UNIT-IV "Quantum Mechanics"

4.1 BOHR'S MODEL OF ATOM

Bohr, in 1913, suggested a model of atom for which he was awarded Nobel Prize in Physics. Rutherford's experiment on α-particle led Bohr to the conclusion that the atom consists of a positively charged nucleus at its centre.

4.1.1 BOHR'S POSTULATES

In order to account for the stability of the atom and the line spectra of hydrogen atom, he gave the following postulates:

❖ The atom consists of a central nucleus having a net positive charge.

❖ The electrons revolve round the nucleus in circular orbits. The coulomb's attractive force on these negatively charged revolving electrons provides the necessary centripetal force.

❖ An electron cannot revolve round the nucleus in any arbitrary orbit but only those orbits are possible in which the angular momentum of an electron is equal to an integral multiple of $\dfrac{h}{2\pi}$ where 'h' is **Planks' constant**. These orbits are called **stationary orbits** and an electron revolving in these orbits does not radiate energy. This postulate is called **Bohr's Quantization.**

❖ The radiation of energy only takes place when an electron jumps from one stationary orbit to the other. The frequency of radiation is given by

$$h\nu = E_1 - E_2$$

$$\text{or} \qquad \nu = \frac{E_1 - E_2}{h} \qquad\qquad \text{---(i)}$$

where E_1 is the energy in the first orbit and E_2 that in the second orbit. The Eq. (i) is called **Bohr's frequency condition**.

4.1.2 BOHR'S THEORY OF HYDROGEN ATOM

Consider an atom the nucleus of which has a positive charge *Ze*, *Z* being the atomic number and '*e*' the charge on a proton. Let an electron of charge '*e*' move around the nucleus with velocity '*v*' in an orbit of radius '*r*'.

The force of attraction between the nucleus and the electron is

$$F = \frac{kZe \cdot e}{r^2} = \frac{kZe^2}{r^2} \qquad\qquad \text{--- (ii)}$$

where k is a constant, the value of which in S.I. units is $\frac{1}{4\pi\varepsilon_o} = 9 \times 10^9 \, Nm^2C^{-2}$.

As the electrons move along a circular orbit, the centripetal force provided by the attractive force on the electron is

$$F_c = \frac{mv^2}{r} \qquad\qquad \text{--- (iii)}$$

Now according to second postulate,

$$F = F_c \qquad \Rightarrow \frac{kZe^2}{r^2} = \frac{mv^2}{r} \qquad \text{or} \qquad mv^2r = kZe^2 \quad \text{--- (iv)}$$

Radius of Bohr's Orbit

According to Bohr's quantization rule, angular momentum,

$$mvr = \frac{nh}{2\pi}$$

$$\text{or} \qquad m^2v^2r^2 = \frac{n^2h^2}{4\pi^2} \qquad\qquad \text{--- (v)}$$

Dividing (v) by (iv), we get

$$\frac{m^2v^2r^2}{mv^2r} = \frac{nh^2}{4\pi^2} \cdot \frac{1}{kZe^2} \qquad \Rightarrow r = \frac{n^2h^2}{4\pi^2mkZe^2} \quad \text{--- (vi)}$$

Thus the radius of the orbits varies as the square of *n*, known as the principal quantum number.

Note: *Radius of Bohr's n^{th} orbit, $r_n \propto n^2$.*

Bohr's Radius

For hydrogen atom, $Z = 1$. The radius of first orbit of hydrogen atom is called **Bohr's radius**. Therefore, setting $n = 1$ and $Z = 1$ in Eq. (vi) along with the values of other constants, we have

Bohr's radius, $a_0 = 5.29 \times 10^{-11}$ m ≈ 0.53 Å

Velocity of electron

$$\text{As } mvr = \frac{nh}{2\pi} \qquad \Rightarrow \qquad v = \frac{nh}{2\pi mr} \qquad \text{--- (vii)}$$

Substituting the value of 'r' from Eq. (vi) in Eq. (vii), we get

$$v = \frac{nh}{2\pi m\left(\dfrac{n^2h^2}{4\pi^2 mkZe^2}\right)} = \frac{2\pi kZe^2}{nh}$$

Putting the values of n, h, Z, e etc. we have

$$v = 2.18 \times 10^6 \ ms^{-1}$$

Total Energy of the electron

The energy of an electron in any orbit is the sum of its kinetic and potential energies.

$$\text{Now} \quad K.E. = \frac{1}{2}mv^2 = \frac{kZe^2}{2r} \qquad \text{[from Eq. (iv)]}$$

The potential energy is given by the work done in bringing the electron of charge '$-e$' from distance 'r' from the nucleus of charge 'Ze' to infinity which is given by

$$P.E. = -\int_{r}^{\infty} \frac{kZe \cdot e}{r^2}dr = -\frac{kZe^2}{r}$$

Hence the total energy, $E = K.E. + P.E. = \dfrac{kZe^2}{2r} - \dfrac{kZe^2}{r} = -\dfrac{kZe^2}{2r}$ --- (viii)

Substituting the value of 'r' from Eq. (vi) in Eq. (viii), we have

$$E_n = -\frac{2\pi^2 k^2 Z^2 me^4}{n^2 h^2} \qquad \text{--- (ix)}$$

It represents the energy of the nth orbit. Here 'n' may have values 1, 2, 3, 4 etc.

For hydrogen atom, $Z = 1$ and substituting $k = \dfrac{1}{4\pi\varepsilon_o}$, we have

$$E_n = -2n^2\left(\frac{1}{4\pi\varepsilon_o}\right)^2 \cdot \frac{(1)^2 me^4}{n^2 h^2} = -\frac{me^4}{8\varepsilon_o^2 n^2 h^2} \qquad \text{--- (x)}$$

Putting for $m = 9.1 \times 10^{-31}$ kg; $e = 1.6 \times 10^{-19}$ C;

$\varepsilon_o = 8.854 \times 10^{-12}$ C²N⁻¹m⁻²; h = 6.6 ×10⁻³⁴ Js, we get

$$E_n = -\frac{13.6}{n^2} \text{ eV} \qquad\qquad (1 \text{ eV} = 1.6 \times 10^{-19} \text{ J})$$

Thus total energy of the electron in an orbit varies inversely as the square on 'n'.

