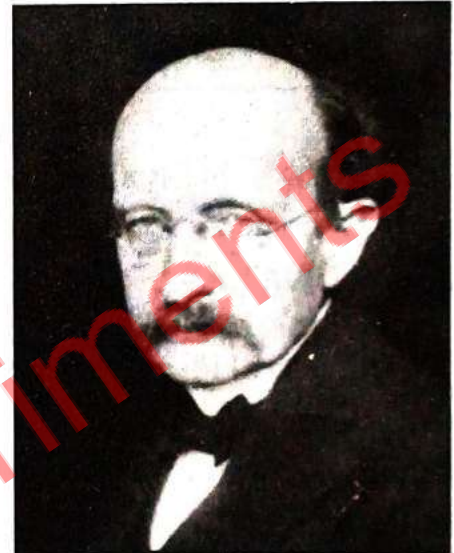# INTRODUCTION TO QUANTUM MECHANICS

" Anybody who has been seriously engaged in scientific work of any kind realises that over the entrance to the gates of the temple of science are written the words : 'Ye must have faith. ' It is a quality which the scientist cannot dispense with"

– Max Planck

1.1. INTRODUCTION

Until the advent of quantum mechanics till late nineteenth century, many physicists believed that they had made great progress in physics and there was not much more that needed to be discovered.

At that time the classical physics was widely accepted. However, by the early 20th century, physicists discovered that the laws of classical mechanics break down in the atomic world. As a result, new laws of physics applicable to the atomic world were developed. These were referred to as **quantum mechanics**. In quantum mechanics, particles have wave-like properties governed by a particular wave equation called the **Schrodinger wave equation**.

Timeline of Quantum Mechanics

1900 :	Max Planck suggested that the radiation is quantised *i.e.*, it comes in integral multiple of the quantity to explain the blackbody radiation.
1905 :	Albert Einstein stated that light, which has wave-like properties also consists of discrete quantised bundles of energy called **photons**.
1913 :	Neil Bohr stated that electrons in atoms have wave-like properties and constructed a theory of atomic structure based on quantum idea.
1924 :	Louis de-Broglie suggested that all particles are associated with waves. This leads to *wave particle duality*.
1925 :	Werner Heisenberg formulated matrix mechanics, the first version of quantum mechanics.
1926 :	Erwin Schrodinger formulated a version of quantum mechanics based on waves. He wrote down the so called Schrodinger wave equation that governs how the waves evolve in space and time.
1926 :	Max Planck gave the probability interpretation of quantum mechanics.
1927 :	Paul Dirac combined quantum mechanics and special theory of relativity to describe electron.

1.2. SCALE OF QUANTUM PHYSICS

Classical Physics deals with macroscopic phenomena where a certain number of dynamical variables are associated with physical system and each of these dynamical variables posses a well defined value at each instant. In Classical mechanics, most of the effects are directly observable with simple instruments. The evaluation of a physical system in time is entirely determined in Classical Physics, if its state at a given initial instant is known. Classical Physics progressed towards greater simplicity after the formulation of rational mechanics by Newton because during that entire period, no experimental fact or discovery led to any doubt concerning its correctness. However, by the early 20th century, with the discovery of various phenomena like radioactivity, X-rays, photoelectric effect etc, it became clear that the phenomena on atomic or subatomic scales (length scale of the order of 10^{-8} cm) do not fit into the frame of Classical Physics and their explanation is based upon entirely new principles. It was also found that the dynamical variables like energy and momentum take only discrete values in different states of an atom in microscopic world rather than continuous values expected according to Classical Physics. These new concepts led to the development of a new mechanics known as **Quantum Mechanics**, which could satisfactory explain many observed facts in microscopic world.

Quantum mechanics developed in two stages. In 1900, Max Planck's hypothesis was the beginning of Ist stage. This theory was semiclassical and was not completely satisfactory. Then the second stage began when Erwin Schrodinger developed wave mechanics in 1926.

1.3. FAILURES OF CLASSICAL MECHANICS

1.3.1. Stability of the Atom

Through his famous α-particle scattering experiment, Rutherford established that there is a small, heavy positively charged region present in the centre of the atom, which is called **nucleus** and negatively charged light electrons surrounding this nucleus. On the basis of classical theory, for the system to be stable, these negatively charged electrons should revolve continuously around the positively charged nucleus. But an electron during its revolution undergoes a change in the direction of its velocity at every instant of its motion and therefore, it is continuously accelerated. According to electrodynamics, energy is radiated continuously in the form of electromagnetic radiations by an accelerated charged particle. So, the revolving electron must emit radiations and therefore, its energy must continuously decrease thus leading to a decrease in the radius of the orbit. This means that electron must follow a spiral path around the nucleus and ultimately it must fall inside the nucleus after losing its entire energy. Thus, the atom must collapse after short duration according to classical mechanics, but it is not so. The atom is a stable structure. So, classical mechanics could not explain the stability of the atom.

1.3.2. Line Spectrum of Hydrogen Atom

$$\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

According to classical mechanics, the electron revolving around the nucleus can have any energy and thus, electromagnetic radiations of all the wavelengths can be emitted by an excited hydrogen atom *i.e.*, the spectrum of hydrogen is expected to be continuous on the basis of classical mechanics. But it was observed experimentally that hydrogen spectrum contains certain well defined bright lines. Thus, the line spectrum of hydrogen could not be explained by classical mechanics.

1.3.3. Black Body Radiation

An object that can absorb the electromagnetic radiations of all the wavelengths incident on it is called an **ideal black body**. The black body at thermal equilibrium, emits the radiations distributed over a continuous range of wavelengths, that is dependent only on the temperature of the black body.

The spectral variation of emitted energy with wavelength at different temperatures is shown in fig. 1.1.

This curve shows that energy is not uniformly distributed but there is a peak in the radiation spectrum at a particular wavelength that is proportional to temperature. As the temperature increases, this peak shifts towards lower wavelengths.
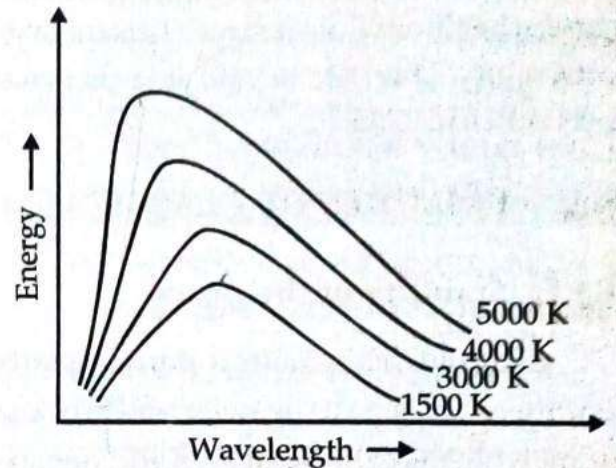
A number of attempts were made in order to explain the origin of

Fig. 1.1

continuous black body radiation spectrum. Rayleigh and Jeans in 1900 tried to explain this spectrum with the help of classical thermodynamics and electromagnetism and they gave the following expression for radiated energy density u_λ emitted at absolute temperature T in the wavelength range λ to $\lambda + d\lambda$ from black body:

$$u_\lambda \, d\lambda = \frac{8\pi}{\lambda^4} \, k \, T \, d\lambda \qquad \qquad ...(1.1)$$

where k is Boltzmann constant and it has a value equal to $1.38 \times 10^{-23} \, \text{JK}^{-1}$.

