$$|A|^2 \frac{\pi}{\sqrt{2}} = 1$$

$$\therefore A = \left(\frac{\sqrt{2}}{\pi} \right)^{1/2}$$

$$\therefore \psi(x) = \left(\frac{\sqrt{2}}{\pi} \right)^{1/2} \frac{1+ix}{1+ix^2}$$

Example 3 : Find the expectation value of momentum and position for a particle having wave function

$$\Psi(x, t) = A e^{-x^2/2a + ikx}$$

The range of x is from $-\infty$ to $+\infty$.

Solution : If A is the normalisation constant, then $\int \Psi \Psi^* dx = 1$

$$\therefore \int_{-\infty}^{\infty} A e^{-x^2/2a + ikx} A^* e^{-x^2/2a - ikx} dx = 1$$

$\left(-\frac{x^2}{2a} + ikx \right) + \left(-\frac{x^2}{2a} - ikx \right)$
 $-x^2/a$

$$\text{or } |A|^2 \int_{-\infty}^{\infty} e^{-x^2/a} dx = 1 \quad \dots(i)$$

Expectation value of $\langle x \rangle$ is given as

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} \Psi x \Psi^* dx \\ &= |A|^2 \int_{-\infty}^{\infty} x e^{-x^2/a} dx \end{aligned}$$

But the integral on RHS is an odd integral. Therefore, it is zero.

$$\therefore \langle x \rangle = 0$$

The expectation value of $\langle p_x \rangle$ is given as

$$\begin{aligned} \langle p_x \rangle &= -i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} dx \\ &= -i\hbar \int_{-\infty}^{\infty} A e^{-x^2/2a + ikx} \frac{\partial}{\partial x} (A^* e^{-x^2/2a - ikx}) dx \\ &= -i\hbar |A|^2 \int_{-\infty}^{\infty} e^{-x^2/2a + ikx} \frac{\partial}{\partial x} (e^{-x^2/2a - ikx}) dx \\ &= -i\hbar |A|^2 \int_{-\infty}^{\infty} e^{-x^2/2a + ikx} \left(-\frac{x}{a} - ik \right) e^{-x^2/2a - ikx} dx \end{aligned}$$

$$\begin{aligned}\therefore \langle p_x \rangle &= -i\hbar |A|^2 \int_{-\infty}^{\infty} \left(e^{-x^2/2a + ikx} \left(-\frac{x}{a} \right) e^{-x^2/2a - ikx} - e^{-x^2/2a + ikx} ik e^{-x^2/2a - ikx} \right) dx \\ &= |A|^2 \frac{i\hbar}{a} \int_{-\infty}^{\infty} x e^{-x^2/a} dx + \hbar k |A|^2 \int_{-\infty}^{\infty} e^{-x^2/a} dx\end{aligned}$$

The first integrand on RHS is odd integral and hence is zero. In the second term, we use equation (i).

$$\therefore \langle p_x \rangle = \hbar k$$

Example 4 : Consider the wave function of a particle

$$\Psi(x) = A \left(1 - \frac{x}{a} \right) \text{ for } a/2 < x < a$$

Find the normalisation constant A and also obtain $\langle x \rangle$.

Solution: $|\Psi(x)|^2 = |A|^2 \left(1 - \frac{x}{a} \right)^2 = |A|^2 \left(1 - \frac{2x}{a} + \frac{x^2}{a^2} \right)$

We have $\int_{a/2}^a |\Psi(x)|^2 dx = 1$

$$\therefore |A|^2 \int_{a/2}^a \left(1 - \frac{2x}{a} + \frac{x^2}{a^2} \right) dx = 1$$

$$|A|^2 \left[x - \frac{x^2}{a} + \frac{x^3}{3a^2} \right]_{a/2}^a = 1$$

$$|A|^2 \left[a - \frac{a^2}{a} + \frac{a^3}{3a^2} - \left(\frac{a}{2} - \frac{a^2}{4a} + \frac{a^3}{24a^2} \right) \right] = 1$$

$$|A|^2 \left(\frac{a}{24} \right) = 1$$

$$\therefore |A| = \sqrt{\frac{24}{a}}$$

$$\therefore \Psi(x) = \sqrt{\frac{24}{a}} \left(1 - \frac{x}{a} \right)$$

Expectation value of x is given as

$$\langle x \rangle = \int_{a/2}^a x |\Psi(x)|^2 dx$$

Therefore,

$$\begin{aligned}
 \langle x \rangle &= |A|^2 \int_{a/2}^a x \left(1 - \frac{2x}{a} + \frac{x^2}{a^2} \right) dx \\
 &= \frac{24}{a} \int_{a/2}^a \left(x - \frac{2x^2}{a} + \frac{x^3}{a^2} \right) dx \\
 &= \frac{24}{a} \left[\frac{x^2}{2} - \frac{2x^3}{3a} + \frac{x^4}{4a^2} \right]_{a/2}^a \\
 &= \frac{24}{a} \left[\frac{a^2}{2} - \frac{2a^3}{3a} + \frac{a^4}{4a^2} - \left(\frac{a^2}{8} - \frac{2a^3}{24a} + \frac{a^4}{64a^2} \right) \right] \\
 &= \frac{24}{a} \left[\frac{a^2}{2} - \frac{2a^3}{3a} + \frac{a^4}{4a^2} - \frac{a^2}{8} + \frac{2a^3}{24a} - \frac{a^4}{64a^2} \right] \\
 &= \frac{24}{a} a^2 \left[\frac{1}{2} - \frac{2}{3} + \frac{1}{4} - \frac{1}{8} + \frac{2}{24} - \frac{1}{64} \right] \\
 \therefore \langle x \rangle &= 0.625 a
 \end{aligned}$$

Example 5 : Normalise the wave function

$$\Psi(x) = A e^{-x^2/2a^2 + ikx}$$

The range of x is from $-\infty$ to $+\infty$.

Solution : If A is the normalisation constant, then $\int \Psi \Psi^* dx = 1$

$$\therefore \int_{-\infty}^{\infty} A e^{-x^2/2a^2 + ikx} A^* e^{-x^2/2a^2 - ikx} dx = 1$$

or $|A|^2 \int_{-\infty}^{\infty} e^{-x^2/a^2} dx = 1$

We have the general integral $\int_{-\infty}^{\infty} e^{-\beta x^2} dx = \sqrt{\frac{\pi}{\beta}}$

Therefore,

$$|A|^2 \sqrt{\frac{\pi}{1/a^2}} = 1$$

$$|A|^2 a \sqrt{\pi} = 1$$

$$\therefore |A| = \frac{1}{\sqrt{a \pi}}$$

$$\psi(x) = \frac{1}{\sqrt{a \pi}} e^{-x^2/2a^2 + ikx}$$

Example 6 : Find the current density if the wave function is $\psi(x) = Ae^{ikx}$

Solution : The current density is given as

$$\vec{J} = \frac{\hbar}{2mi} [\Psi^* \nabla \Psi - \Psi \nabla \Psi^*]$$

The wave function represents motion along an x - axis. Hence

$$J_x = \frac{\hbar}{2mi} \left[\Psi^* \frac{d\Psi}{dx} - \Psi \frac{d\Psi^*}{dx} \right]$$

We have $\psi(x) = Ae^{ikx}$ and $\psi^*(x) = A^*e^{-ikx}$

$$\begin{aligned} \therefore J_x &= \frac{\hbar}{2mi} \left[A^*e^{-ikx} \frac{dAe^{ikx}}{dx} - Ae^{ikx} \frac{dA^*e^{-ikx}}{dx} \right] \\ &= \frac{\hbar}{2mi} AA^* [e^{-ikx} (ik)e^{ikx} - e^{ikx} (-ik)e^{-ikx}] \\ &= \frac{\hbar}{2mi} AA^* [(ik) - (-ik)] \\ &= \frac{\hbar}{2mi} AA^* (2ik) \end{aligned}$$

$$\therefore J_x = \frac{\hbar k}{m} |A|^2$$

$$\therefore \hbar k = p = mv$$

$$\therefore J_x = \frac{mv}{m} |A|^2 = v |A|^2$$

Example 7 : Consider the particle whose wave function is given as

$$\begin{aligned} \psi(x) &= x e^{-\alpha x} & x &> 0 \\ &= 0 & x &< 0 \end{aligned}$$

(1) Normalise the wave function.

(2) Find $\langle x \rangle$

(3) Find the value of x at which probability is maximum.

Solution : (1) To normalise the wave function, let us write the wave function as

$$\psi(x) = A x e^{-\alpha x}$$

where A is the normalisation constant.

The condition for normalisation is given as

$$\int_0^{\infty} |\psi(x)|^2 dx = 1$$

Here the range of x is from 0 to ∞ , since $\psi(x) = 0$ for $x < 0$.

$$\therefore \int_0^{\infty} |A|^2 x^2 e^{-2\alpha x} dx = 1$$

$$|A|^2 \int_0^{\infty} x^2 e^{-2\alpha x} dx = 1$$

We have general integral $\int_0^{\infty} x^n e^{-\beta x} dx = \frac{n!}{(\beta)^{n+1}}$

Therefore, $\int_0^{\infty} x^2 e^{-2\alpha x} dx = \frac{2!}{(2\alpha)^3} = \frac{1}{4\alpha^3}$

Hence $|A|^2 \frac{1}{4\alpha^3} = 1$

$\therefore |A| = (4\alpha^3)^{1/2} = 2\alpha\sqrt{\alpha}$

$\therefore \psi(x) = 2\alpha\sqrt{\alpha} x e^{-\alpha x}$

(2) Expectation value of x is given as

$$\begin{aligned}\langle x \rangle &= \int_0^{\infty} x |\psi(x)|^2 dx \\ &= \int_0^{\infty} 4\alpha^3 x^3 e^{-2\alpha x} dx\end{aligned}$$

$$= 4\alpha^3 \int_0^{\infty} x^3 e^{-2\alpha x} dx$$

$$= 4\alpha^3 \frac{3!}{(2\alpha)^4}$$

$$= \frac{3!}{4\alpha} = \frac{6}{4\alpha}$$

$\therefore \langle x \rangle = \frac{3}{2\alpha}$

(3) The peak of the probability function $P(x)$ occurs when $\frac{dP}{dx} = 0$.

We have

$$\psi(x) = 2\alpha\sqrt{\alpha} x e^{-\alpha x}$$

$\therefore P(x) = |\psi(x)|^2 = 4\alpha^3 x^2 e^{-2\alpha x}$

$\therefore \frac{dP}{dx} = 4\alpha^3 [2x e^{-2\alpha x} - 2\alpha x^2 e^{-2\alpha x}]$

For peak value of probability

$$4\alpha^3 [2x e^{-2\alpha x} - 2\alpha x^2 e^{-2\alpha x}] = 0$$

$\therefore 2x e^{-2\alpha x} - 2\alpha x^2 e^{-2\alpha x} = 0$

or $x - \alpha x^2 = 0$

$\therefore x = \frac{1}{\alpha}$

Thus, the probability will have the peak value at $x = \frac{1}{\alpha}$

Example 8 : The wave function for the ground state of the hydrogen atom is given as

$$\Psi(r) = A e^{-r/a_0} \quad \text{where } a_0 = \text{Bohr's radius}$$

Normalise the wave function and find the expectation value of r .

Solution : The range of r is from 0 to ∞ .

The normalisation condition is

$$\int_0^{\infty} |\Psi(r)|^2 d\tau = 1$$

$$\therefore |A|^2 \int_0^{\infty} e^{-2r/a_0} d\tau = 1$$

$d\tau$ is a typical volume element of the space and it is $d\tau = 4\pi r^2 dr$

$$\therefore |A|^2 \int_0^{\infty} e^{-2r/a_0} 4\pi r^2 dr = 1$$

$$4\pi |A|^2 \int_0^{\infty} r^2 e^{-2r/a_0} dr = 1$$

$$4\pi |A|^2 \frac{2!}{(2/a_0)^3} = 1$$

$$\pi |A|^2 a_0^3 = 1$$

$$\therefore |A| = \frac{1}{\sqrt{\pi a_0^3}}$$

$$\therefore \Psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad \dots(i)$$

The expectation value of r is given as

$$\langle r \rangle = \int_0^{\infty} r |\Psi(r)|^2 d\tau$$

Using equation (i) above, we get

$$= \frac{1}{\pi a_0^3} \int_0^{\infty} r e^{-2r/a_0} 4\pi r^2 dr$$

$$= \frac{1}{\pi a_0^3} 4\pi \int_0^{\infty} r^3 e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4}$$

$$\langle r \rangle = \frac{3}{2} a_0$$

Example 9 : The wave function of a certain particle is $\psi = A \cos^2 x$ for $-\pi/2 \leq x \leq \pi/2$.

(a) find the value of A

(b) Find the probability that the particle be found between $x = 0$ and $x = \pi/4$.

Solution : (a) The condition for normalisation is

$$\int_{-\pi/2}^{\pi/2} |\psi(x)|^2 dx = 1$$

$$\therefore \int_{-\pi/2}^{\pi/2} |A|^2 \cos^4 x dx = 1$$

or $|A|^2 \int_{-\pi/2}^{\pi/2} \cos^4 x dx = 1$

$$|A|^2 2 \int_0^{\pi/2} \cos^4 x dx = 1 \quad (\text{as } \cos x \text{ is an even function})$$

We have general reduction formula

$$\int \cos^n x dx = \frac{\sin x \cos^{n-1} x}{n} + \frac{n-1}{n} \int \cos^{n-2} x dx$$

$$\begin{aligned} \therefore \int \cos^4 x dx &= \frac{\sin x \cos^3 x}{4} + \frac{3}{4} \int \cos^2 x dx \\ &= \frac{\sin x \cos^3 x}{4} + \frac{3}{4} \left(\frac{\sin x \cos x}{2} + \frac{1}{2} \int dx \right) \\ &= \frac{\sin x \cos^3 x}{4} + \frac{3}{4} \left(\frac{\sin x \cos x}{2} + \frac{1}{2} x \right) \end{aligned}$$

...(i)

$$\begin{aligned} \therefore \int_0^{\pi/2} \cos^4 x dx &= \left[\frac{\sin x \cos^3 x}{4} + \frac{3}{4} \left(\frac{\sin x \cos x}{2} + \frac{1}{2} x \right) \right]_0^{\pi/2} \\ &= \frac{1}{4} \times 1 \times 0 + \frac{3}{4} \left(\frac{1}{2} \times 1 \times 0 + \frac{1}{2} \cdot \frac{\pi}{2} \right) - 0 \\ &= \frac{3\pi}{16} \end{aligned}$$

Hence

$$|A|^2 2 \frac{3\pi}{16} = 1$$

$$\therefore |A| = \sqrt{\frac{8}{3\pi}}$$

Therefore,

$$\Psi(x) = \sqrt{\frac{8}{3\pi}} \cos^2 x$$

(b) The probability of particle finding in the range 0 to $\pi/4$ is

$$P(x) = \int_0^{\pi/4} |A|^2 \cos^4 x dx$$

$$= \frac{8}{3\pi} \int_0^{\pi/4} \cos^4 x \, dx$$

The reduction formula is

$$\begin{aligned} \therefore \int_0^{\pi/4} \cos^4 x \, dx &= \left[\frac{\sin x \cos^3 x}{4} + \frac{3}{4} \left(\frac{\sin x \cos x}{2} + \frac{1}{2} x \right) \right]_0^{\pi/4} \\ &= \frac{1}{4} \frac{1}{\sqrt{2}} \left(\frac{1}{\sqrt{2}} \right)^3 + \frac{3}{4} \left(\frac{1}{2} \frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}} + \frac{1}{2} \frac{\pi}{4} \right) - 0 \\ &= \frac{1}{4} \left(\frac{1}{4} + \frac{3}{4} + \frac{3\pi}{8} \right) = \frac{8+3\pi}{32} \end{aligned}$$

$$\therefore P(x) = \frac{8}{3\pi} \times \frac{8+3\pi}{32}$$

or $P(x) = 0.4623$

Example 10 : A wave function of a free particle moving in the range $-\infty$ to $+\infty$ is given by

$$\psi(x) = x e^{-\alpha x^2}$$

Normalise the wave function.

Solution : In order to normalise the wave function, multiply the rhs by constant A.

$$\therefore \psi(x) = A x e^{-\alpha x^2}$$

Condition for normalisation is

$$\int |\Psi|^2 \, dx = 1 \quad \text{or} \quad \int \Psi \Psi^* \, dx = 1$$

$$\therefore \int_{-\infty}^{\infty} A x e^{-\alpha x^2} A^* x e^{-\alpha x^2} \, dx = 1$$

$$\therefore A A^* \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} \, dx = 1$$

or $|A|^2 \int_{-\infty}^{\infty} x^2 e^{-2\alpha x^2} \, dx = 1$

We have the general integral $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} \, dx = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta}}$

Thus, $\int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} \, dx = \frac{1}{2(2\alpha)} \sqrt{\frac{\pi}{(2\alpha)}}$

$$\therefore |A|^2 \frac{1}{2(2\alpha)} \sqrt{\frac{\pi}{(2\alpha)}} = 1$$

$$\therefore |A|^2 = 4\alpha \sqrt{\frac{2\alpha}{\pi}}$$

or

$$A = 2 \left(\frac{2\alpha^3}{\pi} \right)^{1/4}$$

∴

$$\psi(x) = 2 \left(\frac{2\alpha^3}{\pi} \right)^{1/4} x e^{-\alpha x^2/2}$$

QUESTIONS AND PROBLEMS

1. Give the physical interpretation of a wave function, associated with a moving particle.
2. Give the requirements that a wave function should satisfy. *Imp*
3. Obtain the Schrödinger's time dependent equation.
4. Obtain Schrödinger's time independent equation from time dependent equation.
5. Show that time part of the wave function is $e^{-iEt/\hbar}$.
6. Obtain the equation of continuity. Give its physical significance. *Imp Imp Imp*
- Imp* 7. What is meant by eigen functions and eigen values of an operator?
8. Define an operator. Give a few illustrations of some operators used in quantum mechanics operators.
9. How are the expectation values of physical quantities are obtained?
10. State and prove Ehrenfest theorems.
11. Show that $\frac{d\langle x \rangle}{dt} = \frac{\langle p_x \rangle}{m}$ and $\frac{d\langle p_x \rangle}{dt} = \langle -\frac{dV}{dx} \rangle$ *Imp*
12. Give the normalisation condition for a wave function.
13. Normalise the wave function $\psi(x) = e^{-\alpha x^2}$ in the range $-\infty$ and $+\infty$.
14. Normalise the wave function $\psi(x) = x e^{-\alpha x^2}$ in the range $-\infty$ and $+\infty$. Also find $\langle x \rangle$ and $\langle x^2 \rangle$.
15. Obtain the equation of probability current density.
16. Find the eigen value of the operator $\frac{d^2}{dx^2}$ for the eigen function $e^{-i\alpha x}$.
17. The eigen function for momentum operator is e^{ikx} . Find the eigen value. (Ans : $\hbar k$)
18. Normalise the wave function

$$\psi(x) = e^{-|x|} \sin \alpha x$$

in the range $-\infty$ to $+\infty$.

$$(Ans: \text{Normalisation constant} = \sqrt{\frac{2(1+\alpha^2)}{\alpha^2}})$$

n by

CHAPTER 3

OPERATOR MECHANISM

INTRODUCTION

In the previous chapter we have studied what is meant by an operator, eigen values and expectation values of a physical variable. In this chapter we will study some properties of the operators. Also, we will introduce the concept of commutation brackets used in quantum mechanics. The commutation relations involving position and momentum coordinates are of basic importance in quantum mechanics. These relations will be derived.

3.1 HERMITIAN OPERATOR

If \hat{A} is an operator corresponding to certain observable quantity and ψ is the wave function of the system, then the expectation value is given by

$$\langle A \rangle = \int_{\tau} \psi^* \hat{A} \psi \, d\tau$$

$\langle A \rangle$ is a real number. Consequently, \hat{A} must satisfy the condition

$$\int_{\tau} \psi^* (\hat{A} \psi) \, d\tau = \int_{\tau} (\hat{A} \psi)^* \psi \, d\tau \quad \dots(3.1)$$

for every state ψ of the system. The operator which obeys the above condition is called *hermitian operator*. It will be seen below that eigen value of hermitian operator are all real.

Example 1: Prove that eigen values of the hermitian operator are real *Imp.*

Solution: Eigen value equation for any operator \hat{A} has the following form

$$\hat{A} \psi = a \psi$$

$$\hat{A} \psi = \lambda \psi$$

where λ is the eigen value of the operator \hat{A} corresponding to the function ψ . Then,

$$\int_{\tau} \psi^* (\hat{A} \psi) \, d\tau = \int_{\tau} \psi^* (\lambda \psi) \, d\tau = \lambda \int_{\tau} \psi^* \psi \, d\tau$$

If the eigen function is normalised $\int_{\tau} \psi^* \psi \, d\tau = 1$, then

$$\int_{\tau} \psi^* \hat{A} \psi \, d\tau = \lambda \quad \dots (i)$$

Also

$$\int_{\tau} (\hat{A} \psi)^* \psi \, d\tau = \int_{\tau} (\lambda^* \psi^*) \psi \, d\tau = \lambda^* \int_{\tau} \psi^* \psi \, d\tau = \lambda^*$$

$$\int_{\tau} (\hat{A}\psi)^* \psi d\tau = \lambda^* \quad \dots (ii)$$

where λ^* is the complex conjugate of λ .

For hermitian operator we have

$$\int_{\tau} \psi^* \hat{A}\psi d\tau = \int_{\tau} (\hat{A}\psi)^* \psi d\tau$$

Using (i) and (ii), we find that

$$\therefore \lambda = \lambda^*$$

This is possible only when λ is real. This is true for all eigen values of the operator \hat{A} . Thus eigen values of hermitian operators are all real.

Example 2 : Show that the momentum operator $-i\hbar \frac{\partial}{\partial x}$ is hermitian operator. Obtain eigen functions for momentum operator.

Solution : For hermitian operator we have

$$\int_{\tau} \psi^* \hat{A}\psi d\tau = \int_{\tau} (\hat{A}\psi)^* \psi d\tau \quad \dots (i)$$

If momentum operator is hermitian, it should satisfy following condition

$$\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right) dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \psi}{\partial x} \right)^* \psi dx$$

$$\text{or} \quad -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \psi dx \quad \dots (ii)$$

Consider the integral

$$\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right) dx = -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx \quad \dots (iii)$$

Integration by parts of the following integral is

$$\int_a^b \frac{u(x) dv(x)}{dx} dx = [u(x)v(x)]_a^b - \int_a^b \frac{du(x)}{dx} v(x) dx$$

Thus,

$$\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx = [\psi^* \psi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \psi dx$$

Both ψ^* and ψ tend to zero at infinity, $(\psi^*\psi) \rightarrow 0$. Hence,

$$\psi^*\psi \rightarrow 0 \text{ at } \infty \quad (\psi^*\psi) \rightarrow 0$$

$$\int_{-\infty}^{\infty} \psi^* \frac{\partial \psi}{\partial x} dx = - \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \psi dx$$

Using the above equation on the RHS of equation (iii), we get

$$\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right) dx = i\hbar \int_{-\infty}^{\infty} \frac{\partial \psi^*}{\partial x} \psi dx \quad [\psi^*\psi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \frac{\partial \psi}{\partial x} \psi^* dx$$

$$= - \int_{-\infty}^{\infty} \left(i\hbar \frac{\partial \psi^*}{\partial x} \right) \psi dx$$

$$\int_{-\infty}^{\infty} \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x} \right) dx = \int_{-\infty}^{\infty} \left(-i\hbar \frac{\partial \psi}{\partial x} \right)^* \psi dx$$

$$\text{or} \quad \int_{\tau} \psi^* \hat{p}_x \psi d\tau = \int_{\tau} (\hat{p}_x \psi)^* \psi d\tau \quad \dots(\text{iv})$$

Comparing equation (iv) with equation (i) we find that momentum operator is hermitian.

Let λ be the eigen value of the momentum operator \hat{p}_x . Then

$$\hat{p}_x \psi = \lambda \psi$$

$$\therefore -i\hbar \frac{\partial \psi}{\partial x} = \lambda \psi$$

$$\text{or} \quad -i\hbar \frac{d\psi}{dx} = \lambda \psi$$

$$\therefore \frac{d\psi}{\psi} = i \frac{\lambda}{\hbar} dx$$

If we integrate this equation, we get

$$\psi = C e^{(i\lambda/\hbar)x}$$

where C is constant.

The above equation gives eigen functions of \hat{p}_x

3.2 SIMULTANEOUS EIGEN FUNCTIONS : COMMUTATORS

□ If \hat{A} and \hat{B} are two operators, and ψ is a function satisfying following equations

$$\hat{A} \psi = a\psi \quad \dots(3.2)$$

and

$$\hat{B} \psi = b\psi \quad \dots(3.3)$$

In the above ψ is the simultaneous eigen function of operators \hat{A} and \hat{B} belonging to the eigen values a and b respectively.

Equations (3.2) and (3.3) imply that

$$\hat{B} \hat{A} \psi = \hat{B} (a\psi) = a \hat{B} \psi = ab\psi$$

and

$$\hat{A} \hat{B} \psi = \hat{A} (b\psi) = b \hat{A} \psi = ba\psi$$

as a and b are scalars, we have $ab = ba$.

Hence by subtraction of above two equations, we get

$$(\hat{A} \hat{B} - \hat{B} \hat{A}) \psi = 0 \quad \dots(3.4)$$

This equation shows that ψ is also an eigen function of the operator $\hat{A} \hat{B} - \hat{B} \hat{A}$ belonging to the eigen value zero. Thus, the condition (3.4) is necessary that ψ be a simultaneous eigen function of \hat{A} and \hat{B} . For simplicity it is denoted by $[\hat{A}, \hat{B}]$

\therefore

$$[\hat{A}, \hat{B}] = \hat{A} \hat{B} - \hat{B} \hat{A} \quad \dots(3.5)$$

$[\hat{A}, \hat{B}]$ is called commutator bracket.

If $[\hat{A}, \hat{B}] = 0$, then the two operators \hat{A} and \hat{B} are said to commute.

The commutator $[\hat{A}, \hat{B}]$ satisfies the following rules

(1) $[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$

(2) $[\hat{A}, \hat{B} \hat{C}] = [\hat{A}, \hat{B}] \hat{C} + \hat{B} [\hat{A}, \hat{C}]$

(3) $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$ or $[\hat{A}, \hat{B} - \hat{C}] = [\hat{A}, \hat{B}] - [\hat{A}, \hat{C}]$

(4) $[\hat{A} \hat{B}, \hat{C}] = [\hat{A}, \hat{C}] \hat{B} + \hat{A} [\hat{B}, \hat{C}]$

(5) $[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$

(6) $[x\hat{A}, \hat{B}] = x[\hat{A}, \hat{B}]$ and $[\hat{A}, y\hat{B}] = y[\hat{A}, \hat{B}]$, where x and y are scalars.

Proofs of the above properties are discussed in the problems latter.

3.3 BASIC COMMUTATORS IN QUANTUM MECHANICS

Basic operators in quantum mechanics are position, momentum, Hamiltonian, angular momentum operators. Here after the caps (^) indicating that the symbols represent the operators are avoided for simplicity.

The momentum operators corresponding to x , y and z components of \hat{p} are

$$p_x = -i\hbar \frac{\partial}{\partial x}$$

$$p_y = -i\hbar \frac{\partial}{\partial y}$$

and

$$p_z = -i\hbar \frac{\partial}{\partial z}$$

Let us consider the action of commutator $[x, p_x]$ on the arbitrary wave function $\psi(x, y, z)$

3.2)

$$[x, p_x] \psi = \left[x, -i\hbar \frac{\partial}{\partial x} \right] \psi$$

$$\begin{aligned}
 &= -i\hbar \left[x, \frac{\partial}{\partial x} \right] \psi \\
 &= -i\hbar \left(x \frac{\partial}{\partial x} - \frac{\partial}{\partial x} x \right) \psi \\
 &= -i\hbar \left(x \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x} (x\psi) \right) \\
 &= -i\hbar \left(x \frac{\partial \psi}{\partial x} - x \frac{\partial \psi}{\partial x} - \psi \right) \\
 &= i\hbar \psi
 \end{aligned}$$

$$\therefore [x, p_x] = i\hbar \quad \dots(3.6)$$

Similarly

$$[y, p_y] = i\hbar \quad \text{and} \quad [z, p_z] = i\hbar$$

It is to be noted that the commutator of a position co-ordinate (say x) and the corresponding momentum operator (p_x) is non-vanishing and has value $i\hbar$.

Let us consider commutator

$$\begin{aligned}
 [x, p_y] \psi &= \left[x, -i\hbar \frac{\partial}{\partial y} \right] \psi \\
 &= -i\hbar \left[x, \frac{\partial}{\partial y} \right] \psi \\
 &= -i\hbar \left(x \frac{\partial}{\partial y} - \frac{\partial}{\partial y} x \right) \psi \\
 &= -i\hbar \left(x \frac{\partial \psi}{\partial y} - \frac{\partial}{\partial y} (x\psi) \right) \\
 &= -i\hbar \left(x \frac{\partial \psi}{\partial y} - x \frac{\partial \psi}{\partial y} \right) \\
 &= 0
 \end{aligned}$$

$$\therefore [x, p_y] = 0$$

Similarly

$$[y, p_x] = 0; [y, p_z] = 0$$

$$[z, p_y] = 0; [z, p_x] = 0$$

Thus, the commutator of position co-ordinate and momentum component which does not correspond to it is always zero.

The vanishing and non-vanishing commutators involving (x, y, z) and (p_x, p_y, p_z) can be put together in the form of a single relation using x_1, x_2, x_3 for x, y, z respectively and p_1, p_2, p_3 for p_x, p_y, p_z respectively. This relation is

$$[x_i, p_j] = i\hbar \delta_{ij}, \quad i, j = 1, 2, 3, \dots$$

where kronecker delta function (δ_{ij}) satisfies the following properties

$$\begin{aligned}
 \delta_{ij} &= 1 & \text{if } i &= j \\
 \delta_{ij} &= 0 & \text{if } i &\neq j
 \end{aligned}$$

It may be mentioned here that the commutator relation $[x, p_x] = i\hbar$ is in a way alternative form of the uncertainty principle viz. $\Delta x \Delta p_x \geq \hbar/2$. The commutator of two operators corresponding to physical quantities which cannot be measured simultaneously with arbitrary accuracy is always non-zero We know that x and p_x cannot be measured simultaneously with arbitrary accuracy.

If the commutator of the operators corresponding to two physical quantities vanishes, then these quantities can be measured simultaneously with arbitrary accuracy. For example, simultaneous measurement of x does not affect the measurement p_y . Therefore, x and p_y can be measured simultaneously with arbitrary accuracy. Consequently, $[x, p_y] = 0$.

3.4 ANGULAR MOMENTUM COMMUTATION RELATIONS

In classical mechanics, the angular momentum of a particle relative to the origin of a certain co-ordinate system is a vector quantity is given by

$$\vec{L} = \vec{r} \times \vec{p}$$

where \vec{r} is the position vector and \vec{p} is the linear momentum vector.