Note: *Total energy increases as the electron reaches in higher orbits, but kinetic energy decreases.*

Energy Quantisation

Since 'n' can have values 1, 2, 3, 4, ..., the electron in hydrogen atom can have only the following values of the energy:

For $n = 1$, $E_1 = -\dfrac{me^4}{8\varepsilon_o^2 h^2}$

For $n = 2$, $E_2 = \dfrac{1}{4} \cdot \left(-\dfrac{me^4}{8\varepsilon_o^2 h^2} \right) = \dfrac{1}{4} E_1$

For $n = 3$, $E_3 = \dfrac{1}{9} \cdot \left(-\dfrac{me^4}{8\varepsilon_o^2 h^2} \right) = \dfrac{1}{9} E_1$

$-\quad -\quad -\quad -\qquad\quad -$

$-\quad -\quad -\quad -\qquad\quad -$

For $n = \infty$, $E_\infty = 0$

Thus an electron can have only some definite value of energy. It is called the **Energy Quantisation.**

Note: *In free state (out of atom), electron can have any energy (continuous state) and is said to be **localized**.*

Electron Transition

If E_1 and E_2 are energies of the electron in initial stationary orbit of principal quantum number n_1 and final stationary orbit of quantum number n_2, then

$$E_1 = -\frac{me^4}{8\varepsilon_o^2 h^2 n_1^2} \qquad\qquad \text{and } E_2 = -\frac{me^4}{8\varepsilon_o^2 h^2 n_2^2}$$

When an electron jumps from energy level n_2 to energy level n_1, the difference of the two energies is emitted as light of frequency 'ν' given by

$$h\,\nu = E_2 - E_1 = -\frac{me^4}{8\varepsilon_o^2 h^2 n_2^2} + \frac{me^4}{8\varepsilon_o^2 h^2 n_1^2} = \frac{me^4}{8\varepsilon_o^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or $$\nu = \frac{me^4}{8\varepsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{or } \frac{c}{\lambda} = \frac{me^4}{8\varepsilon_o^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$\Rightarrow$ $$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_o^2 ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{or } \overline{\nu} = \frac{me^4}{8\varepsilon_o^2 ch^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

or $$\overline{\nu} = R_\infty\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] \qquad \text{--- (xi)}$$

The quantity $\overline{\nu} = \dfrac{1}{\lambda}$, is called the **wave number**. The factor $R_\infty = \dfrac{me^4}{8\varepsilon_o^2 ch^3}$ is

called **Rydberg's Constant**. Its value is 1.097×10^7 m^{-1}.

For a hydrogen like atom, like ionized helium (He^4), where $Z \neq 1$, we have

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

Note: *Bohr's theory is applicable only to atoms containing one electron only e.g., He$^+$, Li^{++} etc.*

📖 *SAMPLE PROBLEMS*:

1. A hydrogen atom is excited into n = 4 state by collisions with other atoms. The atom emits one photon as it falls back to the ground state (n = 1). Calculate the wavelength of the photon.

Sol. The wavelength of photon is given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Here $\qquad\qquad R_H = 1.097 \times 10^7$ m^{-1}; $\qquad n_1 = 1$; $\qquad n_2 = 4$

$\therefore$ $$\frac{1}{\lambda} = 1.097 \times 10^{-10}\ m = 972\ \text{Å}$$

2. The energy of the hydrogen atom in the ground state is –13.6 eV. Determine the energies of those energy levels whose quantum numbers are 2 and 3.

Sol. The energy of an electron in the nth orbit of hydrogen atom is given by

$$E_n = -\frac{13.6}{n^2}\,\text{eV}$$

For $n = 2$; $E_2 = -\frac{13.6}{(2)^2}\,\text{eV}$

For $n = 3$; $E_3 = -\frac{13.6}{(3)^2}\,\text{eV}$

3. The total energy of an electron in the first exited state of hydrogen atom is –3.4 eV.

(i) What is the kinetic energy of electron in this state?

(ii) What is the potential energy of electron in this state?

Sol. The relation between potential energy E_p and kinetic energy E_k of electron in any orbit is given by

$$E_p = -2E_k$$

∴   Total energy $E_n = E_p + E_k = -2\,E_k + E_k = -E_k$

(i) Kinetic energy of electron, $E_k = -E_n = -(-3.4\text{ eV}) = $ **3.4 eV**

(ii) Potential energy of electron, $E_p = -2\,E_k = -2 \times 3.4 = $ **– 6.8 eV**

4.1.3 EFFECT OF THE FINITE NUCLEAR MASS ON BOHR'S MODEL OF AN ATOM

In the Bohr theory, we have assumed that the nucleus of the H atom is so heavy that it remains fixed at the centre of the circular orbit, while the electron revolve round it. But this will be true only when the mass of the nucleus is infinitely large as compared to that of the electron. In fact the nucleus has finite mass. The nucleus of H atom is about 1836 times as heavy as electron and hence the assumption that the nucleus is fixed is not justified. Therefore, the nucleus and the electron revolve round a common centre of mass with same angular velocity. The nucleus has an orbit of smaller radius as compared to electron orbit.

Let us consider the electron and the nucleus at a distance 'r'. The electron of mass 'm' and nucleus of mass 'M' both revolve at distances x and $(r - x)$ respectively,

about their common centre of mass '*C*' which remains fixed in space as shown in Fig. 4.1

Since the system is in equilibrium, the moment of *m* and *M* about C will be equal. Now, according to centre of mass theory,

$$M(r-x) = mx \qquad \text{--- (i)}$$

Adding $m(r-x)$ on both sides, we have

Fig.4.1

$$(M+m)(r-x) = mr$$

or $\qquad r - x = \dfrac{m}{(m+M)} r \qquad \text{--- (ii)}$ nd

and from (i) and (ii), $\qquad x = \dfrac{M}{(m+M)} r \qquad \text{--- (iii)}$

The total orbital angular momentum of the atom is the sum of the angular momentum of electron and the nucleus. Thus,

$$L = M(r-x)^2 \omega + mx^2 \omega$$

$$= M \left(\frac{m}{m+M} r \right)^2 \omega + m \left(\frac{M}{m+M} r \right)^2 \omega$$

$$= \frac{mM}{m+M} r^2 \omega = \mu r^2 \omega \qquad \text{--- (iv)}$$

where μ is the reduced mass of the electron-nucleus system and it is less than *m* by a factor $\dfrac{1}{\left(1 + \dfrac{m}{M} \right)}$.

Now from the Bohr's quantization condition, we have

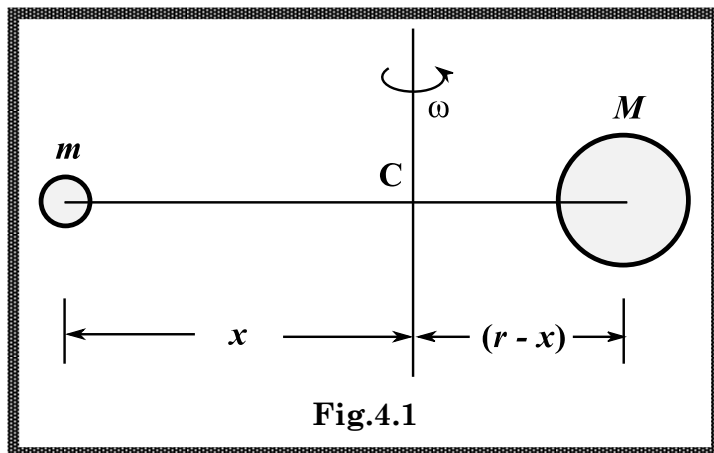$$\mu r^2 \omega = \frac{nh}{2\pi}, \qquad n = 1, 2, 3,\dots$$

$$\Rightarrow \qquad \mu v r = \frac{nh}{2\pi} \qquad\qquad\text{--- (v)}$$

Further, the energy of the electron in the nth orbit of a one electron atom is

$$E_n = \frac{\mu Z^2 e^4}{8\varepsilon_0^2 n^2 h^2} \qquad\qquad\text{--- (vi)}$$

Since μ is slightly less than m, the electron energies are slightly less negative than if the nucleus were at rest (i.e. infinitely heavy).