According to eqn. (1.1), as $\lambda \to 0$, the energy density should become infinite but it was in complete disagreement with the experiment according to which, the energy density should be finite. Then, Wein also tried to explain the variation of emitted energy density (in the wavelengths range λ to $\lambda + d\lambda$) with wavelength and on the basis of classical theory, he derived the following expression for the energy emitted in wavelength range from λ to $\lambda + d\lambda$ by assuming that oscillators emitting radiations are of molecular size. The expression is
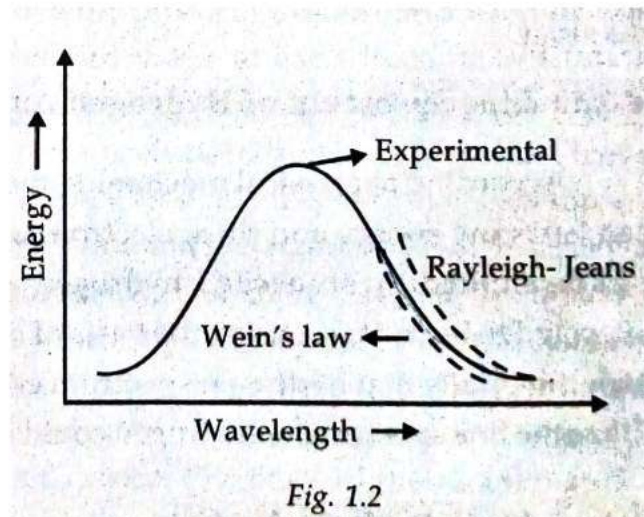

Fig. 1.2

$$u_\lambda \, d\lambda = \frac{8\pi h c}{\lambda^5} \, e^{-hc/\lambda kT} \, d\lambda \qquad \qquad ...(1.2)$$

It was found that this equation could explain the experimental curves only in low wavelength regions but failed in high wavelength regions.

So, on the basis of classical theory, a single relation could not be derived that could explain the energy distribution in a black body spectrum over the complete range of wavelengths.

In addition to the above mentioned drawbacks, some other drawbacks of classical mechanics, are as follows :

- It could not explain the origin of discrete spectra of atom since according to classical mechanics the energy changes are always continuous. This difficulty was later on resolved by Bohr to some extent.

- The classical mechanics could not explain a large number of observed phenomenon like photoelectric effect, Compton effect, Raman effect etc.

- Specific heat of solids and their variation with temperature could not be explained by classical theory.

1.10. dE-BROGLIE HYPOTHESIS – DUAL NATURE OF MATTER

Light exhibits the phenomena of interference, diffraction, polarisation, photoelectric effect, Compton effect etc. The phenomena of interference, diffraction and polarisation could be explained only on the basis of wave theory of light. This means that light possesses wave nature. While on the other hand, the phenomena of photoelectric effect and Compton effect could only be explained on the basis of quantum theory of light, according to which light consists of discrete quanta of energy $h\nu$, known as **photons**. These photons behave like corpuscles. This means that light possesses particle nature. Thus, light is said to possess dual nature i.e., wave nature as well as particle nature. This dual characteristic property of light is known as 'Dual Nature of Light.'

Louis de-Broglie in 1924, proposed that the matter should also exhibit dual nature like light. He argued that if radiation can act like a wave sometimes and like particle at other times, then things like electrons should also exhibit wave properties, under appropriate conditions. The experiments such as those in which $\dfrac{e}{m}$ of material particles in measured, illustrate the particle nature of matter.

According to de-Broglie, a moving material particle has some wave properties associated with it. The waves associated with these moving material particle are called **matter waves** or **de-Broglie waves**. de-Broglie gave an expression for the wavelength of matter waves and it was experimentally verified by Davisson and Germer in 1927 and by G.P. Thomson in 1928.

de-Broglie Wave Equation : To find the wavelength of waves associated with a moving material particle, let us consider a photon of frequency ν. According to quantum theory, the energy of this photon is given by

$$E = h\nu \qquad\qquad ...(1.31)$$

where h is Planck's constant.

If photon is assumed to be a particle of mass m, then its energy

$$E = mc^2 \qquad \text{...(1.32)}$$

From eqns (1.31) and (1.32), we get $hv = mc^2$

or

$$mc = \frac{hv}{c} = \frac{h}{\lambda} \qquad \text{...(1.33)}$$

Because $\lambda = \dfrac{c}{v}$ is wavelength of radiation, therefore,

$$\lambda = \frac{h}{mc} = \frac{h}{p} \qquad \text{...(1.34)}$$

where $p = mc$ is the momentum of the photon.

Louis de-Broglie argued that the wave character is also associated with all particles in motion and the wavelength of wave associated with them is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \qquad \text{...(1.35)}$$

where m is the mass and v is the velocity of moving particle respectively.

The eqn. (1.35) is called **de-Broglie wave** equation and λ is known as **de-Broglie wavelength.**

1.10.1. de-Broglie Wavelength of Accelerated Charged Particle

Consider a charged particle, whose charge is q and it is accelerated under a potential difference of V volts, then energy acquired by this charge is qV. This energy must be equal to the kinetic energy of charge, when initially it was at rest.

Thus
$$qV = \frac{1}{2}mv^2,$$

where m is the mass and v is velocity of accelerated charge.

$$\therefore \qquad v = \sqrt{\frac{2qV}{m}}$$

Hence, the momentum of accelerated charge is given by

$$p = mv$$

or

$$p = m\sqrt{\frac{2qV}{m}} = \sqrt{2mqV}$$

de-Broglie wavelength of accelerated charge, $\lambda = \dfrac{h}{p}$

or

$$\lambda = \frac{h}{\sqrt{2mqV}} \qquad \qquad \text{...(1.47)}$$

For electrons : $\quad m = 9.1 \times 10^{-31}$ kg

$$q = 1.6 \times 10^{-19} \text{ C}$$

$$h = 6.62 \times 10^{-34} \text{ Js}$$

So, $\qquad \lambda = \dfrac{12.27 \times 10^{-10} \text{ m}}{\sqrt{V}}$

or $\qquad \lambda = \dfrac{12.27 \text{ Å}}{\sqrt{V}} \qquad \qquad \text{...(1.48)}$

When a material particle is in thermal equilibrium at temperature T, then they have Maxwellian distribution of velocities and the kinetic energy of each particle,

$$E = kT \qquad \qquad \text{....(1.49)}$$

where k is Boltzmann's constant having value equal to 1.38×10^{-23} J/k.

So, using eqn. (1.46), de-Broglie wavelength of a material particle at temperature T is

$$\lambda = \frac{h}{\sqrt{2mkT}} \qquad \qquad \text{...(1.50)}$$

1.10.2. Experimental Verification of Wave-Particle Dualism

Davisson and Germer in 1927 and G.P. Thomson in 1928 confirmed the wave properties of matter experimentally.

1. Davisson and Germer's Experiment : In 1927, two American Physicists Davisson and Germer first of all predicted electron waves experimentally proposed by de-Broglie.

Hence, a wave packet is a type of wave motion in which the amplitude of the wave is very large in a small region and negligibly small in the rest of the space. The span of a wave packet is finite. The velocity of the wave packet when determined, comes out to be equal to the velocity of material particle. The probability of finding the particle is maximum where amplitude of the wave packet is the largest.

1.13. GROUP VELOCITY

Group velocity is the velocity, with which a wave packet i.e., a group of waves moves. It is also defined as the velocity with which the centre of mass of slowing varying envelope (representing the wave packet) moves in a medium. The significance of group velocity is that this is the velocity with which energy contained in the wave packet is transmitted.

Expression for Group Veloctiy : Consider a group of waves consisting only two components of equal amplitude and having frequencies ω_1 and ω_2 differing by a small amount. Let these waves be represented by wave function of amplitude a i.e.,

$$\psi_1 = a \cos(\omega_1 t - k_1 x) \qquad \qquad ...(1.59)$$

$$\psi_2 = a \cos(\omega_2 t - k_2 x) \qquad \qquad ...(1.60)$$

where $k_1 = \dfrac{2\pi}{\lambda_1}$ and $k_2 = \dfrac{2\pi}{\lambda_2}$ are wave vectors or propagation constants of two superimposing waves. Here $\dfrac{\omega_1}{k_1}$ and $\dfrac{\omega_2}{k_2}$ represent their respective phase (wave) velocities. Let us assume that $\dfrac{\omega_1}{k_1} \neq \dfrac{\omega_2}{k_2}$ i.e., it is a dispersive medium. The resultant wave function, due to superposition of the two waves, can be written as

$$\psi = \psi_1 + \psi_2 \qquad \qquad ...(1.61)$$

or $$\psi = a\left[\cos(\omega_1 t - k_1 x) + \cos(\omega_2 t - k_2 x)\right]$$

or $$\psi = 2a \cos\left[\left(\frac{\omega_1 + \omega_2}{2}\right)t - \left(\frac{k_1 + k_2}{2}\right)x\right] \cos\left[\left(\frac{\omega_1 - \omega_2}{2}\right)t - \left(\frac{k_1 - k_2}{2}\right)x\right]$$

$$\left[\because \cos A + \cos B = 2\cos\frac{A+B}{2}\cos\frac{A-B}{2}\right]$$

or $$\psi = 2a \cos(\omega t - kx)\cos\left(\frac{\Delta\omega t}{2} - \frac{\Delta k t}{2}\right)$$

where $\qquad \omega = \dfrac{\omega_1 + \omega_2}{2}, \ k = \dfrac{k_1 + k_2}{2}, \ \Delta\omega = \omega_1 - \omega_2$ and $\Delta k = k_1 - k_2$

or $\qquad \psi = 2a \cos\left[\dfrac{\Delta\omega}{2} t - \dfrac{\Delta k}{2} x\right] \cos(\omega t - kx)$ $\qquad$ ...(1.62)