We have $\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z$ and $\vec{p} = \hat{i}p_x + \hat{j}p_y + \hat{k}p_z$

$$\therefore \vec{L} = (\hat{i}x + \hat{j}y + \hat{k}z) \times (\hat{i}p_x + \hat{j}p_y + \hat{k}p_z)$$

$$\text{or } \vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= \hat{i}(y p_z - z p_y) - \hat{j}(x p_z - z p_x) + \hat{k}(x p_y - y p_x)$$

$$\therefore \vec{L} = \hat{i}L_x + \hat{j}L_y + \hat{k}L_z$$

Therefore,

$$L_x = (y p_z - z p_y) \quad \dots(3.7)$$

$$L_y = -(x p_z - z p_x) = (z p_x - x p_z) \quad \dots(3.8)$$

$$L_z = (x p_y - y p_x) \quad \dots(3.9)$$

In order to study the dynamical quantity *angular momentum* in quantum mechanics, we will construct the corresponding operators. This is done by using the components of momentum operators $p_x = -i\hbar \frac{\partial}{\partial x}$, $p_y = -i\hbar \frac{\partial}{\partial y}$ and $p_z = -i\hbar \frac{\partial}{\partial z}$. With these operators angular momentum components in equations (3.7), (3.8) and (3.9) can be written in operator form as

$$L_x = i\hbar \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \quad \dots(3.10)$$

$$L_y = i\hbar \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \quad \dots(3.11)$$

and $L_z = i\hbar \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \quad \dots(3.12)$

Commutation rules for the components of orbital angular momentum with position:

Consider commutation rule for L_x and x .

$$[a, b] = [ab - ba]$$

$$\begin{aligned} [L_x, x] \psi &= \left[i\hbar \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right), x \right] \psi \\ &= i\hbar \left[\left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right), x \right] \psi \\ &= i\hbar \left(\left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) x - x \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \right) \psi \\ &= i\hbar \left(z \frac{\partial x \psi}{\partial y} - y \frac{\partial x \psi}{\partial z} - x z \frac{\partial \psi}{\partial y} + y x \frac{\partial \psi}{\partial z} \right) \\ &= i\hbar \left(\underbrace{zx \frac{\partial \psi}{\partial y}} - \underbrace{yx \frac{\partial \psi}{\partial z}} - \underbrace{xz \frac{\partial \psi}{\partial y}} + \underbrace{yx \frac{\partial \psi}{\partial z}} \right) \\ &= 0 \end{aligned}$$

$$\therefore [L_x, x] = 0$$

Similarly, $[L_y, y] = 0$ and $[L_z, z] = 0$

Consider commutation rule for L_x and y .

$$\begin{aligned} [L_x, y] \psi &= \left[i\hbar \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right), y \right] \psi \\ &= i\hbar \left[\left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right), y \right] \psi \\ &= i\hbar \left(\left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) y - y \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \right) \psi \\ &= i\hbar \left(z \frac{\partial(y \psi)}{\partial y} - y \frac{\partial(y \psi)}{\partial z} - y z \frac{\partial \psi}{\partial y} + y^2 \frac{\partial \psi}{\partial z} \right) \\ &= i\hbar \left(\underbrace{zy \frac{\partial \psi}{\partial y}} + \underbrace{z \psi} - \underbrace{y^2 \frac{\partial \psi}{\partial z}} - \underbrace{yz \frac{\partial \psi}{\partial y}} + \underbrace{y^2 \frac{\partial \psi}{\partial z}} \right) \\ &= i\hbar z \psi \end{aligned}$$

$$\therefore [L_x, y] = i\hbar z$$

...(3.13)

Similarly we can prove that

$$\begin{aligned} [L_y, z] &= i\hbar x, & [L_z, x] &= i\hbar y, \\ [L_x, z] &= -i\hbar y, & [L_z, y] &= -i\hbar x \end{aligned}$$

Commutation rules for the various components of orbital angular momentum:

Consider the commutation relation between L_x and L_y

$$[L_x, L_y] = L_x L_y - L_y L_x$$

Let us consider the first term on RHS

$$\begin{aligned} L_x L_y &= i\hbar \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) i\hbar \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \\ &= -\hbar^2 \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \end{aligned}$$

$$\begin{aligned}
&= -\hbar^2 \left(z \frac{\partial}{\partial y} \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) - y \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \right) \\
&= -\hbar^2 \left(z \frac{\partial}{\partial y} \left(x \frac{\partial}{\partial z} \right) - z \frac{\partial}{\partial y} \left(z \frac{\partial}{\partial x} \right) - y \frac{\partial}{\partial z} \left(x \frac{\partial}{\partial z} \right) + y \frac{\partial}{\partial z} \left(z \frac{\partial}{\partial x} \right) \right) \\
&= -\hbar^2 \left(y \frac{\partial}{\partial x} + yz \frac{\partial^2}{\partial z \partial x} - yx \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial y \partial x} + zx \frac{\partial^2}{\partial y \partial z} \right)
\end{aligned}$$

Similarly

$$\begin{aligned}
L_y L_x &= i\hbar \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) i\hbar \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \\
&= -\hbar^2 \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \\
&= -\hbar^2 \left(x \frac{\partial}{\partial z} \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) - z \frac{\partial}{\partial x} \left(z \frac{\partial}{\partial y} - y \frac{\partial}{\partial z} \right) \right) \\
&= -\hbar^2 \left(x \frac{\partial}{\partial z} \left(z \frac{\partial}{\partial y} \right) - x \frac{\partial}{\partial z} \left(y \frac{\partial}{\partial z} \right) - z \frac{\partial}{\partial x} \left(z \frac{\partial}{\partial y} \right) + z \frac{\partial}{\partial x} \left(y \frac{\partial}{\partial z} \right) \right) \\
&= -\hbar^2 \left(x \frac{\partial}{\partial y} + zy \frac{\partial^2}{\partial x \partial z} - xy \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial x \partial y} + xz \frac{\partial^2}{\partial z \partial y} \right) \\
\therefore L_x L_y - L_y L_x &= -\hbar^2 \left(y \frac{\partial}{\partial x} + yz \frac{\partial^2}{\partial z \partial x} - yx \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial y \partial x} + zx \frac{\partial^2}{\partial y \partial z} \right) \\
&\quad + \hbar^2 \left(x \frac{\partial}{\partial y} + zy \frac{\partial^2}{\partial x \partial z} - xy \frac{\partial^2}{\partial z^2} - z^2 \frac{\partial^2}{\partial x \partial y} + xz \frac{\partial^2}{\partial z \partial y} \right) \\
\therefore L_x L_y - L_y L_x &= -\hbar^2 \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) = i\hbar \times i\hbar \left(y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) = i\hbar L_z
\end{aligned}$$

Thus,

$$[L_x, L_y] = i\hbar L_z \quad \dots(3.14)$$

Alternative method to prove above relation:

$$\begin{aligned}
[L_x, L_y] &= [yp_z - zp_y, zp_x - xp_z] \\
&= [yp_z, zp_x] - [yp_z, xp_z] - [zp_y, zp_x] + [zp_y, xp_z] \quad \dots(i)
\end{aligned}$$

Let us consider the first term on RHS viz. $[yp_z, zp_x]$. We know that the measurement of p_z affects that of z and not p_x . Hence we may immediately write the following

$$[yp_z, zp_x] = y[p_z, z]p_x \quad \dots(ii)$$

Similarly, fourth bracket on RHS of equation (i) becomes

$$[zp_y, xp_z] = xp_y[z, p_z] \quad \dots(iii)$$

It is to be remembered that the relative order of z and p_z must be maintained as these are non-commuting operators satisfying the relation $[z, p_z] = i\hbar$. However, terms like xp_y may be written

in any order because $[x, p_y] = 0$ and therefore, $x p_y = p_y x$. Second and third brackets on RHS of equation (i) vanish as they involve commuting operators. Therefore, equation (i) becomes

$$\begin{aligned}[L_x, L_y] &= y p_x [p_z, z] + x p_y [z, p_z] \\ &= -y p_x [z, p_z] + x p_y [z, p_z]\end{aligned}$$

But $[z, p_z] = i\hbar$

Therefore,

$$[L_x, L_y] = i\hbar (x p_y - y p_x)$$

or

$$[L_x, L_y] = i\hbar L_z$$

By cyclic permutations, we can obtain

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

and

$$[L_z, L_y] = -i\hbar L_x$$

$$[L_x, L_z] = -i\hbar L_y$$

Commutation relation of L^2 with components L_x , L_y and L_z :

We have

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Let us consider $[L^2, L_x]$

$$\begin{aligned}[L^2, L_x] &= [L_x^2 + L_y^2 + L_z^2, L_x] \\ &= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]\end{aligned}$$

We know that

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}]$$

Therefore,

$$\begin{aligned}[L^2, L_x] &= L_x [L_x, L_x] + [L_x, L_x] L_x + L_y [L_y, L_x] + [L_y, L_x] L_y + L_z [L_z, L_x] + [L_z, L_x] L_z \\ &= L_x \times 0 + 0 \times L_x + L_y (-i\hbar L_z) + (-i\hbar L_z) L_y + L_z (i\hbar L_y) + (i\hbar L_y) L_z \\ &= 0\end{aligned}$$

Similarly,

$$[L^2, L_y] = 0$$

and

$$[L^2, L_z] = 0$$

Thus, L^2 commutes with any of the three components of angular momentum operators.

Ladder operators:

Ladder operators involving L_x and L_y are defined as

$$L_+ = L_x + iL_y$$

and

$$L_- = L_x - iL_y$$

1. Let us consider commutation of L_z with L_+

$$\begin{aligned}[L_z, L_+] &= [L_z, L_x + iL_y] \\ &= [L_z, L_x] + [L_z, iL_y] \\ &= [L_z, L_x] + i[L_z, L_y]\end{aligned}$$

$$\begin{aligned}
 &= i\hbar L_y + i(-i\hbar L_x) \\
 &= i\hbar L_y + \hbar L_x \\
 &= \hbar (L_x + iL_y)
 \end{aligned}$$

$$\therefore [L_z, L_+] = \hbar L_+ \quad \dots(3.15)$$

2. Let us consider commutation of L_z with L_-

$$\begin{aligned}
 [L_z, L_-] &= [L_z, L_x - iL_y] \\
 &= [L_z, L_x] - [L_z, iL_y] \\
 &= [L_z, L_x] - i[L_z, L_y] \\
 &= i\hbar L_y - i(-i\hbar L_x) \\
 &= i\hbar L_y - \hbar L_x \\
 &= -\hbar (L_x - iL_y)
 \end{aligned}$$

$$\therefore [L_z, L_-] = -\hbar L_- \quad \dots(3.16)$$

3. Let us consider commutation of L_+ with L_-

$$\begin{aligned}
 [L_+, L_-] &= [L_x + iL_y, L_x - iL_y] \\
 &= [L_x, L_x] - i[L_x, L_y] + i[L_y, L_x] - i^2 [L_y, L_y] \\
 &= [L_x, L_x] - i[L_x, L_y] + i[L_y, L_x] + [L_y, L_y] \\
 &= 0 - i(i\hbar L_z) + i(-i\hbar L_z) + 0
 \end{aligned}$$

$$\therefore [L_+, L_-] = 2\hbar L_z \quad \dots(3.17)$$

Angular momentum operators in spherical polar co-ordinates :

Angular momentum operators in cartesian co-ordinates are given by equations (3.10), (3.11) and (3.12)

We can convert these in spherical polar co-ordinates by using transformation relation between (x, y, z) and (r, θ, ϕ) .

$$\begin{aligned}
 x &= r \sin \theta \cos \phi \\
 y &= r \sin \theta \sin \phi \\
 z &= r \cos \theta
 \end{aligned}$$

With these transformations equations it can be shown that

$$L_x = i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

$$L_y = i\hbar \left(-\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)$$

And

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

Eigen functions and eigen values of L_z

We now try to find the eigen value of L_z . Let

$$L_z \psi = \lambda \psi \quad \dots(3.17a)$$

where $\psi = \psi(r, \theta, \phi)$ and λ is the eigen value.

Let us assume that $\psi(r, \theta, \phi)$ can be written as

$$\psi(r, \theta, \phi) = F(r, \theta) G(\phi)$$

We have

$$L_z = -i\hbar \frac{\partial}{\partial \phi}$$

Therefore, equation(3.17a) becomes

$$-i\hbar \frac{\partial \psi}{\partial \phi} = \lambda \psi$$

$$-i\hbar \frac{\partial F G}{\partial \phi} = \lambda F G$$

$$-i\hbar F \frac{\partial G}{\partial \phi} = \lambda F G$$

(Since F does not depend on ϕ)

$$\therefore -i\hbar \frac{dG}{d\phi} = \lambda G$$

$$\text{or} \quad \frac{dG}{G} = \frac{i\lambda}{\hbar} d\phi$$

On integration we get,

$$\ln G = \ln A + \frac{i\lambda}{\hbar} \phi$$

$$\therefore G = A e^{i\lambda\phi/\hbar}$$

Ignoring the multiplication constant, we have

$$G = e^{i\lambda\phi/\hbar}$$

$$\therefore \psi = F(r, \theta) e^{i\lambda\phi/\hbar}$$

Now ψ must be a single valued function of (r, θ, ϕ) . In this case increase in ϕ by 2π should not change the function, so that

$$F(r, \theta) e^{i\lambda\phi/\hbar} = F(r, \theta) e^{i\lambda(\phi+2\pi)/\hbar}$$

$$= F(r, \theta) e^{i\lambda\phi/\hbar} e^{2\pi i\lambda/\hbar}$$

$$\therefore e^{i\lambda 2\pi/\hbar} = 1$$

$$\text{or} \quad \cos\left(\frac{2\pi\lambda}{\hbar}\right) + i \sin\left(\frac{2\pi\lambda}{\hbar}\right) = 1$$

This gives

$$\cos\left(\frac{2\pi\lambda}{\hbar}\right) = 1 \quad \text{and} \quad \sin\left(\frac{2\pi\lambda}{\hbar}\right) = 0$$

Therefore,

$$\frac{2\pi\lambda}{\hbar} = 2m\pi, \quad \text{where } m \text{ is an integer with } m = 0, 1, 2, \dots$$

$$\therefore \lambda = m\hbar, \quad m = 0, 1, 2, \dots$$

Thus eigen values of L_z operator are $m\hbar$, where $m = 0, 1, 2, \dots$

Raising and lowering of operators :

Let ψ_m be an eigen function of operator L_z with eigen value $m\hbar$. Let us consider the operator $L_+ = L_x + iL_y$, such that L_z is operating on $(L_x + iL_y)\psi_m$.

a)

$$\begin{aligned} L_z(L_x + iL_y)\psi_m &= (L_zL_x + iL_zL_y)\psi_m \\ &= L_zL_x\psi_m + iL_zL_y\psi_m \end{aligned} \quad \dots(3.18)$$

We have

$$L_zL_x - L_xL_z = i\hbar L_y \quad \text{and} \quad L_zL_y - L_yL_z = -i\hbar L_x$$

or

$$L_zL_x = L_xL_z + i\hbar L_y \quad \text{and} \quad L_zL_y = L_yL_z - i\hbar L_x$$

Using these in equation (3.18), we get

$$\begin{aligned} L_z(L_x + iL_y)\psi_m &= (L_xL_z + i\hbar L_y)\psi_m + i(L_yL_z - i\hbar L_x)\psi_m \\ &= (L_xL_z + iL_yL_z)\psi_m + i\hbar(L_x + iL_y)\psi_m \\ &= (L_x + iL_y)L_z\psi_m + \hbar(L_x + iL_y)\psi_m \\ &= (L_x + iL_y)(L_z\psi_m + \hbar\psi_m) \\ &= (L_x + iL_y)(m\hbar\psi_m + \hbar\psi_m) \\ &= (L_x + iL_y)(m+1)\hbar\psi_m \end{aligned}$$

$$\therefore L_z(L_x + iL_y)\psi_m = (m+1)\hbar(L_x + iL_y)\psi_m \quad \dots(3.19)$$

We find that, when $(L_x + iL_y)$ operates on eigen function ψ_m , the eigen value of L_z operator increases by \hbar . In this sense (L_+) is called raising operator.

Similarly we can show that

$$L_z(L_x - iL_y)\psi_m = (m-1)\hbar(L_x - iL_y)\psi_m$$

Eigen value of L_z decreases by \hbar , when $(L_x - iL_y)$ operates on eigen function ψ_m . Therefore, L_- is called lowering operator.

3.5 PARITY AND PARITY OPERATOR

If we have function $f(x)$ such that

$$f(x) = f(-x)$$

i.e. if there is no change in the sign of the function when the direction of variable (x) is reversed, the function has a even parity. For example,

$$f(x) = x^2 + 2 \quad \therefore f(-x) = x^2 + 2$$

the function has even parity.

$$\text{If} \quad f(x) = -f(-x)$$

i.e. if there is change in the sign of the function when the direction of the variable is reversed, the function has odd parity.

For example, if

$$f(x) = x^3, \quad \text{then} \quad f(-x) = -x^3 = -f(x)$$

the function has odd parity.

The function $\cos x$ has even parity since $\cos(-x) = \cos(x)$. Similarly the function $\sin x$ has odd parity as $\sin(-x) = -\sin(x)$.

If we have function,

$$f_1(x) = A \sin x$$

and

$$f_2(x) = B \cos x.$$

What is parity of function $f_1(x)$ and $f_2(x)$?

$\sin x$ has odd parity and $\cos x$ has even parity, therefore, the function $f_1(x)$ has odd parity and $f_2(x)$ has even parity.

In general, let $\psi(x)$ be an eigen function, such that

$$P \psi(x) = \epsilon \psi(-x)$$

Where P is parity operator and ϵ is the eigen value.

If $\epsilon = +1$, the function $\psi(x)$ has *even parity*.

If $\epsilon = -1$, the function $\psi(x)$ has *odd parity*.

Concept of parity is very much important in quantum mechanics. All eigen functions that are bound state solutions of Schrödinger's steady state equations for a potential $V(r)$ have definite parities *i.e.* either the eigen functions have *odd parity* or *even parity*. The reason is that the probability density $\psi\psi^*$ will then have same value at the point $(-x, -y, -z)$ as that of point (x, y, z) , which is the requirement of the fact that the potential has the same value at that point.

Let us now consider Schrödinger's time independent equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x)$$

If we change x to $-x$, the equation becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(-x)}{dx^2} + V(-x) \psi(-x) = E \psi(-x)$$

If $V(x)$ is symmetric about $x = 0$, then $V(-x) = V(x)$. Thus, from above two equations we have two eigen functions $\psi(x)$ and $\psi(-x)$ that give the same energy eigen value. If these two eigen functions are not linearly independent, then they must differ by a multiplicative constant *i.e.*

$$\psi(x) = \epsilon \psi(-x) \quad \dots(3.20)$$

If we change x to $-x$ in equation (3.10), we have

$$\psi(-x) = \epsilon \psi(x) \quad \dots(3.21)$$

Using equation (3.21) in (3.20), we get

$$\psi(x) = \epsilon \epsilon \psi(x) = \epsilon^2 \psi(x)$$

Thus, we get

$$\epsilon^2 = 1$$

\therefore

$$\epsilon = +1 \text{ or } \epsilon = -1$$

Therefore, we have

$$\psi(x) = \psi(-x) \quad \text{for } \epsilon = +1$$

$$\text{and } \psi(x) = -\psi(-x) \quad \text{for } \epsilon = -1$$

If $\epsilon = +1$, $\psi(x)$ has even parity and if $\epsilon = -1$, the function has odd parity.]

Parity concept in three dimensional case :

[Let us consider wave functions which, in general, depend upon three variables x, y and z . Let us change

$$x \rightarrow -x$$

$$y \rightarrow -y$$

and

$$z \rightarrow -z$$

i.e.

$$\vec{r} \rightarrow -\vec{r}$$

$$\psi(x, y, z) \rightarrow \psi(-x, -y, -z)$$

$$\psi(\vec{r}) \rightarrow \psi(-\vec{r})$$

space inversion

This transformation is called space inversion. It is shown in Fig. 3.1

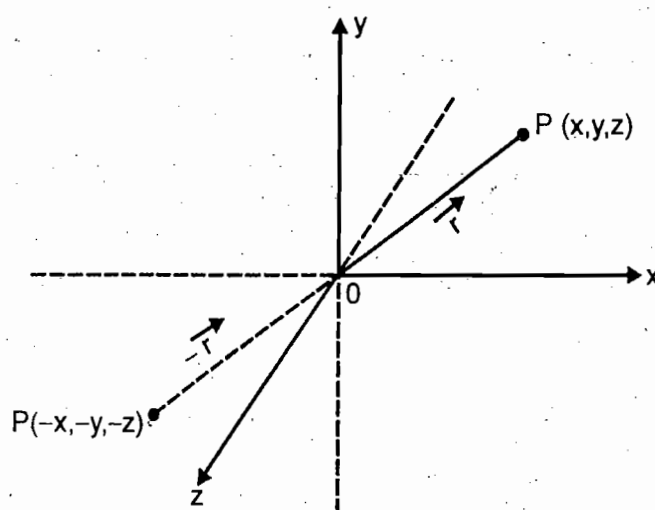


Fig. 3.1 -

If, $\psi(x, y, z) = \psi(-x, -y, -z)$ i.e. $\psi(\vec{r}) = \psi(-\vec{r})$, the function has even parity.

If, $\psi(x, y, z) = -\psi(-x, -y, -z)$ i.e. $\psi(\vec{r}) = -\psi(-\vec{r})$, the function has odd parity. \square

Parity in spherical polar coordinates:

\square Quite often we have to use spherical polar co-ordinates (r, θ, ϕ) . So let us see how to determine the parity of wave function $\psi(r, \theta, \phi)$. The transformation $\vec{r} \rightarrow -\vec{r}$ corresponds to going from P to P' as shown in Fig. 3.2. Fig. 3.2 shows that when the signs of rectangular co-ordinates (of point P) are changed in the parity operation, the coordinates of new point P' are obtained by transformations

$$r \longrightarrow r,$$

$$\theta \longrightarrow \pi - \theta$$

and $\phi \longrightarrow \pi + \phi$

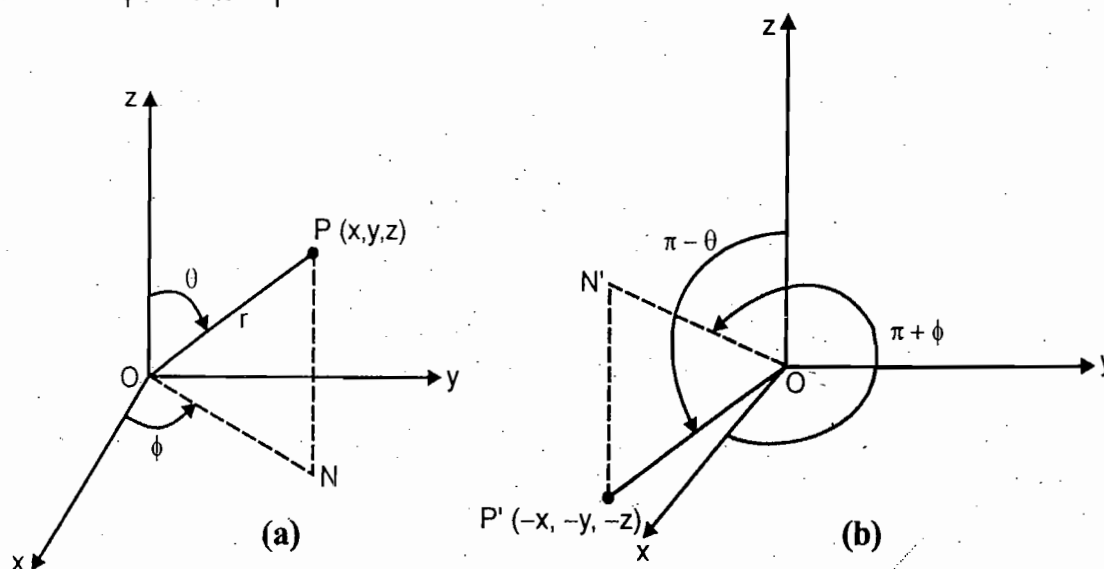


Fig. 3.2

If $\psi(r, \theta, \phi) = \psi(r, \pi - \theta, \pi + \phi)$, the wave function has *even* parity.

If $\psi(r, \theta, \phi) = -\psi(r, \pi - \theta, \pi + \phi)$, the wave function has *odd* parity. \square

Example 3 : Determine the parity for the following functions

$$e^{-\alpha r}, \cos \theta e^{-\alpha r} \text{ and } \cos \theta e^{-\alpha r} e^{i\phi}$$

Solution :

$$(1) \psi(r) = e^{-\alpha r}$$

The parity of function (even or odd) decided by transformation $r \rightarrow r, \theta \rightarrow \pi - \theta, \phi \rightarrow \pi + \phi$. Obviously, the function has even parity.

$$(2) \psi(r, \theta, \phi) = \cos \theta e^{-\alpha r}$$

$$\therefore \psi(r, \pi - \theta, \pi + \phi) = \cos(\pi - \theta) e^{-\alpha r} \\ = -\cos \theta e^{-\alpha r}$$

$$\cos(\pi - \theta) \\ = -\cos \theta$$

$$(\because \cos(\pi - \theta) = -\cos \theta)$$

$$\therefore \psi(r, \theta, \phi) = -\psi(r, \pi - \theta, \pi + \phi)$$

Therefore, the function has odd parity.

$$(3) \psi(r, \theta, \phi) = \cos \theta e^{-\alpha r} e^{i\phi}$$

$$\therefore \psi(r, \pi - \theta, \pi + \phi) = \cos(\pi - \theta) e^{-\alpha r} e^{i(\pi + \phi)} \\ = \cos(\pi - \theta) e^{-\alpha r} e^{i\phi} e^{i\pi} = 1$$

$$e^{i\pi} = -1$$

$$(\because \cos(\pi - \theta) = -\cos \theta \text{ and } e^{i\pi} = -1)$$

$$\therefore \psi(r, \theta, \phi) = \psi(r, \pi - \theta, \pi + \phi)$$

Therefore, the function has even parity.

Example 4 : By mathematical induction show that

$$[x, p^n] = i \hbar n p^{n-1}$$

Solution : The essence of the principle of mathematical induction is as under.

Suppose that a certain mathematical relation is true for $n = k$ and we are able to prove that it is true for $n = k + 1$ and also that the relation is true for one value of n over its range, then in general it is true for any value of n . Using this principle we shall now prove the required result.

We know that

$$[x, p] = i \hbar$$

Thus the relation $[x, p^n] = i \hbar n p^{n-1}$ is true for $n = 1$.

Let us assume that the relation is true for $n = k$, i.e.

$$[x, p^k] = i\hbar k p^{k-1}$$

Now we will show that it is true for $n = k + 1$

$$\begin{aligned} [x, p^{k+1}] &= [x, p p^k] \\ &= p[x, p^k] + [x, p] p^k \\ &= p i\hbar k p^{k-1} + i\hbar p^k \\ &= (k+1)i\hbar p^{k+1} \end{aligned}$$

Thus the result is true for $n = k + 1$. We have already seen that the result is true for $n = 1$. Using the above relation, we see that it is true for $n = 2, n = 3 \dots$ Hence it is true for any value of n .

$$\therefore [x, p^n] = i\hbar n p^{n-1}$$

Example 5 : Prove that $[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$

$$\begin{aligned} \text{Solution : We have } [\hat{A}, \hat{B} + \hat{C}] &= \hat{A}(\hat{B} + \hat{C}) - (\hat{B} + \hat{C})\hat{A} \\ &= \hat{A}\hat{B} + \hat{A}\hat{C} - \hat{B}\hat{A} - \hat{C}\hat{A} \\ &= \hat{A}\hat{B} - \hat{B}\hat{A} + \hat{A}\hat{C} - \hat{C}\hat{A} \\ &= [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \end{aligned}$$

$$\therefore [\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}]$$

Thus, Commutators obey the law of distribution w. r. t. addition.

Example 6 : Prove that $[[\hat{A}, \hat{B}]\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$

$$\begin{aligned} \text{Solution : We have } [[\hat{A}, \hat{B}]\hat{C}] &= \hat{A}(\hat{B}\hat{C}) - (\hat{B}\hat{C})\hat{A} \\ &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} \end{aligned}$$

Subtracting and adding $\hat{B}\hat{A}\hat{C}$ on RHS of above equation we get

$$\begin{aligned} [\hat{A}, \hat{B}\hat{C}] &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{C} + \hat{B}(\hat{A}\hat{C} - \hat{C}\hat{A}) \\ &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \end{aligned}$$

$$\therefore [[\hat{A}, \hat{B}]\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$$

Example 7 : Prove that $[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$

$$\begin{aligned} \text{Solution : We have } [\hat{A}, [\hat{B}, \hat{C}]] &= [\hat{A}, \hat{B}\hat{C} - \hat{C}\hat{B}] \\ &= \hat{A}(\hat{B}\hat{C} - \hat{C}\hat{B}) - (\hat{B}\hat{C} - \hat{C}\hat{B})\hat{A} \\ &= \hat{A}\hat{B}\hat{C} - \hat{A}\hat{C}\hat{B} - \hat{B}\hat{C}\hat{A} + \hat{C}\hat{B}\hat{A} \end{aligned}$$

Similarly $[\hat{B}, [\hat{C}, \hat{A}]] = \hat{B}\hat{C}\hat{A} - \hat{B}\hat{A}\hat{C} - \hat{C}\hat{A}\hat{B} + \hat{A}\hat{C}\hat{B}$

And $[\hat{C}, [\hat{A}, \hat{B}]] = \hat{C}\hat{A}\hat{B} - \hat{C}\hat{B}\hat{A} - \hat{A}\hat{B}\hat{C} + \hat{B}\hat{A}\hat{C}$

$$\begin{aligned} \therefore [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] \\ = \hat{A}\hat{B}\hat{C} - \hat{A}\hat{C}\hat{B} - \hat{B}\hat{C}\hat{A} + \hat{C}\hat{B}\hat{A} \\ + \hat{B}\hat{C}\hat{A} - \hat{B}\hat{A}\hat{C} - \hat{C}\hat{A}\hat{B} + \hat{A}\hat{C}\hat{B} \\ + \hat{C}\hat{A}\hat{B} - \hat{C}\hat{B}\hat{A} - \hat{A}\hat{B}\hat{C} + \hat{B}\hat{A}\hat{C} \end{aligned}$$

All the terms on R.H.S. get cancelled in pairs.

$$\therefore [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$$

Example 8 : Show that $[\hat{A}, \hat{B}^{-1}] = \hat{B}^{-1} [\hat{B}, \hat{A}] \hat{B}^{-1}$

Solution : Consider the right hand side

$$\begin{aligned} \hat{B}^{-1} [\hat{B}, \hat{A}] \hat{B}^{-1} &= \hat{B}^{-1} (\hat{B}\hat{A} - \hat{A}\hat{B}) \hat{B}^{-1} \\ &= \hat{B}^{-1} (\hat{B}\hat{A}\hat{B}^{-1} - \hat{A}\hat{B}\hat{B}^{-1}) \\ &= \hat{B}^{-1} \hat{B} \hat{A} \hat{B}^{-1} - \hat{B}^{-1} \hat{A} \hat{B} \hat{B}^{-1} \\ &= \hat{A} \hat{B}^{-1} - \hat{B}^{-1} \hat{A} \quad (\because \hat{B}^{-1} \hat{B} = \hat{B} \hat{B}^{-1} = 1) \\ &= [\hat{A}, \hat{B}^{-1}] \end{aligned}$$

$$\therefore [\hat{A}, \hat{B}^{-1}] = \hat{B}^{-1} [\hat{B}, \hat{A}] \hat{B}^{-1}$$

Example 9 : By mathematical induction show that

$$[x^n, p] = i\hbar n x^{n-1}$$

Solution : The essence of the principle of mathematical induction is as under. Suppose that a certain mathematical relation is true for $n = k$ and we are able to prove that it is true for $n = k + 1$ and also that the relation is true for value of n over its range, then in general it is true for any value of n . Using this principle we shall now prove the required result.

For $n=1$,

$$[x, p] = i\hbar$$

Let the relation is true for $n = k$, i.e.

$$[x^k, p] = i\hbar k x^{k-1}$$

Now we will show that it is true for $n = k + 1$

$$[x^{k+1}, p] = [x x^k, p]$$

$$\begin{aligned}
 &= x[x^k, p] + [x, p]x^k \\
 &= x i \hbar k x^{k-1} + i \hbar x^k \\
 &= (k+1)i\hbar x^{k+1}
 \end{aligned}$$

Because the result is true for $n = k + 1$, hence in general it will be true for any positive integer.

$$\therefore [x^n, p] = i \hbar n x^{n-1}$$

Example 10 : Show that the time dependence of the expectation value of a dynamical variable can be expressed as

$$\frac{d\langle A \rangle}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{i}{\hbar} \langle [H, \hat{A}] \rangle$$

where H is Hamiltonian operator and \hat{A} is operator corresponding to some physical variable.

