4.1 ➤ SCHRÖDINGER WAVE EQUATION

In wave mechanics a material particle is equivalent to a wave-packet. To locate the position of the particle within the wave packet, Schrödinger gave an equation which we shall derive here.

(i) Time independent Schrödinger equation :

Consider a system of stationary waves to be associated with the particle. Let $\psi(\mathbf{r}, t)$ be the wave characteristic for the de-Broglie wave at any location $\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$ at time t. Then the differential equation of the wave motion in three dimensions in accordance with Maxwell's wave-equation can be written as,

i.e.,
$$\nabla^2\psi = \frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2} \quad \text{or} \quad \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2}, \qquad \text{...(1)}$$

where u is the wave velocity.

The solution of equation (1) gives ψ as a periodic displacement* in terms of time, *i.e.*,

$$\psi(\mathbf{r}, t) = \psi_0\, e^{-i\omega t} \qquad \text{...(2)}$$

where ψ_0 is the amplitude at the point considered. It is function of position $\mathbf{r}$ *i.e.*, of co-ordinates (x, y, z) and not of time t.

The equation (2) may be expressed as

$$\psi(\mathbf{r}, t) = \psi_0(\mathbf{r})\, e^{-i\omega t}. \qquad \text{...(3)}$$

Differentiating equation (3) twice with respect to t, we get

$$\frac{\partial\psi}{\partial t} = -\, i\omega\, \psi_0(\mathbf{r})\, e^{-i\omega t} \quad \text{and} \quad \frac{\partial^2\psi}{\partial t^2} = -\,\omega^2\, \psi_0(\mathbf{r})\, e^{-i\omega t}.$$

Substituting this is equation (1), we get

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\omega^2}{u^2}\,\psi. \qquad \text{...(4)}$$

$$\omega = 2\pi\nu = \frac{2\pi u}{\lambda},$$

But

$$\frac{\omega}{u} = \frac{2\pi}{\lambda}. \quad ...(5)$$

e.,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \nabla^2\psi. \quad ...(6)$$

Also

Using (5) and (6), equation (4) becomes

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0. \quad ...(7)$$

So for we have not introduced wave mechanical concept and so that treatment is general. For introducing the concept of wave mechanics, we must put for de Broglie equation

$$\lambda = \frac{h}{mv}. \quad ...(8)$$

Substituting in equation (7), we get

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0. \quad ...(9)$$

If E and V are the total and potential energies of the particle respectively, then its kinetic energy $\frac{1}{2}mv^2$ is given by

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

which gives

$$m^2v^2 = 2m\,(E - V).$$

Substituting this in equation (9), we get

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0. \quad \text{...(10)}$$

The above equation is called *Schrödinger time independent wave equation*. The quantity ψ is usually referred as *wave function*.

Let us now substitute in equation (10),

$$\hbar = \frac{h}{2\pi}. \quad \text{...(11)}$$

Then the Schrödinger time-independent wave equation, in usually used form, may be written as

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi = 0. \quad \text{...(12)}$$

This is Schrödinger's time independent wave equation.

(ii) Time-dependent Schrö

independent wave equation.

(ii) Time-dependent Schrödinger Equation : Time-dependent Schrödinger equation may be obtained by eliminating E from equation (12).

Differentiating equation (3) with respect to t, we get

$$\frac{\partial \psi}{\partial t} = -i\omega\psi_0(\mathbf{r})\,e^{-i\omega t}$$

$$= -i\,(2\pi\nu)\,\psi_0(\mathbf{r})\,e^{-i\omega t}$$

$$= -2\pi i\nu\psi(\mathbf{r}) \qquad \text{[using (3)]}$$

$$= -\frac{2\pi i E}{h}\psi \qquad \left(\text{since } E = h\nu, \text{ i.e., } \nu = \frac{E}{h}\right)$$

$$= -\frac{iE}{\hbar}\psi \times \frac{i}{i} \qquad \text{[using (11)]}$$

which gives

$$E\psi = i\hbar\frac{\partial \psi}{\partial t}. \qquad ...(13)$$

Substituting value of $E\psi$ from above equation in (12), we get

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial \psi}{\partial t} - V\psi\right] = 0$$

or

$$\nabla^2\psi = -\frac{2m}{\hbar^2}\left[i\hbar\frac{\partial \psi}{\partial t} - V\psi\right]$$

i.e.,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial \psi}{\partial t}. \qquad ...(14)$$