The graphical representation of eqn. (1.62) is shown in fig. 1.15 (a).
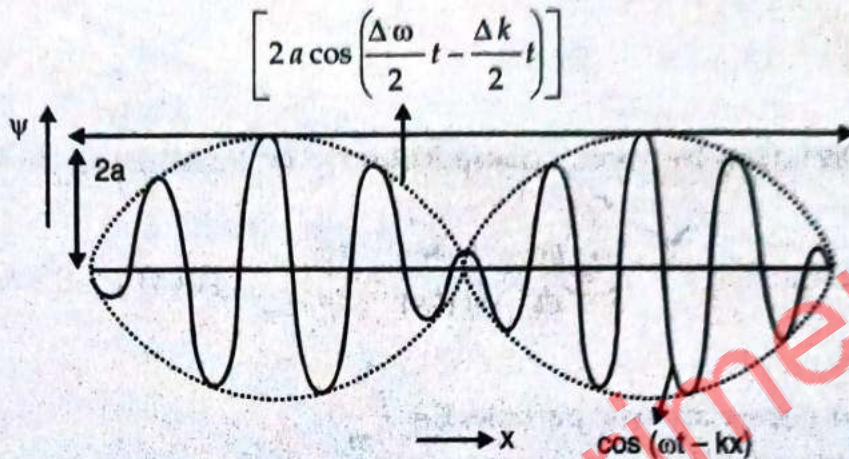

Fig. 1.15 (a) : A modulated wave of angular frequency ω and wave vector k

The phase and group velocity can be expressed from eqn. (1.62) as follows :

(a) A wave of frequency ω, wave vector k has a velocity relation as

$$v_p = \frac{\omega}{k} = \frac{2\pi v}{\dfrac{2\pi}{\lambda}} = v\lambda$$

This is the **phase velocity** or **wave velocity**.

(b) A second wave of frequency $\dfrac{\Delta\omega}{2}$, propagation constant $\dfrac{\Delta k}{2}$ and group velocity $v_g = \dfrac{\Delta\omega}{\Delta k}$.

It consists of a group of waves of first type and is a very slowly varying (moving) envelop of propagation constant $\dfrac{\Delta k}{2}$ and frequency $\dfrac{\Delta\omega}{2}$. This envelope is represented by the dotted curve in fig. 1.15(a). The velocity v_g is called **group velocity** or **the velocity of wave group**. If Δω and Δk are very small then

$$v_g = \frac{d\omega}{dk} = \underset{k \to 0}{\text{Lim}}\left(\frac{\Delta\omega}{\Delta k}\right) \qquad ...(1.63)$$

1.13.1. Relation between Group Velocity (v_g) and Particle Velocity (v)

We know that $\quad v_g = \dfrac{d\omega}{dk} = \dfrac{d(\hbar\omega)}{d(\hbar k)} = \dfrac{dE}{dp}$ ...(1.65) $[\because E = \hbar\omega \text{ and } p = \hbar k]$

(i) For non-relativistic particle, $E = \dfrac{p^2}{2m}$

$\therefore \qquad v_g = \dfrac{dE}{dp} = \dfrac{2p}{2m} = \dfrac{p}{m} = \dfrac{mv}{m} = v$ (1.66)

i.e., group velocity of wave packet is equal to the velocity of the particle itself in non-relativistic case.

1.13.2. Relation between Phase Velocity (v_p) and Group Velocity (v_g) for Non-Relativistic Free Particle

For non-relativistic free particle, $E = \dfrac{p^2}{2m}$.

From eqn. (1.68), we have $v_p = \dfrac{\omega}{k} = \dfrac{E}{p} = \dfrac{p^2}{2m \cdot p}$

or $$v_p = \dfrac{p}{2m} = \dfrac{mv}{2m} = \dfrac{v}{2}$$

But $$v_g = v \qquad \text{[From eqn. (1.66)]}$$

$\therefore$ $$v_p = \dfrac{v_g}{2} \qquad \qquad ...(1.70)$$

i.e., phase velocity is half of the group velocity for a non-relativistic free particle.

Now, $$v_p = \dfrac{\omega}{k}$$

$\therefore$ $$\omega = v_p.k$$

But $$v_g = \dfrac{d\omega}{dk} = \dfrac{d}{dk}(v_p k)$$

or
$$v_g = v_p + k \frac{dv_p}{dk}$$
...(1.71)

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

$$\Rightarrow \quad \frac{dk}{d\lambda} = -\frac{2\pi}{\lambda^2} = -\frac{1}{\lambda} \cdot \frac{2\pi}{\lambda} = -\frac{k}{\lambda}$$

or
$$\frac{k}{dk} = -\frac{\lambda}{d\lambda}$$

Putting this in eqn. (1.71), we get

$$v_g = v_p - \lambda \left(\frac{dv_p}{d\lambda} \right)$$
...(1.72)

Eqn. (1.72) gives the relationship between group velocity and phase velocity. In case of non-dispersive medium, v_p does not depend on k and therefore $\frac{dv_p}{dk} = 0$ and $v_g = v_p$.

1.15. HEISENBERG'S UNCERTAINTY PRINCIPLE

According to classical mechanics, a moving particle occupies a definite position in space and it has a definite momentum. Both its position as well as momentum can be measured simultaneously and accurately or we can say that the motion of a classical particle is described by a sharply defined trajectory.

But Heisenberg pointed out that when a moving particle is represented as a wave packet, then there is a fundamental limit to the accuracy with which the particle properties can be measured. The position of the particle is uncertain within the size of the wave packet because the particle can be present anywhere within the wave packet. Also, the wave packet has a velocity spread. Hence, the velocity or momentum of the wave packet is also not known with certainty. So, it is impossible to measure the position and momentum of a particle simultaneously and precisely *i.e.*, the trajectory of a quantum particle is not sharply defined.

Heisenberg uncertainty principle states that "*it is impossible to measure accurately and simultaneously both the position of a particle along a particular direction (say x-axis) and momentum of the particle in the same direction, p_x*". If Δx is uncertainty in the measurement of position along x-direction and Δp_x is uncertainty in the measurement of momentum in the same direction, then the product of these two uncertainties is of the order of $\hbar = \dfrac{h}{2\pi}$ *i.e.*,

$$\Delta x . \Delta p_x \approx \hbar \qquad \qquad ...(1.74)$$

where h is Planck's constant.

Similarly, $\qquad \qquad \Delta y . \Delta p_y \approx \hbar$ and $\Delta z . \Delta pz \approx \hbar \qquad ...(1.75)$

Thus, if value of Δx is smaller, then value of Δp_x will be more. The relations given by eqns (1.74) and (1.75) are known as position-momentum uncertainty relation.

Heisenberg's uncertainty relation is universal and is applicable to all the pairs of cannonical conjugate variables, whose product has dimensions of action (joule-sec). *e.g.*, position and momentum, energy and time, angle and angular momentum etc.

1.15.1. Energy-Time Uncertainty Relation

If ΔE is the uncertainty in the determination of energy of the system and Δt is the uncertainty in measurement of time to which this determination refers, then

$$\Delta E . \Delta t \approx \hbar \qquad \qquad ...(1.76)$$

Eqn. (1.76) is known as energy-time uncertainty relation. This eqn. shows that energy of the particle will be poorly defined if the time for which the system remains in a particular energy state is short and if the time of stay is long, then the energy will be more defined.