When an electron jumps from n_2 to n_1 state the excess energy is radiated in the form of the quantum of frequency ν given by

$$\nu = \frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or} \qquad \overline{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{\mu Z^2 e^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\text{or} \qquad \overline{\nu} = R_M Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad\qquad\text{--- (vii)}$$

Here,
$$R_M = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c} \qquad\qquad\text{--- (viii)}$$

where R_M is Rydberg constant for a finite mass nucleus.

The finite nuclear mass causes a slight variation in Rydberg constant from atom to atom. The Rydberg constant for an infinitely heavy mass is

$$R_\infty = \frac{m e^4}{8\varepsilon_0^2 h^3 c} \qquad\qquad\text{--- (ix)}$$

Dividing (viii) by (ix), we have

$$\frac{R_M}{R_\infty} = \frac{\mu}{m} = \frac{mM}{(m+M)m} = \frac{M}{(m+M)} = \frac{1}{\left(1+\dfrac{m}{M}\right)}$$

$$\text{or} \qquad R_M = \frac{R_\infty}{\left(1+\dfrac{m}{M}\right)} \qquad\qquad\text{--- (x)}$$

$$\therefore \qquad R_M < R_\infty$$

For an H atom, with infinite nuclear mass, $R_\infty = 1.09737 \times 10^7 \, \text{m}^{-1}$ and with a finite nuclear mass, $R_M = 1.09677 \times 10^7 \, \text{m}^{-1}$.

4.2 CONCEPT OF WAVE FUNCTION AND ITS PHYSICAL SIGNIFICANCE

We know that waves in water are described by the periodic variation in height of the water surface. The waves on a string are on account of change in displacement $y(x, t)$ of the string. In case of sound waves in air or a medium, it is pressure $p(x, t)$ which varies in space and time. In light waves, the fields, $\vec{E}$ and $\vec{B}$ varies. In order to characterize the de Broglie wave associated with a material particle, we require a quantity that varies in space and time. The variable quantity is called the **wave function** for the particle and is usually designated by Ψ which is function of coordinates (*x, y, z*) and time *t*. The value of the wave function associated with a moving body at the particular point *x, y, z* in space at the time *t* is related to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ.

Significance of Wave Function

The displacement of a wave can have positive or negative values. Likewise, the wave function $\Psi(x, y, z, t)$ should be related to either positive or negative probability. As probability cannot be negative, so $\Psi(x, y, z, t)$ cannot be a direct measure of the presence of the particle but it indicates the presence of the particle. As such Ψ cannot, by itself, be an observable quantity. Hence, we conclude that Ψ ***has no direct physical significance attached to it***.

Probability Interpretation of a Wave function

However, *the square of absolute value of* Ψ *i.e.* $|\Psi|^2$, *called as* **probability density**, *when evaluated at a particular place at particular time has a definite physical interpretation as* $|\Psi|^2$ *is proportional to probability of finding the body there at that time.* From uncertainty principle, for a body having a well-defined

momentum, the uncertainty in position is infinite and the wave associated with it will be of infinite extent. Hence, $|\Psi|^2$ will be small and there is a slight possibility of body's presence.

Wave function is usually a complex quantity having both real and imaginary parts. The probability density $|\Psi|^2$ for a complex Ψ is, therefore, taken as the product of $\Psi^*\Psi$ of Ψ and its ***complex conjugate*** Ψ^*. Hence $\Psi^*\Psi$ is always a positive real quantity.

The probability of finding the system in a volume element $d\tau$ is then $|\Psi|^2 d\tau$. This quantity is when integrated from $-\infty$ to ∞ must give the total probability, which is equal to unity. That is

$$\int_{-\infty}^{\infty} |\Psi|^2 d\tau = 1$$

This is referred to as ***normalization condition*** and is useful in normalizing an acceptable wave function to affirm its position probability.

Finally, Ψ must have the following characteristics:

  (i) Ψ must be continuous and single-valued everywhere.

  (ii) $\partial\Psi/\partial x$, $\partial\Psi/\partial y$ and $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.

  (iii) Ψ must be normalizable, which means that Ψ must go to 0 as $x \to \pm\infty$, $y \to \pm\infty$, $z \to \pm\infty$ in order that $\int_V |\Psi|^2 d\tau$ over all space be a finite constant.

Another important parameter is the ***probability current density*** $\vec{j}(\vec{r},t)$, which is the flow of probability across unit area in unit time. It is a vector defined as

$$\vec{j}(r,t) = \frac{i\hbar}{2m}\left(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi\right)$$

The concept of $\vec{j}(\vec{r},t)$ leads to the result that *if the probability of finding a particle in some region increases with time, the probability of finding it outside this region decreases by the same amount.*

4.3 DERIVATION OF TIME DEPENDENT SCHRÖDINGER WAVE EQUATION

Erwin Schrodinger, in 1926, formulated the wave equation governing the propagation of matter waves associated with moving systems using de Broglie concept. This equation is called as **Schrodinger wave equation** which plays the same role in *Quantum Mechanics* as *Newton's second law* does in *Classical Mechanics*.

4.3.1 WAVE EQUATION IN ONE DIMENSION FOR A FREE PARTICLE

A subatomic particle such as electron, proton, neutron etc. can be represented by a *wave packet* formed due to the superposition of a number of harmonic waves having varied wavelength λ. A wave packet of a free particle moving along the positive X-direction with a definite momentum having wave number $k = \dfrac{2\pi}{\lambda}$ and angular frequency ω moving can be described by

$$\psi(x, t) = Ae^{i(kx - \omega t)} \qquad\qquad \text{--- (i)}$$

where *A* is the wave amplitude.

According to *de Broglie hypothesis*

$$p = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar k \qquad \Rightarrow k = \frac{p}{\hbar} \qquad\qquad \text{--- (ii)}$$

Also, the kinetic energy of the free particle of mass *m* is

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = h\nu = \hbar\omega \Rightarrow \omega = \frac{E}{\hbar} \qquad\qquad \text{--- (iii)}$$

Using these values in Eq. (i), we get

$$\psi(x, t) = Ae^{\frac{i}{\hbar}(px - Et)} \qquad\qquad \text{--- (iv)}$$

Differentiating Eq. (iv) w.r.t. *x*, we get

$$\frac{\partial \Psi}{\partial x} = \left(\frac{ip}{\hbar} \right) A \exp\left[\frac{i}{\hbar}(px - Et) \right] = \frac{ip}{\hbar} \Psi \qquad\qquad \text{--- (v)}$$

Again differentiating w.r.t. x, we have

$$\frac{\partial^2 \Psi}{\partial x^2} = \left(\frac{ip}{\hbar}\right)^2 \Psi = -\frac{p^2}{\hbar} \Psi \qquad \text{--- (vi)}$$