This equation may be written as

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial \psi}{\partial t}. \qquad ...(15)$$

This equation contains the time and hence is called ***time-dependent Schrödinger equation.***

The operator $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$ is called Hamiltonian and is represented by H; while operator $i\hbar\frac{\partial}{\partial t}$, operated on ψ, gives E which may be seen from (13). This equation (15) may be written as

$$H\psi = E\psi. \qquad ...(16)$$

The above forms of the Schrödinger's equation describe the motion of a *non-relativisitic material particle.*

Operators in quantum mechanics

- The principal mathematical difference between classical mechanics and quantum mechanics is that whereas in the former physical observables are represented by functions (such as position as a function of time), in quantum mechanics they are represented by mathematical operators.
- An operator is a symbol for an instruction to carry out some action, an operation, on a function. In most of the examples we shall meet, the action will be nothing more complicated than multiplication or differentiation. Thus, one typical operation might be multiplication by x, which is represented by the operator X x. Another operation might be differentiation with respect to x, represented by the operator d/dx.

Linear operators

The operators we shall meet in quantum mechanics are all linear. A linear operator is one for which

$$\Omega(af + bg) = a\Omega f + b\Omega g$$

where a and b are constants and f and g are functions. Multiplication is a linear operation; so is differentiation and integration.

Eigenfunctions and eigenvalues

In general, when an operator operates on a function, the outcome is another function. Differentiation of sin x, for instance, gives cos x. However, in certain cases, the outcome of an operation is the same function multiplied by a constant. Functions of this kind are called ‘eigenfunctions’ of the operator. More formally, a function f (which may be complex) is an eigenfunction of an operator Ω if it satisfies an equation of the form

$$\Omega f = \omega f$$

where ω is a constant. Such an equation is called an eigenvalue equation. The function e^{ax} is an eigenfunction of the operator d/dx because $(d/dx)\, e^{ax} = a\, e^{ax}$, which is a constant (a) multiplying the original function.

4.6 ➤ OPERATORS ASSOCIATED WITH DIFFERENT OBSERVABLES

An operator is a rule by means of which a given function is changed into another function.

The measurable quantities like energy, momentum, position etc. are called observables.

Each observable has a definite operator associated with each.

Energy operator : For example the Schrödinger equation

$$H\psi = E\psi$$

informs that the ***operator associated with the energy E is Hamiltonian H.***, *i.e.*, $E_{op} = H$.

The time independent form of E_{op} is

$$E_{op} = H = \frac{\hbar^2}{2m}\nabla^2 + V.$$

The time dependent Schrödinger equation is

$$H\psi = i\hbar\frac{\partial\psi}{\partial t} \quad i.e., \quad (H)\,\psi = \left(i\hbar\frac{\partial}{\partial t}\right)\psi$$

i.e.,time dependent value of Hamiltonian is

$$\boxed{H = i\hbar\frac{\partial}{\partial t}}$$

Thus we have

$$\boxed{E_{op} = H = -\frac{\hbar^2}{2m}\nabla^2 + V = i\hbar\frac{\partial}{\partial t}\,.} \qquad ...(1)$$

Momentum operator :

As Hamiltonian $$H = K.E. + P.E. = \frac{p^2}{2m} + V.$$

Also $$H = -\frac{\hbar}{2m}\nabla^2 + V.$$

$$\therefore \quad \frac{p^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$$

i.e., $$p^2 = -\hbar^2\nabla^2.$$

Thus the operator associated with momentum p_{op} is

$$p_{op}{}^2 = -\hbar^2\nabla^2 = \frac{\hbar^2}{i^2}\nabla^2$$

i.e., $$\boxed{p_{op} = \frac{\hbar}{i}\nabla.} \qquad ...(2)$$

If p_x, p_y, p_z are components of momentum **p**, then

$$(\hat{\mathbf{i}}\,p_x + \hat{\mathbf{j}}\,p_y + \hat{\mathbf{k}}\,p_z) = \frac{\hbar}{i}\left(\hat{\mathbf{i}}\frac{\partial}{\partial x} + \hat{\mathbf{j}}\frac{\partial}{\partial y} + \hat{\mathbf{k}}\frac{\partial}{\partial z}\right).$$