1.15.2. Angular Displacement and Angular Momentum Uncertainty Relation

If ΔJ is the uncertainty in the measurement of angular momentum and $\Delta\theta$ is the uncertainty in the measurement of angular displacement, then the product of these two uncertainties is of the order of $\hbar$ i.e.,

$$\Delta J . \Delta\theta \approx \hbar \qquad \qquad ...(1.77)$$

Eqn. (1.77) is known as angle-angular momentum uncertainty relation.

The exact statement of Heisenberg's uncertainty principle is *"The product of the uncertainties involved in measurement of any pair of cannonical conjugate variables like position and momentum, energy and time, angle and angular momentum etc. can never be less than that of the order of $\hbar/2$"*

i.e.,

$$\left. \begin{array}{l} \Delta x . \Delta p_x \geq \hbar/2 \\ \Delta y . \Delta p_y \geq \hbar/2 \\ \Delta z . \Delta p_z \geq \hbar/2 \end{array} \right\} \qquad \qquad ...(1.78)$$

$$\Delta E . \Delta t \geq \hbar/2 \qquad \qquad ...(1.79)$$

and

$$\Delta J . \Delta\theta \geq \hbar/2 \qquad \qquad ...(1.80)$$

1.17.1. Non-existence of Electrons in Nucleus

The radius of the nucleus of an atom is of the order of 10^{-14} m. Hence, if the electron is assumed to be confined inside the nucleus, then the uncertainty in the position of the electron should be equal to the diameter of nucleus i.e.

$$\Delta x = 2 \times 10^{-14} \text{ m}$$

According to Heisenberg's uncertainty principle,

$$\Delta x . \Delta p_x \approx \hbar$$

or

$$\Delta p_x \approx \frac{\hbar}{\Delta x} \approx \frac{h}{2\pi \Delta x}$$

$\therefore$

$$\Delta p_x = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 2 \times 10^{-14}} = 5.275 \times 10^{-21} \text{ kgms}^{-1}$$

If Δp_x is the order of uncertainty in the momentum of the electron, then its momentum must be atleast comparable to Δp_x if electron is confined inside the nucleus.

$\therefore$

$$p_x \approx \Delta p_x = 5.275 \times 10^{-21} \text{ kgms}^{-1}$$

The corresponding kinetic energy of the electron can be written as

$$E = \frac{p_x^2}{2m}, \text{ where } m \text{ is mass of electron.}$$

or $\qquad E = \dfrac{(5.275 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31}}$ J

$\qquad = \dfrac{(5.275 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19}}$ eV

$\qquad = 9.7 \times 10^7$ eV

$\therefore \qquad E = 97$ MeV

This shows that if electrons exist inside the nucleus, then their K.E. should be of the order of 97 MeV. But experimental data indicates that the energy of the electrons emitted by nuclei is not greater than 4 MeV. Thus, the electrons can not be present within the nucleus.

1.17.2. Existence of Neutrons, Protons and α-particles Inside the Nucleus

The radius of the nucleus of the atom is of the order of 10^{-14} m. Hence, if neutrons, protons and α–particles are assumed to be present inside the nucleus, then the uncertainty in the measurement of their position should be equal to the diameter of the nucleus, i.e., $\Delta x = 2 \times 10^{-14}$ m.

According to Heisenberg's uncertainty principle,

$$\Delta x . \Delta p_x \approx \hbar$$

or $\qquad \Delta p_x \approx \dfrac{h}{\Delta x} \approx \dfrac{h}{2\pi \Delta x}$

$\therefore \qquad \Delta p_x = \dfrac{6.625 \times 10^{-34}}{2 \times 3.14 \times 2 \times 10^{-14}}$

$\qquad = 5.275 \times 10^{-21}$ kgms^{-1}

If Δp_x is the order of uncertainty in the measurement of momentum, then their momentum must be atleast comparable to Δp_x, if neutrons, protons and α-particles are present inside the nucleus.

Thus, $\qquad p_x \approx \Delta p_x = 5.275 \times 10^{-21}$ kgms^{-1}

The corresponding K.E. of neutron (or proton) inside the nucleus can be given as

$$E = \dfrac{p_x^2}{2m}, \text{ where } m \text{ is the mass of proton or neutron.}$$

or $\qquad E = \dfrac{(5.275 \times 10^{-21})^2}{2 \times 1.67 \times 10^{-27}}$ J

or
$$E = 8.4 \times 10^{-15} \, J = \frac{8.4 \times 10^{-15}}{1.6 \times 10^{-19}} \, eV$$

or
$$E = 52 \, KeV$$

This energy is less than the energy carried by neutrons and protons emitted from the nucleus. Thus, neutrons and protons exist inside the nucleus.

The rest mass of α-particle is approximately four times the rest mass of proton. So, α-particle should have an energy of the order of 13 KeV. The energy of α-particles emitted from nucleus is found to be more than 13 KeV. Hence, α-particles can exist inside the nucleus.

1.18. DIFFERENCE BETWEEN CLASSICAL AND QUANTUM MECHANICS

1. Classical mechanics deals with particles/objects of macroscopic size whereas quantum mechanics deals with particles of microscopic size.

2. Classical mechanics, also known as Newtonian mechanics, has been developed on the basis of Newton's laws of motion having basic equation $(\vec{F} = m\,\vec{a})$ whereas method of approach to obtain the laws of motion in quantum mechanics is on the basis of Schrodinger's wave equation.

3. In classical mechanics, the future behaviour (*i.e.*, the position and momentum) of a particle can be completely known if its initial position and momentum as well as the forces acting on it are known, whereas in quantum mechanics there is an inherent uncertainty in the determination of initial position and momentum of a particle. It is therefore not possible to completely describe the future position and momentum of a particle without any uncertainty. In other words, in classical mechanics the trajectory of the particle is sharply defined whereas quantum mechanically the trajectory of the particle is not sharply defined.

4. Classical mechanics deals with certainties whereas quantum mechanics deals with probabilities.

5. Experiments such as the photoelectric effect, Compton effect, Raman effect cannot be explained in classical mechanics but hold good in quantum mechanics.

SOLVED NUMERICAL PROBLEMS

Example 1 : The work function of sodium metal is 2.3 eV. What is the longest wavelength of light that can cause photoelectric emission from sodium ?

Solution : Work function

$$W = h v_0 = \frac{hc}{\lambda_0} = 2.3 \text{ eV} = 2.3 \times 1.6 \times 10^{-19} \text{J}$$

or

$$\lambda_0 = \frac{hc}{W}$$

or

$$\lambda_0 = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{2.3 \times 1.6 \times 10^{-19}} \text{ m}$$

$$= 5.400 \times 10^{-7} \text{m} = 5400 \text{ Å}$$

Example 2 : The photoelectric work function of potassium is 2.0 eV. UV radiations of wavelength 3600 Å is made to fall on it. Find the maximum kinetic energy of photoelectrons in eV and also the maximum velocity of photoelectrons.

Solution : From Einstein's photoelectric equation, we know that

$$h v = W + \frac{1}{2} m v_{max}^2$$

Example 6 : Calculate the de-Broglie wavelength of neutron of energy 28.8 eV. Given, mass of neutron, $m = 1.67 \times 10^{-27}$ kg.

Solution : The de-Broglie wavelength is given as

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2mE}}$$

Here,

$$E = 28.8 \text{ eV} = 28.8 \times 1.6 \times 10^{-19} \text{ J}$$

$$\therefore \quad \lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times 28.8 \times 1.6 \times 10^{-19}}} \text{ m}$$

$$= 0.05 \text{ Å}.$$

Example 7 : Calculate the de-Broglie wavelength of α-particle accelerated through a potential difference of 2000 V. Given mass of α-particle $= 6.68 \times 10^{-27}$ kg.