Solution : Expectation value of A is given as

$$\langle A \rangle = \int \Psi^*(x, t) \hat{A} \Psi(x, t) dx$$

then

$$\frac{d\langle A \rangle}{dt} = \frac{\partial}{\partial t} \int \Psi^*(x, t) \hat{A} \Psi(x, t) dx$$

$$= \int \left[\frac{\partial \Psi^*}{\partial t} \hat{A} \Psi + \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi + \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} \right] dx$$

$$= \int \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi dx + \int \left[\frac{\partial \Psi^*}{\partial t} \hat{A} \Psi + \Psi^* \hat{A} \frac{\partial \Psi}{\partial t} \right] dx \quad \dots (i)$$

Schrödinger's time dependent equation is given as

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

or

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

\therefore

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar} H\Psi = -\frac{i}{\hbar} H\Psi$$

Complex conjugate of above equation is

$$\frac{\partial \Psi^*}{\partial t} = \frac{i}{\hbar} (H\Psi)^*$$

Using $\frac{\partial \Psi}{\partial t}$ and $\frac{\partial \Psi^*}{\partial t}$ in equation (i), we get

$$\frac{d\langle A \rangle}{dt} = \int \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi dx + \int \left[\frac{i}{\hbar} (H\Psi)^* \hat{A} \Psi + \Psi^* \hat{A} \left(-\frac{i}{\hbar} H\Psi\right) \right] dx$$

$$\begin{aligned}
 H\Psi &= E\Psi \\
 &= -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}
 \end{aligned}$$

Since the Hamiltonian operator is hermitian it satisfies the condition given in equation (3.1). With this condition the above equation becomes

$$\frac{d\langle A \rangle}{dt} = \int \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi dx + \int \left[\frac{i}{\hbar} \Psi^* H \hat{A} \Psi + \Psi^* \hat{A} (-i/\hbar) H \Psi \right] dx$$

$$\frac{d\langle A \rangle}{dt} = \int \Psi^* \frac{\partial \hat{A}}{\partial t} \Psi dx + \frac{i}{\hbar} \int [\Psi^* H \hat{A} \Psi - \Psi^* \hat{A} H \Psi] dx$$

$$= \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{i}{\hbar} \int \Psi^* [H \hat{A} - \hat{A} H] \Psi dx$$

$$= \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{i}{\hbar} \int \Psi^* [H, \hat{A}] \Psi dx$$

$$\therefore \frac{d\langle A \rangle}{dt} = \left\langle \frac{\partial A}{\partial t} \right\rangle + \frac{i}{\hbar} \langle [H, \hat{A}] \rangle$$

QUESTIONS AND PROBLEMS

1. Define hermitian operator.
2. Show that eigen values of hermitian operators are all real.
3. Show that momentum operator $-i\hbar \frac{\partial}{\partial x}$ is hermitian.
4. Show that $[x, p_x] = i\hbar$ *Imp*
5. Prove that $[x, p^n] = i\hbar n p^{n-1}$
6. Prove that $[x^n, p] = i\hbar n x^{n-1}$
7. Using cartesian components of operators L_x, L_y and L_z prove that

$$[L_x, L_y] = i\hbar L_z$$
 and

$$[L^2, L_x] = 0$$
8. Prove that $[L_z, y] = -i\hbar x$
9. Show that if two operators \hat{A} and \hat{B} have a common set of eigen functions, then they commute with each other.
10. Show that $[A, B^{-1}] = B^{-1}[B, A]B^{-1}$
11. Prove that $[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0$.
12. Show that eigen value of operator L_z is integral multiple of \hbar .
13. Write a note on raising and lowering operators.
14. Define ladder operators. Show that the ladder operator L_+ increases the eigen value of operator L_z by \hbar .
15. Explain the concept of parity. Show that eigen values of parity operator are +1 and -1.
16. Find the parity of function (i) $Ae^{-\alpha x^2}$ (ii) $\cos \theta e^{-\alpha r}$.

CHAPTER 4

APPLICATIONS OF SCHRÖDINGER EQUATION

INTRODUCTION

In this chapter we shall obtain some interesting predictions concerning quantum mechanical phenomenon. We will consider some problems in which constraints are applied on the motion of a particle. Constraints are applied by using the different forms of potentials. The predictions corresponding to these constraints will be obtained by solving time-independent Schrödinger equation. The eigen functions and eigen values will also be obtained. Quantization of energy is one of the very interesting features of quantum mechanical problems. Some problems involving quantization of energy will be studied in this chapter.

4.1 FREE PARTICLE OR ZERO POTENTIAL

The simplest form of the time independent Schrödinger equation is the case in which the particle is moving through constant potential *i.e.* $V(x) = \text{constant}$. Since the force $F = -\frac{dV}{dx}$ acting on the particle is zero. Thus, the particle m is a free particle. We know that in classical mechanics the free particle is either at rest or moving with constant momentum p . In either case the total energy of the particle $E = \frac{p^2}{2m} + V = \frac{p^2}{2m}$ is constant.

To predict the quantum mechanical behavior of a free particle, we will solve the Schrödinger's time independent equation. We have M'07

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0$$

With $V = 0$, we get

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \dots(4.1)$$

$$\text{Let } k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \frac{d^2\psi}{dx^2} + k^2 \psi = 0 \quad \dots(4.2)$$

The solutions of this equation are eigen functions. The possible solutions of equation (4.2) are e^{-ikx} and e^{ikx} .

The solution of time part is given as $\phi(t) = e^{-iEt/\hbar}$. Since we have $E = \hbar\omega$, therefore, $\phi(t) = e^{-i\omega t}$. The wave function is

$$\Psi(x, t) = \psi(x) \phi(t)$$

$$\therefore \Psi(x, t) = e^{ikx} e^{-i\omega t} = e^{i(kx - \omega t)} \quad \dots(4.3)$$

$$\text{or } \Psi(x, t) = e^{-ikx} e^{-i\omega t} = e^{-i(kx + \omega t)} \quad \dots(4.4)$$

Equation (4.3) represents the wave propagating along the positive x axis and equation (4.4) represents wave propagating along the negative x axis.

Let us consider the equation (4.3) and let A be the normalization constant, then a wave propagating along positive x axis is given by

$$\Psi(x, t) = A e^{i(kx - \omega t)} \quad \dots(4.5)$$

The probability density is :

$$\Psi^* \Psi = A^* A = \text{constant}$$

Thus the particle is equally likely to be found anywhere and hence the uncertainty in the position is $\Delta x = \infty$. From $\Delta x \Delta p \geq \hbar/2$, we get $\Delta p = 0$ i.e. the momentum of the particle is definite. That is the particle has precise value of momentum as indicated by de Broglie equation $p = h/\lambda = \hbar k$. Since the particle can be found anywhere, there is infinite time available to measure the energy of the particle traveling over an infinite length. From this uncertainty in time $\Delta t = \infty$. From equation $\Delta E \Delta t \geq \hbar/2$, the uncertainty in energy $\Delta E = 0$. Thus, we get precise value of the energy. This is also indicated by de Broglie-Einstein equation $E = \hbar\omega$. As the wave function contains single value of k and ω , p and E are single valued.

There is difficulty in the normalization of free particle wave function. According to normalization condition

$$\int_{-\infty}^{\infty} \Psi^* \Psi dx = AA^* \int_{-\infty}^{\infty} dx = 1$$

$$\therefore AA^* \int_{-\infty}^{\infty} dx = 1$$

The amplitude must be vanishingly small as $\int_{-\infty}^{\infty} dx$ has an infinite value. Therefore, the

probability of finding the particle will be vanishingly small everywhere. Thus there is difficulty in connection with the normalization of the free particle wave function. However, we should not worry too much about this mathematical difficulty because firstly, we cannot have a particle which is completely free from the forces. Secondly, in actual practice the range of motion of the particle is not infinite.

Energy spectrum of the free particle :

The energy of the free particle is $E = \frac{p^2}{2m}$. For particle moving in the + X direction, p is positive and moving along -X axis, p is negative. But p^2 is positive and can have any value between 0 and ∞ . Therefore, range of energy is also from 0 to ∞ . Thus, the energy spectrum of a free particle is continuous.

4.2 INFINITE DEEP POTENTIAL WELL

Let us consider one-dimensional motion along X-axis of a particle between two points $x = 0$ and $x = a$. The particle is free to move between 0 and a . But it cannot cross to the left of $x = 0$ and to the right of $x = a$. This situation is represented by the potential function V given by

$$\begin{aligned} V &= \infty & x &\leq 0 \\ V &= 0 & 0 < x < a \\ V &= \infty & x &\geq a \end{aligned}$$

The Fig. 4.1 represents infinitely deep potential well.

This potential has feature that it will bind the particle within $x = 0$ and $x = a$, with any finite energy $E \geq 0$. In classical mechanics any of these energies are possible and the energy spectrum is continuous. But in quantum mechanics as constraints are applied, it will be shown below that only certain discrete energy values are allowed. A particle moving under the influence of an infinite square well potential is often called a particle in a one-dimensional rigid box.

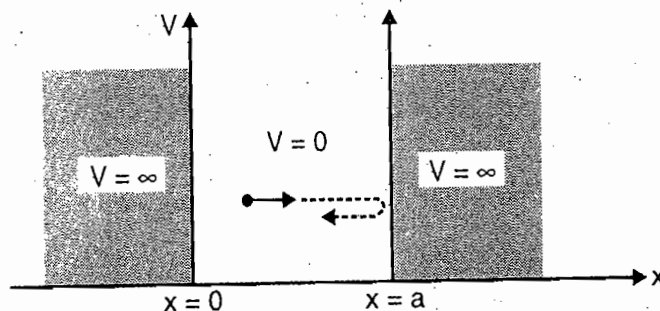


Fig. 4.1 : Graphical representation of infinite potential well

In the region within the potential well, the time-independent Schrödinger's equation can be solved to obtain eigen values of energy and corresponding eigen functions.

Schrödinger's time independent equation is given as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

In the region $0 < x < a$, above equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Let

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

This is second order linear homogeneous differential equation in ψ . Its general solution may be written as

$$\psi(x) = A \sin kx + B \cos kx$$

where A and B are arbitrary constants and can be obtained by using the boundary conditions on ψ .

Outside the region $0 < x < a$ the wave function $\psi(x) = 0$

Also, at the boundaries of the potential well, $\psi(x) = 0$

Therefore, at $x = 0$, $\psi(x) = 0$, which gives

$$(I) \quad B = 0$$

Using in equation (4.9), we get

$$\psi(x) = A \sin(kx) \quad \dots(4.10)$$

At $x = a$, $\psi(x) = 0$, which gives

$$(II) \quad A \sin(ka) = 0$$

This is true if $A = 0$ or $\sin ka = 0$. But, $A \neq 0$, because otherwise $\psi = 0$ everywhere. Which is not possible because then probability of finding the particle inside the well is zero. This contradicts the particle is present and moving between $x = 0$ and $x = a$.

Therefore, only alternative is $\sin ka = 0$.

Thus we choose k such that $\sin ka = 0$. This is possible only if

$$ka = n\pi \quad \text{where } n = 1, 2, 3, 4, 5, \dots$$

$$\text{or} \quad k = \frac{n\pi}{a} \quad \dots(4.11)$$

$$\therefore \quad \psi(x) = A \sin\left(\frac{n\pi}{a}x\right) \quad \dots(4.12)$$

Since we have $k^2 = \frac{2mE}{\hbar^2}$, therefore,

$$\frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

Thus, we get energy eigen value

$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Since energy E depends on index ' n ', we may write

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \dots(4.13)$$

where $n = 1, 2, 3, 4, \dots$

Thus, we see that only certain values of energy are allowed as given by equation (4.13). As n is an integer, there is thus infinite sequence of discrete energy levels which correspond to positive integer n . This integer n is called a *quantum number*. The quantum state with lowest n ($= 1$) is called the ground state. The levels corresponding to $n = 2, 3, 4, \dots$ etc. are called excited states.

Let us consider the energy for $n = 1$ level. The energy is

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2} \quad \text{Zero pt energy} \quad \dots(4.14)$$

This is also called the zero-point energy. It is the lowest possible energy the particle can have if it is bound in the infinite potential well region. Classically, the lowest energy is zero. But quantum mechanically the ground state cannot have zero energy value. The phenomenon is basically a result of Heisenberg's uncertainty principle. If the particle is bound by the infinite potential well of the width a , then the uncertainty in its position will be $\Delta x = a$. Consequently, the uncertainty in the momentum will be $\Delta p = \hbar/2a$ and hence have corresponding energy. Thus the uncertainty principle cannot allow the particle to be bound by the potential and having zero energy. The higher energy levels are

$$E_2 = 4 \frac{\pi^2 \hbar^2}{2ma^2} = 4E_1$$

$$E_3 = 9 \frac{\pi^2 \hbar^2}{2ma^2} = 9E_1$$

and so on...

h is
his

The energy spectrum is shown in Fig. 4.2.

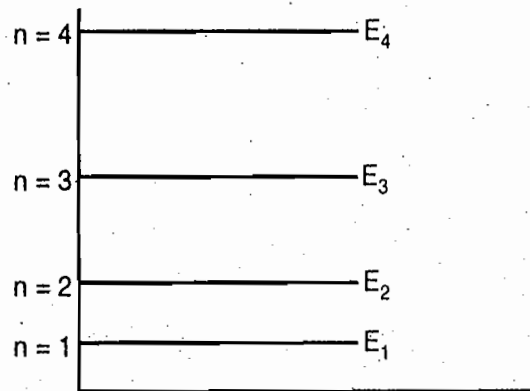


Fig. 4.2 : Energy spectrum

Wave functions :

The wave functions are given by the equation (4.12). As it is characteristic of n we may write

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a}x\right) \quad A = \sqrt{2/a} \quad \dots(4.15)$$

As the particle is confined to move between $x = 0$ and $x = a$, the condition for normalisation is

$$\int_0^a |\psi_n(x)|^2 dx = 1 \quad A^* \sin\left(\frac{n\pi}{a}x\right) A \sin\left(\frac{n\pi}{a}x\right) \quad \sin^2 x = \frac{1 - \cos 2x}{2}$$

$$\therefore \int_0^a |A|^2 \sin^2\left(\frac{n\pi}{a}x\right) dx = 1$$

$$|A|^2 \int_0^a \sin^2\left(\frac{n\pi}{a}x\right) dx = 1 \quad \dots(4.16)$$

We have $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$, therefore, equation (4.16) becomes

$$|A|^2 \int_0^a \frac{1}{2} \left[1 - \cos\left(\frac{2n\pi}{a}x\right) \right] dx = 1$$

$$\frac{|A|^2}{2} \int_0^a \left[1 - \cos\left(\frac{2n\pi}{a}x\right) \right] dx = 1$$

$$\frac{|A|^2}{2} \int_0^a \left[dx - \cos\left(\frac{2n\pi}{a}x\right) dx \right] = 1$$

$$\frac{|A|^2}{2} \left[x - \frac{\sin\left(\frac{2n\pi}{a}x\right)}{\frac{2n\pi}{a}} \right]_0^a = 1$$

$$\frac{|A|^2}{2} a = 1$$

$$\therefore |A| = \sqrt{\frac{2}{a}}$$

Thus, on normalisation we get

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad \dots(4.17)$$

This is the wave function corresponding to energy eigen value E_n .

The ground state function ($n = 1$) is:

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right) \quad \dots(4.18)$$

In Fig. 4.3 (a) and the first three wave functions ψ_1 , ψ_2 and ψ_3 are shown and in Fig. 4.3 (b) corresponding probability densities $|\psi_1|^2$, $|\psi_2|^2$ and $|\psi_3|^2$ are shown

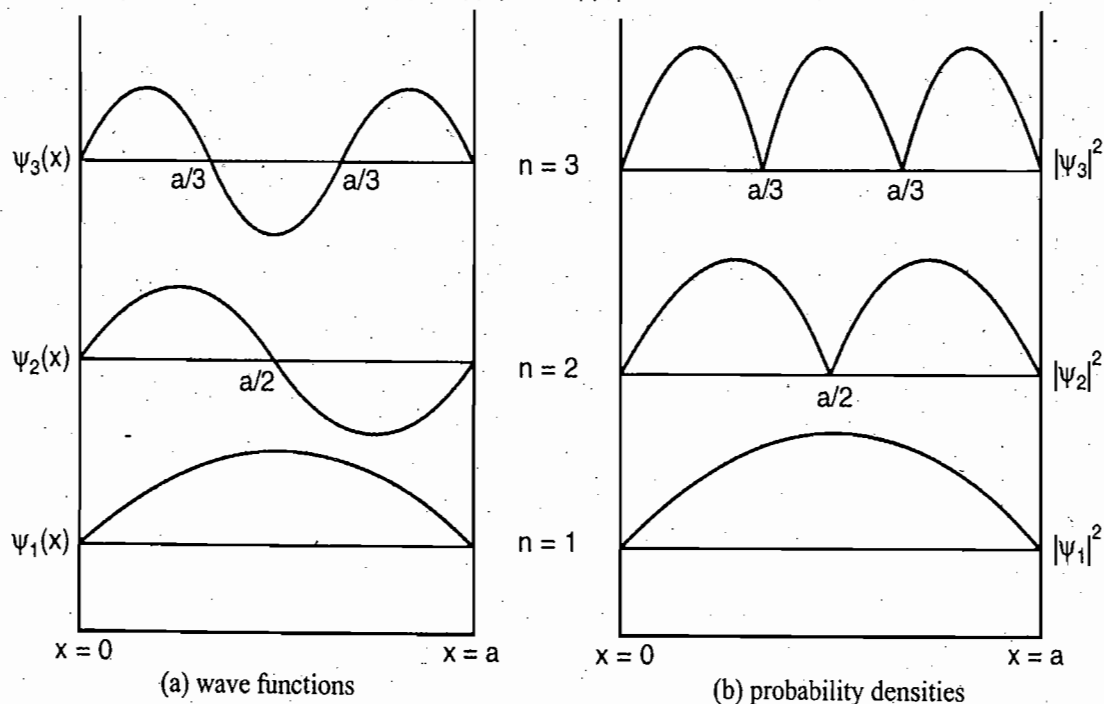


Fig. : 4.3

4.3 PARTICLE IN THREE DIMENSIONAL RIGID BOX $\psi = \psi_1 \psi_2 \psi_3$

Now we shall consider the case of a particle enclosed in a rectangular box of sides a , b and c in length. The potential function $V(x, y, z)$ is zero inside the box and outside the box the potential is infinite. As the potential is infinite outside the box, the particle is confined to move only inside the box and cannot come out of it. Thus, the box is called rigid box. Mathematically the potential may be represented as

$$V = \begin{cases} 0 & 0 < x < a \\ & 0 < y < b \\ & 0 < z < c \end{cases}$$

elsewhere

The rectangular box is shown in Fig. 4.4

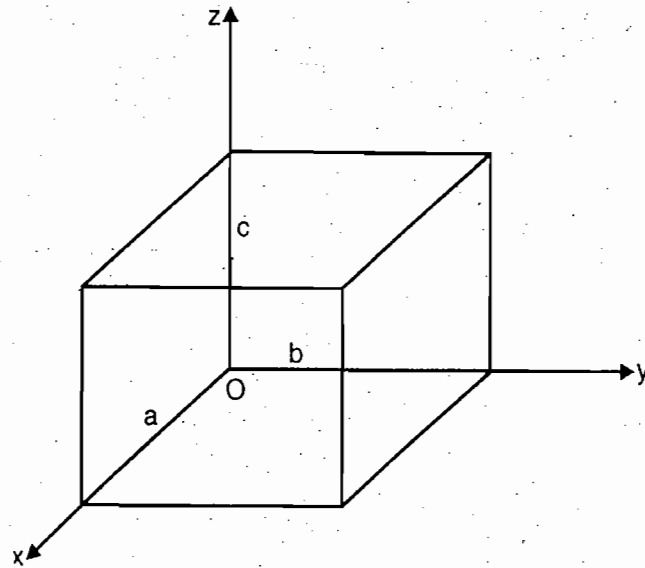


Fig. 4.4

Three dimensional time-independent Schrödinger's equation is given as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

Inside the box, we have $V=0$, therefore, the Schrödinger's equation takes the form

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0$$

$V=0$
 $\psi = \psi_1 \psi_2 \psi_3$
 $\frac{\partial}{\partial} \psi_1 \psi_2 \psi_3$
 $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$... (4.19)

where $\psi = \psi(x, y, z)$.

Equation (4.19) in Cartesian coordinate system may be written as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \dots (4.20)$$

Equation (4.20) can be solved by separation of variables method.

Let $\psi(x, y, z) = \psi_1(x) \psi_2(y) \psi_3(z)$ $\psi = \psi_1 \psi_2 \psi_3$... (4.21)

Using equation (4.21) in equation (4.20), we get

$$\frac{\partial^2 \psi_1 \psi_2 \psi_3}{\partial x^2} + \frac{\partial^2 \psi_1 \psi_2 \psi_3}{\partial y^2} + \frac{\partial^2 \psi_1 \psi_2 \psi_3}{\partial z^2} + \frac{2mE}{\hbar^2} \psi_1 \psi_2 \psi_3 = 0$$

$$\therefore \psi_2 \psi_3 \frac{\partial^2 \psi_1}{\partial x^2} + \psi_1 \psi_3 \frac{\partial^2 \psi_2}{\partial y^2} + \psi_1 \psi_2 \frac{\partial^2 \psi_3}{\partial z^2} + \frac{2mE}{\hbar^2} \psi_1 \psi_2 \psi_3 = 0$$

Dividing above equation throughout by $\psi_1 \psi_2 \psi_3$, we get

$$\frac{1}{\psi_1} \frac{\partial^2 \psi_1}{\partial x^2} + \frac{1}{\psi_2} \frac{\partial^2 \psi_2}{\partial y^2} + \frac{1}{\psi_3} \frac{\partial^2 \psi_3}{\partial z^2} + \frac{2mE}{\hbar^2} = 0$$

or

$$\frac{1}{\psi_1} \frac{d^2 \psi_1}{dx^2} + \frac{1}{\psi_2} \frac{d^2 \psi_2}{dy^2} + \frac{1}{\psi_3} \frac{d^2 \psi_3}{dz^2} + \frac{2mE}{\hbar^2} = 0$$

\therefore

$$\frac{1}{\psi_1} \frac{d^2 \psi_1}{dx^2} + \frac{1}{\psi_2} \frac{d^2 \psi_2}{dy^2} + \frac{1}{\psi_3} \frac{d^2 \psi_3}{dz^2} = - \frac{2mE}{\hbar^2} \quad \dots (4.22)$$

Let $k^2 = \frac{2mE}{\hbar^2}$,

$$\therefore \frac{1}{\psi_1} \frac{d^2 \psi_1}{dx^2} + \frac{1}{\psi_2} \frac{d^2 \psi_2}{dy^2} + \frac{1}{\psi_3} \frac{d^2 \psi_3}{dz^2} = - k^2 \quad \dots (4.23)$$

$f(x) \quad f(y) \quad f(z)$
 $-k_1^2 \quad -k_2^2 \quad -k_3^2$

On LHS, the first term depends on x only, second term depends on y only and the third term depends on z only. On RHS the term $-k^2$ is constant. Since x, y, z are independent variables, each of the first three terms must be constants. Denoting them by $-k_1^2, -k_2^2$ and $-k_3^2$ respectively, we have

$$\frac{1}{\psi_1} \frac{d^2 \psi_1}{dx^2} = -k_1^2 \quad \dots(4.24)$$

$$\frac{1}{\psi_2} \frac{d^2 \psi_2}{dy^2} = -k_2^2 \quad \dots(4.25)$$

$$\frac{1}{\psi_3} \frac{d^2 \psi_3}{dz^2} = -k_3^2 \quad \dots(4.26)$$

Using above three equations in equation (4.23), we get

$$k_1^2 + k_2^2 + k_3^2 = k^2 \quad \dots(4.27)$$

Equations (4.24), (4.25) and (4.26) can be written as

$$\frac{d^2 \psi_1}{dx^2} + k_1^2 \psi_1 = 0 \quad \dots(4.28)$$

$$\frac{d^2 \psi_2}{dy^2} + k_2^2 \psi_2 = 0 \quad \dots(4.29)$$

$$\frac{d^2 \psi_3}{dz^2} + k_3^2 \psi_3 = 0 \quad \dots(4.30)$$

The general solution of equation (4.28) may be written as

$$\psi_1(x) = A_1 \sin k_1 x + B_1 \cos k_1 x \quad \dots(4.31)$$

where A_1 and B_1 are arbitrary constants and can be obtained by using boundary conditions on ψ .

Outside the region $0 < x < a$ the wave function $\psi_1(x) = 0$

Also at the boundaries of the rigid box, $\psi_1(x) = 0$

Thus, at $x = 0$, $\psi_1(x) = 0$. Substitution in equation (4.31) gives

$$B_1 = 0$$

Using in equation (4.31), we get

$$\psi_1(x) = A_1 \sin(k_1 x) \quad \dots(4.32)$$

At $x = a$, $\psi_1(x) = 0$, which gives

$$A_1 \sin(k_1 a) = 0$$

In the above, $A_1 \neq 0$. Because then ψ_1 will be zero every inside the box between $x = 0$ and $x = a$. There is always some probability of finding the particle within $x = 0$ and $x = a$. Therefore, $\sin(k_1 a) = 0$.

$$\therefore k_1 a = n_1 \pi \quad \text{where } n_1 = 1, 2, 3, 4, \dots$$

or

$$k_1 = \frac{n_1 \pi}{a} \quad \dots(4.33)$$

where $n_1 = 1, 2, 3, 4, 5, \dots$

$$\therefore \psi_1(x) = A_1 \sin\left(\frac{n_1 \pi}{a} x\right) \quad \dots(4.34)$$

If we normalize equation in the range 0 to a , we get

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_1\pi}{a}x\right) \quad \dots(4.35)$$

Similarly, solutions of equations (4.29) and (4.30) respectively can be written as

$$\psi_2(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_2\pi}{b}y\right)$$

$$\psi_3(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_3\pi}{c}z\right)$$

where $n_3 = 1, 2, 3, \dots$

Using ψ_1, ψ_2 and ψ_3 in equation (4.21), we get resultant wave function ψ . As it depends on the integers n_1, n_2 and n_3 , we may write $\psi = \psi_1 \psi_2 \psi_3$

$$\psi_{n_1 n_2 n_3} = \sqrt{\frac{2}{a}} \sin\left(\frac{n_1\pi}{a}x\right) \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n_2\pi}{b}y\right) \cdot \sqrt{\frac{2}{c}} \sin\left(\frac{n_3\pi}{c}z\right)$$

$$\text{or } \psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_1\pi}{a}x\right) \cdot \sin\left(\frac{n_2\pi}{b}y\right) \cdot \sin\left(\frac{n_3\pi}{c}z\right) \quad \dots(4.36)$$

Using k_1, k_2 and k_3 in equation (4.27), we get

$$\frac{n_1^2 \pi^2}{a^2} + \frac{n_2^2 \pi^2}{b^2} + \frac{n_3^2 \pi^2}{c^2} = k^2$$

$$\text{Since } k^2 = \frac{2mE}{\hbar^2}$$

$$\therefore \pi^2 \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) = \frac{2mE}{\hbar^2}$$

$$\therefore E = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad \dots(4.37)$$

Since energy eigen values depend on the indices n_1, n_2 and n_3 , we may write

$$E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right) \quad \dots(4.38)$$

The ground state of the system corresponds to $n_1 = n_2 = n_3 = 1$ and is given by

$$E_{111} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) = \frac{\hbar^2 \pi^2}{2m} \left(\frac{3}{a^2} \right)$$

Let us consider the special case of motion of a particle in cubical box ($a = b = c$). For this case, we get

$$\psi_{n_1 n_2 n_3} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_1\pi}{a}x\right) \sin\left(\frac{n_2\pi}{a}y\right) \sin\left(\frac{n_3\pi}{a}z\right) \quad \dots(4.39)$$

and energy eigen value

$$E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2ma^2} (n_1^2 + n_2^2 + n_3^2) \quad \dots(4.40)$$

The ground state energy or zero-point energy can be obtained by using $n_1 = n_2 = n_3 = 1$ in equation (4.40), and it is $E_{111} = 3 \frac{\hbar^2 \pi^2}{2ma^2}$.

The ground state wave function is given as

$$\psi_{111} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{\pi}{a}z\right) \quad \dots(4.41)$$

The next higher energy level i.e. first excited state energy corresponds to following three combinations of n_1, n_2 and n_3

n_1	n_2	n_3
1	1	2
1	2	1
2	1	1

All these three combination will have the same energy $E_{112} = E_{121} = E_{211} = 6 \frac{\hbar^2 \pi^2}{2ma^2}$

The wave functions corresponding to above three states are

$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}z\right) \quad \text{for } n_1=1, n_2=1, n_3=2$$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}z\right) \quad \text{for } n_1=1, n_2=2, n_3=1$$

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{2\pi}{a}x\right) \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{\pi}{a}z\right) \quad \text{for } n_1=2, n_2=1, n_3=1$$

Thus, it is clear that there are three possible states of the particle corresponding to the same energy value $E = 6 \frac{\hbar^2 \pi^2}{2ma^2}$.

When there are more than one eigen functions corresponding to the same energy eigen value, the energy state of the particle is called *degenerate* and the order of degeneracy is equal to the number of eigen functions corresponding to the same energy. Thus, first excited state is *three fold degenerate*.

Second excited state corresponds to the set of three combinations of n_1, n_2, n_3 , which are

n_1	n_2	n_3
1	2	2
2	2	1
2	1	2

This state is three fold degenerate corresponding to same energy eigen value $E = 9 \frac{\hbar^2 \pi^2}{2ma^2}$.

The third excited state is corresponds to the $n_1 = 2, n_2 = 2, n_3 = 2$. This state is non-degenerate having energy $E = 12 \frac{\hbar^2 \pi^2}{2ma^2}$.

In the above, we discussed the motion of a particle in a 3-dimensional rigid box. We can also consider motion in 2-dimensional box. The formula for energy in this case is

$$E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} \right)$$

in

The corresponding energy eigen functions are

$$\Psi_{n_1 n_2} = \sqrt{\frac{4}{ab}} \sin\left(\frac{n_1 \pi}{a} x\right) \cdot \sin\left(\frac{n_2 \pi}{b} y\right)$$

For square box with sides equal to a , we have

41)

$$E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2ma^2} (n_1^2 + n_2^2)$$

ree

The ground state energy in this case corresponds to $n_1 = n_2 = 1$ and it is equal to $E = \frac{\hbar^2 \pi^2}{ma^2}$.

The higher energy levels can be easily determined.

4.4 ONE DIMENSIONAL POTENTIAL WELL OF FINITE DEPTH (SQUARE WELL POTENTIAL)

The square well potential is shown in the Fig. 4.5.

It may be mathematically expressed as

$$\begin{aligned} V &= V_0 & x &\leq -a \\ V &= 0 & -a < x < a \\ V &= V_0 & x &\geq a \end{aligned}$$

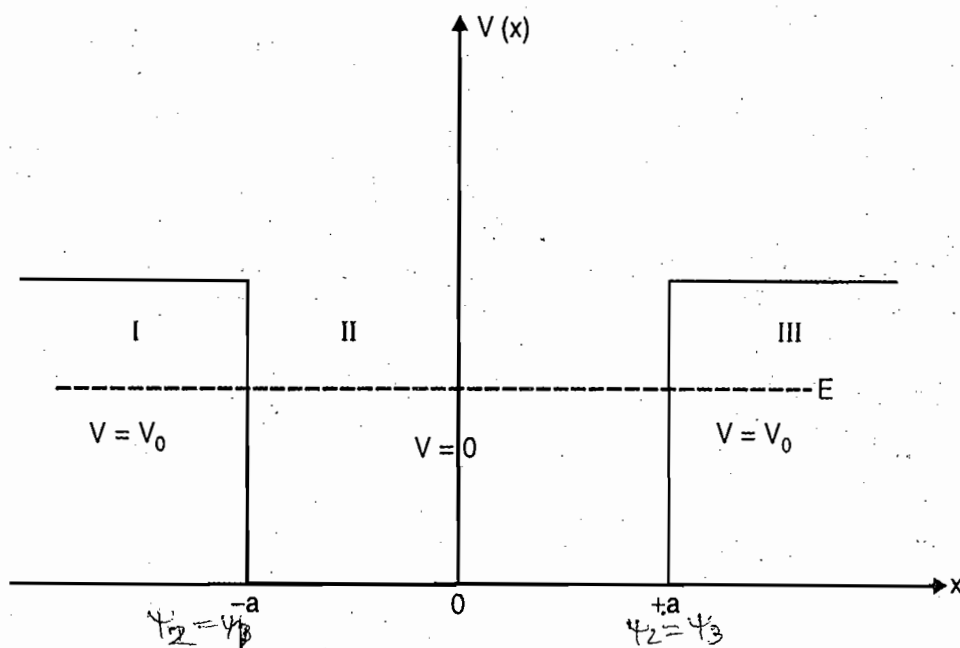


Fig. 4.5 : Finite potential well potential

If the particle has total energy $E < V_0$, then according to classical mechanics, it can only be in region II ($-a < x < a$). Because in region III and I the momentum $p = \sqrt{2m(E - V_0)}$ will be imaginary and it is not possible. Thus, the particle is permanently trapped to the region $-a < x < a$ and bounces back and forth between the ends of the region with momentum of constant magnitude $p = \sqrt{2mE}$.