$\therefore$ Therefore operators associated with momentum components are

$$(p_x)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial x},\ (p_y)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial y},\ (p_z)_{op} = \frac{\hbar}{i}\frac{\partial}{\partial z}.$$

Kinetic energy operator : As

$$H = KE + PE = T_{op} + V_{op}.$$

Also

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V. \qquad ...(3)$$

$\therefore$ Kinetic energy,

$$T_{op} = -\frac{\hbar^2}{2m}\nabla^2. \qquad ...(4)$$

Velocity operator :

$$(KE)_{op} = \frac{1}{2}m{\upsilon_{op}}^2 = -\frac{\hbar^2}{2m}\nabla^2.$$

$\therefore$ Operator associated with velocity υ_{op} is given by

$${\upsilon_{op}}^2 = -\frac{\hbar^2}{m^2}\nabla^2 = \frac{\hbar^2}{i^2}\frac{\nabla^2}{m^2} \qquad ...(5)$$

$\therefore$

$$\upsilon_{op} = \frac{\hbar}{im}\nabla.$$

The ***operator associated with potential energy***

$$V_{op} = V. \qquad ...(6)$$

The operator associated with position $r_{op} = r$.

Accordingly the ***following table represents the operators associated with different*** ***-vables.***

Observable	Associated operator	
	symbol	operator
Energy	E_{op} or H	$-\frac{\hbar^2}{2m}\nabla^2 + V$ or $i\hbar\frac{\partial}{\partial t}$
Kinetic energy	T_{op}	$-\hbar^2\frac{\nabla^2}{2m}$
Potential energy	V_{op}	V
Momentum	$\boldsymbol{p}_{op}$	$\frac{\hbar}{i}\nabla$
	$(p_x)_{op}$	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
	$(p_y)_{op}$	$\frac{\hbar}{i}\frac{\partial}{\partial y}$
	$(p_z)_{op}$	$\frac{\hbar}{i}\frac{\partial}{\partial z}$
Velocity	$\boldsymbol{v}_{op}$	$\frac{\hbar}{im}\nabla$
	$(v_x)_{op}$	$\frac{\hbar}{im}\frac{\partial}{\partial x}$
	$(v_y)_{op}$	$\frac{\hbar}{im}\frac{\partial}{\partial y}$
	$(v_z)_{op}$	$\frac{\hbar}{im}\frac{\partial}{\partial z}$

Observable	Associated operator	
	symbol	operator
Position	r_{op}	r
	x_{op}	x
	y_{op}	y
	z_{op}	z

4.9 ➤ POSTULATES OF QUANTUM MECHANICS

The mathematical formulation of "Quantum mechanics" is based on the following postulates :

1. There is **wave-function** associated with every physical state of the system which contains the entire description.

   According to this postulate the wave function is a function of all position coordinates and time and contains the information about the properties of the system. This information may be definite or in statistical form.

2. Every physical observable is associated with an operator specially linear operator. The physical observable may be energy, momentum, velocity, position etc. The operators associated with energy and momentum are

$$\textbf{energy } \hat{E} = i\hbar\frac{\partial}{\partial t} \quad \textbf{or} \quad \textbf{Hamiltonian momentum } \hat{p} = \frac{\hbar}{i}\nabla.$$

   In terms of components $\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, $\hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$, $\hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$

3. The measurements of an observable can provide the values (λ) gives by the equation

$$\hat{p}\,\varphi = \lambda\varphi \qquad ...(1)$$

   This is called eigen value equation and the values (λ) are called the eigen values. The condition imposed an wave function φ is $\int \varphi^{\infty}\,\varphi\, d\psi < \infty$ and φ is single valued function.