Solution : The de-Broglie wavelength is given as

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

Here, $m = 6.68 \times 10^{-27}$ kg, $q = 2e = 2 \times 1.6 \times 10^{-19}$ C,

$h = 6.625 \times 10^{-34}$ Js

and   V = 2000 volts

$\therefore$ $\lambda = \dfrac{6.625 \times 10^{-34}}{\sqrt{2 \times 6.68 \times 10^{-27} \times 2 \times 1.6 \times 10^{-19} \times 2000}}$

$= \dfrac{6.625 \times 10^{-34}}{\sqrt{85.504 \times 10 \times 10^{-22}}}$

$= \dfrac{6.625}{29.24} \times 10^{-12}$ m

$= 2.3 \times 10^{-13}$ m $= 2.3 \times 10^{-3}$ Å.

Example 8 : **Calculate the wavelength of thermal neutrons at 27 °C, assuming energy of a particle at absolute temperature T is of the order of kT, where k is Boltzmann constant.**

Solution : The de-Broglie wavelength is given by

$$\lambda = \frac{h}{\sqrt{2mE}}$$

But $E = kT$ so, $\lambda = \dfrac{h}{\sqrt{2mkT}}$

$h = 6.625 \times 10^{-34}$ Js, $m = 1.67 \times 10^{-27}$ kg

$k = 1.38 \times 10^{-23}$ J/K,

$T = 27\,^{\circ}C = (27 + 273)$ K $= 300$ K

$\therefore$ $\lambda = \dfrac{6.625 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-27} \times 1.38 \times 10^{-23} \times 300}}$ m

$= \dfrac{6.625 \times 10^{-34}}{3.72 \times 10^{-24}}$ m

$= 1.78 \times 10^{-10}$ m $= 1.78$ Å.

Example 9 : The average time an electron remains in the excited state in an atom is 10^{-6} sec. If this is the uncertainty in the measurement of time, estimate the uncertainty in the measurement of energy of the transition.

Solution : Heisenberg's time-energy uncertainty relation is given as

$$\Delta E \cdot \Delta t \approx \hbar$$

Here $\Delta t = 10^{-6}$ sec, $\hbar = \dfrac{h}{2\pi} = 1.05 \times 10^{-34}$ Js

$\therefore$

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{1.05 \times 10^{-34}}{10^{-6}}$$

$$= 1.05 \times 10^{-28} \text{ J}$$

$$= \frac{1.05 \times 10^{-28}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 0.0656 \times 10^{-8} \text{ eV}.$$

Example 10 : Calculate the uncertainty in the momentum of proton which is confined to a nucleus of radius equal to 10^{-13} cm. From this result, estimate the kinetic energy of proton inside the nucleus.

Solution : From Heisenberg's uncertainty principle, we know that

$$(\Delta x)_{max} (\Delta p)_{min} = \hbar$$

Maximum uncertainty in position of proton, $(\Delta x)_{max}$ is equal to diameter of nucleus.

$\therefore$

$$(\Delta x)_{max} = 2 \times 10^{-13} \text{ cm} = 2 \times 10^{-15} \text{ m}$$

$$\hbar = 1.05 \times 10^{-34} \text{ Js}$$

Now,

$$(\Delta p)_{min} = \frac{\hbar}{(\Delta x)_{max}} = \frac{1.05 \times 10^{-34}}{2 \times 10^{-15}} \text{ kgm/s}$$

$$= 0.525 \times 10^{-19} \text{ kgm/s}$$

As momentum p of proton inside nucleus cannot be less than $(\Delta p)_{min}$.

$$\therefore \qquad p = (\Delta p)_{min} = 0.525 \times 10^{-19}\, kgm/s$$

and K.E. of proton inside nucleus, $E = \dfrac{p^2}{2m}$

Here, $m = 1.67 \times 10^{-27}\, kg$ for proton

$$\therefore \qquad E = \dfrac{(0.525 \times 10^{-19})^2}{2 \times 1.67 \times 10^{-27}}$$

$$= 0.0825 \times 10^{-11}\, J$$

$$= \dfrac{0.0825 \times 10^{-11}}{1.6 \times 10^{-19}}\, eV$$

$$= 0.0516 \times 10^8\, eV$$

Hence, $\qquad E = 5.16\, MeV.$

Example 11 : The velocity of a proton is 10^8 m/s and the fundamental error in its measurement is 0.01%. Calculate the fundamental error in the measurement of its position.

Solution : The uncertainty in velocity of proton,

$$\Delta v = \dfrac{0.01}{100} \times 10^8 = 10^4\, m/s$$

$\therefore$ The uncertainty in momentum, $\Delta p = m\, \Delta v$

where m is mass of proton $= 1.67 \times 10^{-27}\, kg$

Thus, $\qquad \Delta p = 1.67 \times 10^{-27} \times 10^4$

$$= 1.67 \times 10^{-23}\, kgm/s$$

Using Heisenberg's uncertainty principle, we have

$$\Delta x \cdot \Delta p \approx \hbar$$

So, uncertainty in position of proton, $\Delta x \approx \dfrac{\hbar}{\Delta p}$

$$\Delta x = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 1.67 \times 10^{-23}}$$

$$= 0.629 \times 10^{-11} \text{ m}$$

Example 12 : A ball of 0.1 g is thrown with a velocity 10^3 cm/sec through a circular hole of radius 10^{-4} cm. What is the uncertainty introduced in the angle of emergence ?

Solution : Given $m = 0.1 \text{ g} = 0.1 \times 10^{-3}$ kg or 10^{-4} kg

$$v = 10^3 \text{ cm/s} = 10 \text{ m/s}$$

$\therefore$ Momentum, p of ball $= mv = 10^{-4} \times 10 = 10^{-3}$ kgm/s

By Heisenberg's uncertainty principle,

$$\Delta x \cdot \Delta p \approx \hbar \implies \Delta p \approx \frac{\hbar}{\Delta x}$$

Here, $\Delta x = 2 \times 10^{-4} \text{ cm} = 2 \times 10^{-6}$ m

Thus, $$\Delta p = \frac{6.625 \times 10^{-34}}{2 \times 3.14 \times 2 \times 10^{-6}}$$

$$= 0.525 \times 10^{-28} \text{ kgm/s}$$

Hence, uncertainty in the angle of emergence

$$\Delta\theta \approx \frac{\Delta p}{p} = \frac{0.525 \times 10^{-28}}{10^{-3}}$$

$$= 0.525 \times 10^{-25} \text{ radians.}$$

2.2. POSTULATES OF QUANTUM MECHANICS

The postulates of quantum mechanics are as follows :

1. Associated with any particle moving in a conservative field of force, is a wave function, which determines everything that can be known about the system.

2. With every physical observable q, there is associated an operator Q, which when operating upon the wave function associated with a definite value of that observable will yield that value times the wave function.

3. Any operator Q associated with a physically measurable property q will be Hermitian.

4. The set of eigenfunctions of operator Q will form a complete set of linearly independent functions.

5. For a system described by a given wave function, the expectation value of any property q can be found by performing the expectation value integral with respect to the wave function.

6. The time evolution of the wave function is given by the time dependent Schrodinger equation.

2.3. WAVE FUNCTION AND ITS PHYSICAL SIGNIFICANCE

A wave function consists of both real as well as imaginary part *i.e.*, it is in general complex. Thus, it cannot be measured by means of any actual physical instrument. All possible information about the physical system is contained in the wave function. The wave function $\psi(\vec{r}, t)$ provides a complete quantum mechanical description of the behaviour of a particle of mass m with potential energy V at position $\vec{r}$ at any time t. Since the motion of the particle is connected to the propagation of an associated wave function, so these two must be associated in space. That is the particle is most likely to be found in some regions of space, where the magnitude of wave function is large and in other regions of space, where the magnitude of $\psi(\vec{r}, t)$ is small, the particle is not likely to be present. This shows that $\psi(\vec{r}, t)$ can be interpreted in terms of statistical terms. Max Born in 1926 gave a fundamental postulate that if the particle is described by a wave function $\psi(\vec{r}, t)$, then the probability of finding the particle within the volume element $dV = dx\, dy\, dz$ about point $\vec{r}$ at time t is

$$P(\vec{r}, t)\, dV = |\psi(\vec{r}, t)|^2\, dV$$

or

$$P(\vec{r}, t)\, dV = |\psi(\vec{r}, t)|^2\, dV = \psi^*(\vec{r}, t)\psi(\vec{r}, t)\, dV$$

where $\psi^*(\vec{r}, t)$ is the complex conjugate of $\psi(\vec{r}, t)$ and $P(\vec{r}, t)$ is the probability density. So, we can calculate the probability of finding the particle in the vicinity of a particular point, provided we know the wave function associated with the physical system. $|\psi(x, t)|^2$ is called the *probability per unit distance* or *probability density* (one dimension). Thus ψ itself has no physical significance but $|\psi|^2$ gives the probability of experimentally finding the particle described by ψ at point $\psi(x, y, z)$ at any time t. $|\psi|^2 = 1$ leads to strong probability for presence of the particle, but $|\psi|^2 = 0$ leads to absence of the particle.