For $E > V_0$, particle can go into region III and I but with decreasing kinetic energy $T = E - V_0$.

Case I : $E < V_0$

Let us first consider the case $E < V_0$.

We have one dimensional time independent Schrödinger's equation

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

$$\text{I} \quad V = V_0 \quad E < V_0$$

$$\text{II} \quad V = 0$$

$$\text{III} \quad V = V_0 \quad E < V_0 \quad \dots (4.42)$$

$$x \rightarrow -\infty \quad e^{-\alpha x} = 0$$

$$x \rightarrow \infty \quad e^{\alpha x} = 0$$

rate

also

In region I, $V = V_0$. Since $E < V_0$, we may write equation (4.42) as follows

$$\frac{d^2\psi_1}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi_1 = 0$$

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \text{ then } \dots(4.43)$$

In region II, Schrödinger's equation is

$$\frac{d^2\psi_2}{dx^2} + \frac{2mE}{\hbar^2}\psi_2 = 0$$

$$\psi = A \sin \alpha x + B \cos \alpha x$$

$$\frac{d^2\psi}{dx^2} - \alpha^2\psi = 0 \text{ then } \dots(4.44)$$

In region III, Schrödinger's equation is

$$\frac{d^2\psi_3}{dx^2} - \frac{2m}{\hbar^2}(V_0 - E)\psi_3 = 0$$

$$\psi = A e^{\alpha x} + B e^{-\alpha x} \dots(4.45)$$

Let

$$k^2 = \frac{2mE}{\hbar^2} \dots(4.46)$$

and

$$\alpha^2 = \frac{2m(V_0 - E)}{\hbar^2} \dots(4.47)$$

With above two equations, equations (4.43), (4.44) and (4.45) become

$$\frac{d^2\psi_1}{dx^2} - \alpha^2\psi_1 = 0 \text{ --- (I) } \psi_1(x) \text{ soln } \dots(4.48)$$

$$\frac{d^2\psi_2}{dx^2} + k^2\psi_2 = 0 \quad \psi_2 \dots(4.49)$$

and

$$\frac{d^2\psi_3}{dx^2} - \alpha^2\psi_3 = 0 \quad \psi_3 \dots(4.50)$$

The general solution of equation (4.48) is given by

$$\psi_1(x) = C e^{\alpha x} + D e^{-\alpha x} \dots(4.51)$$

In region I, $\psi_1(x)$ should vanish as $x \rightarrow -\infty$. From equation (4.51), we get $e^{-\alpha x} \rightarrow \infty$ as $x \rightarrow -\infty$. Therefore, to get acceptable solution in region I we must set $D = 0$ in equation (4.51). Hence

$$\psi_1(x) = C e^{\alpha x} \dots(4.52)$$

The general solution of equation (4.49) is given by

$$\psi_2(x) = A \sin kx + B \cos kx \dots(4.53)$$

The general solution of equation (4.50) is given by

$$\psi_3(x) = F e^{\alpha x} + G e^{-\alpha x}$$

In region III, $\psi_3(x)$ should vanish as $x \rightarrow \infty$. However, we get $e^{\alpha x} \rightarrow \infty$ as $x \rightarrow \infty$. Therefore, to get acceptable solution in region III we must have $F = 0$. Hence,

$$\psi_3(x) = G e^{-\alpha x} \dots(4.54)$$

The values of constants A, B, C and G can be determined by using the boundary conditions.

Now consider the boundary conditions

(1) First boundary condition:

$$\text{At } x = a, \quad |\psi_2(x)|_{x=a} = |\psi_3(x)|_{x=a}$$

$$\therefore \psi_2 = \psi_3 \quad A \sin ka + B \cos ka = G e^{-\alpha a}$$

and

$$\left(\frac{d\psi_2}{dx}\right)_{x=a} = \left(\frac{d\psi_3}{dx}\right)_{x=a}$$

$$\therefore (Ak \cos ka - Bk \sin ka) = -\alpha G e^{-\alpha a} \dots(4.56)$$

$$(\psi_2 = \psi_3) \pm (\psi_2 = \psi_1) \text{ at } x = -a$$

$$\frac{d}{dx}(\psi_2 = \psi_3) \pm \frac{d}{dx}(\psi_2 = \psi_1) \text{ at } x = -a$$

(+) & (-) for both

(2) Second boundary condition

$$\text{At } x = -a \quad \psi_2 = \psi_1$$

$$|\psi_2(x)|_{x=-a} = |\psi_1(x)|_{x=-a}$$

$$\therefore -A \sin ka + B \cos ka = C e^{-\alpha a} \quad \dots(4.57)$$

$$\text{and} \quad \left(\frac{d\psi_2}{dx}\right)_{x=-a} = \left(\frac{d\psi_1}{dx}\right)_{x=-a}$$

$$\therefore (Ak \cos ka + Bk \sin ka = \alpha C e^{-\alpha a}) \quad \dots(4.58)$$

Adding equations (4.55) and (4.57), we get

$$2B \cos ka = (G + C) e^{-\alpha a} \quad \dots(4.59)$$

Subtracting equation (4.57) from (4.55), we get

$$2A \sin ka = (G - C) e^{-\alpha a} \quad \dots(4.60)$$

Adding equations (4.56) and (4.58), we get

$$2Ak \cos ka = \alpha(C - G) e^{-\alpha a} \quad \dots(4.61)$$

Subtracting equation (4.56) from (4.58), we get

$$2Bk \sin ka = \alpha(C + G) e^{-\alpha a} \quad \dots(4.62)$$

Dividing equation (4.62) by (4.59), we get

$$\frac{k \sin ka}{\cos ka} = \alpha$$

$$\text{or} \quad k \tan ka = \alpha \quad \dots(4.63)$$

provided $B \neq 0$ and $G + C \neq 0$

Dividing equation (4.61) by (4.60), we get

$$\frac{k \cos ka}{\sin ka} = -\alpha$$

$$\text{or} \quad k \cot ka = -\alpha \quad \dots(4.64)$$

provided $A \neq 0$ and $G - C \neq 0$.It is easily shown below that equations (4.63) and (4.64) cannot be satisfied *simultaneously*.

This can be proved as under:

Suppose the equations (4.63) and (4.64) hold good simultaneously. Then, adding equations (4.63) and (4.64), we get

$$k \tan ka + k \cot ka = 0$$

$$\text{or} \quad \tan^2 ka = -1$$

But this cannot be valid as both k and a are real. Thus it is only possible either to satisfy equation (4.63) but not (4.64) or to satisfy equation (4.64) but not (4.63). Consequently, there are two classes of solutions for square well potential.

Class I Solutions:Suppose $k \tan ka = \alpha$ is trueSince $k \cot ka = -\alpha$ is not true, we must have $A = 0$ and $G - C = 0$ or $G = C$.

Using these constants in equations (4.52), (4.53) and (4.54), we get

$$\psi_1(x) = C e^{\alpha x} \quad x \leq 0$$

$$\psi_2(x) = B \cos kx \quad 0 < x < a$$

$$\psi_3(x) = C e^{-\alpha x} \quad x \geq 0$$

The parity of these functions is *even* parity as $\psi(x) = \psi(-x)$.

* & * *
add & subtract

For k

$$A = 0$$

$$G = C$$

For $-k$ $G = -C$

$$B = 0 \quad \cancel{G = C}$$

Class II solutions: For these class solutions,

$$k \cot ka = -\alpha \quad \text{is true.}$$

As $k \tan ka$ is not true, we must have $B = 0$ and $G + C = 0$ or $G = -C$.

Using these constants in equations (4.52), (4.53) and (4.54), we get

$$\begin{aligned}\psi_1(x) &= C e^{\alpha x} & x \leq 0 \\ \psi_2(x) &= A \sin kx & 0 < x < a \\ \psi_3(x) &= -C e^{-\alpha x} & x \geq a\end{aligned}$$

The parity of these functions is *odd* as $\psi(x) = -\psi(-x)$.

Energy eigen values for Class I solutions :

Let us first find energy eigen values for first class solutions. We have

$$k \tan ka = \alpha$$

Multiplying on both sides by a , we get

$$ka \tan ka = \alpha a$$

Let $\xi = ka$ and $\eta = \alpha a$

$$\therefore \quad \xi \tan \xi = \eta \quad \dots(4.65)$$

Thus, η is function of ξ .

On adding equations (4.46) and (4.47), we get

$$k^2 + \alpha^2 = \frac{2mE}{\hbar^2} + \frac{2m(V_0 - E)}{\hbar^2}$$

$$\text{or} \quad k^2 + \alpha^2 = \frac{2mV_0}{\hbar^2}$$

Multiplying on both sides by a^2 , we get

$$k^2 a^2 + \alpha^2 a^2 = \frac{2mV_0}{\hbar^2} a^2$$

$$\text{or} \quad \xi^2 + \eta^2 = \frac{2mV_0}{\hbar^2} a^2 \quad \dots(4.66)$$

$$\text{or} \quad \xi^2 + \eta^2 = r^2$$

In the above equation, $r = \sqrt{\frac{2mV_0}{\hbar^2}} a$

Equation (4.66) represents a circle of radius $r = \sqrt{\frac{2mV_0}{\hbar^2}} a$ on $\xi - \eta$ plane. Such a family of circles is shown in Fig. 4.6. The diagram is restricted to the first only. Let us consider equation (4.65), the function $\eta = \xi \tan \xi$ has zeros at $\xi = 0, \pi, 2\pi, 3\pi, \dots$ and asymptotes at $\xi = \pi/2, 3\pi/2, 5\pi/2, \dots$. Because $\tan \xi \rightarrow 0$ as $\xi \rightarrow 0, \pi, 2\pi, 3\pi$ and $\tan \xi \rightarrow \infty$ as $\xi \rightarrow \pi/2, 3\pi/2, 5\pi/2, \dots$. The pair of equations (4.65) and (4.66) can be solved to obtain allowed values of k . The quantization of energy can be seen by graphical method. The energy eigen values correspond to points of intersection of plot of equation (4.65) and (4.66) on $\xi - \eta$ plane. As ξ and η are obviously restricted to positive values, the points of intersection are taken in first quadrant as shown in Fig. 4.6. Each point of intersection corresponds to one allowed value of energy. The energy eigen values can be actually obtained by numerical methods.

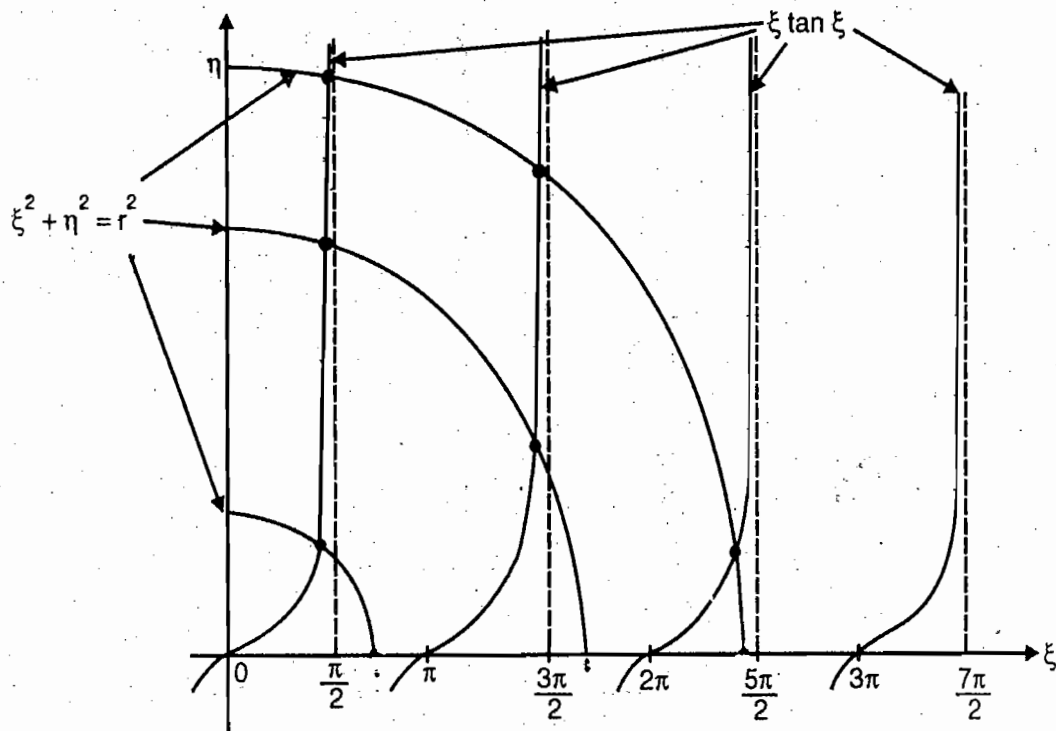


Fig. 4.6 Class I solutions

It is clear from the Fig. 4.6 that the number of allowed solutions of equation (4.65) and (4.66) depends on the radius of quarter circle given by equation (4.66). Each point of intersection gives an eigen value for $E < V_0$ corresponding to the eigen functions of the class I (i.e. even functions). If $r = \sqrt{\frac{2mV_0}{\hbar^2}} a < \pi$, there is only one point of intersection. Therefore, there exists one eigen value.

If $\pi < \sqrt{\frac{2mV_0}{\hbar^2}} a < 2\pi$, there exists two eigen values.

For $2\pi < \sqrt{\frac{2mV_0}{\hbar^2}} a < 3\pi$, there are three eigen values.

Eigen values for Class II solutions:

The eigen values corresponding to eigen functions of second class (i.e. odd functions) can be found in a similar manner. Multiplying equation (4.64) by a on both sides we get

$$ka \cot ka = -\alpha a$$

$$\text{or} \quad \xi \cot \xi = -\eta \quad \dots(4.67)$$

The intersection of curves of equations (4.67) and (4.66) in the first quadrant of ξ - η plane gives the energy eigen values. The plot is shown in Fig. 4.7.

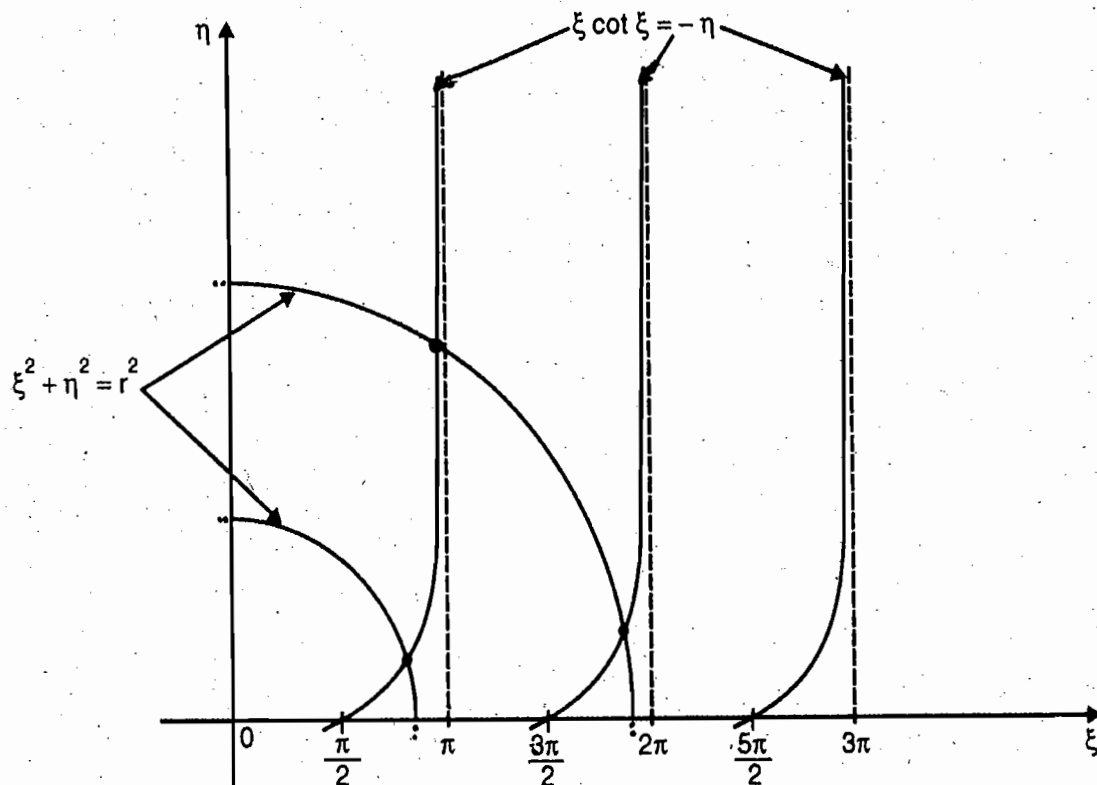


Fig. 4.7 Class II solutions

It will be apparent that there will be no energy eigen value for the second class if

$$\sqrt{\frac{2mV_0}{\hbar^2}} a < \frac{\pi}{2}.$$

If $\frac{\pi}{2} \leq \sqrt{\frac{2mV_0}{\hbar^2}} a \leq \frac{3\pi}{2}$, there is one eigen value. If $\frac{3\pi}{2} \leq \sqrt{\frac{2mV_0}{\hbar^2}} a \leq \frac{5\pi}{2}$ there are two eigen values and so on.

In this way, one can determine the number of energy eigen values knowing m , V_0 and a . Actual values of the energies, however, have to be determined with the help of a suitable numerical method as mentioned earlier also.

4.5 STEP POTENTIAL

The step potential function is defined as

$$V(x) = \begin{cases} 0 & \text{for } x \leq 0 \\ V_0 & \text{for } x > 0 \end{cases} \quad \left. \begin{array}{l} \text{Region I} \\ \text{Region II} \end{array} \right\} \quad \dots (4.68)$$

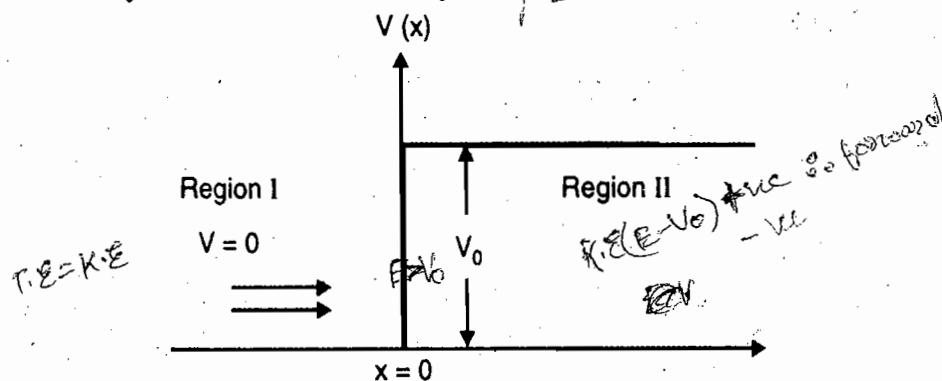


Fig. 4.8 : Step potential

Let a particle of energy E move from left to right, i.e. along the positive direction of x -axis (Fig 4.8).

We will first consider classical motion of a particle.

Classical treatment :

Cases I: $E > V_0$: In region I, $V = 0$. Therefore, total energy E of particle is equal to its kinetic energy. If the particle with this kinetic energy arrives at $x = 0$ boundary, it will be able to cross over to the region II as $E > V_0$. As Kinetic energy $(E - V_0)$ in region II is positive, the particle will move in forward direction. Thus for the case $E > V_0$, the reflection probability will be $R = 0$ and transmission probability $T = 1$.

Case II : $E < V_0$: Suppose a stream of particles is moving from region I towards region II. In region I, total energy E of particle is equal to its kinetic energy because $V=0$. If the particle with this kinetic energy arrive at $x = 0$ boundary, it will not be able to cross over to the region II as $E < V_0$. Because Kinetic energy $(E - V_0)$ in region II will be negative. Classically the particle with negative kinetic energy does not exist. Thus for the case $E < V_0$, the particle will definitely be reflected back at the boundary $x = 0$. Thus, the reflection probability will be $R = 1$ and transmission probability $T = 0$.

Now we shall see what is prediction of quantum theory for this problem.

Quantum Mechanical motion :

As the potential is independent of time, we use time-independent Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(4.69)$$

For region I, $V=0$. Therefore, the Schrödinger equation takes the form

$$\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 = 0 \quad \dots(4.70)$$

Let $k_1^2 = \frac{2mE}{\hbar^2}$. Therefore, equation (4.70) becomes

$$\frac{d^2\psi_1}{dx^2} + k_1^2 \psi_1 = 0 \quad \dots(4.71)$$

The general solution of this equation is

$$\psi_1 = A e^{ik_1x} + B e^{-ik_1x} \quad \dots(4.72)$$

incident wave reflected wave

Some particles may be reflected by the potential barrier and some transmitted. The first term $A e^{ik_1x}$ represents the *incident wave* and the second term $B e^{-ik_1x}$ represents *reflected wave*.

The Schrödinger wave equation for region II is $V = V_0$

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_2 = 0 \quad \dots(4.73)$$

We will consider two cases viz, $E > V_0$ and $E < V_0$.

Case I: ($E > V_0$): M.C.T

Let $k_2^2 = \frac{2m}{\hbar^2} (E - V_0)$. With this equation (4.73) becomes

$$\frac{d^2\psi_2}{dx^2} + k_2^2 \psi_2 = 0 \quad \dots(4.74)$$

The general solution of equation (4.74) is given by

$$\psi_2 = C e^{ik_2x} + D e^{-ik_2x} \quad \dots(4.75)$$

In region II, the term Ce^{ik_2x} represents a transmitted wave. There is no barrier after $x = 0$, and so no particles can flow to the left direction for $x > 0$. Thus, $D = 0$ in equation (4.75). So the solution in region II is

$$\psi_2 = Ce^{ik_2x} \quad \text{transmitted wave} \quad \dots(4.76)$$

To determine constants A, B and C in equations (4.72) and (4.76), we use the boundary conditions on wave functions.

At $x = 0$, $\psi_1 = \psi_2$

$$\therefore \frac{d}{dx}(\psi_1 = \psi_2) \quad [\psi_1]_{x=0} = [\psi_2]_{x=0} \quad A + B = C \quad \dots(4.77)$$

And

$$\left(\frac{d\psi_1}{dx}\right)_{x=0} = \left(\frac{d\psi_2}{dx}\right)_{x=0} \quad k_1(A - B) = k_2C \quad \dots(4.78)$$

Multiplying (4.77) by k_1 and adding to (4.78), we get

$$2k_1A = (k_1 + k_2)C$$

$$\therefore C = \frac{2k_1}{k_1 + k_2} A \quad \dots(4.79)$$

Substituting this value in equation (4.77), we get

$$B = \frac{k_1 - k_2}{k_1 + k_2} A \quad \dots(4.80)$$

The wave function for incident waves is given as

$$\psi_{in} = Ae^{ik_1x}$$

Its complex conjugate is $\psi_{in}^* = A^* e^{-ik_1x}$

The equation of probability current density is given as

$$\vec{J} = \frac{\hbar}{2mi} [\psi^* \nabla \psi - \psi \nabla \psi^*]$$

The current density for incident waves is

$$J_{in} = \frac{\hbar}{2mi} \left(\psi_{in}^* \frac{d\psi_{in}}{dx} - \psi_{in} \frac{d\psi_{in}^*}{dx} \right)$$

Using ψ_{in} and ψ_{in}^* in J_{in} , we get

$$J_{in} = \frac{\hbar k_1}{m} |A|^2 \quad \dots(4.81)$$

The wave function for reflected waves is given as

$$\psi_{ref} = Be^{-ik_1x}$$

Its complex conjugate is $\psi_{ref}^* = B^* e^{ik_1x}$

The current density for reflected waves is

$$J_{ref} = \frac{\hbar}{2mi} \left(\psi_{ref}^* \frac{d\psi_{ref}}{dx} - \psi_{ref} \frac{d\psi_{ref}^*}{dx} \right)$$

Using ψ_{ref} and ψ_{ref}^* in J_{ref} , we get

$$J_{ref} = \frac{\hbar k_1}{m} |B|^2 \quad \dots(4.82)$$

The transmitted wave is given as

$$\psi_2 = \psi_{tr} = C e^{ik_2x}$$

So the current density for transmitted wave will be

$$J_{tr} = \frac{\hbar k_2}{m} |C|^2 \quad \dots(4.83)$$

The probability of transmission T is given by

$$T = \frac{J_{tr}}{J_{in}} \quad \frac{t_2}{\epsilon n}$$

Using equations (4.83) and (4.81), we get

$$T = \frac{k_2 |C|^2}{k_1 |A|^2}$$

Using value of C from equation (4.79), we get

$$T = \frac{k_2}{k_1} \cdot \frac{4k_1^2}{(k_1 + k_2)^2}$$

or

$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2} \quad \dots(4.84)$$

The probability of reflection R is given by

$$R = \frac{J_{ref}}{J_{in}} \quad \frac{\epsilon_2}{\epsilon n}$$

Using equations (4.82) and (4.81), we get

$$\therefore R = \frac{|B|^2}{|A|^2}$$

Using equation (4.80) in above equation, we get

$$R = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} \quad \dots(4.85)$$

From equations (4.84) and (4.85), we get

$$R + T = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} + \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

$$\therefore R + T = 1$$

Case II: ($E < V_0$) Under this condition equation (4.73) becomes

$$\frac{d^2 \psi_2}{dx^2} - \frac{2m}{\hbar^2} (V_0 - E) \psi_2 = 0 \quad \dots(4.86)$$

$$\text{Let } \alpha^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$\therefore \frac{d^2 \psi_2}{dx^2} - \alpha^2 \psi_2 = 0 \quad \dots(4.87)$$

The transmitted wave equation is the solution of equation (4.87) in forward direction, which will be

$$\psi_2 = \psi_{tr} = C e^{-\alpha x} \quad \dots(4.88)$$

The current density for transmitted waves is

$$J_{tr} = \frac{\hbar}{2mi} \left(\psi_{tr}^* \frac{d\psi_{tr}}{dx} - \psi_{tr} \frac{d\psi_{tr}^*}{dx} \right)$$

We have

$$\psi_{tr}^* = C e^{-\alpha x}$$

Using ψ_{tr} and ψ_{tr}^* in J_{tr} , we get

$$J_{tr} = 0$$

Hence, $T = 0$

By definition, $R + T = 1$. Therefore, $R = 1$.

Thus, there is complete reflection.

The wave functions in region I and II for $E \geq V_0$ and $E < V_0$ are shown in Fig. 4.9.

Classically, for $E < V_0$, $R = 1$ and $T = 0$. Thus quantum mechanical results are the same as those of classical results for this case. However, the function has tail into the *classically forbidden region*. This tail is represented by the term $e^{-\alpha x}$ (See Fig. 4.9 b). the tail becomes shorter and shorter as E becomes smaller and smaller as compared to V_0 . There is some probability even though small of finding the particle in the region $x > 0$. This phenomenon is called *barrier penetration*. It may be noted that $T = 0$ does not contradict with the fact that there is some probability of finding the particle in region II, because there is no wave traveling continuously along + X axis in region II. We may say that the particle penetrates through the potential barrier at $x = 0$. However, it returns back into the region I after spending short time in region II.

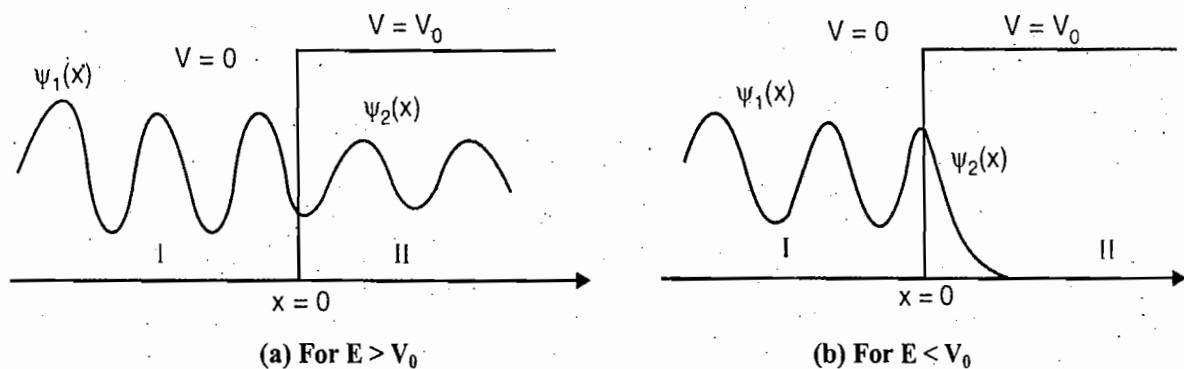


Fig. 4.9

4.6 POTENTIAL BARRIER

In this section we consider a potential barrier, illustrated in Fig. 4.10

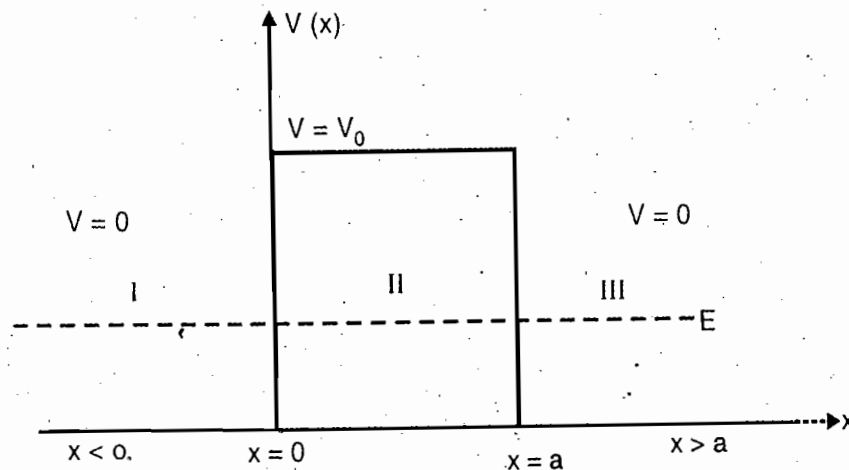


Fig. 4.10 : Potential barrier

The potential can be written as follows

$$\begin{aligned} V &= 0 & x < 0 \\ V &= V_0 & 0 \leq x \leq a \\ V &= 0 & x > a \end{aligned}$$

Classical motion: Suppose a particle of total energy E is moving from left to right in region I ($x < 0$). When it is incident on the barrier at $x = 0$, there are two possibilities. First, if the energy of particle $E < V_0$, the particle is reflected back and second, if $E > V_0$ the particle crosses over through the barrier into the region II ($x > a$).

Quantum Mechanical Motion : Now we will see quantum mechanical results.

We have one-dimensional time-independent Schrödinger's equation.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0 \quad \dots(4.89)$$

In region I ($V = 0$), above equation becomes

$$\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2} \psi_1 = 0 \quad \dots(4.90)$$

In region II ($V = V_0$), equation (4.89) becomes

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2} (E - V_0)\psi_2 = 0 \quad \dots(4.91)$$

In region III ($V = 0$), equation (4.89) becomes

$$\frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2} \psi_3 = 0 \quad \dots(4.92)$$

Consider two cases

Case I: $E > V_0$.