   Equation (1) states that the operator P associated with observable in state φ gives eigen values (λ); leaving function unchanged.

4. This postulates gives the rule for extracting information from the wave functions. If states that the expectation value of observable f of a system in state φ is given by

$$\langle f \rangle = \frac{\int \varphi^* \hat{f}\, \varphi\, d\Psi}{\int \varphi^* \varphi\, d\Psi}$$

   where $\hat{f}$ is operator associated with observable f.

The expectation value represents the arithmetic mean over a large number of simultaneous measurements in identical states φ. In general, Quantum mechanics allows a fluctuation in these measurements, while classical mechanics assumes that every observable in principle, is absolutely determinate.

The operators $\hat{f}$ which admit only real eigen values are called **Hermitian operators.**

4.10 ➤ PARTICLE IN A BOX

(a) One Dimensional Box

Consider a particle within a one-dimensional box extending from $x = 0$ to $x = L$. The potential function is expressed as

$$\left.\begin{aligned} V &= 0 \text{ for } 0 \le x \le L \\ V &= \infty \text{ for } x < 0 \text{ and } x > L, \end{aligned}\right\} \qquad \text{...(1)}$$

Since wave function ψ has to be continuous, it follows that $\frac{\partial^2 \psi}{\partial x^2}$ must be finite everywhere. As particle is always within the box, the probability of finding the particle outside the box is zero. This implies that $\psi \to 0$ everywhere outside the box.

Inside the box, the Schrödinger equation is written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0. \qquad \text{...(2)}$$

Substituting

$$\frac{2mE}{\hbar^2} = k^2 \qquad \text{...(3)}$$

we get

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0. \qquad \text{...(4)}$$

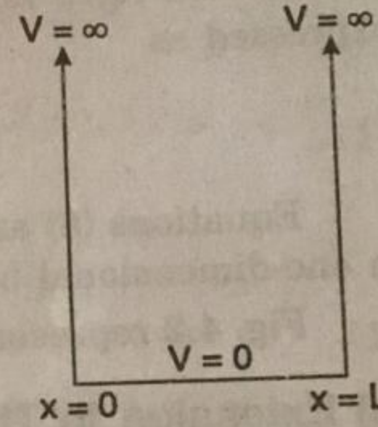

Fig. 4.1

The general solution of this equation may be expressed as

$$\psi = A \sin(kx + \phi) \qquad \text{...(5)}$$

where A and ϕ are constants to be determined by boundary conditions.

We have $\psi = 0$ at $x = L$, so that (5) gives

$$0 = A \sin \phi$$

As $A \neq 0$, $$\sin \phi = 0 \quad \text{or} \quad \phi = 0. \qquad \text{...(6)}$$

Further $\psi = 0$ at $x = L$, so that (5) gives

$$0 = A \sin (kL + 0) \qquad \text{(using } \phi = 0\text{)}$$

i.e., $$\sin kL = 0 \quad \text{or} \quad kL = n\pi$$

or $$k = \frac{n\pi}{L}. \qquad \text{...(7)}$$

In view of this equation (3) gives

$$\frac{2mE}{\hbar^2} = \left(\frac{n\pi}{L}\right)^2.$$

This gives $$E = E_n \text{ (say)} = \frac{n^2\pi^2\hbar^2}{2mL^2}. \qquad \text{...(8)}$$

For other *values of energy equation* (2) *has no solution.* Thus, we note that the energy-values of the particle in a box are quantised given by (8).

The corresponding *eigen functions* from (5), (6) and (7) are

$$\psi = \psi_n \text{ (say)} = A \sin \frac{n\pi x}{L}. \qquad \text{...(9)}$$

The *probability density* is $|\psi|^2 = \psi^*\psi = A^2 \sin^2 \frac{n\pi x}{L}$. ...(10)

Obviously the probability density is zero at $x = 0$ at $x = L$.