Note : If $\psi = A + iB$, then its complex conjugate is $\psi^* = A - iB$

$\therefore$ $|\psi|^2 = \psi^* \psi = A^2 + B^2$. Hence $|\psi|^2$ is always a positive real quantity.

2.3.1. Conditions Satisfied by Wave Function

Due to the above interpretation of $|\psi|^2$ as a probability density, the solution that can be allowed for ψ from the Schrodinger equation are subjected to satisfy the following conditions :

(i) ψ must be finite everywhere. Because if it is infinite at a particular point then it will lead to an infinitely large probability of finding the particle at that point and this would violate the uncertainty principle.

(ii) ψ must be single valued at each and every point in space because if ψ has more than one value at any point, then it leads to more than one value of probability of finding the particle at that point, which is not acceptable.

(iii) Both ψ and its first order derivative must be continuous everywhere except at those points at which potential energy is infinite. This is required because in Schrodinger wave equation $\dfrac{\partial^2 \psi}{\partial x^2}$ must be finite everywhere.

(iv) ψ must be such that it describes the particle completely that is a knowledge of ψ at $t = 0$ must be enough to get its value at any time t (later).

(v) ψ must be normalisable, which means that ψ must go to zero as $x \to \pm\infty, y \to \pm\infty$ and $z \to \pm\infty$ in order that $\int |\psi|^2 \, dV$ over all space be a finite constant.

2.5. TIME INDEPENDENT OR STATIONARY STATE SCHRODINGER WAVE EQUATION

The time dependent Schrodinger equation in one dimension for a particle in a field is given as

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right] \psi \qquad \text{...(2.31)}$$

In the case, where the potential energy V is independent of time and depends only on the position and the total energy E is constant then position and time coordinates can be separated in eqn. (2.31). Thus ψ may be represented in the form

$$\psi(x, t) = \phi(x)\, u(t) \qquad \text{...(2.32)}$$

Here ϕ is a function of x alone and u is a function of t alone.

Differentiating eqn. (2.32) w.r.t. t, we get

$$\frac{\partial \psi}{\partial t} = \phi \frac{\partial u}{\partial t}$$

Differentiating eqn. (2.32) w.r.t. x, we get

$$\frac{\partial \psi}{\partial x} = u \frac{\partial \phi}{\partial x}$$

Differentiating this equation again w.r.t. x, we get

$$\frac{\partial^2 \psi}{\partial x^2} = u \frac{\partial^2 \phi}{\partial x^2}$$

From equation $i\hbar \frac{\partial \psi}{\partial t} = E \psi$, we get

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

or
$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} E \phi u \qquad \qquad ...(2.33)$$

Putting the values of ψ, $\frac{\partial \psi}{\partial t}$ and $\frac{\partial^2 \psi}{\partial x^2}$ in eqn. (2.31), we get

$$i\hbar \left(-\frac{i}{\hbar} E \phi u \right) = -\frac{\hbar^2}{2m} u \frac{\partial^2 \phi}{\partial x^2} + V u \phi$$

or
$$E\phi = -\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V \phi$$

or
$$\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + E\phi - V\phi = 0$$

or
$$\frac{\partial^2 \phi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V)\phi = 0 \qquad \qquad ...(2.34)$$

As ϕ is a function of x only in 1-D, so we can write $\frac{\partial^2 \phi}{\partial x^2} = \frac{d^2 \phi}{dx^2}$. Putting it in eqn. (2.34), we get

$$\frac{d^2 \phi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \phi = 0 \qquad \qquad ...(2.35)$$

which is **one-dimensional time independent Schrodinger wave equation.**

In 3-D, ϕ is a function of $\vec{r}$ i.e., (x, y, z) and thus, the time independent Schrodinger wave equation in three dimensions can be written as

$$\nabla^2 \phi(\vec{r}) + \frac{2m}{\hbar^2} (E - V) \phi(\vec{r}) = 0 \qquad \qquad ...(2.36)$$

where $\nabla^2 \phi(\vec{r}) = \dfrac{\partial^2 \phi}{\partial x^2} + \dfrac{\partial^2 \phi}{\partial y^2} + \dfrac{\partial^2 \phi}{\partial z^2}.$

SOLVED NUMERICAL PROBLEMS

Example 1 : The wave function of a particle confined to a box of length L is $\psi(x) = \sqrt{\dfrac{2}{L}} \sin \dfrac{\pi x}{L}$ in the region $0 < x < L$ and zero everywhere else. Calculate the probability of finding the particle in the region $0 < x < \dfrac{L}{2}$.

Solution : The probability of finding the particle in the region 0 to L/2 is given by

$$P = \int_{0}^{L/2} \psi^* \psi \, dx$$

$$= \int_{0}^{L/2} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \cdot \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_{0}^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx$$

$$= \frac{2}{L} \int_{0}^{L/2} \left(\frac{1 - \cos \dfrac{2\pi x}{L}}{2} \right) dx$$

$$= \frac{2}{L.2} \left[\int_{0}^{L/2} dx - \int_{0}^{L} \cos \frac{2\pi x}{L} \, dx \right]$$

$$= \frac{1}{L} \left[x - \frac{\sin \dfrac{2\pi x}{L}}{\dfrac{2\pi}{L}} \right]_{0}^{L/2}$$

$$= \frac{1}{L} \left(\frac{L}{2} - 0 \right)$$

$$\therefore \qquad P = \frac{1}{2}.$$

Thus the probability of finding the particle is half.

APPLICATIONS OF SCHRODINGER WAVE EQUATION

"The mathematical framework of quantum theory has passed countless successful tests and is now universally accepted as a consistent and accurate description of all atomic phenomena"

– *Erwin Schrodinger*

3.1. FREE PARTICLE IN ONE-DIMENSIONAL BOX

In quantum mechanics, a box means a region of space in which the particle experiences no force *i.e.,* the potential energy of particle is zero in this region and infinite outside this region. One dimensional box means that the particle is allowed to move only along a straight line say along x-axis.

Consider a particle of mass m confined to move in one-dimensional box of length a along x-axis under the following conditions :

(i) The walls of the box are rigid and perfectly elastic so that the particle rebounds with the same kinetic energy after making elastic collision with the wall and the total energy E of the particle remains constant.

(ii) The walls of the box are non-penetrable so that there is no probability of finding the particle outside the box.

Such a one-dimensional box is shown in fig. 3.1 and its potential energy function can be defined as

$$V(x) = \begin{cases} 0 \text{ for } 0 < x < a \text{ i.e., inside the box} \\ \infty \text{ for } x < 0 \text{ and } x > a \text{ i.e., outside the box} \end{cases} \quad ...(3.1)$$
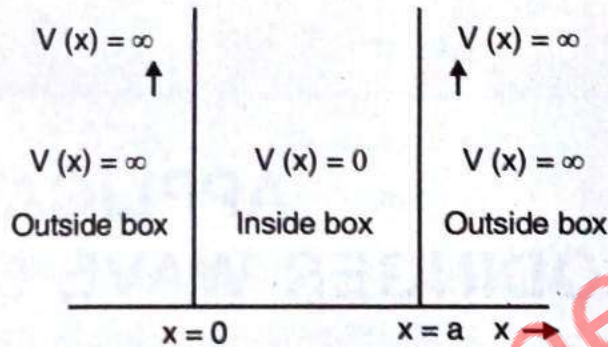

Fig. 3.1 : One dimensional box

One dimensional time independent Schrodinger equation is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0 \quad ...(3.2)$$

For $0 < x < a$ i.e., inside box, $V = 0$ and eqn. (3.2) takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad ...(3.3)$$

or

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad ...(3.4)$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad ...(3.5)$$

The general solution of eqn. (3.5) can be written as

$$\psi(x) = A e^{ikx} + Be^{-ikx} \quad ...(3.6)$$

where A and B are arbitrary constants, which are to be determined by using boundary conditions. The boundary condition on ψ is that ψ must be continuous at the point of discontinuity of potential i.e., at $x = 0$ and $x = a$.