Multiplying both sides by $-\frac{\hbar^2}{2m}$, we have

$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \Psi}{\partial x^2} = \frac{p^2}{2m} \Psi \qquad \text{--- (vii)}$$

Now, differentiating Eq. (iv) w.r.t. t, we get

$$i\hbar \frac{\partial \Psi}{\partial t} = E\Psi \qquad \text{--- (viii)}$$

For a classical particle,

$$E = \frac{p^2}{2m} \qquad \text{--- (ix)}$$

Hence from Eqns. (vii), (viii) and (ix), we have

$$-\frac{\hbar^2}{2m} \cdot \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t} \qquad \text{--- (x)}$$

Eq. (x) represents a *one-dimensional time-dependent Schrodinger equation for a free particle.*

In three dimensions, the wave equation is represented as

$$\psi(x, t) = Ae^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

And the Schrodinger Eq. (viii) becomes

$$-\frac{\hbar^2}{2m} \cdot \nabla^2 \Psi = i\hbar \frac{\partial \Psi}{\partial t} \qquad \text{--- (xi)}$$

where $$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad \text{--- (xii)}$$

is the *Laplacian operator.*

Energy and Momentum Operators

Eqns. (v) and (viii) can be written as

$$\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi = p\Psi \quad \text{and} \quad \left(i\hbar\frac{\partial}{\partial t}\right)\Psi = E\Psi$$

This suggests that the energy E and the momentum p can be considered as differential operators i.e.

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad \text{and} \quad p \rightarrow -i\hbar\frac{\partial}{\partial x} \qquad \text{--- (xiii)}$$

In three dimensions, we have

$$E \rightarrow i\hbar\frac{\partial}{\partial t} \quad \text{and} \quad \vec{p} \rightarrow -i\hbar\vec{\nabla} \qquad \text{--- (xiv)}$$

Particle under the influence of a force field

When a particle moves under the influence of a force $F(r)$ along arbitrary direction, the potential energy $V(r)$ is a function of r only and is independent of time i.e., the force field is a *conservative field*. The total energy E of the particle in a potential $V(r)$ is given by

$$E = \frac{p^2}{2m} + V(r, t) \qquad \text{--- (xv)}$$

Substituting for operators of E, $\vec{p}$ and $V(r)$ in Eq. (xv) and allowing the resulting operator equation to operate on the wave function $\Psi(\vec{r}, t)$, we get

$$i\hbar\frac{\partial\Psi}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(r, t) \qquad \text{--- (xvi)}$$

4.4 DERIVATION OF TIME INDEPENDENT SCHRÖDINGER WAVE EQUATIONS

In a number of situations, the potential energy of a particle is independent of time i.e., the forces that act on it, and hence V vary with the position of the particle only. In such cases, we can separate the variables in Eq. (xvi) and obtain two equations, one depending on the variable t and other on the variable $\vec{r}$.

4.4.1 WAVE EQUATION IN THREE DIMENSIONS FOR A PARTICLE MOVING UNDER THE INFLUENCE OF A FORCE

If the potential V does not explicitly depend on time, then the total energy E is constant. The wave function $\Psi(\vec{r}, t)$ can be expressed as the product of *time-independent part* $\psi(r)$ and *time-dependent part* $\phi(t)$, i.e.,

$$\Psi(\vec{r}, t) = \psi(\vec{r})\,\phi(t) \qquad\qquad \text{--- (xvii)}$$

Substituting Eq. (xvii) in Eq. (xvi), we get

$$\psi(\vec{r}) \cdot i\hbar \frac{d\phi(t)}{dt} = \phi(t)\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{r})$$

Dividing both sides by $\psi(\vec{r})\phi(t)$, we get

$$\frac{i\hbar}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\psi(\vec{r})}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{r}) \qquad\qquad \text{--- (xviii)}$$

The L.H.S. of Eq. (xviii) is a function of t only, while the R.H.S. is a function of $\vec{r}$ only. This is possible only if both sides are equal to a constant, say E. Equating each side to E, we get

$$i\hbar\frac{d\phi(t)}{dt} = E\phi(t) \qquad\qquad \text{--- (xix)}$$

and

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(\vec{r}) = E\psi(\vec{r}) \qquad\qquad \text{--- (xx)}$$

Eq. (xx) is the ***Time Independent Schrodinger Equation*** in three dimensions for a particle moving under a potential field which is independent of time.

Characteristics of Schrodinger Equation

1. The time-dependent Schrodinger equation contains *first order time derivative* and *second order space derivative* of Ψ terms linearly. Consequently, not only harmonic waves but also a linear combination of these, are the solutions of Schrodinger equation. For example, if $\psi_1(x, t)$ and $\psi_2(x, t)$ are two harmonic functions, then the superposition of the wave functions, $\psi(x, t) = \psi_1(x, t) + \psi_2(x, t)$ is also a solution of the Schrodinger equation.

2. The solution of Schrodinger equation is a complex function representing matter wave but the solution $y(x, t)$ of classical equation $\dfrac{\partial^2 y(x, t)}{\partial x^2} = \dfrac{1}{c^2} \cdot \dfrac{\partial^2 y(x, t)}{\partial t^2}$ is

always real. This differentiates Schrodinger equation from the classical wave equation.

3. The operator $-\dfrac{\hbar^2}{2m}\nabla^2 + V(r)$ is called **Hamiltonian operator,** denoted by $H(\vec{r})$, and is independent of time. It is also called as *total energy operator*.

4.5 EXPECTATION VALUE

The expectation value of a dynamical quantity is defined as the average of the results of a large number of measurements on an independent system represented by identical wave functions or single measurements on each of a large number of identical systems.

1. **Expectation value of position (*x*)**

    Suppose we are to determine the positions of an N number of particles with each of them described by the same wave function $\psi(x, t)$. Let the position of each particle between positions *x* and *x* + *dx* at time *t* be measured. Then the probability that a particle will have position between *x* and *x* + *dx* is

    $$P = \frac{Number\ of\ particles\ having\ positions\ between\ x\ and\ x + dx}{N} \quad \text{--- (i)}$$

    But the probability *P* having position between *x* and *x* + *dx* is

    $$P = \psi^*(x, t)\psi(x, t)\,dx \qquad \text{--- (ii)}$$

    where $\psi(x, t)$ is assumed to be normalized.

    $\therefore$ Number of particles having positions between *x* and *x* + *dx* is

    $$N\psi^*(x, t)\psi(x, t)\,dx$$

If there are N_1 particles distributed at x_1, N_2 particles at x_2, and so on over all space, then

$$N_1 x_1 + N_2 x_2 + \ldots\ldots\ldots N_n x_n = \int_{-\infty}^{\infty} x N \psi^*(x, t)\psi(x, t)\,dx \qquad \text{--- (iii)}$$

where $N = \sum\limits_{i=1}^{n} N_i$ is the total number of particles.

or $\qquad \dfrac{N_1 x_1 + N_2 x_2 + \ldots\ldots N_n x_n}{N} = \displaystyle\int\limits_{-\infty}^{\infty} x\, \psi^*(x, t)\psi(x, t)\, dx$ --- (iv)

But $\dfrac{N_1 x_1 + N_2 x_2 + \ldots\ldots N_n x_n}{N} = \langle x \rangle =$ the expectation value of position of the particle.

$$\therefore \quad \langle x \rangle = \int\limits_{-\infty}^{\infty} \psi^*(x, t) x\, \psi(x, t)\, dx = \int\limits_{-\infty}^{\infty} \psi^*(x, t)\hat{x}\, \psi(x, t)\, dx \qquad \text{--- (v)}$$

because $\hat{x} = x =$ position operator.