Since the particle is always within the box, the *normalisation condition* is

$$\int_0^L \psi^*\psi \, dx = 1 \quad \text{or} \quad \int_0^L A^2 \sin^2 \frac{n\pi x}{L} \, dx = 1$$

or $$A^2 \cdot \frac{L}{2} = 1.$$

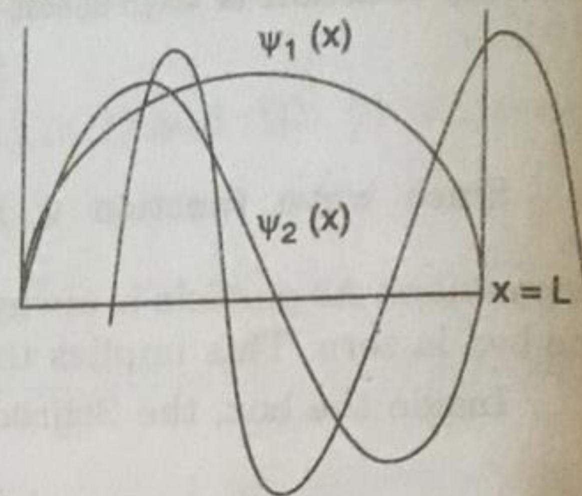

Fig. 4.2

This gives *normalisation constant*, $A = \sqrt{2/L}$. Thus the *normalised eigen function* ψ_n belonging to eigen value E_n is expressed as

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right). \quad \text{...(11)}$$

Equations (8) and (11) represent required *eigen values* and *eigen functions* for a particle in one-dimensional box.

Fig. 4.2 represents the first three normalized wave-functions $\psi(x)$ for a particle in a box.

(b) Extension to Three Dimensional Box

If, we consider the particle in three-dimensional box with edges parallel to X, Y, Z axes of length l_x, l_y, l_z, the particle can move freely within the region $0 < x < l_x$, $0 < y < l_y$, $0 < z < l_z$.

The potential function rises suddenly to large value at the walls and remains infinite outside the boundaries. The Schrödinger equation in three-dimensions for the particle inside the box $(V = 0)$ is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E\psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} E\psi = 0. \quad \text{...(12)}$$

Substituting $\psi(x, y, z) = X(x), Y(y), Z(z)$ where $X(x)$ is function of X alone, $Y(y)$ is function of y alone and Z is a function of z alone.

Separating (12) into three one-dimensional equations, we get

$$\frac{\partial^2 X}{\partial x^2} + \frac{2m}{\hbar^2} E_x X = 0 \quad \text{...(13a)}$$

$$\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2} E_y Y = 0 \quad \text{...(13b)}$$

$$\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2} E_z Z = 0 \quad \text{...(13c)}$$

with

$$E_x + E_y + E_z = E.$$

These equations are similar to one-dimensional equation already solved.

$\therefore$ The solutions of (13) are given by

$$X(x) = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi x}{l_x}$$

$$Y(y) = \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi y}{l_y}$$

$$Z(z) = \sqrt{\frac{2}{l_z}} \sin \frac{n_z \pi z}{l_z}.$$

With $E_x = \frac{n_x^2 \pi^2 \hbar^2}{2ml_x^2}$, $E_y = \frac{n_y^2 \pi^2 \hbar^2}{2ml_y^2}$, $E_z = \frac{n_z^2 \pi^2 \hbar^2}{2ml_z^2}$; n_x, n_y, n_z being integers.

The *eigen-values of particle in box are therefore*

$$E = E_x + E_y + E_z = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right]. \quad \text{...(14)}$$

The *complete wave function is* $\psi(x, y, z) = X(x), Y(y)\, Z(z)$

$$= 2\sqrt{\frac{2}{l_x l_y l_z}} \sin \frac{n_x \pi x}{l_x} \sin \frac{n_y \pi y}{l_y} \sin \frac{\pi_z \pi z}{l_z}. \quad \text{...(15)}$$

As n_x, n_y, n_z may take integral values only, the energy values of particle in a box are not continuous but discrete determined by all possible integral choices of n_x, n_y, n_z.