Since the particle is confined within the box only, so the probability $|\psi(x)|^2$ of finding the particle outside the box must be zero. Thus, $\psi(x)$ must also be zero outside the box

i.e., $\qquad\qquad \psi(x) = 0 \text{ for } x \le 0 \text{ and } x \ge a \qquad ...(3.7)$

From the boundary condition at $x = 0$, i.e., $\psi(x) = 0$ at $x = 0$, we have

$$0 = A + B \qquad \text{...(3.8) [Using eqn. (3.6)]}$$

From the boundary condition at $x = a$ i.e., $\psi = 0$ at $x = a$, we have

$$Ae^{ika} + Be^{-ika} = 0 \qquad \text{...(3.8a) [Using eqn. (3.6)]}$$

From eqn. (3.8), we get $B = -A$

Putting this value in eqn. (3.8a), we get

$$Ae^{ika} - Ae^{-ika} = 0$$

or

$$2i \, A \left[\frac{e^{ika} - e^{-ika}}{2i} \right] = 0$$

or

$$2iA \sin ka = 0 \qquad \text{...(3.9)} \qquad \left[\because \frac{e^{ika} - e^{-ika}}{2i} = \sin ka \right]$$

$$\Rightarrow \qquad \text{either } A = 0 \text{ or } \sin ka = 0$$

But $A \neq 0$ because if $A = 0$, then $B = -A = 0$, hence ψ becomes zero everywhere which means the particle is not present in the box.

Hence, $\qquad \sin ka = 0$

or $\qquad \sin ka = \sin n\pi$

or $\qquad ka = n\pi$

or $\qquad k = \dfrac{n\pi}{a}$, where $n = 1, 2, 3, ...$ $\qquad$ ...(3.10)

Putting this value of k in eqn. (3.5), we get

$$\frac{n\pi}{a} = \sqrt{\frac{2mE}{\hbar^2}}$$

or

$$\frac{n^2 \pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

or

$$E = \frac{n^2 \pi^2 \hbar^2}{2m a^2} \qquad \text{...(3.11)}$$

It is clear that $n \neq 0$ because $n = 0$ gives the result $\psi = 0$ everywhere which means that particle is not present within the box. Also for $n = -1, -2, ...$, we have the same wave function as that for the corresponding positive values of n i.e., negative values of n do not yield any independent solutions.

Hence, the allowed values of n are 1, 2, 3, ... and eqn. (3.11) can be written as

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} \quad \text{with} \quad n = 1, 2, 3, ...$$ ...(3.12)

Now, the solution of eqn. (3.4) is given by

$$\psi(x) = A\, e^{ikx} - A\, e^{-ikx} \qquad \text{[Using eqn. (3.8) in eqn. (3.6)]}$$

$$= 2i\, A \left(\frac{e^{ikx} - e^{-ikx}}{2i} \right)$$

or $$\psi(x) = 2iA \sin kx$$

or $$\psi(x) = N \sin kx \qquad \qquad ...(3.13)$$

where $N = 2iA$ is another constant.

The value of N can be found by using normalisation condition on $\psi(x)$ i.e. the total probability of finding the particle inside the box is unity

i.e., $$\int_0^a \psi^*(x)\, \psi(x)\, dx = 1$$

or $$\int_0^a N^* \sin kx \cdot N \sin kx \, dx = 1 \qquad \text{[Using eqn. (3.13)]}$$

or $$|N|^2 \int_0^a \sin^2 kx \, dx = 1$$

or $$|N|^2 \int_0^a \left(\frac{1 - \cos 2kx}{2} \right) dx = 1$$

$$\frac{|N|^2}{2} \left[\int_0^a dx - \int_0^a \cos 2kx \, dx \right] = 1$$

or $$\frac{|N|^2}{2} \left[x - \frac{\sin 2kx}{2k} \right]_0^a = 1$$

or $$\frac{|N|^2}{2} \left[a - \frac{1}{2k} (\sin 2ka - \sin 0) \right] = 1$$

$$\frac{|N|^2}{2}\left[a - \frac{1}{2.\frac{n\pi}{a}}\left(\sin 2\frac{n\pi}{a}a - \sin 0\right)\right] = 1 \qquad \left[\because k = \frac{n\pi}{a}\right]$$

$$\frac{|N|^2}{2}\left[a - \frac{a}{2n\pi}(\sin 2n\pi - \sin 0)\right] = 1$$

$$\frac{|N|^2}{2}[a - 0] = 1$$

$$|N|^2 = \frac{2}{a}$$

$$N = \sqrt{\frac{2}{a}} \qquad \qquad ...(3.14)\ [\textit{Neglecting the phase factor}]$$

Hence, eqn. (3.13) becomes

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \qquad \qquad ...(3.15)$$

Eqn. (3.15) represents the normalised wave function for the particle inside the box.

Let us consider the eigen functions and the corresponding probability density for various values of n.

For $n = 1$, $\qquad \psi_1(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi}{a}x\right)$

and $\qquad |\psi_1(x)|^2 = \frac{2}{a}\sin^2\left(\frac{\pi x}{a}\right)$.

For $n = 2$, $\qquad \psi_2(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{2\pi x}{a}\right)$

and $\qquad |\psi_2(x)|^2 = \frac{2}{a}\sin^2\left(\frac{2\pi x}{a}\right)$

For $n = 3$, $\qquad \psi_3(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{3\pi x}{a}\right)$

and $\qquad |\psi_3(x)|^2 = \frac{2}{a}\sin^2\left(\frac{3\pi x}{a}\right)$
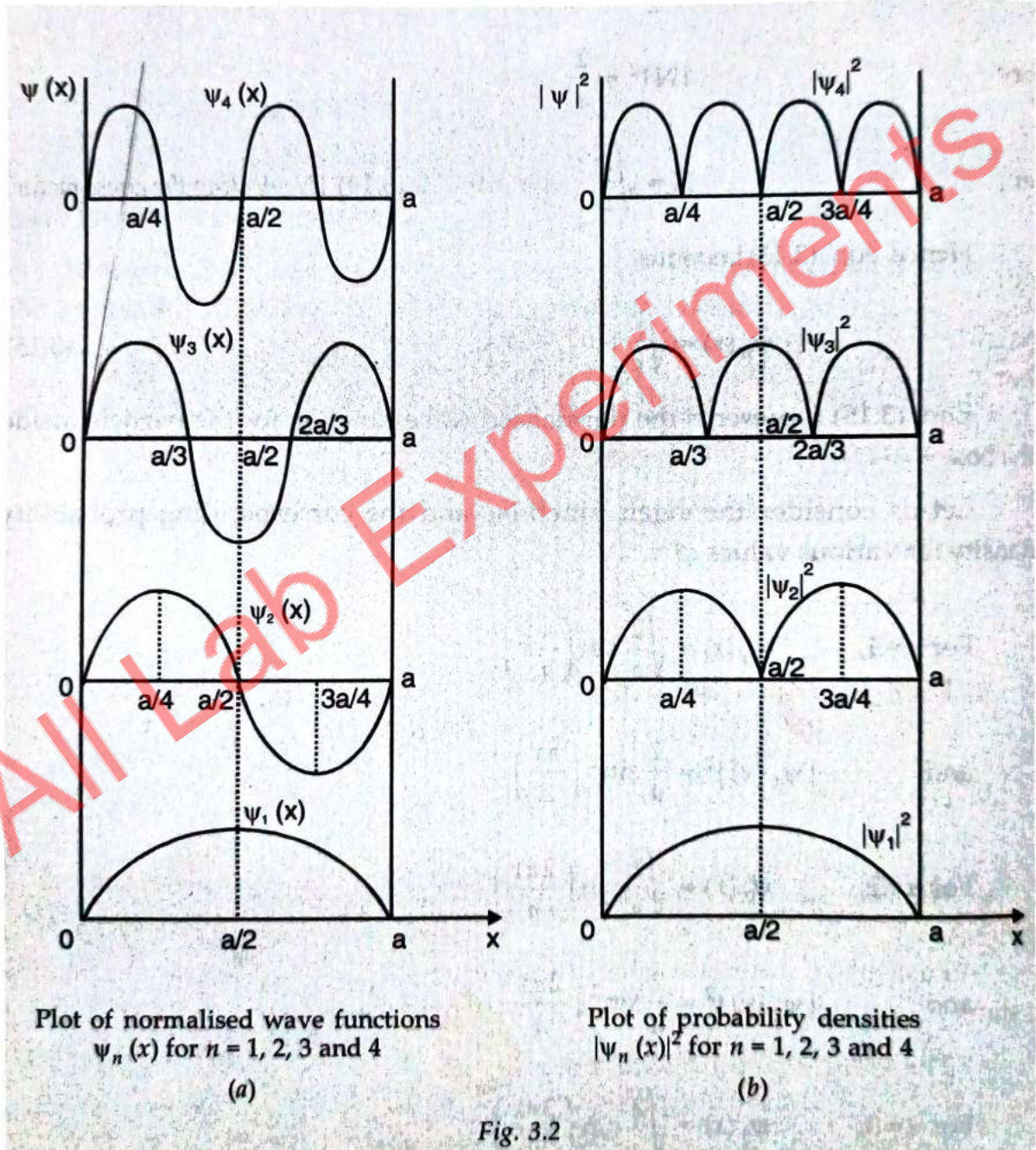
For $n = 4$, $\psi_4(x) = \sqrt{\dfrac{2}{a}} \sin\left(\dfrac{4\pi x}{a}\right)$