2. Expectation value of momentum (*p*)

If p_x be the *x*-component of momentum of a particle, then the expectation value of p_x is

$$\langle p_x \rangle = \int\limits_{-\infty}^{+\infty} \psi^*(x, t)\hat{p}_x\, \psi(x, t)\, dx \qquad \text{--- (vi)}$$

where $\hat{p}_x$ is the operator corresponding to p_x, where

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

$$\therefore \quad \langle p_x \rangle = \int\limits_{-\infty}^{+\infty} \psi^*(x, t)(-i\hbar)\frac{\partial}{\partial x}\psi(x, t)\, dx = -i\hbar \int\limits_{-\infty}^{+\infty} \psi^*(x, t)\frac{\partial}{\partial x}\psi(x, t)\, dx \quad \text{--- (vii)}$$

3. Expectation value of PE *V(x)*

$$\langle V \rangle = \int\limits_{-\infty}^{+\infty} \psi^*(x, t)V(x)\, \psi(x, t)\, dx \qquad \text{--- (viii)}$$

4. Expectation value of KE (*K*)

$$\langle K \rangle = \int\limits_{-\infty}^{+\infty} \psi^*(x, t)\hat{K}\, \psi(x, t)\, dx \qquad \text{--- (ix)}$$

But $\quad \hat{K} = \dfrac{(\hat{p}_x)^2}{2m} = \dfrac{1}{2m}\left(-i\hbar\dfrac{\partial}{\partial x}\right)^2 = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$. Therefore, from Eq. (ix)

$$\langle K \rangle = \int\limits_{-\infty}^{+\infty} \psi^*(x, t)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\psi(x, t)\, dx \qquad \text{--- (x)}$$

or $\quad \langle K \rangle = -\dfrac{\hbar^2}{2m}\displaystyle\int\limits_{-\infty}^{+\infty} \psi^*(x, t)\frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x}\right) dx = -\dfrac{\hbar^2}{2m}\left[\left\{\psi^*\frac{\partial \psi}{\partial x}\right\}_{-\infty}^{+\infty} - \int\limits_{-\infty}^{+\infty}\frac{\partial \psi^*}{\partial x}\cdot\frac{\partial \psi}{\partial x}\, dx\right]$

On account of the normalization condition, $\int\limits_{-\infty}^{+\infty}\psi^*\psi\,dx = 1$, ψ^* is zero both at $x = +\infty$

and $x = -\infty$. So, $\left\{\psi^*\dfrac{\partial\psi}{\partial x}\right\}_{-\infty}^{+\infty} = 0$.

$$\therefore \qquad \langle K \rangle = \frac{\hbar^2}{2m}\int\limits_{-\infty}^{+\infty}\frac{\partial\psi^*}{\partial x}\cdot\frac{\partial\psi}{\partial x}\,dx = \frac{\hbar^2}{2m}\int\limits_{-\infty}^{+\infty}\left|\frac{\partial\psi}{\partial x}\right|dx \qquad\qquad \text{--- (xi)}$$

This leads to the conclusion that the physical quantities corresponding to the expectation values are always real quantities and leads to real eigenvalues of the associated quantum mechanical operator.

5. Expectation value of energy for an eigenstate $\psi_n(\vec{r}, t)$

We have, $\langle E \rangle = \int\limits_{V}\psi_n^*(\vec{r}, t)\,\hat{E}\,\psi_n(\vec{r}, t)\,d\tau = \int\limits_{V}\psi_n^*(\vec{r})\,e^{\frac{iE_n t}{\hbar}}\left(i\hbar\frac{\partial}{\partial t}\right)\psi_n(\vec{r})\,e^{-\frac{iE_n t}{\hbar}}\,d\tau$

$$\left\{\because\ \hat{E} = i\hbar\frac{\partial}{\partial t}\ and\ \psi_n(\vec{r}, t) = \psi_n(r)e^{-\frac{iE_n t}{\hbar}}\right\}$$

$$= i\hbar\int\limits_{V}\psi_n^*(\vec{r})\,e^{\frac{iE_n t}{\hbar}}\,(-iE_n/\hbar)\,\psi_n(\vec{r})\,e^{-\frac{iE_n t}{\hbar}}\,d\tau$$

$$= E_n\int\limits_{V}\psi_n^*(\vec{r})\,\psi_n(\vec{r})\,d\tau \qquad\qquad\qquad \text{--- (xii)}$$

But $\quad\int\limits_{V}\psi_n^*(\vec{r})\,\psi_n(\vec{r})\,d\tau = 1 \qquad\qquad \left\{\because \psi_n(\vec{r})\ is\ normalized\right\}$

$\therefore \quad \langle E \rangle = E_n$

i.e. the energy of nth E_n is real and is constant in time as in case of a stationary state.

📖
👆 ***SAMPLE PROBLEMS:***

1. Show that the expectation value of $\langle p_x \rangle$ is real.

    Sol. We have, $\qquad\qquad \langle p_x \rangle = \int\limits_{-\infty}^{+\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,dx = -i\hbar\int\limits_{-\infty}^{+\infty}\psi^*\frac{\partial\psi}{\partial x}\,dx$

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

where we have added the second term and subtracted the same term in the first term.

or
$$\langle p_{x}\rangle = -i\hbar \int\limits_{-\infty}^{+\infty}\frac{\partial}{\partial x}\left(\psi^{*}\psi \right)dx + \int\limits_{-\infty}^{+\infty}\psi\left(i\hbar \frac{\partial}{\partial x} \right)\psi^{*}\,dx$$

$$= -i\hbar\left[\psi^{*}\psi \right]_{-\infty}^{+\infty} + \langle p_{x}\rangle^{*}$$

since the wave function vanishes at ∞, the first term is zero. Hence, $\langle p_{x}\rangle$ is real.

2. *Calculate the expectation value of the coordinate x corresponding to the wave function* $\psi_{n}(x) = \sqrt{\dfrac{2}{a}}\sin\dfrac{n\pi x}{a}$, $0 \le x \le a$, *n* = 1, 2, ..