Let $k^2 = \frac{2mE}{\hbar^2} \quad \dots(4.93)$

and $\alpha^2 = \frac{2m(E - V_0)}{\hbar^2} \quad \dots(4.94)$

With above two equations, equations (4.90), (4.91) and (4.92) become

$$\frac{d^2\psi_1}{dx^2} + k^2\psi_1 = 0 \quad \dots(4.95)$$

$$\frac{d^2\psi_2}{dx^2} + \alpha^2\psi_2 = 0 \quad \dots(4.96)$$

and $\frac{d^2\psi_3}{dx^2} + k^2\psi_3 = 0 \quad \dots(4.97)$

The general solution of equation (4.95) is given by

$$\psi_1(x) = A e^{ikx} + B e^{-ikx} \quad \dots(4.98)$$

In equation (4.98), the term $A e^{ikx}$ represents the wave incident along + X direction towards the barrier at $x = 0$ and $B e^{-ikx}$ represents reflected wave i.e.

$$\psi_{in} = A e^{ikx} \text{ and } \psi_{ref} = B e^{-ikx}$$

The general solution of equation (4.96) is given by

$$\psi_2(x) = F e^{i\alpha x} + G e^{-i\alpha x} \quad \dots(4.99)$$

The general solution of equation (4.97) is given by

$$\psi_3(x) = C e^{ikx} + D e^{-ikx}$$

Once particle is transmitted in the region III, there will be wave propagating along + x axis only. Hence we set $D = 0$ in above equation. Thus, the wave function in the region III, will be

$$\psi_3(x) = C e^{ikx} \quad \dots(4.100)$$

It also represents the transmitted wave. Thus,

$$\psi_{tr} = C e^{ikx}$$

A, B, C, D, F and G are constants. Their values can be chosen by using the boundary conditions.

First boundary condition:

$$\text{At } x=0 \quad \psi_1 = \psi_2$$

$$d\psi_1 = d\psi_2$$

$$|\psi_1(x)|_{x=0} = |\psi_2(x)|_{x=0}$$

$$\therefore [A e^{ikx} + B e^{-ikx}]_{x=0} = [F e^{i\alpha x} + G e^{-i\alpha x}]_{x=0}$$

$$\therefore A + B = F + G \quad \times k \quad \dots(4.101)$$

$$\text{and} \quad \left(\frac{d\psi_1}{dx}\right)_{x=0} = \left(\frac{d\psi_2}{dx}\right)_{x=0} \quad + = \alpha$$

$$[A i k e^{ikx} - B i k e^{-ikx}]_{x=0} = [i\alpha F e^{i\alpha x} - i\alpha G e^{-i\alpha x}]_{x=0}$$

$$\therefore k(A - B) = \alpha(F - G) \quad \dots(4.102)$$

Second boundary condition:

$$\text{At } x=a \quad \psi_2 = \psi_3$$

$$|\psi_2(x)|_{x=a} = |\psi_3(x)|_{x=a}$$

$$\therefore [F e^{i\alpha x} + G e^{-i\alpha x}]_{x=a} = [C e^{ikx}]_{x=a}$$

$$\text{or} \quad F e^{i\alpha a} + G e^{-i\alpha a} = C e^{ika} \quad \times k \quad (x) \quad (x) = G \quad \dots(4.103)$$

$$\text{and} \quad \left(\frac{d\psi_2}{dx}\right)_{x=a} = \left(\frac{d\psi_3}{dx}\right)_{x=a} \quad = B = F$$

$$[i\alpha F e^{i\alpha x} - i\alpha G e^{-i\alpha x}]_{x=a} = [ik C e^{ikx}]_{x=a}$$

$$\therefore \alpha F e^{i\alpha a} - \alpha G e^{-i\alpha a} = k C e^{ika} \quad \dots(4.104)$$

Multiplying equation (4.101) by k and adding in (4.102), we get

$$2kA = (k + \alpha)F + (k - \alpha)G$$

$$\therefore A = \frac{(k + \alpha)}{2k}F + \frac{(k - \alpha)}{2k}G \quad \dots(4.105)$$

Multiplying equation (4.101) by k and subtracting (4.102) from it, we get

$$2kB = (k - \alpha)F + (k + \alpha)G$$

$$\therefore B = \frac{(k - \alpha)}{2k}F + \frac{(k + \alpha)}{2k}G \quad \dots(4.106)$$

Multiplying equation (4.103) by α and adding to (4.104), we get

$$2\alpha F e^{i\alpha a} = (k + \alpha) C e^{ika}$$

$$\therefore F = \frac{(k + \alpha)}{2\alpha} C e^{ika} e^{-i\alpha a} \quad \dots(4.107)$$

Multiplying equation (4.103) by α and subtracting (4.104) from it, we get

$$2\alpha G e^{-i\alpha a} = (\alpha - k) C e^{ika}$$

$$\therefore G = \frac{(\alpha - k)}{2\alpha} C e^{ika} e^{i\alpha a} \quad \dots(4.108)$$

Using constants F and G from equations (4.107) and (4.108), in equations (4.105) and (4.106), we get

$$A = \frac{(k+\alpha)(k+\alpha)}{2k} C e^{ika} e^{-iaa} + \frac{(k-\alpha)(\alpha-k)}{2k} C e^{ika} e^{iaa}$$

$$\text{or } A = \frac{C e^{ika}}{4k\alpha} [(k+\alpha)^2 e^{-iaa} - (k-\alpha)^2 e^{iaa}] \quad \dots(4.109)$$

$$\text{and } B = \frac{(k-\alpha)(k+\alpha)}{2k} C e^{ika} e^{-iaa} + \frac{(k+\alpha)(\alpha-k)}{2k} C e^{ika} e^{iaa}$$

$$= \frac{C e^{ika}}{4k\alpha} [(k^2 - \alpha^2) e^{-iaa} - (k^2 - \alpha^2) e^{iaa}]$$

$$= \frac{C e^{ika}}{4k\alpha} (\alpha^2 - k^2) [e^{iaa} - e^{-iaa}]$$

$$\text{or } B = \frac{C e^{ika}}{4k\alpha} (\alpha^2 - k^2) 2i \sin \alpha a \quad \dots(4.110)$$

$$(\because e^{ix} - e^{-ix} = 2i \sin x)$$

Complex conjugate of equation (4.109), we get

$$A^* = \frac{C^* e^{-ika}}{4k\alpha} [(k+\alpha)^2 e^{iaa} - (k-\alpha)^2 e^{-iaa}] \quad \dots(4.111)$$

$$\therefore AA^* = \frac{C e^{ika}}{4k\alpha} [(k+\alpha)^2 e^{-iaa} - (k-\alpha)^2 e^{iaa}] \frac{C^* e^{-ika}}{4k\alpha} [(k+\alpha)^2 e^{iaa} - (k-\alpha)^2 e^{-iaa}]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^2 e^{-iaa} - (k-\alpha)^2 e^{iaa}] [(k+\alpha)^2 e^{iaa} - (k-\alpha)^2 e^{-iaa}]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^4 + (k-\alpha)^4 - (k+\alpha)^2(k-\alpha)^2 e^{-2iaa} - (k+\alpha)^2(k-\alpha)^2 e^{2iaa}]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^4 + (k-\alpha)^4 - (k+\alpha)^2(k-\alpha)^2 [e^{2iaa} + e^{-2iaa}]]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^4 + (k-\alpha)^4 - (k+\alpha)^2(k-\alpha)^2 (2 \cos 2\alpha a)]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^4 + (k-\alpha)^4 - 2(k+\alpha)^2(k-\alpha)^2 (1 - 2 \sin^2 \alpha a)]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^4 + (k-\alpha)^4 - 2(k+\alpha)^2(k-\alpha)^2 + 4(k+\alpha)^2(k-\alpha)^2 \sin^2 \alpha a]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^2 - (k-\alpha)^2]^2 + 4(k+\alpha)^2(k-\alpha)^2 \sin^2 \alpha a]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k+\alpha)^2 - (k-\alpha)^2]^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a]$$

$$= \frac{CC^*}{16k^2\alpha^2} [(k^2 + \alpha^2 + 2k\alpha) - (k^2 + \alpha^2 - 4k\alpha)]^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a]$$

$$\therefore AA^* = \frac{CC^*}{16k^2\alpha^2} [16k^2\alpha^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a] \quad \dots(4.112)$$

Complex conjugate of equation (4.110) gives

$$B^* = \frac{C^* e^{-ika}}{4k\alpha} (\alpha^2 - k^2) 2(-i) \sin \alpha a \quad \dots(4.113)$$

$$\therefore BB^* = \frac{C e^{ika}}{4k\alpha} (\alpha^2 - k^2) 2i \sin \alpha a \times \frac{C^* e^{-ika}}{4k\alpha} (\alpha^2 - k^2) 2(-i) \sin \alpha a$$

$$\text{or } BB^* = \frac{CC^*}{16k^2\alpha^2} 4(\alpha^2 - k^2)^2 \sin^2 \alpha a \quad \dots(4.114)$$

We have,

For the incident wave $\psi_{in} = A e^{ikx}$,

For the reflected wave $\psi_{ref} = B e^{-ikx}$

and for the transmitted wave $\psi_{tr} = C e^{ikx}$

The current density of incident waves is

$$J_{in} = \text{Re} \left(\psi_{in}^* \frac{\hbar}{mi} \frac{d\psi_{in}}{dx} \right) = \frac{\hbar k}{m} |A|^2 \quad \dots(4.115)$$

The current density of reflected wave is

$$J_{ref} = \text{Re} \left(\psi_{ref}^* \frac{\hbar}{mi} \frac{d\psi_{ref}}{dx} \right) = \frac{\hbar k}{m} |B|^2 \quad \dots(4.116)$$

The current density of transmitted wave is

$$J_{tr} = \text{Re} \left(\psi_{tr}^* \frac{\hbar}{mi} \frac{d\psi_{tr}}{dx} \right) = \frac{\hbar k}{m} |C|^2 \quad \dots(4.117)$$

The coefficient of transmission is given by

$$T = \frac{J_{tr}}{J_{in}} = \frac{|C|^2}{|A|^2} = \frac{CC^*}{AA^*}$$

From equation (4.112), we get

$$\frac{CC^*}{AA^*} = \frac{16k^2\alpha^2}{[16k^2\alpha^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a]}$$

$$\therefore T = \frac{16k^2\alpha^2}{[16k^2\alpha^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a]}$$

$$\text{or } T = \frac{1}{\left[1 + \frac{4(k^2 - \alpha^2)^2}{16k^2\alpha^2} \sin^2 \alpha a \right]} \quad \dots(4.118)$$

$$\therefore k^2 = \frac{2mE}{\hbar^2} \text{ and } \alpha^2 = \frac{2m(E - V_0)}{\hbar^2}$$

$$\therefore k^2 - \alpha^2 = \frac{2mV_0}{\hbar^2}$$

$$\therefore \frac{4(k^2 - \alpha^2)^2}{16k^2\alpha^2} = \frac{4(2mV_0/\hbar^2)^2}{16(2mE/\hbar^2)(2m(E - V_0)/\hbar^2)} = \frac{V_0^2}{4E(E - V_0)}$$

Using the above in equation (4.118), the transmission coefficient is given by

$$T = \frac{1}{\left[1 + \frac{V_0^2 \sin^2 \alpha a}{4E(E - V_0)} \right]} \quad \dots(4.119)$$

The coefficient of reflection is given as

$$R = \frac{J_{ref}}{J_{in}} = \frac{|B|^2}{|A|^2} = \frac{BB^*}{AA^*}$$

Dividing equation (4.114) by equation (4.112), we get

$$\frac{BB^*}{AA^*} = \frac{CC^*}{16k^2\alpha^2} 4(\alpha^2 - k^2)^2 \sin^2 \alpha a \times \frac{16k^2\alpha^2}{[16k^2\alpha^2 + 4(k^2 - \alpha^2)^2 \sin^2 \alpha a] CC^*}$$

$$R = \frac{4(k^2 - \alpha^2) \sin^2 \alpha a}{[16k^2 \alpha^2 + 4(k^2 - \alpha^2) \sin^2 \alpha a]}$$

$$= \frac{1}{\left[\frac{16k^2 \alpha^2}{4(k^2 - \alpha^2) \sin^2 \alpha a} + 1 \right]}$$

$$\text{or } R = \frac{1}{\left[\frac{4E(E - V_0)}{V_0^2 \sin^2 \alpha a} + 1 \right]} \quad \dots(4.120)$$

This is formula for the reflection coefficient.

We can prove that $R + T = 1$. Using equations (4.119) and (4.120), we have

$$R + T = \frac{1}{\left[1 + \frac{V_0^2 \sin^2 \alpha a}{4E(E - V_0)} \right]} + \frac{1}{\left[\frac{4E(E - V_0)}{V_0^2 \sin^2 \alpha a} + 1 \right]}$$

$$= \frac{4E(E - V_0)}{[4E(E - V_0) + V_0^2 \sin^2 \alpha a]} + \frac{V_0^2 \sin^2 \alpha a}{[4E(E - V_0) + V_0^2 \sin^2 \alpha a]}$$

$$\therefore R + T = 1$$

It is seen from equation (4.119) that, in general, T is less than unity. Therefore, there is general partial reflection and partial transmission across the potential barrier between $x = 0$ and $x = a$. However, $\sin \alpha a = 0$ for those values of energies for which $\alpha a = \pi, 2\pi, 3\pi$ etc. Then $T = 1$ i.e. there is *perfect* transmission through the barrier. This means that all the particles pass through the barrier as if it was absent. This is a very interesting phenomenon. However, kinetic energy of the particles will be reduced as long as the particles are in region II.

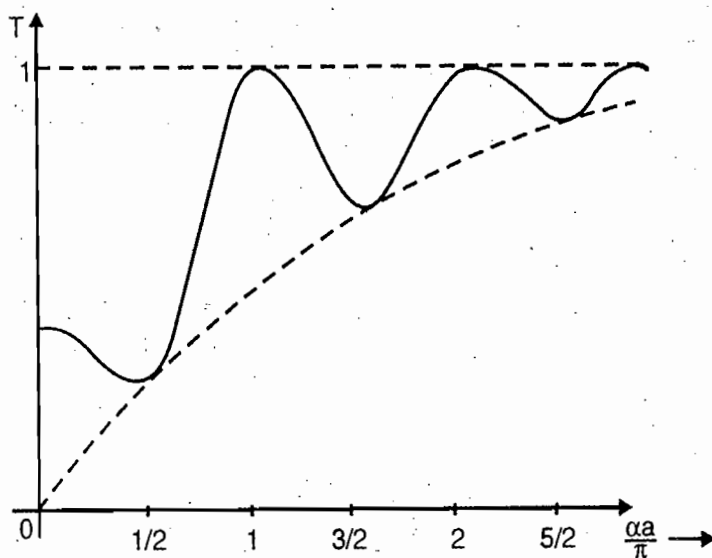


Fig. 4.11

The variation of T w.r.t $\frac{\alpha a}{\pi}$ is shown graphically in Fig. 4.11. The coefficient of transmission goes through alternate maxima and minima with increase in $\frac{\alpha a}{\pi}$. The maxima always corresponds to $T = 1$. Also, as $\frac{\alpha a}{\pi} \rightarrow \infty$, $T \rightarrow 1$. This corresponds to $E \gg V_0$. When T is maximum R is

minimum and vice versa. However R_{\max} will not be 1. It will always less than 1. We know that classically, there is no reflection of particles if $E > V_0$ ($R = 0$, $T = 1$). However quantum mechanically there is some probability of reflection for $E > V_0$ but $R \rightarrow 0$ as $E \rightarrow \infty$.

The appearance of maxima and minima in the flux of particles is similar to the interference phenomenon in the case of light waves.

Case II : $E < V_0$

The case for $E < V_0$ can be easily derived from the case $E > V_0$. From equation (4.94) we have

$$\alpha^2 = \frac{2m(E - V_0)}{\hbar^2}$$

$$\therefore \alpha^2 = -\frac{2m(V_0 - E)}{\hbar^2}$$

Let $\beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$. For $V_0 > E$, β^2 is positive.

$$\therefore \alpha^2 = -\beta^2$$

$$\text{or } \alpha = i\beta.$$

Using $\alpha = i\beta$ in equations (4.119) and (4.120) we get R and T for $E < V_0$. Therefore,

$$T = \frac{1}{\left[1 + \frac{V_0^2 \sin^2 i\beta a}{4E(E - V_0)} \right]} \quad \dots(4.121)$$

and

$$R = \frac{1}{\left[\frac{4E(E - V_0)}{V_0^2 \sin^2 i\beta a} + 1 \right]} \quad \dots(4.122)$$

We have $\sin i\theta = i \sinh \theta$, where $\sinh \theta$ represents the hyperbolic function.

Therefore,

$$T = \frac{1}{\left[1 + \frac{V_0^2 (i)^2 \sinh^2 \beta a}{4E(E - V_0)} \right]}$$

or

$$T = \frac{1}{\left[1 + \frac{V_0^2 \sinh^2 \beta a}{4E(V_0 - E)} \right]} \quad \dots(4.123)$$

and

$$R = \frac{1}{\left[\frac{4E(V_0 - E)}{V_0^2 \sinh^2 \beta a} + 1 \right]} \quad \dots(4.124)$$

It is seen that for $E < V_0$ there is always some probability of transmission. Classically the probability of transmission for $E < V_0$ is $T = 0$, i.e. there is no transmission. Thus, this type of transmission is completely quantum mechanical phenomenon. This is also called *tunneling effect*.

If a particle impinging on the potential barrier with energy less than the height of the potential barrier, there is always some probability of transmission through the barrier. This phenomenon of crossing the barrier is called the tunneling effect.

4.7 ONE DIMENSIONAL HARMONIC OSCILLATOR

First we will consider the classical motion of one-dimensional simple harmonic oscillator

Classical motion :

In linear simple harmonic motion, the restoring force F is proportional to the displacement of a particle from the mean position and directed towards the mean position, so that

$$\boxed{F = -kx} \quad F = ma = m \frac{d^2x}{dt^2}$$

$$\therefore m \frac{d^2x}{dt^2} = -kx$$

$$\text{or} \quad \frac{d^2x}{dt^2} + \omega^2 x = 0$$

$$\text{where } \boxed{\omega^2 = k/m} \quad \text{or} \quad k = m\omega^2$$

The solution of above equation is:

$$\boxed{x} = a \sin(\omega t + \phi)$$

where a is the amplitude of oscillation.

Thus, particle oscillates between $+a$ and $-a$ with frequency

$$\boxed{v} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

The total energy of the oscillator is

$$\text{Total } E = \frac{1}{2} k a^2 = \text{constant}$$

where a is amplitude called classical limit. It is different for different energies.

We can say that the particle must be moving around in the classically allowed region: $|x| < a = (2E/k)^{1/2}$. All subdivisions within the classically allowed region are not equally probable, as the particle is whizzing through equilibrium, while spending more time in the parts through which it is slowly moving. The time (dt) that a particle spends in a small region dx depends on its speed and is given by $dt = dx/v$. The probability (dP) of finding the particle in dx is then proportional to the time it spends there is $dP = 2dt/T$, where T is the period of oscillation.

$$\therefore dP = \frac{2 dt}{T} = \frac{2}{T} \frac{dt}{dx} dx$$

$$= \frac{2}{T} \left(\frac{1}{v} \right) dx$$

$$\therefore v = \omega \sqrt{a^2 - x^2} \quad \text{and } T = 2\pi/\omega, \text{ we get}$$

$$dP = \frac{1}{\pi \sqrt{a^2 - x^2}} dx = P(x) dx \quad \dots(4.125)$$

where $\boxed{P(x)} = \frac{1}{\pi \sqrt{a^2 - x^2}}$ is called the probability density.

The plot of classical probability density against displacement is shown in Fig. 4.12.

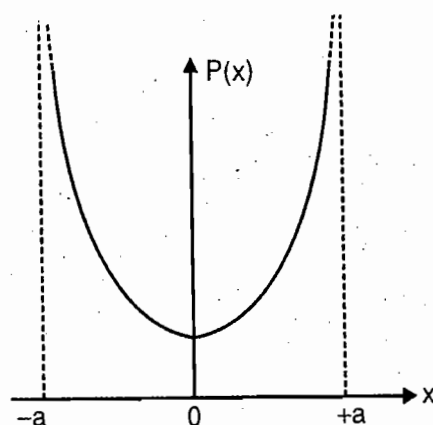


Fig. 4.12 : Classical probability density plot

Quantum mechanical motion :

The simple harmonic oscillator has potential energy

$$V = \frac{1}{2} kx^2$$

The plot of potential energy against displacement is shown in Fig. 4.13.

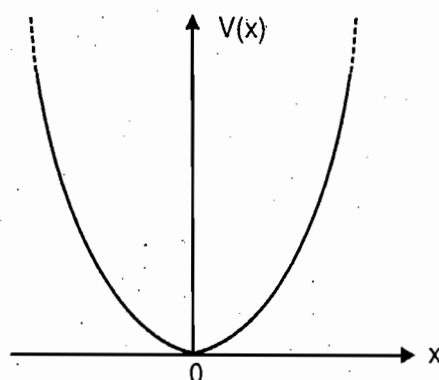


Fig. 4.13 : Potential energy

The Schrodinger equation for harmonic oscillator is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0 \quad \dots(4.127)$$

It is convenient to simplify equation (4.127) by introducing the dimensionless quantities. Let us introduce dimensionless variable

$$\xi = \alpha x$$

... (4.128)

where α is constant having dimensions of inverse of length.

$$\therefore \frac{d\psi}{dx} = \frac{d\psi}{d\xi} \frac{d\xi}{dx}$$

$$\therefore \frac{d\psi}{dx} = \alpha \frac{d\psi}{d\xi}$$

And

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx} \left(\frac{d\psi}{dx} \right) = \frac{d}{dx} \left(\alpha \frac{d\psi}{d\xi} \right) = \frac{d\xi}{dx} \frac{d}{d\xi} \left(\alpha \frac{d\psi}{d\xi} \right) = \alpha^2 \frac{d^2\psi}{d\xi^2}$$

Using these values in equation (4.127)), we get

$$\alpha^2 \frac{d^2 \psi}{d\xi^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} k \frac{\xi^2}{\alpha^2} \right) \psi = 0$$

$$\therefore \alpha^2 \frac{d^2 \psi}{d\xi^2} + \left(\frac{2mE}{\hbar^2} - \frac{mk\xi^2}{\hbar^2 \alpha^2} \right) \psi = 0 \quad \frac{\xi}{\alpha} \propto \xi^2$$

Dividing throughout by α^2 , we get

$$\frac{d^2 \psi}{d\xi^2} + \left(\frac{2mE}{\hbar^2 \alpha^2} - \frac{mk\xi^2}{\hbar^2 \alpha^4} \right) \psi = 0 \quad \dots(4.129)$$

Since α is constant, let us choose α in such a way that

$$\frac{mk}{\hbar^2 \alpha^4} = 1 \quad \text{or} \quad \alpha^4 = \frac{mk}{\hbar^2} \quad \text{i.e.} \quad \alpha = \left(\frac{mk}{\hbar^2} \right)^{1/4} \quad \dots(4.130)$$

We also introduce another constant λ , defined as

$$\lambda = \frac{2mE}{\hbar^2 \alpha^2} \quad \dots(4.131)$$

Using $k = m\omega^2$ in equation (4.130), we get

$$\alpha = \left(\frac{m\omega}{\hbar} \right)^{1/2} \quad \dots(4.132)$$

and

$$\lambda = \frac{2E}{\hbar\omega} \quad \dots(4.133)$$

Therefore, equation (4.129), will take the form

$$\frac{d^2 \psi}{d\xi^2} + (\lambda - \xi^2) \psi = 0 \quad \dots(4.134)$$

We desire to obtain solutions $\psi(\xi)$ which satisfy equation (4.134) throughout the region $-\infty$ to $+\infty$ for ξ , and which are acceptable functions *i.e.*, each function must be continuous, single valued and finite throughout the region.

Let us consider asymptotic solution *i.e.* $\xi \rightarrow \infty$. When ξ is large we can neglect λ in comparison with ξ . Then equation (4.134) becomes

$$\frac{d^2 \psi}{d\xi^2} - \xi^2 \psi = 0$$

The general solution of the above equation will be of the form

$$\psi(\xi) = A e^{-\xi^2/2} + B e^{\xi^2/2}$$

As $\xi \rightarrow \infty$, $e^{-\xi^2/2} \rightarrow 0$ and $e^{\xi^2/2} \rightarrow \infty$. Thus acceptable solution will be

$$\psi(\xi) = A e^{-\xi^2/2}$$

We proceed to obtain the solution of wave equation (4.134) throughout configuration space $(-\infty < \xi < +\infty)$, based upon the asymptotic solution. Let us assume that the solution is of the form:

$$\psi(\xi) = A H(\xi) e^{-\xi^2/2} \quad \dots(4.135)$$

where A is constant, and $H(\xi)$ is some function of ξ .

From equation (4.135),

$$\frac{d\psi}{d\xi} = AH'(\xi) e^{-\xi^2/2} - \xi A H(\xi) e^{-\xi^2/2}$$

$$\text{and } \frac{d^2\psi}{d\xi^2} = AH''(\xi) e^{-\xi^2/2} - \xi AH'(\xi) e^{-\xi^2/2} - AH(\xi) e^{-\xi^2/2} - \xi AH'(\xi) e^{-\xi^2/2} + \xi^2 AH(\xi) e^{-\xi^2/2}$$

$$\therefore \frac{d^2\psi}{d\xi^2} = AH''(\xi) e^{-\xi^2/2} - 2\xi AH'(\xi) e^{-\xi^2/2} - AH(\xi) e^{-\xi^2/2} + \xi^2 AH(\xi) e^{-\xi^2/2}$$

Using $\frac{d^2\psi}{d\xi^2}$ and $\psi(\xi)$ in equation (4.134), we get

$$AH''(\xi) e^{-\xi^2/2} - 2\xi AH'(\xi) e^{-\xi^2/2} - AH(\xi) e^{-\xi^2/2} + \xi^2 AH(\xi) e^{-\xi^2/2} + (\lambda - \xi^2) AH(\xi) e^{-\xi^2/2} = 0$$

$$\therefore A e^{-\xi^2/2} [H''(\xi) - 2\xi H'(\xi) + (\lambda - 1)H(\xi)] = 0 \quad \dots(4.136)$$

As $e^{-\xi^2/2}$ is an arbitrary function, we get

$$H''(\xi) - 2\xi H'(\xi) + (\lambda - 1)H(\xi) = 0$$

$$\text{or } H'' - 2\xi H' + (\lambda - 1)H = 0 \quad \dots(4.137)$$

where the primes denote differentiation with respect to ξ .

Equation (4.137) is the Hermite differential equation for 'H' in the variable ' ξ '. We try to obtain the solution of this equation in the form of Frobenius power series.

$$\text{Let, } H(\xi) = \sum_{m=0}^{\infty} a_m \xi^m$$

$$\therefore H'(\xi) = \sum_{m=1}^{\infty} a_m m \xi^{m-1}$$

$$\text{and } H''(\xi) = \sum_{m=2}^{\infty} a_m m(m-1) \xi^{m-2}$$

Using all these values in equation (4.137), we get

$$\sum_{m=2}^{\infty} a_m m(m-1) \xi^{m-2} - 2\xi \sum_{m=1}^{\infty} a_m m \xi^{m-1} + (\lambda - 1) \sum_{m=0}^{\infty} a_m \xi^m = 0$$

$$\sum_{m=2}^{\infty} a_m m(m-1) \xi^{m-2} - 2 \sum_{m=1}^{\infty} a_m m \xi^m + (\lambda - 1) \sum_{m=0}^{\infty} a_m \xi^m = 0$$

In above equation, replace m by m+2 in first term. Therefore,

$$\sum_{m=0}^{\infty} a_{m+2} (m+2)(m+1) \xi^m - 2 \sum_{m=0}^{\infty} a_m m \xi^m + (\lambda - 1) \sum_{m=0}^{\infty} a_m \xi^m = 0$$

$$\therefore \sum_{m=0}^{\infty} [a_{m+2} (m+2)m - 2a_m m + (\lambda - 1)a_m] \xi^m = 0 \quad \dots(4.138)$$

Since ' ξ ' is arbitrary, the coefficient of each and every power of ξ in the above equation must be zero. Therefore, considering coefficient of ξ^m , we get

$$a_{m+2} (m+2)(m+1) - 2a_m m + (\lambda - 1)a_m = 0.$$

$$\therefore a_{m+2} = \frac{(2m+1-\lambda)}{(m+1)(m+2)} a_m \quad \dots(4.139)$$

This expression is called *recursion formula*. If we know a_0 , we can calculate a_2, a_4, a_6 etc. Similarly if we know a_1 , we can find a_3, a_5, a_7 etc. Thus $H(\xi)$ is an infinite power series of odd and even powers of ξ such as

$$H(\xi) = [a_0 + a_2\xi^2 + a_4\xi^4 + \dots] + [a_1\xi + a_3\xi^3 + a_5\xi^5 + \dots]$$

For arbitrary values of the energy parameter λ , the above given series consists of an infinite number of terms and does not correspond to satisfactory wave function. Let us examine the convergence of the power series solution defined by equation (4.139), as $m \rightarrow \infty$.

Consider

$$\lim_{m \rightarrow \infty} \frac{a_{m+2}}{a_m} = \lim_{m \rightarrow \infty} \frac{(2m+1-\lambda)}{(m+1)(m+2)} = \frac{2}{m} \quad \dots(4.140)$$

Considering the series expansion of e^{ξ^2} , we have

$$\begin{aligned} e^{\xi^2} &= 1 + \xi^2 + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + \dots + \frac{\xi^m}{(m/2)!} + \frac{\xi^{m+2}}{(m/2+1)!} + \dots \\ &= b_0 + b_2\xi^2 + b_4\xi^4 + \dots + b_m\xi^m + b_{m+2}\xi^{m+2} + \dots \end{aligned}$$

From this series, we get

$$\frac{b_{m+2}}{b_m} = \frac{\frac{1}{(m/2+1)!}}{\frac{1}{(m/2)!}} = \frac{2}{2+m}$$

Therefore, for limit $m \rightarrow \infty$, we have

$$\lim_{m \rightarrow \infty} \frac{b_{m+2}}{b_m} = \lim_{m \rightarrow \infty} \frac{2}{2+m} = \frac{2}{m} \quad \dots(4.141)$$

Equations (4.140) and (4.141) show the behavior of $H(\xi)$ and e^{ξ^2} respectively, which shows that $H(\xi)$ diverges approximately as e^{ξ^2} and therefore $\psi(\xi) = AH(\xi)e^{-\xi^2/2} = A e^{\xi^2} e^{-\xi^2/2} = A e^{\xi^2/2}$. This gives that as $\xi \rightarrow +\infty$ or $-\infty$ the wave function $\psi(\xi) \rightarrow \infty$, thus making it unacceptable as a wave function.

The only way in which this situation can be avoided is to choose λ in equation (4.139) such a way that the coefficients of powers of ξ vanish after certain value of $m = n$ making $H(\xi)$ a polynomial in ξ instead of an infinite series.

Thus, after a_n all coefficients are zero, this is possible if for $m = n$ in equation (4.139), gives

$$a_{n+2} = \frac{(2n+1-\lambda)}{(n+1)(n+2)} a_n = 0$$

But $a_n \neq 0$, therefore,

$$2n+1-\lambda = 0$$

$$\text{or} \quad \lambda = 2n+1.$$

From equation (4.133), we have

$$\lambda = \frac{2E}{\hbar\omega}$$

$$\therefore \frac{2E}{\hbar\omega} = (2n+1)$$

$$E = \frac{1}{2} (2n + 1) \hbar \omega$$

or $E = \left(n + \frac{1}{2}\right) \hbar \omega$ where $n = 0, 1, 2, 3, 4, 5, \dots$

Since, the allowed energies are different for different 'n', we may write

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega \quad \dots(4.142)$$

Above equation gives the energy spectrum of one-dimensional harmonic oscillator. About the energy spectrum of harmonic oscillator, we note the following

(1) The energy spectrum is *discrete*. There are infinite number of energy levels corresponding to $n = 0, 1, 2, 3, 4, \dots$. However, the classical theory predicts the energy spectrum to be continuous.