and $|\psi_4(x)|^2 = \dfrac{2}{a}\sin^2\left(\dfrac{4\pi x}{a}\right)$ and so on.

First four normalised eigen functions and their corresponding probability densities are plotted in fig. (3.2a) and fig. (3.2b) respectively.

Plot of normalised wave functions
$\psi_n(x)$ for $n = 1, 2, 3$ and 4
(a)

Plot of probability densities
$|\psi_n(x)|^2$ for $n = 1, 2, 3$ and 4
(b)

Fig. 3.2

It is clear from fig. 3.2(a) that there is only one-half wave for the lowest energy state *i.e.*, $n = 1$ and in the successive higher energy states, an additional half wave is present as the energy is increased by one step.

Example 1 : Calculate the first three energy levels of an electron confined in a box 1 Å wide. Given mass of electron = 9.1×10^{-31} kg and $h = 6.624 \times 10^{-34}$ Js.

Solution : For a particle in one-dimensional box we know that

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

Here $m = 9.1 \times 10^{-31}$ kg, $a = 1$ Å or $a = 10^{-10}$ m

On putting $n = 1$, the above equation becomes

$$E_1 = \frac{\pi^2 \hbar^2}{2ma^2}$$

or

$$E_1 = \frac{(3.14)^2 \times (6.624 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31} \times (10^{-10})^2 \times 4\pi^2}$$

or

$$E_1 = \frac{6.624 \times 6.624 \times 10^{-17}}{8 \times 9.1}$$

$$= 0.6027 \times 10^{-17} \text{ J}$$

$$= \frac{0.6027 \times 10^{-17}}{1.6 \times 10^{-19}} \text{ eV}$$

or

$$E_1 = 0.3768 \times 10^2 \text{ eV} = 37.68 \text{ eV}$$

For $n = 2$,

$$E_2 = \frac{4 \times \pi^2 \hbar^2}{2ma^2}$$

$$= 4 \times 37.68 \text{ eV} = 150.72 \text{ eV}$$

For $n = 3$,

$$E_3 = 9 \times \frac{\pi^2 \hbar^2}{2ma^2}$$

$$= 9 \times 37.68 \text{ eV} = 339.12 \text{ eV}$$

Example 2 : Find the values of momentum for first three levels for an electron in a one-dimensional box of length 0.5 Å.

Solution : We know for a particle in one-dimensional box,

$$p_n = \frac{n\pi\hbar}{a} = \frac{n\pi.h}{a.2\pi}$$

or

$$p_n = \frac{nh}{2a}$$

Here $a = 0.5$ Å $= 0.5 \times 10^{-10}$ m

For $n = 1$,

$$p_1 = \frac{h}{2a} = \frac{6.63 \times 10^{-34}}{2 \times 0.5 \times 10^{-10}}$$

$$= 6.63 \times 10^{-24} \text{ kgms}^{-1}$$

For $n = 2$,

$$p_2 = \frac{2h}{2a} = 2 \times 6.63 \times 10^{-24}$$

$$= 13.26 \times 10^{-24} \text{ kgms}^{-1}$$

For $n = 3$,

$$p_3 = \frac{3h}{2a} = 3 \times 6.63 \times 10^{-24}$$

$$= 19.89 \times 10^{-24} \text{ kgms}^{-1}.$$

Example 3 : Find the temperature at which the average energy of the molecules of a perfect gas would be equal to the lowest energy of electron in 1-D box of side 0.5 Å.

Given that $h = 6.63 \times 10^{-34}$ Js, mass of electron $m = 9.1 \times 10^{-31}$ kg, **Boltzmann constant** $k = 1.38 \times 10^{-23}$ JK^{-1}.

Solution : The average kinetic energy of molecule of perfect gas at temperature T is given by

$$E = \frac{3}{2}kT$$

The energy eigen values of a particle in 1-D box of length a is given by

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

For lowest energy, $n = 1$

So, $$E_{lowest} = \frac{\pi^2\hbar^2}{2ma^2} = \frac{\pi^2 h^2}{2ma^2(4\pi^2)}$$

or $$E_{lowest} = \frac{h^2}{8ma^2}$$

According to given condition,

$$\frac{3}{2}kT = \frac{h^2}{8ma^2} \qquad \text{...(i)}$$

Here $k = 1.38 \times 10^{-23}$ J K^{-1}, $m = 9.1 \times 10^{-31}$ kg,

$a = 0.5 \times 10^{-10}$ m, $h = 6.63 \times 10^{-34}$ Js

Putting all these values in eqn. (i), we get

$$\frac{3}{2} \times 1.38 \times 10^{-23} \times T = \frac{(6.63 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.5 \times 10^{-10})^2}$$

$$\frac{3}{2} \times 1.38 \times 10^{-23} \times T = 2.4152 \times 10^{-17}$$

or $$T = \frac{2 \times 2.4152 \times 10^{-17}}{3 \times 1.38 \times 10^{-23}}$$

$$= 11.67 \times 10^5 \text{ K}.$$

Example 4 : Can you observe the energy state for a ball of mass 10 g moving in a box of length 10 cm ?

Solution : We know that the energy eigen values of a particle in 1-D box is given as

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Here, $m = 10$ g $= 10 \times 10^{-3} = 10^{-2}$ kg

$a = 10$ cm $= 10 \times 10^{-2}$ m $= 10^{-1}$ m

So,
$$E_n = \frac{n^2 \pi^2 h^2}{2 \times 10^{-2} \times (10^{-1})^2 \times (4\pi^2)}$$

$$= \frac{n^2 h^2}{8 \times 10^{-4}}$$

$$= \frac{n^2 \times (6.63 \times 10^{-34})^2}{8 \times 10^{-4}} \text{ J}$$

In terms of eV,
$$E_n = \frac{n^2 \times (6.63 \times 6.63 \times 10^{-68})}{8 \times 10^{-4} \times 1.6 \times 10^{-19}} \text{ eV}$$

or
$$E_n = 3.43 \times n^2 \times 10^{-45} \text{ eV}$$

For $n = 1$, $E_1 = 3.43 \times 10^{-45}$ eV

For $n = 2$, $E_2 = 13.72 \times 10^{-45}$ eV

For $n = 3$, $E_3 = 30.87 \times 10^{-45}$ eV

For $n = 4$, $E_4 = 54.88 \times 10^{-45}$ eV and so on.

These energy levels are so close to each other that they cannot be observed separately and a continuum will be observed.