Sol. $\langle x \rangle = \dfrac{2}{a}\int\limits_{0}^{a} x\sin^{2}\dfrac{n\pi x}{a}dx = \dfrac{2}{a}\int\limits_{0}^{a}\dfrac{x}{2}\left(1 - \cos\dfrac{2n\pi x}{a} \right)dx = \dfrac{1}{a}\int\limits_{0}^{a}x\,dx - \dfrac{1}{a}\int\limits_{0}^{a}x\cos\dfrac{2n\pi x}{a}dx$

The second term is zero since

$$\int\limits_{0}^{a}x\cos\dfrac{2n\pi x}{a}dx = \dfrac{a}{2n\pi}\left[x\sin\dfrac{2n\pi x}{a} \right]_{0}^{a} - \dfrac{a}{2n\pi}\int\limits_{0}^{a}\sin\dfrac{2n\pi x}{a}dx$$

$$= 0 + \left(\dfrac{a}{2n\pi} \right)^{2}\left[\cos\dfrac{2n\pi x}{a} \right]_{0}^{a} = 0$$

Thus, $\langle x \rangle = \dfrac{1}{a}\cdot\dfrac{a^{2}}{2} = \dfrac{a}{2}$

3. Show that the expectation value of the linear momentum for the above wave function is zero.

Sol. We have, $\langle p_{x}\rangle = \int\limits_{-\infty}^{+\infty}\psi^{*}\hat{p}_{x}\psi\,dx = \int\limits_{-\infty}^{+\infty}\psi^{*}\left(-i\hbar\dfrac{\partial}{\partial x} \right)\psi\,dx$

$$= -i\hbar\left(\dfrac{2}{a} \right)\int\limits_{0}^{a}\sin\dfrac{\pi x}{a}\dfrac{\partial}{\partial x}\left\{ \sin\dfrac{\pi x}{a} \right\}dx = -i\hbar\left(\dfrac{1}{a} \right)\dfrac{\pi}{a}\int\limits_{0}^{a}2\sin\dfrac{\pi x}{a}\cos\dfrac{\pi x}{a}dx$$

$$= -i\hbar\dfrac{\pi}{a^{2}}\int\limits_{0}^{a}\sin\dfrac{2\pi x}{a}dx = \dfrac{\pi\hbar}{ia^{2}}\dfrac{a}{2\pi}\left[-\cos\dfrac{2\pi x}{a} \right]_{0}^{a} = 0 \qquad \text{Hence Proved.}$$

Compiled By: Dr. Pankaj Biswas (Asst. Prof. School of Physics SMVDU) (M): 9419113597

The above result can be anticipated from the fact that momentum eigenvalues for trapped particle is

$$p_n = \pm\sqrt{2mE_n} = \pm\frac{n\pi\hbar}{a} \qquad\qquad \{\because E = p^2/2m\}$$

The $\pm$ sign is on account of the fact that the trapped particle moves back and forth, and so its average momentum for any value of n is

$$p_{av} = \frac{(+n\pi\hbar/a) + (-n\pi\hbar/a)}{2} = 0 = \langle p_x \rangle$$

4.6 OPERATORS

An operator in Quantum Mechanics is a rule or mathematical tool which transforms one function into another.

If $\hat{A}$ is an operator and $f(x)$ is a function, then operating $\hat{A}$ on $f(x)$ generates a new function $g(x)$ such that

$$\hat{A}f(x) = g(x) \qquad\qquad\qquad \text{--- (i)}$$

For example, if $f(x) = x^n$ and $\hat{A} = \dfrac{d}{dx}$, then

$$\hat{A}f(x) = \frac{d}{dx}(x^n) = nx^{n-1} = g(x)$$

Each dynamical variable (or observable) is represented by an operator.

The following table shows the list of operators:

S. No.	Name of operator	Symbol of the operator	Result of an operation on x^n
1.	Multiplication by a constant	k	kx^n
2.	Taking square root	$\sqrt{}$	$x^{n/2}$
3.	Differentiation	$\dfrac{d}{dx}$	nx^{n-1}
4.	Integration w.r.t. x	$\int x^n dx$	$\dfrac{x^{n+1}}{n+1} + C$
5.	Taking logarithm	$\log_e(\ )$	$n\log_e x$

In Quantum Mechanics, all the operators are ***linear***. A linear operator $\hat{A}$ has the following properties:

1. $\hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x)$

2. $\hat{A}[cf(x)] = c\hat{A}f(x)$, where c is an arbitrary constant.

4.6.1 SOME IMPORTANT OPERATORS IN QUANTUM MECHANICS

(a) *Cartesian Co-ordinate operator*

The operators in to Cartesian coordinates are $\hat{x}, \hat{y}, \hat{z}$ corresponding to x, y, z respectively. When these operators operate on a wave function $f(x)$, the function $f(x)$ is simply multiplied by the corresponding coordinate, e.g.,

$$\hat{x}f(x) = xf(x), \; \hat{y}f(x) = yf(x) \text{ and } \hat{z}f(x) = zf(x)$$

(b) *Linear momentum operator*

The components of linear momentum operator are represented by $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$ corresponding to x, y, z respectively. The values can be found as follows:

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \; \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \; \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \text{ and } \hat{p} = -i\hbar \vec{\nabla}$$

Thus $\hat{p}_x$ operating on ψ gives $-i\hbar(\partial\psi / \partial x)$, and so on.

(c) *Potential energy (PE) operator*

The operator corresponding to *PE* is represented by $\hat{V}$. When $\hat{V}$ operates on a function ψ, the function gets multiplied by V, i.e.,

$$\hat{V}\psi = V\psi$$

(d) *Kinetic energy (KE) operator*

The operator corresponding to *KE* is represented by $\hat{T}$. It can directly be obtained from linear momentum operator since $T = p^2/(2m)$. Thus

$$\hat{T} = \hat{p}_x^2/(2m) = \frac{1}{2m}\left(-i\hbar \frac{\partial}{\partial x}\right)^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

When $\hat{T}$ operates on a function ψ, the function gets operated upon by

$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$, i.e.,

$$\hat{T}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

(e) *Total energy operator*

The operator corresponding to total energy is represented by $\hat{H}$. Since total energy is given by

$$E = T + V = \frac{p_x^2}{2m} + V(x)$$

The corresponding operator equation will be

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{p}_x^2}{2m} + \hat{V}$$

or $\qquad\qquad \hat{H} = -\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V \qquad\qquad$ --- (i)

Eq. (i) is the *Hamiltonian operator* representing the *total energy operator*.

When $\hat{H}$ operates on a function ψ, the function gets operated upon by

$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + V$ i.e.,

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi$$

or $\qquad\qquad \dfrac{\hbar^2}{2m}\dfrac{\partial^2\psi(r)}{\partial x^2} + (E - V)\psi(r) = 0 \qquad\qquad$ --- (ii)

which gives the *time-independent Schrodinger equation* for a particle moving under the influence of force field derivable from potential ($V \neq 0$).