(2) The lowest energy level (corresponding to $n = 0$) has energy $E_0 = \frac{1}{2} \hbar \omega$, called the ground state energy or *zero-point energy*. Classically, the lowest energy is zero, which corresponds to state of rest. Quantum mechanically, the lowest energy is not zero but $\frac{1}{2} \hbar \omega$. This is consequence of uncertainty principle.

The energy spectrum is shown in Fig. 4.14. It is seen that the separation between successive energy levels is the same and is equal to $\hbar \omega$.

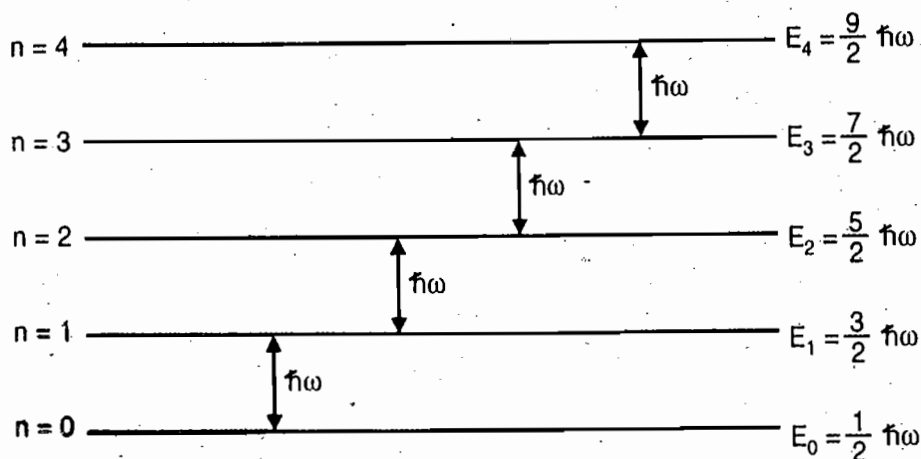


Fig. 4.14 : Energy spectrum of one dimensional oscillator.

Normalization of wave function :

The wave function for one dimensional harmonic oscillator is given as

$$\psi(\xi) = A H(\xi) e^{-\xi^2/2}, \text{ where } A \text{ is constant called normalization constant.}$$

Since $\xi = \alpha x$

$$\therefore \psi(x) = A H(\alpha x) e^{-\alpha^2 x^2/2}$$

Since energy depends on the integer n , the wave function corresponding to different energy levels E_n is expressed as

$$\psi_n(\xi) = A_n H_n(\xi) e^{-\xi^2/2} \quad \dots(4.143)$$

$$\text{or} \quad \psi_n(x) = A_n H_n(\alpha x) e^{-\alpha^2 x^2/2} \quad \dots(4.144)$$

We determine A_n , using normalization condition

$$\int_{-\infty}^{+\infty} \psi \psi^* dx = 1$$

$$\text{i.e.} \quad \int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1$$

$$\therefore \int_{-\infty}^{+\infty} |A_n|^2 H_n^2(\alpha x) e^{-\alpha^2 x^2} dx = 1$$

$$\therefore |A_n|^2 \int_{-\infty}^{+\infty} H_n^2(\alpha x) e^{-\alpha^2 x^2} dx = 1$$

$$\text{We have} \quad \int_{-\infty}^{+\infty} H_n^2(\alpha x) e^{-\alpha^2 x^2} dx = \frac{1}{\alpha} \int_{-\infty}^{+\infty} H_n^2(\xi) e^{-\xi^2} d\xi$$

$$\text{But the integral} \quad \int_{-\infty}^{+\infty} H_n^2(\xi) e^{-\xi^2} d\xi = \sqrt{\pi} 2^n n!$$

$$\therefore |A_n|^2 \frac{\sqrt{\pi} 2^n n!}{\alpha} = 1$$

$$\text{This gives} \quad A_n = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2}$$

Therefore, the normalized wave function for the harmonic oscillator is

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(\alpha x) e^{-\alpha^2 x^2/2} \quad \dots(4.145)$$

where $n = 0, 1, 2, 3, 4, \dots$

For $n = 0$, the wave function is called *ground state wave function*.

The Hermite Polynomials are given as follows

Order	$H_n(\xi)$	$H_n(\alpha x)$
0	$H_0(\xi) = 1$	$H_0(\alpha x) = 1$
1	$H_1(\xi) = 2\xi$	$H_1(\alpha x) = 2\alpha x$
2	$H_2(\xi) = 4\xi^2 - 2$	$H_2(\alpha x) = 4\alpha^2 x^2 - 2$
3	$H_3(\xi) = 8\xi^3 - 12\xi$	$H_3(\alpha x) = 8\alpha^3 x^3 - 12\alpha x$
4	$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$	$H_4(\alpha x) = 16\alpha^4 x^4 - 48\alpha^2 x^2 + 12$

The wave functions for different states are given as follows

(1) Ground state function :

$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} H_0(\alpha x) e^{-\alpha^2 x^2/2}$$

or

$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}}\right)^{1/2} e^{-\alpha^2 x^2/2} \quad \dots(4.146)$$

The probability density is

$$|\psi_0(x)|^2 = \left(\frac{\alpha}{\sqrt{\pi}}\right) e^{-\alpha^2 x^2} \quad \dots(4.147)$$

(2) First Excited state wave function:

$$\psi_1(x) = \left(\frac{\alpha}{2\sqrt{\pi}}\right)^{1/2} H_1(\alpha x) e^{-\alpha^2 x^2/2}$$

or

$$\psi_1(x) = \left(\frac{\alpha}{2\sqrt{\pi}}\right)^{1/2} (2\alpha x) e^{-\alpha^2 x^2/2} \quad \dots(4.148)$$

The probability density is

$$|\psi_1(x)|^2 = \left(\frac{\alpha}{2\sqrt{\pi}}\right) 4\alpha^2 x^2 e^{-\alpha^2 x^2} \quad \dots(4.149)$$

The wave function and probability density for ground state and first four excited state are graphically plotted as shown in following Fig. 4.15.

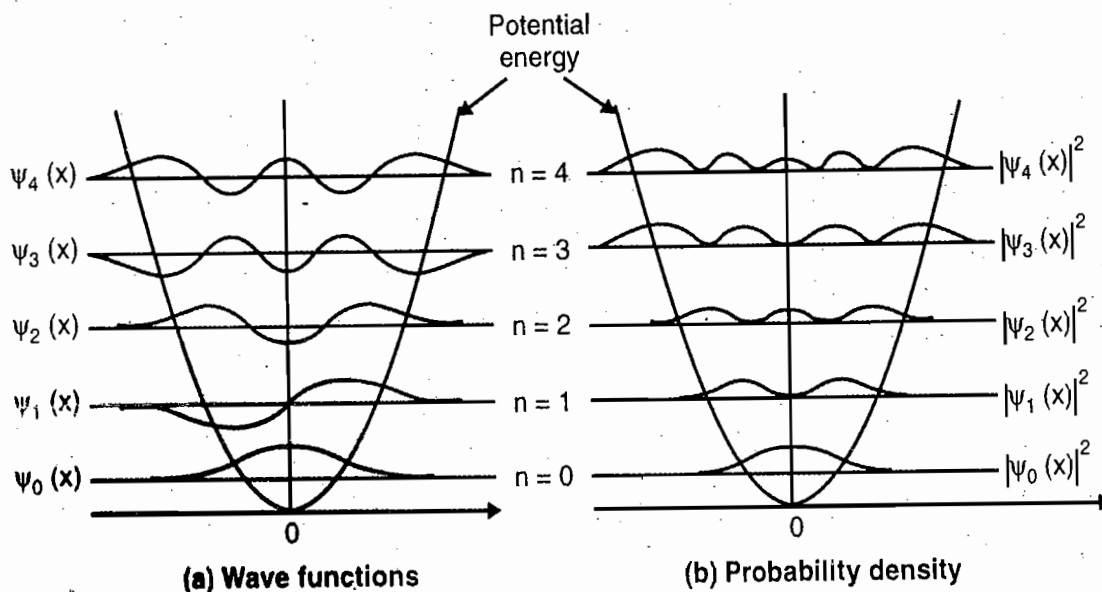


Fig. 4.15

Physical interpretation of harmonic oscillator wave functions :

Wave functions of first four states and their corresponding probability densities are shown in the Fig. 4.16. The dotted curves in Fig. 4.16 (b) represent classical probability densities. Fig. 4.16(b) shows that the quantum mechanical probability density curves do not match with the classical ones for smaller values of n . The classical probability density is

$$P(x) = \frac{1}{\pi\sqrt{a^2 - x^2}} \rightarrow \infty \text{ as } x \rightarrow \pm a$$

where a is the amplitude of the oscillator whose energy is equal to quantum mechanical energy eigen value.

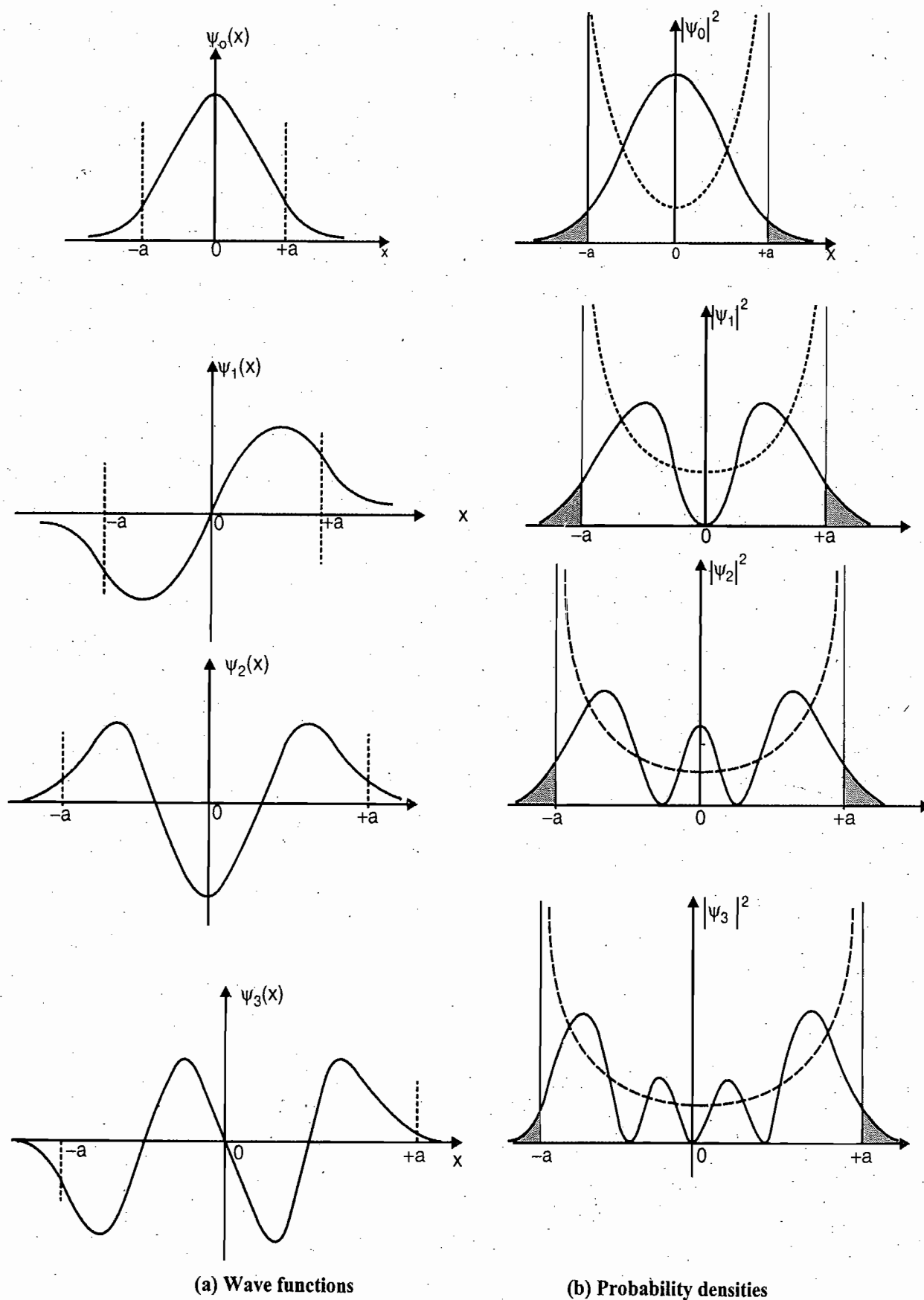


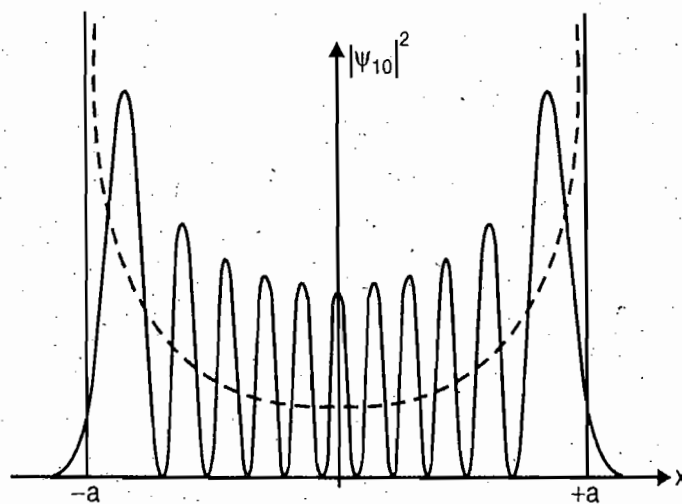
Fig. 4.16

According to classical theory, for a given energy, there is limit beyond which oscillator cannot go, and classical probability density approaches infinity at that limit. The probability density is maximum because the particle spends more time at the extreme points, as its velocity tends to zero. The particle spends least time at the mean position because its velocity is maximum and hence less probability of finding the particle at the mean position.

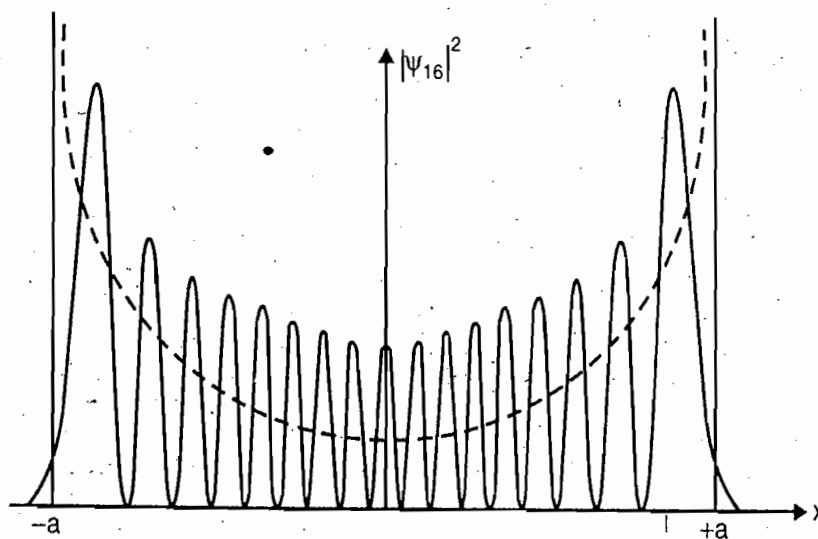
On the other hand, quantum mechanically, there is a small probability outside the classical limits as shown by shaded portion in the Fig. 4.16 (b). This is because the wave function has a 'tail' in the classically forbidden region. This existence of particle outside the classical limits i.e. in the classically forbidden region is called tunneling effect. *Imp*

Correspondence with classical theory :

It is apparent from Fig. 4.16(b) that the probability densities $|\psi_n(x)|^2$ associated with lower states have very little agreement to the corresponding classical densities for the classical harmonic oscillator. However, the agreement between classical and quantum mechanical probability densities improves rapidly as the quantum number n increases.



(a) for $n = 10$



(b) For $n = 16$

Fig. 4.17

Fig. 4.17 shows graphs of probability density $|\psi_n(x)|^2$ for large n (in Fig. 4.17 (a) for $n = 10$ and in (b) $n = 16$). It is seen that quantum mechanical probability density function is an oscillating function. The points of minima correspond to $|\psi_n(x)|^2 = 0$. The maxima are of varying heights. The height of maxima is least at $x = 0$ and it increases on either side of $x = 0$.

The dotted curve shows the averaged out behavior of probability density. It is observed that this curve has the same nature as the classical probability curve. Thus, for large 'n' it is seen that the quantum mechanical probability curve (averaged out) is in agreement with the classical probability curve. This is consistent with Bohr's correspondence principle which states that as the quantum number which characterizes the system $n \rightarrow \infty$ the quantum mechanical results are the same as those predicted by the classical theory.

Parity of the wave function:

The wave function of the simple harmonic oscillator is given as

$$\psi_n(x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(\alpha x) e^{-\alpha^2 x^2/2}$$

Replacing x by $-x$ in the above equation, we get

$$\psi_n(-x) = \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(-\alpha x) e^{-\alpha^2 x^2/2}$$

From the property of Hermite polynomial we have $H_n(-x) = (-1)^n H_n(x)$

Therefore, above equation can be written as

$$\psi_n(-x) = (-1)^n \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} H_n(\alpha x) e^{-\alpha^2 x^2/2}$$

or

$$\psi_n(-x) = (-1)^n \psi_n(x)$$

Thus, if n is even $\psi_n(-x) = \psi_n(x)$ and if n is odd, $\psi_n(-x) = -\psi_n(x)$. Hence, even order solutions i.e. $\psi_0(x)$, $\psi_2(x)$, $\psi_4(x)$ are *even parity* functions and odd order functions i.e. $\psi_1(x)$, $\psi_3(x)$, are *odd parity* functions. Thus, eigen functions of simple harmonic oscillator have definite parity, which is either even or odd.

ILLUSTRATIVE EXAMPLES

Example 1 : The wave function for a particle in infinite potential well is given as

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a} x\right) \quad \text{where } 0 \leq x \leq a. \text{ Find } \langle x \rangle \text{ and } \langle p_x \rangle$$

Solution : A is normalization constant and it is easy to show that its value is $A = \sqrt{\frac{2}{a}}$

$$\therefore \psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

(a) Expectation value of x is given as

$$\langle x \rangle = \int_0^a x |\psi_n(x)|^2 dx$$

$$\begin{aligned}
 \therefore \langle x \rangle &= \int_0^a x |A|^2 \sin^2 \left(\frac{n\pi}{a} x \right) dx \\
 &= \frac{2}{a} \int_0^a x \sin^2 \left(\frac{n\pi}{a} x \right) dx \\
 &= \frac{2}{a} \int_0^a \frac{x}{2} \left(1 - \cos \left(2 \frac{n\pi}{a} x \right) \right) dx \\
 &= \frac{1}{a} \int_0^a \left(x - x \cos \left(2 \frac{n\pi}{a} x \right) \right) dx \\
 &= \frac{1}{a} \left(\int_0^a x dx - \int_0^a x \cos \left(2 \frac{n\pi}{a} x \right) dx \right) \\
 &= \frac{1}{a} \left(\left. \frac{x^2}{2} \right|_0^a - \int_0^a x \cos \left(2 \frac{n\pi}{a} x \right) dx \right)
 \end{aligned}$$

$$\sin^2 \theta = \frac{1 - \cos 2\theta}{2}$$

Integrating second term by parts, we get $u \frac{dv}{dx} - \int \frac{du}{dx} v dx$

$$\begin{aligned}
 \int_0^a x \cos \left(2 \frac{n\pi}{a} x \right) dx &= x \frac{\sin \left(2 \frac{n\pi}{a} x \right)}{2n\pi/a} - \int_0^a \cos \left(2 \frac{n\pi}{a} x \right) dx \\
 &= \left[x \frac{\sin \left(2 \frac{n\pi}{a} x \right)}{2n\pi/a} - \frac{\sin \left(2 \frac{n\pi}{a} x \right)}{2n\pi/a} \right]_0^a = 0
 \end{aligned}$$

This gives $\int_0^a x \cos \left(2 \frac{n\pi}{a} x \right) dx = 0$

$$\therefore \langle x \rangle = \frac{1}{a} \frac{a^2}{2}$$

or $\langle x \rangle = \frac{a}{2}$

(b) Expectation value of p_x is given as

$$\langle p_x \rangle = \int_0^a \psi_n^* \left(-i\hbar \frac{d}{dx} \right) \psi_n dx$$

$$\begin{aligned}
 \langle p_x \rangle &= -i\hbar \int_0^a \psi_n^* \frac{d\psi}{dx} dx \\
 &= -i\hbar \frac{2}{a} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \frac{d}{dx} \sin\left(\frac{n\pi}{a}x\right) dx \\
 &= -i\hbar \frac{2}{a} \frac{n\pi}{a} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \cos\left(\frac{n\pi}{a}x\right) dx \\
 &= -\frac{i\hbar n\pi}{a^2} \int_0^a \sin\left(\frac{2n\pi}{a}x\right) dx \\
 &= \frac{i\hbar n\pi}{a^2} \left[\frac{\cos\left(\frac{2n\pi}{a}x\right)}{2n/\pi} \right]_0^a \\
 \therefore \langle p_x \rangle &= 0
 \end{aligned}$$

Example 2 : A small object of mass $1.00 \mu\text{g}$ is confined to move between two rigid walls separated by distance of 1.00 mm . (a) Calculate the minimum speed of the object. (b) If the speed is $3 \times 10^6 \text{ m/s}$, find the corresponding value of n .

Solution : When a particle is confined to one dimensional rigid box, the energy eigen values are given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \text{where } n = 1, 2, 3, \dots$$

(a) If the particle is in $n = 1$ state i.e. in the ground state, then it has the lowest energy and hence the minimum speed.

Thus,

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

We have

$$a = 1.00 \text{ mm} = 1 \times 10^{-3} \text{ m}$$

$$m = 1.00 \mu\text{g} = 1 \times 10^{-6} \text{ g} = 10^{-9} \text{ kg.}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}$$

$$E_1 = \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 10^{-9} \times (10^{-3})^2}$$

$$= 5.486 \times 10^{-53} \text{ J}$$

The particle has only the kinetic energy, since $V = 0$. Therefore,

$$E_1 = \frac{1}{2} mv^2$$

$$\begin{aligned}\therefore v &= \sqrt{\frac{2E}{m}} = \left(\frac{2 \times 5.486 \times 10^{-53}}{10^{-9}} \right)^{1/2} \\ &= (10.972 \times 10^{-44})^{1/2} \\ &= 3.31 \times 10^{-22} \text{ m/s}\end{aligned}$$

The velocity is so small that the particle is treated at rest *i.e.* in ground state. The particle will require time 3.021×10^{18} seconds or 9.57×10^{10} years to cover the distance equal to width of the one-dimensional rigid box.

(b) Let the particle be in level n with speed $v = 3 \times 10^6$ m/s

We have
$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

$$\therefore \frac{1}{2}mv^2 = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

or
$$n^2 = \frac{m^2 a^2 v^2}{\pi^2 \hbar^2}$$

or
$$n = \frac{m a v}{\pi \hbar}$$

$$= \frac{10^{-9} \times 10^{-3} \times 3 \times 10^6}{3.14 \times 1.055 \times 10^{-34}} = 0.905 \times 10^{28}$$

$$\therefore n = 9 \times 10^{27}$$

n is very high so the particle can not be treated quantum mechanically.

Example 3 : A proton is confined to move in a one-dimensional box of width 0.200 nm.

(a) Find the lowest possible energy of the proton. (b) What is the lowest possible energy of an electron confined to the same box ?

When particle is confined to one dimensional rigid box, the energy eigen value is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

(a) If the particle is in $n = 1$ *i.e.* in the ground state, it has the lowest energy. Thus,

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

We have

$$a = 0.200 \text{ nm} = 0.200 \times 10^{-9} \text{ m} = 2 \times 10^{-10} \text{ m}$$

For proton,

$$m = 1.66 \times 10^{-27} \text{ kg}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}$$

\therefore

$$\begin{aligned}E_1 &= \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 1.66 \times 10^{-27} \times (2 \times 10^{-10})^2} \\ &= 0.826 \times 10^{-21} \text{ J} \\ &= 5.16 \times 10^{-3} \text{ eV}\end{aligned}$$

(b) Now let us work out the problem for electron

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

We have

$$a = 0.200 \text{ nm} = 0.2 \times 10^{-9} \text{ m}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}$$

$$\begin{aligned} E_1 &= \frac{3.14^2 \times (1.055 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31} \times (2 \times 10^{-10})^2} \\ &= 0.1507 \times 10^{-17} = 1.507 \times 10^{-18} \text{ J} \\ &= 9.42 \text{ eV} \end{aligned}$$

Example 4 : A ruby laser emits light of wavelength 693.4 nm. If this light is due to transition from the $n = 2$ to $n = 1$ state of an electron in a one-dimensional box, find the width of the box.

Solution : The energy in the n^{th} level is given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

When electron jumps from $n = 2$ to $n = 1$, the energy difference is

$$E_2 - E_1 = 4 \frac{\pi^2 \hbar^2}{2ma^2} - \frac{\pi^2 \hbar^2}{2ma^2} = 3 \frac{\pi^2 \hbar^2}{2ma^2}$$

This energy difference is emitted in the form a photon with frequency ν . Then

$$E_2 - E_1 = h\nu$$

$$h\nu = 3 \frac{\pi^2 \hbar^2}{2ma^2}$$

$$\frac{hc}{\lambda} = 3 \frac{\pi^2 \hbar^2}{2ma^2}$$

$$a^2 = \frac{3\pi^2 \hbar^2 \lambda}{2mhc}$$

Since, $h = \frac{\hbar}{2\pi}$, we get

$$a = \frac{3h\lambda}{8mc}$$

Given :

$$\lambda = 693.4 \text{ nm} = 693.4 \times 10^{-9} \text{ m}$$

$$c = 3 \times 10^8 \text{ m/s}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$h = 6.625 \times 10^{-34} \text{ J-s}$$

$$a^2 = \frac{3 \times 6.625 \times 10^{-34} \times 693.4 \times 10^{-9}}{8 \times 9.1 \times 10^{-31} \times 3 \times 10^8}$$

$$= 63.1 \times 10^{-20} \text{ m}^2$$

$$a = 7.94 \times 10^{-10} \text{ m} = 7.94 \text{ \AA}$$

Example 5 : Two copper conducting wires of uniform cross sectional area are separated by an oxide layer (CuO). Treat oxide layer as square barrier of height 10 eV and estimate the transmission coefficient for penetration by 7 eV electrons if the layer thickness is (a) 5.00 nm and (b) 1.00 nm.

Solution : For $E < V_0$, the transmission coefficient is given by

$$T = \frac{1}{\left[1 + \frac{V_0^2 \sinh^2 \beta a}{4E(V_0 - E)} \right]}$$

And

$$\beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

 \therefore

$$\beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$$m = 9.11 \times 10^{-31} \text{ kg}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}$$

$$V_0 = 10 \text{ eV} = 10 \times 1.6 \times 10^{-19} \text{ J} = 16 \times 10^{-19} \text{ J}$$

$$E = 7 \text{ eV} = 7 \times 1.6 \times 10^{-19} \text{ J} = 11.2 \times 10^{-19} \text{ J}$$

 \therefore

$$V_0 - E = 4.8 \times 10^{-19}$$

 \therefore

$$\beta = \frac{\sqrt{2 \times 9.1 \times 10^{-31} \times 4.8 \times 10^{-19}}}{1.055 \times 10^{-34}}$$

$$= \frac{\sqrt{87.36 \times 10^{-50}}}{1.055 \times 10^{-34}} = \frac{9.35 \times 10^{-25}}{1.055 \times 10^{-34}}$$

 \therefore

$$\beta = 8.863 \times 10^9 \text{ m}^{-1}$$

(a) For width of the barrier $a = 5.00 \text{ nm} = 5 \times 10^{-9} \text{ m}$

$$\therefore \sinh \beta a = \sinh (8.863 \times 10^9 \times 5 \times 10^{-9}) = \sinh (44.315) = 8.805 \times 10^{18}$$

and

$$\frac{V_0^2}{4E(V_0 - E)} = \frac{(16 \times 10^{-19})^2}{4 \times 11.2 \times 10^{-19} \times 4.8 \times 10^{-19}} = 1.1905$$

 \therefore

$$T = \frac{1}{[1 + 1.1905 \times (8.805 \times 10^{18})^2]} = \frac{1}{[1 + 9.2297 \times 10^{37}]}$$

$$= \frac{1}{9.2297 \times 10^{37}} = 1.08 \times 10^{-38}$$

(b) For width of the barrier $a = 1.00 \text{ nm} = 1 \times 10^{-9} \text{ m}$ \therefore

$$\sinh \beta a = \sinh (8.863 \times 10^9 \times 1 \times 10^{-9}) = \sinh (8.863) = 3532.824$$

and

$$\frac{V_0^2}{4E(V_0 - E)} = \frac{(16 \times 10^{-19})^2}{4 \times 11.2 \times 10^{-19} \times 4.8 \times 10^{-19}} = 1.1905$$

 \therefore

$$T = \frac{1}{[1 + 1.1905 \times (3535.824)^2]} = \frac{1}{[1 + 1.25 \times 10^7]}$$

$$= \frac{1}{1.25 \times 10^7} = 0.8 \times 10^{-7}$$

Example 6 : Using ground state function of the simple harmonic oscillator, show that the ground state energy is $\frac{1}{2} \hbar \omega$.

Solution : Ground state function of the simple harmonic oscillator is given as

$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\alpha^2 x^2 / 2} = A e^{-\alpha^2 x^2 / 2}$$

where

$$\alpha = \sqrt{\frac{m\omega}{\hbar}}$$

Schrödinger's equation for harmonic oscillator is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0$$

In ground state,

$$\frac{d^2\psi_0}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi_0 = 0 \quad \dots(i)$$

$$\frac{d\psi_0}{dx} = \frac{d}{dx} \left(A e^{-\alpha^2 x^2/2} \right) = -\alpha^2 x A e^{-\alpha^2 x^2/2}$$

$$\therefore \frac{d^2\psi_0}{dx^2} = \frac{d}{dx} \frac{d\psi_0}{dx} = \frac{d}{dx} \left(-\alpha^2 x A e^{-\alpha^2 x^2/2} \right) = \alpha^4 x^2 A e^{-\alpha^2 x^2/2} - \alpha^2 A e^{-\alpha^2 x^2/2}$$

$$\text{or} \quad \frac{d^2\psi_0}{dx^2} = (\alpha^4 x^2 - \alpha^2) \psi_0$$

Using in equation (i), we get

$$(\alpha^4 x^2 - \alpha^2) \psi_0 + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi_0 = 0$$

$$\text{or} \quad (\alpha^4 x^2 - \alpha^2) \psi_0 + \frac{2mE}{\hbar^2} \psi_0 - \frac{mk}{\hbar^2} x^2 \psi_0 = 0$$

We have $k = m\omega^2$

$$\therefore (\alpha^4 x^2 - \alpha^2) \psi_0 + \frac{2mE}{\hbar^2} \psi_0 - \frac{m^2\omega^2}{\hbar^2} x^2 \psi_0 = 0$$

$$\left[(\alpha^4 x^2 - \alpha^2) + \frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} x^2 \right] \psi_0 = 0$$

Here ψ_0 is the ground state function of harmonic oscillator, it is not zero.

Therefore, we have

$$\alpha^4 x^2 - \alpha^2 + \frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} x^2 = 0$$

Using $\alpha = \sqrt{\frac{m\omega}{\hbar}}$, we get

$$\frac{m^2\omega^2}{\hbar^2} x^2 - \frac{m\omega}{\hbar} + \frac{2mE}{\hbar^2} - \frac{m^2\omega^2}{\hbar^2} x^2 = 0$$

$$\therefore -\frac{m\omega}{\hbar} + \frac{2mE}{\hbar^2} = 0$$

$$\text{or} \quad \frac{2mE}{\hbar^2} = \frac{m\omega}{\hbar}$$

$$\therefore E = \frac{1}{2} \hbar\omega$$

Example 7 : Using the ground state wave function of the simple harmonic oscillator, find $\langle x \rangle$, $\langle x^2 \rangle$ and $\langle p_x \rangle$.