In three dimensions,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

(f) *Total energy operator in terms of differential w.r.t. time*

The wave function of a system is

$$\psi(x, t) = Ae^{\frac{i}{\hbar}(p_x x - Et)}$$

$$\therefore \quad \frac{\partial \psi}{\partial t} = A\left(-\frac{iE}{\hbar}\right)e^{\frac{i}{\hbar}(p_x x - Et)} = -\frac{i}{\hbar}E\psi = \frac{1}{i\hbar}E\psi$$

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

Since ψ is arbitrary, so

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

(g) Angular momentum operator

The components of angular momentum vector in Cartesian coordinates is

$$L_x = yp_x - xp_y$$

$$L_y = zp_y - yp_z$$

$$L_z = xp_y - yp_x$$

$\therefore$ the operators corresponding to the *x*-, *y*- and *z*-components of angular momentum are

$$\hat{L}_x = \hat{y}\hat{p}_x - \hat{x}\hat{p}_y = y\left(-i\hbar \frac{\partial}{\partial z}\right) - z\left(-i\hbar \frac{\partial}{\partial y}\right),$$

i.e.,
$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

Similarly,
$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$$

and
$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

4.7 EIGENVALUES AND EIGENFUNCTIONS

If an operator $\hat{A}$ operating on a wave function $f(x)$, multiples $f(x)$ by a constant a, i.e.,

$$\hat{A}f(x) = a f(x) \qquad \text{--- (i)}$$

then $f(x)$ is called an *eigenfunction* of $\hat{A}$ belonging to the *eigenvalue a*.

For example, in the equation

$$\frac{d}{dx}\left(e^{5x}\right) = 5e^{5x}$$

e^{5x} is the eigenfunction of the operator $\left(d/dx\right)$ with the eigenvalue 5.

In the equation,

$$\frac{d^2}{d\theta^2}\left(\sin 4\theta\right) = -16\left(\sin 4\theta\right)$$

$\sin 4\theta$ is an eigenfunction of the operator $\left(d^2/d\theta^2\right)$ with the eigenvalue –16.

Note: 1. *Eigenfunction means "proper" function.*

2. *If a is the eigenvalue corresponding to a given operator for a large number of f_i's, then the eigenvalue a is said to be degenerate.*

SAMPLE PROBLEMS:

3. Prove that the operators corresponding to observables in Quantum Mechanics have real expectation values.

Sol. If the wave function Ψ is an eigenfunction of the operator A corresponding to the eigenvalue α, then

$$A\Psi = \alpha\,\Psi \qquad\qquad \text{--- (i)}$$

$\therefore$ the expectation value of a normalized wave function becomes

$$\langle a \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A}\Psi \, d\tau = \int_{-\infty}^{+\infty} \Psi^* \alpha\,\Psi \, d\tau = \alpha \int_{-\infty}^{+\infty} \Psi^* \Psi \, d\tau = \alpha \quad \{\text{using (i) \& norm. condition}\}$$

4. Show that Schrodinger equation is an eigenvalue equation.

Sol. The Hamiltonian operator is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad\qquad \text{--- (i)}$$

Its eigenvalue equation corresponding to the eigenfunction $\psi(r)$ is given by

$$\left[-\frac{\hbar}{2m}\nabla^2 + V(r)\right]\psi(r) = E\,\psi(r) \qquad\qquad \text{--- (ii)}$$

which is simply the time independent Schrodinger equation. Here the eigenvalue E in Eq. (ii) is the total energy of the system.

4.8 PARTICLE IN A ONE-DIMENSIONAL BOX OF INFINITE HEIGHT

Consider the motion of a particle in a hollow rectangular box along the X-axis in non-relativistic region. We assume that

(i) the walls of the box are *rigid, hard and elastic* so that the particle will rebound in the box without any loss of K.E.

(ii) the walls of the box are *non-penetrable* so that the particle will remain confined in the box as the energy of the box is less than the potential energy outside the box as shown in Fig 4.2.

The potential $V(x)$ is given by

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & x < 0 \ and \ x > a \end{cases}$$

--- (i)

(i) Wave equation of the particle

Since inside the box the potential energy $V(x) = 0$, the particle is free, i.e., it is not acted upon by a force field. The *Schrodinger time-independent* equation for the particle is

$V(x) = \infty$ $V(x) = 0$ $V(x) =$

$x < 0$ $0 \leq x \leq a$ $x > a$

$x = 0$ $x = a$ X

Fig. 4.2

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad \text{--- (ii)}$$

E is the *total energy* of the particle and $\hbar = \dfrac{h}{2\pi}$, h being the *Planck's constant*.

$$\text{or} \qquad \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad \text{or} \quad \frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \text{--- (iii)}$$
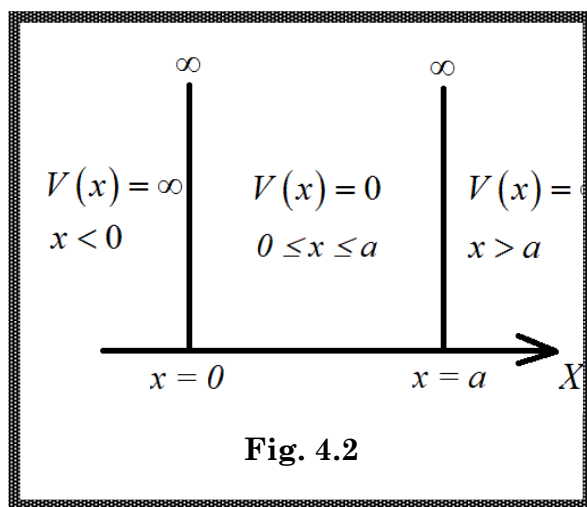
where $\qquad\qquad k = \dfrac{\sqrt{2mE}}{\hbar}$ --- (iv)

is the *propagation constant* for a particular value of energy E of the particle.

It may be noted that in the regions $x < 0$ and $x > a$, the wave function for the particle $\psi(x) = 0$ outside the box.

(i) Energy eigenvalues and eigenfunctions

The solution of the Eq. (iii) is

$$\psi = A\sin kx + B\cos kx \qquad\qquad\text{--- (v)}$$

To determine the constants, we have to use the boundary conditions viz. $\psi = 0$ at $x = 0$ and at $x = a$. The condition $\psi = 0$ at $x = 0$ leads to $B = 0$. Then from Eq. (v)

$$\psi = A\sin kx \qquad\qquad\text{--- (vi)}$$

The condition $\psi = 0$ at $x = a$ gives

$$A\sin ka = 0$$

Since $A \neq 0$ for this would make the function zero everywhere. Hence

$$\sin ka = 0 \qquad \text{or} \quad ka = n\pi, \ \ n = 1, 2, 3, \dots \qquad\text{--- (vii)}$$

The value $n = 0$ is left out since it leads to $\psi = 0$. From Eqs. (iv) and (vii), we have

$$k = \dfrac{n\pi}{a} \qquad\qquad\text{--- (viii)}$$

$$\text{or} \quad \dfrac{2mE_n}{\hbar^2} = \dfrac{n^2\pi^2}{a^2} \qquad\qquad\text{--- (ix)}$$

$$\Rightarrow \quad E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}, \qquad n = 1, 2, 3, \dots \qquad\text{--- (x)}$$

These are the energy eigenvalues for the particle in a one dimensional box. It is observed that $E_n \propto n^2$, i.e., the energy eigenvalues are discrete.

Since $\qquad\qquad \hbar = \dfrac{h}{2\pi}, \qquad \therefore E_n = \dfrac{n^2 h^2}{8ma^2}$ --- (xi)

Putting $n = 1$, in Eq. (xi), we get the lowest energy of the particle

$$E_1 = \dfrac{\pi^2\hbar^2}{2ma^2} = \dfrac{h^2}{8ma^2} \qquad\qquad\text{--- (xii)}$$

E_1 is called the *ground state energy* or **zero point energy** of the particle.

The spacing between n^{th} and $(n + 1)^{th}$ energy levels is

$$\Delta E = (n+1)^2 E_1 - n^2 E_1 = (2n+1)E_1$$

So, ΔE increases for higher values of n (Fig. 4.3).

Putting for the value of k from Eq. (viii), the wave function ψ when $0 \le x \le a$ is

$$\psi_n(x) = A \sin \frac{n\pi x}{a}, \quad n = 1, 2, 3, .. \quad \text{--- (xiii)}$$

Fig. 4.3

(ii)   Normalization of ψ(x)

Since the total probability of finding the particle in $0 \le x \le a$ is unity, we have

$$\int_0^a |\psi_n(x)|^2 \, dx = 1 \qquad \text{or} \quad \int_0^a \left| A \sin \frac{n\pi x}{a} \right|^2 dx = 1$$

or $A^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$ or $A^2 \int_0^a \frac{1}{2}\left(1 - \cos\frac{2n\pi x}{a}\right) dx = 1$

or $\frac{A^2}{2}\left[x - \frac{a}{2\pi n} \sin\frac{2n\pi x}{a} \right]_0^a = 1$

or $\frac{A^2 a}{2} = 1 \qquad \Rightarrow A = \sqrt{\frac{2}{a}}$

$\therefore$ the normalized wavefunction for the particle is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \qquad \text{--- (xiv)}$$

Eq. (xiv) shows that, $\psi_1(x) = 0$ for $x = 0$ and $x = a$.
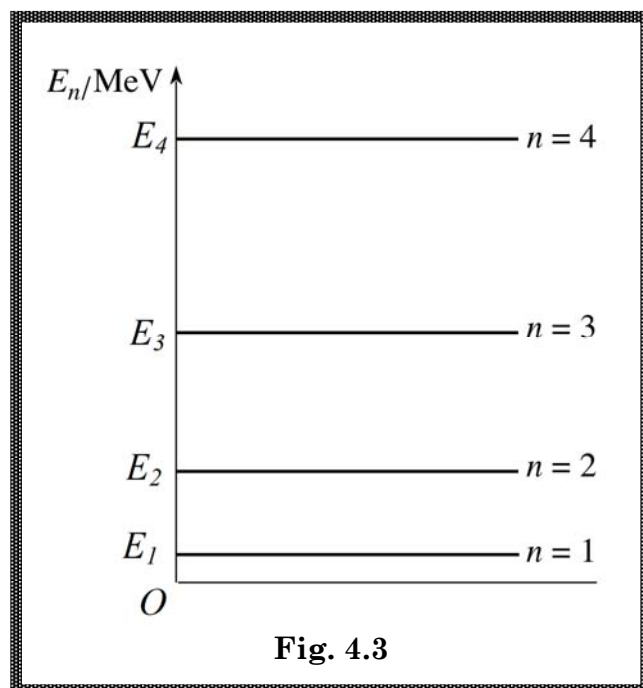
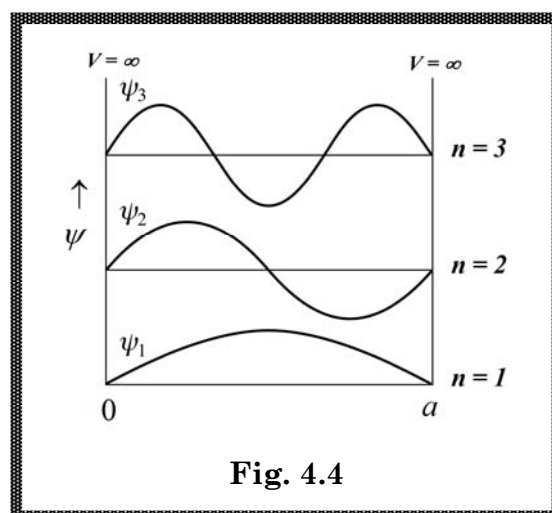So, $\psi_1(x)$ has two nodes at $x = 0$ and $x = a$.

Fig. 4.4

$\psi_2(x)$ has three nodes at $x = 0$, $x = a/2$ and $x = a$.

$\psi_3(x)$ has four nodes at $x = 0$, $x = a/3$, $x = 2a/3$ and $x = a$. These are shown in Fig. 4.4.

To generalize, $\psi_n(x)$ has $(n+1)$ nodes.

(iii) Eigen value of momentum

For the nth state, the momentum p_n is given by

$$p_n^2 = 2mE_n = 2m \times \frac{n^2\pi^2\hbar^2}{2ma^2} = \frac{n^2\pi^2\hbar^2}{a^2}$$

or $$p_n = \pm\frac{n\pi\hbar}{a} = \pm\frac{nh}{2a}$$ --- (xv)

The $\pm$ sign before $\frac{nh}{2a}$ is due to the fact that the particle moves back and forth in the box.

(iv) Probability distribution

The probability density is given by

$$P(x) = |\psi|^2 = \frac{2}{a}\sin^2\frac{n\pi x}{a}$$ --- (xvi)

$P(x)$ is maximum when

$$\frac{n\pi x}{a} = (2n+1)\frac{\pi}{2} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, ...$$

or $x = \dfrac{a}{2n}, \dfrac{3a}{2n}, \dfrac{5a}{2n}, ...$ --- (xvii)

Thus for $n = 1$ state, $P(x)$ is maximum at $x = \dfrac{a}{2}$.

$n = 2$ state, $P(x)$ is maximum at $x = \dfrac{a}{4}, \dfrac{3a}{4}$

Fig. 4.5

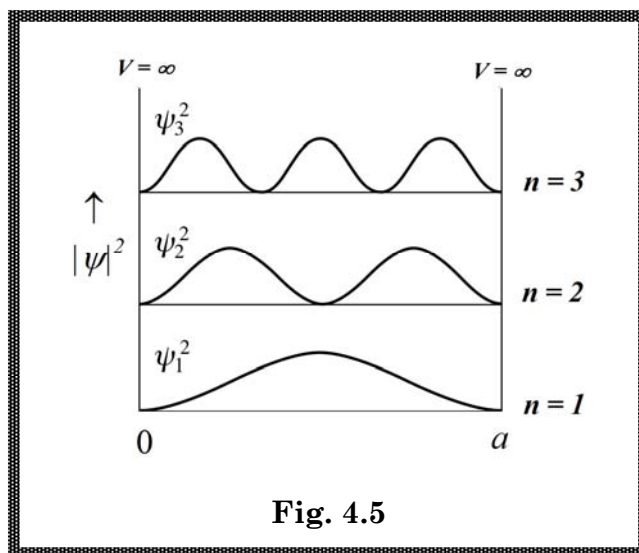$n = 3$ state, $P(x)$ is maximum at $x = \dfrac{a}{6}, \dfrac{3a}{6}, \dfrac{5a}{6}$

Fig. 4.5 shows the variation of probability density for states n = 1, 2 and 3.