Solution : Ground state function of the simple harmonic oscillator is given as

$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\alpha^2 x^2/2}$$

(a) The expectation value of x is given as

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi_0(x)|^2 dx$$

$$\begin{aligned}\therefore \langle x \rangle &= \int_{-\infty}^{\infty} x \left(\frac{\alpha}{\sqrt{\pi}} \right) e^{-\alpha^2 x^2} dx \\ &= \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} x e^{-\alpha^2 x^2} dx\end{aligned}$$

The integral on RHS is an odd integral. Hence, the integral vanishes over the entire range $(-\infty, \infty)$.

$$\therefore \langle x \rangle = 0$$

(b) The expectation value of x^2 is given as

$$\begin{aligned}\langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2 |\psi_0(x)|^2 dx \\ \therefore \langle x^2 \rangle &= \int_{-\infty}^{\infty} x^2 \left(\frac{\alpha}{\sqrt{\pi}} \right) e^{-\alpha^2 x^2} dx \\ &= \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} x^2 e^{-\alpha^2 x^2} dx\end{aligned}$$

We have general integral $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta}}$

$$\begin{aligned}\therefore \langle x^2 \rangle &= \left(\frac{\alpha}{\sqrt{\pi}} \right) \frac{1}{2\alpha^2} \sqrt{\frac{\pi}{\alpha^2}} \\ \therefore \langle x^2 \rangle &= \frac{1}{2\alpha^2} \\ \therefore \alpha &= \sqrt{\frac{m\omega}{\hbar}} \\ \therefore \langle x^2 \rangle &= \frac{\hbar}{2m\omega}\end{aligned}$$

(c) Expectation value of p_x is given as

$$\begin{aligned}\langle p_x \rangle &= \int_{-\infty}^{\infty} \psi_0^* \left(-i\hbar \frac{d}{dx} \right) \psi_0 dx \\ &= -i\hbar \int_{-\infty}^{\infty} \psi_0^* \frac{d\psi_0}{dx} dx\end{aligned}$$

$$\begin{aligned}
 \langle p_x \rangle &= -i\hbar \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} e^{-\alpha^2 x^2} \frac{d}{dx} e^{-\alpha^2 x^2} dx \\
 &= -i\hbar \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} e^{-\alpha^2 x^2} (-\alpha^2 x) e^{-\alpha^2 x^2} dx \\
 &= i\hbar \alpha^2 \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} x e^{-\alpha^2 x^2} dx
 \end{aligned}$$

The integral on RHS is an odd integral over the entire range $(-\infty, \infty)$. Hence the integral vanishes.

$$\therefore \langle p_x \rangle = 0$$

Example 8 : For a particle in a one dimensional rigid box, show that the fractional difference in the energy between adjacent eigen values is

$$\frac{\Delta E_n}{E_n} = \frac{2n+1}{n^2}$$

Use this result to discuss the classical limit of the system.

Solution : The energy eigen value in the n^{th} state of one dimensional rigid box is given as

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

The energy eigen value in the $(n+1)^{\text{th}}$ state is given as

$$E_{n+1} = \frac{(n+1)^2 \pi^2 \hbar^2}{2ma^2}$$

Difference between the eigen values is

$$\begin{aligned}
 \Delta E_n &= E_{n+1} - E_n \\
 &= \frac{(n+1)^2 \pi^2 \hbar^2}{2ma^2} - \frac{n^2 \pi^2 \hbar^2}{2ma^2} \\
 &= [(n+1)^2 - n^2] \frac{\pi^2 \hbar^2}{2ma^2}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \frac{\Delta E_n}{E_n} &= \frac{(n+1)^2 - n^2}{n^2} \\
 &= \frac{n^2 + 2n + 1 - n^2}{n^2}
 \end{aligned}$$

$$\therefore \frac{\Delta E_n}{E_n} = \frac{2n+1}{n^2}$$

For classical limit $n \rightarrow \infty$. Therefore,

$$\lim_{n \rightarrow \infty} \frac{\Delta E_n}{E_n} = \lim_{n \rightarrow \infty} \frac{2n+1}{n^2} = \lim_{n \rightarrow \infty} \frac{2+1/n}{n} = \lim_{n \rightarrow \infty} \frac{2}{n} \rightarrow 0 \text{ as } n \rightarrow \infty$$

$$\therefore \lim_{n \rightarrow \infty} \frac{\Delta E_n}{E_n} = 0$$

or $\Delta E_n \rightarrow 0$ as $n \rightarrow \infty$ i.e. the energy levels are continuous.

Example 9 : The restoring force constant k for the vibrations of the interatomic spacing of the diatomic molecule is 10^3 J/m^2 . If mass of the molecule is $4.9 \times 10^{-26} \text{ kg}$, estimate the zero point energy of the oscillator.

Solution : Given : $m = 4.9 \times 10^{-26} \text{ kg}$
 $k = 10^3 \text{ J/m}^2$

The zero-point energy of the oscillator is $E = \frac{1}{2} \hbar \omega$

For the oscillator of mass m and force constant k , the angular frequency is

$$\omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{10^3}{4.9 \times 10^{-26}}} = \sqrt{\frac{10^{29}}{4.9}} = \sqrt{\frac{10^{30}}{49}} = \frac{10^{15}}{7}$$

$$\therefore E = \frac{1}{2} \times 1.055 \times 10^{-34} \times \frac{1}{7} \times 10^{15} = \frac{1}{14} \times 1.055 \times 10^{-19}$$

$$\text{or } E = 0.0754 \times 10^{-19} \text{ J}$$

$$\therefore E = 0.0471 \text{ eV}$$

Example 10 : Calculate the most probable distance of a particle in the first excited state of the simple harmonic oscillator.

Solution : The wave function in the first excited state of the oscillator is given by

$$\psi_1(x) = \left(\frac{\alpha}{2\sqrt{\pi}} \right)^{1/2} H_1(\alpha x) e^{-\alpha^2 x^2/2}$$

$$\text{or } \psi_1(x) = \left(\frac{\alpha}{2\sqrt{\pi}} \right)^{1/2} (2\alpha x) e^{-\alpha^2 x^2/2} \quad (\text{since } H_1(\alpha x) = 2\alpha x)$$

$$\text{The probability density is } P(x) = |\psi_1(x)|^2 = \left(\frac{\alpha}{2\sqrt{\pi}} \right) 4\alpha^2 x^2 e^{-\alpha^2 x^2}$$

The distance at which the probability is maximum called the most probable distance. It can be obtained by differentiating $P(x)$ w. r. t. x and equating to zero.

$$\begin{aligned} \frac{dP}{dx} &= \left(\frac{\alpha}{2\sqrt{\pi}} \right) 4\alpha^2 \frac{d}{dx} (x^2 e^{-\alpha^2 x^2}) \\ &= \left(\frac{\alpha}{2\sqrt{\pi}} \right) 4\alpha^2 (-2\alpha^2 x^3 e^{-\alpha^2 x^2} + 2x e^{-\alpha^2 x^2}) \end{aligned}$$

$$\frac{dP}{dx} = 0 \text{ gives}$$

$$\left(\frac{\alpha}{2\sqrt{\pi}} \right) 4\alpha^2 (-2\alpha^2 x^3 e^{-\alpha^2 x^2} + 2x e^{-\alpha^2 x^2}) = 0$$

$$\text{or } (-2\alpha^2 x^3 e^{-\alpha^2 x^2} + 2x e^{-\alpha^2 x^2}) = 0$$

$$(-2\alpha^2 x^3 + 2x) e^{-\alpha^2 x^2} = 0$$

$$\text{or } -2\alpha^2 x^3 + 2x = 0$$

$$\therefore x^2 = \frac{1}{\alpha^2}$$

$$\text{or } x = \pm \frac{1}{\alpha}$$

Thus the particle is most likely to be found at positions $x = \frac{1}{\alpha}$ and $x = -\frac{1}{\alpha}$.

Example 11 : For one dimensional harmonic oscillator in its ground state, obtain the expectation value of the potential energy.

Solution : The expectation value of the potential energy is given by

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi_0^* V \psi_0 dx$$

$$V = \frac{1}{2} kx^2$$

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi_0^* \frac{1}{2} kx^2 \psi_0 dx$$

$$= \frac{1}{2} k \int_{-\infty}^{\infty} \psi_0^* x^2 \psi_0 dx$$

$$= \frac{1}{2} k \int_{-\infty}^{\infty} x^2 \left(\frac{\alpha}{\sqrt{\pi}} \right) e^{-\alpha^2 x^2} dx$$

$$= \left(\frac{\alpha}{\sqrt{\pi}} \right) \int_{-\infty}^{\infty} x^2 e^{-\alpha^2 x^2} dx$$

We have general integral $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2\beta} \sqrt{\frac{\pi}{\beta}}$

$$\langle V \rangle = \frac{1}{2} k \left(\frac{\alpha}{\sqrt{\pi}} \right) \frac{1}{2\alpha^2} \sqrt{\frac{\pi}{\alpha^2}}$$

$$= \frac{1}{2} k \frac{1}{2\alpha^2}$$

$$k = m\omega^2 \quad \text{and} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}}$$

$$\langle V \rangle = \frac{1}{4} m\omega^2 \times \frac{\hbar}{m\omega}$$

$$= \frac{1}{4} \hbar\omega$$

Example 12 : Calculate the probability of finding the simple harmonic oscillator outside the classical limit when it is in the ground state.

Solution : The ground state eigen function of the oscillator is given by

$$\psi_0(x) = \left(\frac{\alpha}{\sqrt{\pi}} \right)^{1/2} e^{-\alpha^2 x^2/2}$$

The classical limit of the oscillator is $\pm a$, where a is the amplitude.

The classical energy of the oscillator $E = \frac{1}{2}ka^2 = \frac{1}{2}m\omega^2a^2$

Quantum mechanical ground state energy is $E = \frac{1}{2}\hbar\omega$

$$\therefore \frac{1}{2}\hbar\omega = \frac{1}{2}m\omega^2a^2$$

$$\text{Which gives } a = \pm \sqrt{\frac{\hbar}{m\omega}} = \pm \frac{1}{\alpha}$$

The probability of finding the particle outside the classical region is

$$\begin{aligned} p(x) &= \int_{-1/\alpha}^{-\infty} |\psi_0(x)|^2 dx + \int_{1/\alpha}^{\infty} |\psi_0(x)|^2 dx \\ &= \int_{-1/\alpha}^{-\infty} \left(\frac{\alpha}{\sqrt{\pi}}\right) e^{-\alpha^2 x^2} dx + \int_{1/\alpha}^{\infty} \left(\frac{\alpha}{\sqrt{\pi}}\right) e^{-\alpha^2 x^2} dx \\ &= \frac{\alpha}{\sqrt{\pi}} \left[\int_{-1/\alpha}^{-\infty} e^{-\alpha^2 x^2} dx + \int_{1/\alpha}^{\infty} e^{-\alpha^2 x^2} dx \right] \end{aligned}$$

Since the integrals are even integrals, we can write $\int_{-1/\alpha}^{-\infty} e^{-\alpha^2 x^2} dx = \int_{1/\alpha}^{\infty} e^{-\alpha^2 x^2} dx$

$$\therefore p(x) = \frac{\alpha}{\sqrt{\pi}} \cdot 2 \int_{1/\alpha}^{\infty} e^{-\alpha^2 x^2} dx$$

$$\text{Let } \alpha x = t \quad \therefore dx = \frac{dt}{\alpha}$$

When $x = 1/\alpha$ we get $t = 1$

And when $x = \infty$ we get $t = \infty$

$$\begin{aligned} \therefore p(x) &= \frac{\alpha}{\sqrt{\pi}} \cdot \frac{2}{\alpha} \int_1^{\infty} e^{-t^2} dt \\ &= \frac{2}{\sqrt{\pi}} \int_1^{\infty} e^{-t^2} dt \end{aligned}$$

Therefore,

$$p(x) = \frac{2}{\sqrt{\pi}} \left[\int_0^{\infty} e^{-t^2} dt - \int_0^1 e^{-t^2} dt \right]$$

We have $\int_0^{\infty} e^{-t^2} dt = \frac{\sqrt{\pi}}{2}$

$$\begin{aligned} \therefore p(x) &= \frac{2}{\sqrt{\pi}} \left[\frac{\sqrt{\pi}}{2} - \int_0^1 e^{-t^2} dt \right] \\ &= 1 - \frac{2}{\sqrt{\pi}} \int_0^1 e^{-t^2} dt \quad \dots(i) \end{aligned}$$

Consider the integral $\int_0^1 e^{-t^2} dt$. We use the infinite series expansion for e^{-t^2} . Therefore,

$$\begin{aligned} \int_0^1 e^{-t^2} dt &= \int_0^1 \left(1 - t^2 + \frac{t^4}{2!} - \frac{t^6}{3!} + \frac{t^8}{4!} - \dots \right) dt \\ &= \left[t - \frac{t^3}{3} + \frac{t^5}{2! \times 5} - \frac{t^7}{3! \times 7} + \frac{t^9}{4! \times 9} - \dots \right]_0^1 \\ &= \left[1 - \frac{1}{3} + \frac{1}{2! \times 5} - \frac{1}{3! \times 7} + \frac{1}{4! \times 9} - \dots \right] \\ &= \left[1 - \frac{1}{3} + \frac{1}{2 \times 5} - \frac{1}{6 \times 7} + \frac{1}{24 \times 9} - \dots \right] \\ &= 0.74244 \end{aligned}$$

Using in equation (i), we get the probability of finding the particle outside the classical limits.

$$p(x) = 1 - \frac{2}{\sqrt{\pi}} \times 0.74244$$

$$= 1 - 0.837966 = 0.16203 \text{ approximately}$$

Consequently, the probability of finding the particle inside the classical limit will be 0.837966 or 84%

Example 13 : A beam of mono-energetic electrons each with energy 0.05 eV is incident on a potential step of height 0.025 eV. Calculate the probability of reflection from the potential wall.

Solution : Probability of reflection in the case of step potential is given as

$$R = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

We have $k_1^2 = \frac{2mE}{\hbar^2}$

$$k_2^2 = \frac{2m}{\hbar^2} (E - V_0)$$

We write R as follows

$$R = \frac{k_1^2 + k_2^2 - 2k_1k_2}{k_1^2 + k_2^2 + 2k_1k_2}$$

$$\text{But } k_1^2 + k_2^2 = \frac{2mE}{\hbar^2} + \frac{2m}{\hbar^2} (E - V_0) = \frac{2m}{\hbar^2} (2E - V_0)$$

and $k_1 k_2 = \frac{2m}{\hbar^2} \sqrt{E(E - V_0)}$

$$\therefore R = \frac{2E - V_0 - 2\sqrt{E(E - V_0)}}{2E - V_0 + 2\sqrt{E(E - V_0)}}$$

Divide each term on numerator and denominator by V_0 , we get

$$R = \frac{2\frac{E}{V_0} - 1 - 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0} - 1\right)}}{2\frac{E}{V_0} - 1 + 2\sqrt{\frac{E}{V_0}\left(\frac{E}{V_0} - 1\right)}}$$

Now $E = 0.05 \text{ eV}$ and $V_0 = 0.025 \text{ eV}$

$$\therefore \frac{E}{V_0} = 2$$

This gives

$$\begin{aligned} R &= \frac{2 \times 2 - 1 - 2\sqrt{2(2-1)}}{2 \times 2 - 1 + 2\sqrt{2(2-1)}} \\ &= \frac{4 - 1 - 2\sqrt{2}}{4 - 1 + 2\sqrt{2}} \\ &= \frac{3 - 2 \times 1.42}{3 + 2 \times 1.42} \end{aligned}$$

$$\therefore R = 0.027$$

Example 14 : An electron is trapped in an infinitely deep potential well 3.0 \AA in length. If the electron is in the ground state, what is the probability of finding it within 1.0 \AA of the left hand wall ?

Solution : The eigen function for the particle in a deep potential well of width a is given as

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \quad \text{for } 0 < x < a$$

The ground state wave function is

$$\psi_0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right)$$

The probability of finding the particle in the region from 0 to $a/3$ i.e. up to the distance $1/3^{\text{rd}}$ of total width from the left wall is

$$\begin{aligned} p(x) &= \int_0^{a/3} |\psi_0(x)|^2 dx \\ &= \int_0^{a/3} \frac{2}{a} \sin^2\left(\frac{\pi}{a}x\right) dx \end{aligned}$$

$$p(x) = \frac{2}{a} \int_0^{a/3} \sin^2\left(\frac{\pi}{a}x\right) dx$$

We have $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$, therefore, equation (4.16) becomes

$$p(x) = \frac{2}{a} \int_0^{a/3} \frac{1}{2} \left[1 - \cos\left(\frac{2\pi}{a}x\right) \right] dx$$

$$= \frac{1}{a} \int_0^{a/3} \left[1 - \cos\left(\frac{2\pi}{a}x\right) \right] dx$$

$$= \frac{1}{a} \int_0^{a/3} \left[dx - \cos\left(\frac{2\pi}{a}x\right) dx \right]$$

$$= \frac{1}{a} \left[x - \frac{\sin\left(\frac{2\pi}{a}x\right)}{\frac{2\pi}{a}} \right]_0^{a/3}$$

$$= \frac{1}{a} \left[\frac{a}{3} - \frac{a}{2\pi} \sin\left(\frac{2\pi}{a} \cdot \frac{a}{3}\right) \right]$$

$$= \left[\frac{1}{3} - \frac{1}{2\pi} \sin\left(\frac{2\pi}{3}\right) \right]$$

$$= 0.3333 - 0.1370$$

$$= 0.1963$$

$$\therefore p(x) = 19.63 \%$$

QUESTIONS AND PROBLEMS

1. Explain quantum mechanical motion of a particle through constant potential.
2. With the help of time independent Schrödinger equation obtain the energy eigen values and eigen functions for a particle in one dimensional deep potential well.
3. A particle is enclosed in a three dimensional rigid box. Using the Schrödinger steady state equation obtain the eigen values of energy of the particle. What are degenerate states?
4. A particle of total energy E is moving in a one dimensional potential given by

$$\begin{aligned} V &= 0 & x &\leq 0 \\ &= V_0 & x &> 0 \end{aligned}$$

Calculate the coefficient of reflection and transmission for $E > V_0$ and $E < V_0$.

5. Show that particle in one-dimensional infinite well will have discrete energy states. Plot the first three eigen functions.

6. What do you mean by tunneling through a barrier ? A particle traveling with energy $E > 0$, has a potential barrier defined as

$$V = \begin{cases} 0 & x \leq 0 \\ V_0 & 0 < x < a \\ 0 & x \geq a \end{cases}$$

calculate the transmission coefficient.

7. Show that for a rectangular potential barrier $R + T = 1$.
 8. Show that the transmission probability across a potential barrier of height V_0 for $E < V_0$ is given by

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$$T = \left[1 + \frac{V_0^2 \sinh^2 \beta a}{4E(V_0 - E)} \right]^{-1}$$

9. A particle is moving in a square well represented by

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$$V = \begin{cases} 0 & -a < x < a \\ V_0 & \text{otherwise} \end{cases}$$

Solve the steady state Schrödinger equation for the case $E < V_0$ and explain how the energy eigen values of the particle are determined ?

10. Write down the steady state Schrödinger equation for one-dimensional harmonic oscillator. Solve the same to show that the energy eigen values are given by $E_n = \left(n + \frac{1}{2}\right) \hbar \omega$.
 11. Draw the first four eigen functions of the 1-dimensional harmonic oscillator.
 12. Give the physical interpretation of eigen functions of harmonic oscillator.
 13. Explain the classical and quantum mechanical correspondence in the case of 1-dimensional simple harmonic oscillator.
 14. A beam of mono-energetic electrons each with energy 0.08 eV is incident on a potential step of height 0.04 eV. Calculate the probability of reflection from the potential wall. (Ans: 0.027)
 15. A particle is confined between rigid walls separated by a distance a . Find the probability that it will be found within a distance $a/3$ and $2a/3$ from left wall. (Ans: 60 % approx.)
 16. Calculate the probability of finding the simple harmonic oscillator within the classical limit when it is in the ground state. (Ans : 84%)
 17. Using first excited state function of the simple harmonic oscillator show that the energy eigen value is $\frac{3}{2} \hbar \omega$.
 18. Calculate the ground state energy of the harmonic oscillator of a mass of 1 gm is fixed to a spring which is stretched by 1 cm by a force of 1 N along the x axis.
 19. Calculate the probability of transmission for a 1 MeV proton to be transmitted through a potential barrier of height 4 MeV and width 0.01 \AA . (Ans : 1.5×10^{-3})
 20. Find the probability that a particle in a one dimensional rigid box of width a can be found between $x = 0$ to $x = a/n$, when it is in the n^{th} state. (Ans : $1/n$)
 21. The wave function for a particle in infinite potential well is given as

$$\psi_n(x) = A \sin\left(\frac{n\pi}{a} x\right) \quad \text{where } 0 < x < a$$

Find $\langle x^2 \rangle$

(Ans : $\frac{a^2}{12} \left(1 - \frac{6}{n^2 \pi^2}\right)$)

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CHAPTER 5

SPHERICALLY SYMMETRIC POTENTIALS

INTRODUCTION

So far we have mostly restricted ourselves to see how quantum mechanics can be used to describe motion in one dimension. We have seen that one dimensional motion illustrates such basic features of system as the quantisation of energy. For the applications in atomic physics, solid state physics and nuclear physics, we often require treatment that is three dimensional. For problems involving spherically symmetric potential spherical polar coordinate system is most convenient. In this chapter we will study Schrödinger's equation in spherical polar coordinate system. We will also apply it to spherically symmetric potential and study the quantisation of energy. Hydrogen atom problem will be discussed in a qualitative way. Because of its simplicity, hydrogen atom has advantage that many of its properties can be calculated exactly and without approximation. It has permitted comparison between prediction and experiment for a variety of physical theories from quantum mechanics.

5.1 SCHRÖDINGER'S EQUATION IN SPHERICAL POLAR CO-ORDINATES

Schrödinger's equation in cartesian co-ordinate system is given as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V] \psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is the Laplacian operator in the cartesian form.

The transformation equations between cartesian and spherical polar co-ordinate systems are

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

With these transformations, the Laplacian operator becomes

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

Therefore, Schrödinger's equation in spherical polar coordinate system is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V] \psi = 0 \quad \dots(5.1)$$

where $V = V(r, \theta, \phi)$ and $\psi = \psi(r, \theta, \phi)$.

5.2 FREE AXIS RIGID ROTATOR

A rigid rotator is a system of two particles connected by light rigid rod (*i.e.* with negligible mass). Since the rod is rigid the distance between the particles is always constant. Fig. 5.1 shows the rigid rotator of masses m_1 and m_2 a distance r apart.

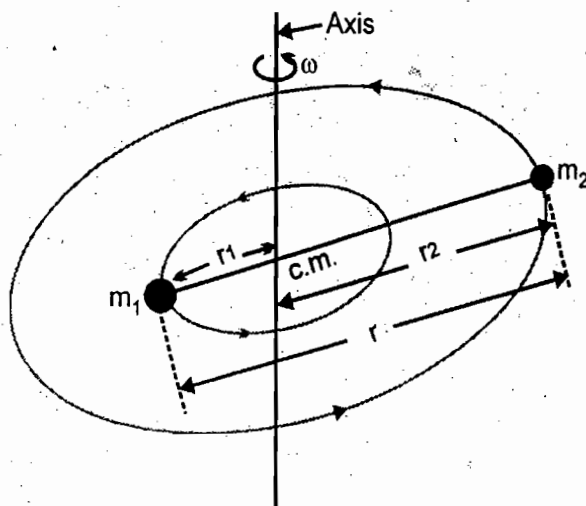


Fig. 5.1 rigid rotator

The axis of rotation is passing through the centre of mass of rigid rotator and perpendicular to the length of the rod. The orientation of axis of rotation in space can be along any direction, so this is called free axis rigid rotator. The moment of inertia about an axis passing through centre of mass and perpendicular to the line joining of m_1 and m_2 is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots(5.2)$$

where r_1 and r_2 are the distances of m_1 and m_2 respectively from the centre of mass. Since the mass is equally distributed about the centre of mass, we have

$$m_1 r_1 = m_2 r_2$$

and

$$r = r_1 + r_2$$

Since,

$$r_1 = \frac{m_2}{m_1} r_2$$

$$r = \frac{m_2}{m_1} r_2 + r_2 = \frac{m_1 + m_2}{m_1} r_2$$

or

$$r_2 = \frac{m_1}{m_1 + m_2} r$$

Similarly,

$$r_1 = \frac{m_2}{m_1 + m_2} r$$

Using r_1 and r_2 in equation (5.2), we get

$$\begin{aligned} I &= \frac{m_1 m_2^2}{(m_1 + m_2)^2} r^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r^2 \\ &= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r^2 \end{aligned}$$

∴

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2$$

The reduced mass of the system is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots(5.3)$$

and moment of inertia of the system about the free axis is

$$I = \mu r^2 \quad \dots(5.4)$$

Equation (5.4) states that the rotation of a rigid rotator is equivalent to the rotation of a single particle of mass μ at perpendicular distance r from the axis of rotation.

Classically the kinetic energy of rotation is

$$K.E. E = \frac{1}{2} I \omega^2$$

where ω is the angular velocity.

Since angular momentum is $L = I\omega$, we can write

$$E = \frac{L^2}{2I} \quad \dots(5.5)$$

The rigid rotator can have any value for ω between 0 to ∞ . Therefore, energy spectrum is continuous.

Now we will solve the problem quantum mechanically. Schrödinger's time independent equation in spherical polar coordinates is given as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V] \psi = 0$$

Multiplying throughout by r^2 , we get

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2}{\hbar^2} [E - V] \psi = 0$$

Since the rigid rotator is free to rotate in any plane and no force acting on it, its potential energy $[V = 0]$. Therefore, we get

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2 E}{\hbar^2} \psi = 0$$

But $[r = \text{constant}]$ therefore, the first term on left hand side of above equation is zero.

Hence, we get

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2 E}{\hbar^2} \psi = 0 \quad \dots(5.6)$$

Since $[I = \mu r^2]$, therefore we get

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2IE}{\hbar^2} \psi = 0 \quad \dots(5.7)$$

Equation (5.7) can be solved by separation of variables method. Let us assume

$$\psi(\theta, \phi) = F(\theta) G(\phi) = FG \quad \dots(5.8)$$

Using in equation (5.7), we get

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial FG}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 FG}{\partial \phi^2} + \frac{2IE}{\hbar^2} FG = 0$$

Let,

$$\lambda = \frac{2IE}{\hbar^2} \quad \dots(5.9)$$

Therefore,

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial FG}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 FG}{\partial \phi^2} + \lambda FG = 0$$

$$\frac{G}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{F}{\sin^2 \theta} \frac{\partial^2 G}{\partial \phi^2} + \lambda FG = 0$$

Multiplying above equation throughout by $\sin^2 \theta$ and dividing by FG , we get

$$\frac{\sin \theta}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} + \lambda \sin^2 \theta = 0$$

or

$$\frac{\sin \theta}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \lambda \sin^2 \theta = - \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} \quad \dots(5.10)$$

m^2

Left hand side of above equation depends upon θ only and right hand side depends upon ϕ only. This is possible only when both sides are equal to same constant say m_l^2 . Therefore, we get

$$\frac{\sin \theta}{F} \frac{d}{d\theta} \left(\sin \theta \frac{dF}{d\theta} \right) + \lambda \sin^2 \theta = m_l^2 \quad \dots(5.11)$$

and
$$-\frac{1}{G} \frac{d^2 G}{d\phi^2} = m_l^2 \quad \dots(5.12)$$

Equation (5.12) can be written as

$$\frac{d^2 G}{d\phi^2} + m_l^2 G = 0 \quad \dots(5.13)$$

The general solution of equation (5.13) can be written as

$$G(\phi) = A e^{im_l \phi} \quad \dots(5.14)$$

where m_l can be positive or negative integer. The range of ϕ is from 0 to 2π . The constant A can be obtained by normalisation condition i.e.

$$\int_0^{2\pi} G^* G d\phi = 1$$

$$\therefore \int_0^{2\pi} A^* e^{-im_l \phi} \cdot A e^{im_l \phi} d\phi = 1$$

$$|A|^2 \int_0^{2\pi} d\phi = 1$$

or

$$|A|^2 2\pi = 1$$

This gives

$$|A| = \frac{1}{\sqrt{2\pi}}$$

$$\therefore G(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \quad \dots(5.15)$$

As the wave function (5.15) must be acceptable solution (i.e. single valued and continuous), then we must have $G(\phi) = G(\phi + 2\pi)$. Because if we rotate ϕ by 2π keeping other variables constant, we are again at the same point.

Therefore,

$$\frac{1}{\sqrt{2\pi}} e^{im_l \phi} = \frac{1}{\sqrt{2\pi}} e^{im_l (\phi + 2\pi)}$$

or

$$e^{i2\pi m_l} = 1$$

$$\therefore \cos(2\pi m_l) + i \sin(2\pi m_l) = 1$$

This gives

$$\cos(2\pi m_l) = 1 \quad \text{and} \quad \sin(2\pi m_l) = 0$$

This is possible only when

$$2\pi m_l = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi \dots\dots$$

$$\therefore m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(5.16)$$

Equation (5.11) can be written as

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dF}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) F = 0 \quad \dots(5.17)$$

This equation can be solved using the following substitution.

$$\cos \theta = x,$$

$$\text{Then, } -\sin \theta d\theta = dx$$

we can write

$$-\frac{d}{dx} = \frac{1}{\sin \theta} \frac{d}{d\theta}$$

$$\therefore \sin \theta \frac{dF}{d\theta} = \frac{\sin^2 \theta}{\sin \theta} \frac{dF}{d\theta} = -(1-x^2) \frac{dF}{dx}$$

Using in equation (5.17), we get

$$-\frac{d}{dx} \left(-(1-x^2) \frac{dF}{dx} \right) + \left[\lambda - \frac{m_l^2}{(1-x^2)} \right] F = 0$$

$$\text{or } (1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \left[\lambda - \frac{m_l^2}{(1-x^2)} \right] F = 0 \quad \dots(5.18)$$

This is associated Legendre's equation. For a given value of m_l it has acceptable solutions only when $\lambda = l(l+1)$, where l is a positive integer given as

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

With equation (5.16), we get

$$l = 0, 1, 2, 3, 4, \dots \quad \dots(5.19)$$

Therefore, we can write equation (5.18) as

$$(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \left[l(l+1) - \frac{m_l^2}{(1-x^2)} \right] F = 0$$

The general solution of above equation is associated Legendre polynomials $P_l^{m_l}(x)$ given as

$$P_l^{m_l}(x) = (1-x^2)^{|m_l|/2} \frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x)$$

where $P_l(x)$ are Legendre polynomials

Hence general solution of equation (5.17) is

$$F_l^{m_l}(\theta) = B P_l^{m_l}(\cos \theta) \quad \dots(5.18)$$

where B is the normalization constant and is given by

$$B = \sqrt{\frac{(2l+1)}{2} \frac{(l-|m_l|)!}{(l+|m_l|)!}}$$

Thus, the total wave function is

$$\psi(\theta, \phi) = F_l^{m_l}(\theta) G_{m_l}(\phi)$$

or

$$\psi(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \sqrt{\frac{(2l+1)}{2} \frac{(l-|m_l|)!}{(l+|m_l|)!}} P_l^{m_l}(\cos \theta) e^{im_l\phi} \quad \dots(5.19)$$

From equation (5.9), we have

$$\lambda = \frac{2IE}{\hbar^2}$$

\therefore

$$\frac{2IE}{\hbar^2} = l(l+1)$$

Thus, the corresponding eigen values are :

$$E_l = \frac{l(l+1)\hbar^2}{2I} \quad \dots(5.20)$$

When

$$l = 0 \quad E_0 = 0$$

$$l = 1 \quad E_1 = 2 \frac{\hbar^2}{2I} = 2B$$

$$l = 2 \quad E_2 = 6 \frac{\hbar^2}{2I} = 6B$$

$$l = 3 \quad E_3 = 12 \frac{\hbar^2}{2I} = 12B$$

and so on...

$$\text{where } B = \frac{\hbar^2}{2I}.$$

The energy level E_0 is called the ground state energy of the rigid rotator. The subsequent levels E_1 , E_2 , etc. are called respectively first, second, etc. rotational energy levels.

The energy level diagram is shown in Fig. 5.2.

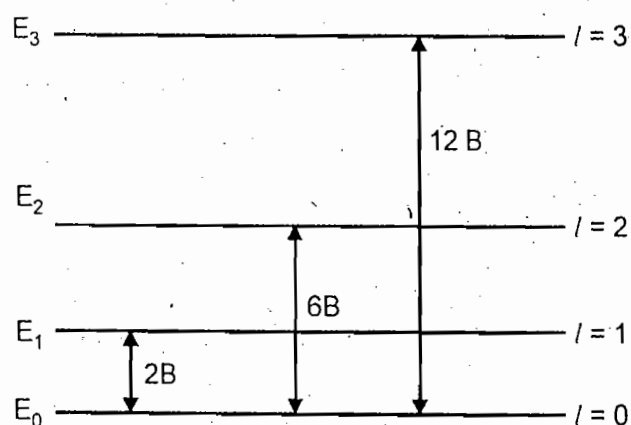


Fig. 5.2

It is seen that the difference between successive energy levels increases with increase in l . Also the spectrum is discrete. The discrete nature of energy levels is confirmed experimentally.

5.3 FIXED AXIS RIGID ROTATOR

Suppose that a rigid rotator with its centre of mass at the origin rotates in the XY plane and axis of rotation is fixed along Z-axis as shown in Fig. 5.3.

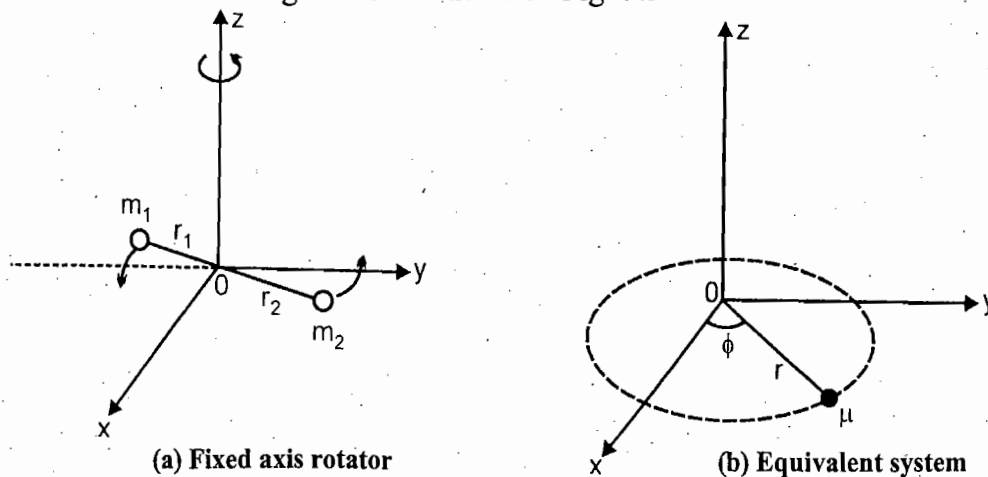


Fig. 5.3

The reduced mass of the system is

1)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \dots(5.3)$$

and the moment of inertia of the system about the axis of rotation is

$$I = \mu r^2 \quad \dots(5.4)$$

To obtain eigen functions and eigen values, we will apply Schrödinger's time independent equation in spherical polar coordinates. It is given by

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V] \psi = 0$$

Multiplying throughout by r^2 , we get

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2}{\hbar^2} [E - V] \psi = 0$$

Since the rigid rotator is free to rotate and no force acting on it, its potential energy $V = 0$.

Therefore,

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2 E}{\hbar^2} \psi = 0 \quad \dots(5.21)$$

But $r = \text{constant}$, therefore, the first term on left hand side of above equation $\frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) = 0$. Also, the rotator is rotating in fixed XY plane i.e. angle made by r with the Z-axis

$\theta = 90^\circ$. Hence we get second term $\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) = 0$. Therefore, equation (5.21) becomes

$$\frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu r^2 E}{\hbar^2} \psi = 0 \quad \dots(5.22)$$

Since $I = \mu r^2$ and $\sin \theta = 1$, we get

$$\frac{d^2 \psi}{d\phi^2} + \frac{2IE}{\hbar^2} \psi = 0 \quad \dots(5.23)$$

1.

Let

$$m_l^2 = \frac{2IE}{\hbar^2} \quad \dots(5.24)$$

Therefore,

$$\frac{d^2 \psi}{d\phi^2} + m_l^2 \psi = 0 \quad \dots(5.25)$$

The general solution of equation (5.25) is given by

$$\psi(\phi) = A e^{im_l \phi}$$

where m_l can be positive or negative integer. The range of ϕ is from 0 to 2π . The constant A can be obtained by normalisation condition and it is given by

$$|A| = \frac{1}{\sqrt{2\pi}}$$

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \quad \dots(5.26)$$

As the wave function (5.26) must be acceptable solution (i.e. single valued and continuous), then we must have $\psi(\phi) = \psi(\phi + 2\pi)$. Because rotating ϕ by 2π , we are again at the same point. Therefore,

$$e^{im_l\phi} = e^{im_l(\phi + 2\pi)}$$

$$\text{or } e^{i2\pi m_l} = 1$$

$$\therefore \cos(2\pi m_l) + i \sin(2\pi m_l) = 1$$

This gives

$$\cos(2\pi m_l) = 1 \text{ and } \sin(2\pi m_l) = 0$$

This is possible only when

$$2\pi m_l = 0, \pm 2\pi, \pm 4\pi, \pm 6\pi, \dots$$

$$\therefore m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad \dots(5.27)$$

From equation (5.24), we get

$$E = \frac{m_l^2 \hbar^2}{2I} \quad \dots(5.28)$$

Equation (5.28) gives the energy eigen value for the fixed axis rigid rotator.

5.4 SCHRÖDINGER'S EQUATION FOR SPHERICALLY SYMMETRIC POTENTIALS

The potential energy of a particle which moves in a central, spherically symmetric force field depends only on the distance between the particle and the center of force i.e. $V = V(r)$.

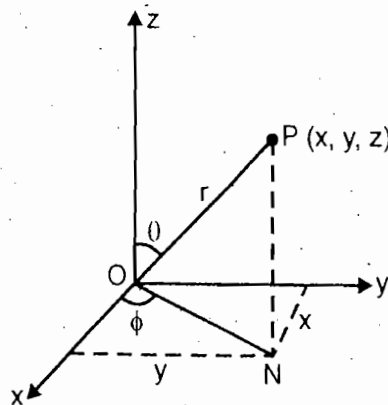


Fig. 5.4 : Spherical polar co-ordinate system

Schrödinger's time independent equation in three dimensions is given by

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(5.29)$$

For spherical symmetric potential, it is more convenient to use the spherical polar coordinate system. Schrödinger's equation in spherical polar coordinate system is

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \dots(5.30)$$

The energy eigen values are determined by the solutions of equation (5.30) which are single valued continuous and have continuous derivatives in r , θ and ϕ .

Equation (5.30) can be solved by separation of variables method. We limit our attention to spherically symmetric potential $V(r)$ which depends only on r and, thus, independent of θ and ϕ . For such a potential equation (5.30) is separable in spherically polar co-ordinates and, therefore, we write the wave function as

$$\psi(r, \theta, \phi) = \underline{R(r) F(\theta) G(\phi)} \quad \text{subs.} \quad \dots(5.31)$$

Substituting in equation (5.30), we get

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial RFG}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial RFG}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 RFG}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) RFG = 0$$

Therefore,

$$\frac{FG}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{RG}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{RF}{r^2 \sin^2 \theta} \frac{\partial^2 G}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - V) RFG = 0$$

Dividing above equation throughout by RFG , we get

$$\frac{1}{r^2} \frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{1}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} + \frac{2m}{\hbar^2} [E - V(r)] = 0$$

Multiplying above equation throughout by $r^2 \sin^2 \theta$, we get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} [E - V(r)] = 0$$

Taking third term on the right side, we get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} [E - V(r)] = - \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} \quad \dots(5.32)$$

Now the LHS of above equation is function of r and θ alone while RHS is function of ϕ alone. Their equality implies that each side must equal to a constant say m_l^2 . Therefore, we get

$$\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{F} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} [E - V(r)] = \underbrace{\left(\frac{m_l^2}{\sin^2 \theta} \right)}_{U(\phi)} \quad \dots(5.33)$$

and

$$- \frac{1}{G} \frac{\partial^2 G}{\partial \phi^2} = m_l^2 \quad \dots(5.34)$$

Equation (5.34) can be written as

$$\frac{d^2 G}{d\phi^2} + m_l^2 G = 0 \quad \dots(5.35)$$

This equation is called ϕ -part equation or azimuthal equation. Since the differential equation is in the azimuthal angle ϕ .

Dividing Equation (5.33) throughout by $\sin^2 \theta$, we get

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{F \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] = \frac{m_l^2}{\sin^2 \theta}$$

Therefore,

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{F \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) \quad \dots(5.36)$$

LHS side of above equation depends on r only and RHS depends on θ only. This requires that both sides are equal to some constant, say λ . Therefore,

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] = \lambda \quad \dots(5.37)$$

$$\text{and } \frac{m_l^2}{\sin^2 \theta} - \frac{1}{F \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial F}{\partial \theta} \right) = \lambda \quad \dots(5.38)$$

Equation (5.37) can be written as

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[E - V(r) - \frac{\lambda}{r^2} \right] R = 0 \quad \dots(5.39)$$

This equation is called radial part equation

Equation (5.38) can be written as

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dF}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) F = 0 \quad \dots(5.40)$$

Equation (5.40) is called θ -part equation.

The ϕ - part equation is given as

$$\frac{d^2 G}{d\phi^2} + m_l^2 G = 0$$

The general solution of this equation can be written as

$$G(\phi) = A e^{im_l \phi} \quad \dots(5.41)$$

The constant m_l must be positive or negative integer. This is because G and its derivative must be continuous and single valued in the domain $0 \leq \phi \leq 2\pi$.

We have

$$m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots \quad \dots(5.42)$$

Consider θ -part equation :

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dF}{d\theta} \right) + \left(\lambda - \frac{m_l^2}{\sin^2 \theta} \right) F = 0$$

Let

$$\cos \theta = x,$$

\therefore

$$-\sin \theta d\theta = dx$$

or

$$-\frac{d}{dx} = \frac{1}{\sin \theta} \frac{d}{d\theta}$$

\therefore

$$\sin \theta \frac{dF}{d\theta} = \frac{\sin^2 \theta}{\sin \theta} \frac{dF}{dx}$$

or

$$\sin \theta \frac{dF}{d\theta} = -(1-x^2) \frac{dF}{dx}$$

Using above in the θ -part equation we get

$$-\frac{d}{dx} \left(-(1-x^2) \frac{dF}{dx} \right) + \left[\lambda - \frac{m_l^2}{(1-x^2)} \right] F = 0$$

or $(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \left[\lambda - \frac{m_l^2}{(1-x^2)} \right] F = 0 \quad \dots(5.43)$

This is *associated Legendre's equation*. For a given value of m_l it has acceptable solutions only when $\lambda = l(l+1)$, where l is a positive integer given as

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

With equation (14), we get

$$l = 0, 1, 2, 3, 4, \dots \quad \dots(5.44)$$

Therefore, we can write equation (5.43) as

$$(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \left[l(l+1) - \frac{m_l^2}{(1-x^2)} \right] F = 0$$

The general solutions of above equation are the associated Legendre polynomials $P_l^{m_l}(x)$ given as

$$P_l^{m_l}(x) = (1-x^2)^{|m_l|/2} \frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x)$$

where $P_l(x)$ are *Legendre polynomials*

Hence general solution of equation (5.40) is

$$F_l^{m_l}(\theta) = B P_l^{m_l}(\cos \theta) \quad \dots(5.45)$$

where B is normalization constant.

With $\lambda = l(l+1)$, we can write radial part equation (5.39) as

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[E - V(r) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(5.46)$$

With the values of l and specified potential $V(r)$, equation (5.46) can be solved to obtain solution $R(r)$ and the energy eigen values.

Thus, the general solution of equation (5.30) is

$$\psi(r, \theta, \phi) = A R(r) P_l^{m_l}(\cos \theta) e^{im_l \phi} \quad \dots(5.47)$$

where A is constant called the normalization constant.

Some of the associated Legendre polynomials are listed in the Table 5.1

Table 5.1

L	m_l	$P_l^{m_l}(\cos \theta)$
0	0	$P_0^0 = 1$
1	0	$P_1^0 = 2 \cos \theta$
1	1	$P_1^1 = \sin \theta$
2	0	$P_2^0 = 4(3 \cos^2 \theta - 1)$
2	1	$P_2^1 = 4 \sin \theta \cos \theta$
2	2	$P_2^2 = \sin^2 \theta$

Spherical Harmonics:

The wave function is

$$\psi(r, \theta, \phi) = R(r) F(\theta) G(\phi)$$

We can write it as

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

where

$$Y(\theta, \phi) = F(\theta) G(\phi)$$

Since F depends on l and m_l and G depends on m_l . We can write

$$Y_l^{m_l}(\theta, \phi) = F_l^{m_l}(\theta) G(\phi)$$

$$Y_l^{m_l}(\theta, \phi) = B P_l^{m_l}(\cos \theta) e^{im_l\phi} \quad \dots(5.48)$$

B is the normalization constant. $Y_l^{m_l}(\theta, \phi)$ is the angular part (θ, ϕ) of the wave function. These are called *spherical harmonics*.

5.5 HYDROGEN ATOM

Hydrogen atom is a system consisting of a nucleus (containing proton) with charge ' e ' and an electron with charge ' $-e$ ' bound by an electrostatic attraction given by Coulomb's force. Coulomb's force of attraction is

$$F = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad \dots(5.49)$$

And hence the potential energy is

$$V(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad \dots(5.50)$$

Let M and m be the masses of nucleus and electron respectively. The reduced mass of the system is

$$\mu = \frac{Mm}{M+m}$$

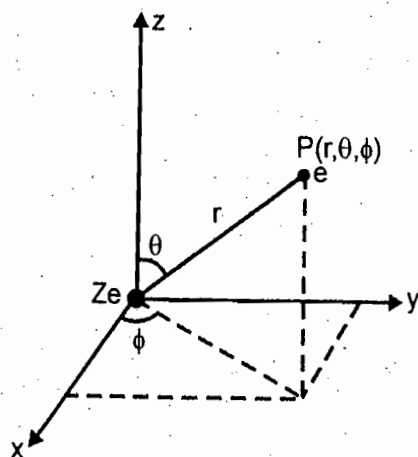


Fig. 5.5

Potential energy V is function of r i.e. potential is spherically symmetric. We will apply Schrödinger's equation in spherical co-ordinate system and it is given as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} [E - V(r)] \psi = 0 \quad \dots(5.51)$$

Using $\psi(r, \theta, \phi) = R(r) F(\theta) G(\phi)$ in equation (5.51) and solving by separation of variables method, we get three equations

(1) Radial equation :

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E - V(r) - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(5.52)$$

(2) θ -part equation :

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dF}{d\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) F = 0 \quad \dots(5.53)$$

(3) ϕ -part equation :

$$\frac{d^2 G}{d\phi^2} + m_l^2 G = 0 \quad \dots(5.54)$$

Solution of ϕ -part equation is given as

$$G(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \quad \dots(5.56)$$

The constant m_l must be positive or negative integer. This is because G and its derivative must be continuous and single valued in the domain $0 \leq \phi \leq 2\pi$.

We have

$$m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots \dots \dots \quad \dots(5.57)$$

m_l is known as *magnetic quantum number*.

As we know that equation (5.53) is associated Legendre equation, its solution is

$$F_l^{m_l}(\theta) = B P_l^{m_l}(\cos \theta) \quad \dots(5.59)$$

where $P_l^{m_l}(\cos \theta)$ are associated Legendre polynomials and B is normalization constant. B can be obtained by condition of normalization of equation (5.59) in the range $0 \leq \theta \leq \pi$. It is given by

$$B = \sqrt{\frac{(2l+1)}{2} \frac{(l-|m_l|)!}{(l+|m_l|)!}} \quad \dots(5.60)$$

And l is positive integer given as

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots \dots \dots \quad \dots(5.61)$$

With equation (5.50) in equation (5.52), we get

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)}{r^2} \right] R = 0 \quad \dots(5.62)$$

Comparing this equation with following equation

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2\mu}{\hbar^2} [E - V(r)] R = 0$$

We then find that the effective potential is

$$V_{\text{eff}} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)}{r^2}$$

With the given value of l , it is found that there are bound state solutions for equation (5.62), which are acceptable (*i.e.* single valued, continuous and finite) only if the total energy E of the system has the form as under:

$$E_n = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} \quad \dots(5.63)$$

where n is the integer and can have value

$$n = l+1, l+2, l+3, \dots \dots \dots \quad \dots(5.64)$$

With l from equation (5.61) and m_l from equation (5.57), we get

$$n = 1, 2, 3, 4, 5, \dots \quad \dots(5.65)$$

The acceptable solution of radial part equation (5.62) more conveniently be written as

$$R_{nl}(r) = C e^{-\alpha r} (\alpha r)^l L(\alpha r) \quad \dots(5.66)$$

where $L(\alpha r)$ is polynomial in (αr)

$$\alpha = \frac{1}{na_0} \text{ where } a_0 \text{ is Bohr's radius given by } a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}$$

and C is normalization constant.

Therefore the general eigen function of the hydrogen atom is

$$\psi(r, \theta, \phi) = N e^{-\alpha r} (\alpha r)^l L(\alpha r) P_l^{m_l}(\cos \theta) e^{im_l\phi} \quad \dots(5.67)$$

where N is normalization constant and is given by

$$N = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}} \cdot \sqrt{\frac{(2l+1)}{2} \frac{(l-|m_l|)!}{(l+|m_l|)!}} \cdot \frac{1}{\sqrt{2\pi}}$$

Some of the eigen functions of hydrogen atom are listed in Table 5.2.

Table 5.2

n	l	m_l	$\psi_{nlm_l}(r, \theta, \phi)$	Energy states
1	0	0	$\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$	Ground state
2	0	0	$\Psi_{200} = \frac{1}{4\sqrt{2\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	First excited state
2	1	0	$\Psi_{210} = \frac{1}{4\sqrt{2\pi a_0^3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \cos \theta$	
2	1	± 1	$\Psi_{21\pm 1} = \frac{1}{8\sqrt{\pi a_0^3}} \left(\frac{r}{a_0}\right) e^{-r/2a_0} \sin \theta e^{\pm i\phi}$	
3	0	0	$\Psi_{300} = \frac{1}{81\sqrt{3\pi a_0^3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	Second excited state
3	1	0	$\Psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi a_0^3}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$	
3	1	± 1	$\Psi_{31\pm 1} = \frac{1}{81\sqrt{\pi a_0^3}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$	

Eigen values:

The solution of radial part of the hydrogen atom shows that the allowed values of total energy of bound states are :

$$E_n = - \frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = - \frac{13.6}{n^2} \text{ eV ,}$$

which is same as predicted by Bohr's theory. Both quantum mechanical predictions and Bohr's predictions are in exact agreement with the experimental results.

Quantum numbers :

The energy eigen values depend on the quantum number 'n' only. But the eigen functions depend on three quantum numbers n, l, m_l since they are products of three functions $R_{nl}(r)$, $F_l^{m_l}(\theta)$ and $G_{m_l}(\phi)$. These three quantum numbers arise because Schrödinger's time independent equation contains three variables r, θ and ϕ , one for each space co-ordinate.

From equations (5.57), (5.61) and (5.64), the conditions for three quantum numbers

$$m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \dots$$

$$l = |m_l|, |m_l| + 1, |m_l| + 2, |m_l| + 3, \dots$$

and

$$n = l + 1, l + 2, l + 3, \dots$$

These conditions more conveniently can be written as

$$n = 0, 1, 2, 3, 4, \dots$$

$$l = 0, 1, 2, 3, \dots (n - 1)$$

and

$$m_l = -l, (-l + 1), (-l + 2), \dots -1, 0, +1, \dots (l + 1), l.$$

The role of 'n' is in specifying the energy eigen value E_n as given by equation (5.63), it is some times called *principal quantum number*. The orbital angular momentum number depends on quantum number l . Therefore, l is also called *orbital quantum number*. If an atom is placed in an external magnetic field, its energy depends on m_l . Consequently m_l is also called *magnetic quantum number*.

Thus, for a given n , l takes values as $0, 1, 2, \dots (n - 1)$ and for a given l , m_l takes values as $-l, (-l + 1), (-l + 2), \dots -1, 0, +1, \dots (l + 1), l$.

For each m_l there are two possible values of m_s which are $+\frac{1}{2}$ and $-\frac{1}{2}$. m_s is called *spin quantum number*.

Degeneracy

For a given value of principal quantum number n , the energy of the atomic level is fixed as predicted by the Bohr's theory (Equation (5.13)). But for a given value of n there are generally several different values of l and for each value of l there are different values of m_l . As the eigen functions depend on n, l and m_l , we have a number of possible eigen functions corresponding to a given energy eigen value E_n . Behaviour of the atom is described by the eigen functions. So the atom has different states having completely different eigen functions for given n with the same energy eigen values. This is referred as *degeneracy* of the energy level, and the eigen functions corresponding to the same energy are called *degenerate*.

As m_l takes values $-l, -l + 1, -l + 2, \dots -1, 0, +1, \dots l + 1, l$ that is $(2l + 1)$ values. Each l takes values as $0, 1, 2, \dots (n - 1)$. Therefore, for each n the number of independent eigen functions will be

$$\sum_{l=0}^{n-1} (2l + 1) = 2 \sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = n^2$$

$$\begin{aligned} n &= 0 \text{ to } (n-1) \\ m_l &= -l \text{ to } +l = 2l+1 \end{aligned}$$

Thus for each n , there are n^2 corresponding degenerate eigen functions. If we take into account spin quantum number (s), which has two possible values of its orientations $m_s = \pm 1/2$, there are $2n^2$ degenerate states corresponding to each energy eigen value E_n .

Table 5.3 shows possible values of quantum numbers for $n = 1, 2, 3$ and number of degenerate eigen functions.

Table 5.3

N	1	2		3		
L	0	0	1	0	1	2
m_l	0	0	-1, 0, +1	0	-1, 0, +1	-2, -1, 0, 1, 2
Number of degenerate eigen functions for each l	1	1	3	1	3	5
Number of degenerate eigen functions for each n	1	4		9		

ILLUSTRATIVE EXAMPLES

Example 1 : The moment of inertia of CO molecule is $1.46 \times 10^{-46} \text{ kg-m}^2$. Calculate the rotational energy and angular velocity in the lowest level of CO molecule.

Solution : The rotational energy level is given as

$$E_l = \frac{l(l+1)\hbar^2}{2I}$$

For the lowest rotational energy level $l=1$, therefore,

$$E_1 = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{I}$$

$$\hbar = 1.055 \times 10^{-34} \text{ J-s}, I = 1.46 \times 10^{-46} \text{ kg-m}^2$$

$$\therefore E_1 = \frac{(1.055 \times 10^{-34})^2}{1.46 \times 10^{-46}} = 7.62 \times 10^{-23} \text{ J}$$

$$\therefore E_1 = \frac{7.62 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ eV} = 4.763 \times 10^{-4} \text{ eV}$$

We have

$$E = \frac{1}{2} I \omega^2$$

$$\omega = \sqrt{\frac{2E}{I}} = \sqrt{\frac{2 \times 7.62 \times 10^{-23}}{1.46 \times 10^{-46}}}$$

$$= 3.23 \times 10^{11} \text{ rad/s}$$

Example 2 : Compute the expectation value of r in the ground state of the hydrogen atom. Also compute the most probable value of r in this state, given that

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad \text{where } a_0 \text{ is Bohr radius.}$$

Solution : (a) The expectation value of r is given as

$$\langle r \rangle = \int_0^\infty r |\psi_{100}|^2 d\tau,$$

where $d\tau$ is volume element and for spherically symmetric system $(d\tau = 4\pi r^2 dr)$

$$\therefore \langle r \rangle = \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} 4\pi r^2 dr$$

$$= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$

We have the general integral $\int_0^\infty x^n e^{-\beta x} dx = \frac{n!}{(\beta)^{n+1}}$

Therefore,

$$\langle r \rangle = \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4}$$

\therefore

$$\langle r \rangle = \frac{3}{2} a_0$$

(b) Most probable distance can be obtained by differentiating probability density w. r. t. r and equating to zero.

The radial probability density is given as

$$P(r) = 4\pi r^2 |\psi_{100}|^2$$

$$P(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

$$\frac{dP}{dr} = \frac{4}{a_0^3} \left[-\frac{2}{a_0} e^{-2r/a_0} r^2 + 2r e^{-2r/a_0} \right]$$

$$= \frac{4}{a_0^3} 2r \left(1 - \frac{r}{a_0} \right) e^{-2r/a_0}$$

For most probable distance $\frac{dP}{dr} = 0$

$$\therefore \frac{4}{a_0^3} 2r \left(1 - \frac{r}{a_0} \right) e^{-2r/a_0} = 0$$

or

$$1 - \frac{r}{a_0} = 0$$

or

$$r = a_0$$

This is the location of the maximum in the radial probability density.

Example 3 : Calculate the expectation value of the potential energy in the ground state of the hydrogen atom.

Smp **Solution :** The ground state of the hydrogen atom is given as

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \quad \text{where } a_0 \text{ is Bohr radius.}$$

The potential energy of the hydrogen atom is

$$V = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

The expectation value of V is given as

$$\langle V \rangle = \int_0^\infty V |\psi_{100}|^2 d\tau,$$

where $d\tau$ is volume element and for spherically symmetric system $d\tau = 4\pi r^2 dr$

$$\langle V \rangle = \frac{1}{\pi a_0^3} \int_0^\infty \left(-\frac{e^2}{4\pi\epsilon_0 r} \right) e^{-2r/a_0} 4\pi r^2 dr$$

$$= -\frac{4}{a_0^3} \frac{e^2}{4\pi\epsilon_0} \int_0^\infty r e^{-2r/a_0} dr$$

We have the general integral $\int_0^\infty x^n e^{-\beta x} dx = \frac{n!}{(\beta)^{n+1}}$

Therefore,

$$\langle V \rangle = -\frac{4}{a_0^3} \frac{e^2}{4\pi\epsilon_0} \frac{1!}{(2/a_0)^2} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{a_0}$$

\therefore

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

\therefore

$$\langle V \rangle = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 \hbar^2}$$

Example 4 : The radial part solution for ground state hydrogen atom is given as

$$R_{10}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

Show that its ground state energy is $-\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2}$

Solution : The radial part equation of hydrogen atom is given as

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)}{r^2} \right] R = 0$$

For ground state $R(r) = R_{10}(r)$ and $l = 0$

Therefore,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR_{10}}{dr} \right) + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] R_{10} = 0$$

$$\text{or } \frac{d^2 R_{10}}{dr^2} + \frac{2}{r} \frac{dR_{10}}{dr} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] R_{10} = 0 \quad \dots(i)$$

We have

$$R_{10} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

$$\therefore \frac{dR_{10}}{dr} = -\frac{1}{\sqrt{\pi a_0^3}} \frac{1}{a_0} e^{-r/a_0}$$

$$\text{and } \frac{d^2 R_{10}}{dr^2} = \frac{1}{\sqrt{\pi a_0^3}} \frac{1}{a_0^2} e^{-r/a_0}$$

Using in equation (i), we get

$$\frac{1}{\sqrt{\pi a_0^3}} \frac{1}{a_0^2} e^{-r/a_0} - \frac{2}{r} \frac{1}{\sqrt{\pi a_0^3}} \frac{1}{a_0} e^{-r/a_0} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} = 0$$

$$\therefore \frac{1}{a_0^2} - \frac{2}{ra_0} + \frac{2\mu}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} \right] = 0$$

$$\text{or } \frac{1}{a_0^2} + \frac{2\mu E}{\hbar^2} = -\frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 r} + \frac{2}{ra_0}$$

Using $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$ in above equation, we get

$$\frac{\mu^2 e^4}{(4\pi\epsilon_0)^2 \hbar^4} + \frac{2\mu E}{\hbar^2} = -\frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 r} + \frac{2\mu e^2}{4\pi\epsilon_0 \hbar^2 r}$$

$$\frac{\mu^2 e^4}{(4\pi\epsilon_0)^2 \hbar^4} + \frac{2\mu E}{\hbar^2} = 0$$

$$\therefore E = -\frac{\mu e^4}{(4\pi\epsilon_0)^2 2\hbar^2}$$

This is the required result.

Example 5. How much more likely an electron in ground state in a hydrogen atom to be found at the distance a_0 from the nucleus than at the distance $a_0/2$?

Solution : Ground state wave function of hydrogen atom is

$$\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

The radial probability density is given as

$$P(r) = 4\pi r^2 |\psi_{100}|^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

$$\therefore \frac{P(r_1)}{P(r_2)} = \frac{r_1^2 e^{-2r_1/a_0}}{r_2^2 e^{-2r_2/a_0}}$$

Here $r_1 = a_0$ and $r_2 = a_0/2$

$$\therefore \frac{P(a_0)}{P(a_0/2)} = \frac{(a_0)^2 e^{-2}}{(a_0/2)^2 e^{-1}} = \frac{4}{e} = 1.470$$

Note that 'e' in the above is the naperian base (e) with value $e = 2.7210$

$$\therefore P(a_0) = 1.47 P(a_0/2)$$

Thus the electron is 47 % more likely to be at a_0 than $a_0/2$.

Example 6 : How many hydrogen atom states are there with $n = 5$? How are they distributed among the sub shells?

Solution : For every n level there are n^2 sublevels. Thus, for $n = 5$ there are 25 sub shells.

They are obtained as follows.

l takes values as 0, 1, 2,($n - 1$)

for each l , m_l takes values from $-l$ to $+l$ i.e. $(2l + 1)$ values

For $n = 5$

l	0	1	2	3	4
m_l	0	+1, 0, -1	2, 1, 0, -1, -2	3, 2, 1, 0, -1, -2, -3	4, 3, 2, 1, 0, -1, -2, -3, -4
No. of eigen states	1	3	5	7	9
Notation	5s	5p	5d	5f	5g

QUESTIONS AND PROBLEMS

- Write down the Schrödinger's time independent equation in spherical polar co-ordinates and separate its variables.
- Obtain Schrödinger's equation for a rigid rotator with a free axis and solve it to obtain energy eigen values and eigen functions.
- Obtain Schrödinger's equation for a rigid rotator with fixed axis and solve it to obtain eigen values and eigen functions.
- Solve the Schrödinger's time independent equation for spherically symmetric potential and obtain eigen functions.
- Discuss qualitatively the radial and angular part solutions of the Schrödinger's equation for hydrogen atom.
- What do you mean by degeneracy of the level? Explain the same in the case of hydrogen atom.
- State and explain the concept of quantum numbers associated with hydrogen atom.
- The moment of inertia of HCl molecule is 2.7×10^{-40} g-cm². What would be the separation between $l = 0$ and $l = 1$ energy levels. (Ans : 4.05×10^{-15} ergs)
- The OH radical has a moment of inertia of 1.48×10^{-40} g-cm². Calculate angular velocity in $l = 5$ state. (Ans : 3.90×10^{13} rad/s.)
- Write down the quantum numbers for all the hydrogen atom states belonging to the subshell for which $n = 4$ and $l = 3$.
- Compute the expectation value of $\frac{1}{r}$ in the ground state of the hydrogen atom. (Ans : $1/a_0$)
- For hydrogen atom in its ground state, calculate the probability density of finding the electron between two spheres of radii a_0 and $1.01a_0$.
- Find the expectation value of r^2 in the ground state of the hydrogen atom. (Ans : $3a_0^2$).
