## 2·12. Equation of motion of Matter Waves.

**(i) Time-independent. Schroedinger equation.** The non-dissipation of the wave-packet of the material particle has been explained by assuming the necessity of the guiding wave obeying Schroedinger wave equation which we shall derive here.

Consider a system of stationary waves to be associated with the particle, Let $(x, y, z)$ be the co-ordinates of the particle and $\psi$ the wave displacement for the de Broglie waves at any time $t$. Then the differential equation of the wave motion in three dimensions can be written in classical way as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2}, \quad \ldots(1)$$

where $u$ is the wave velocity.

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

$$\psi\,(x, y, z, t)=\psi_0\,(x, y, z)\,e^{-i\omega t}, \quad \ldots(2)$$

where $\psi_0$ is the amplitude at the point considered. It is function of $(x, y, z)$, *i.e.*, the position $\mathbf{r}$ and not of time $t$, where

$$\mathbf{r}=\mathbf{i}x+\mathbf{j}y+\mathbf{k}z.$$

The equation (2) may be expressed as

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

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

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

$$=-\omega^2\psi.$$

Substituting this in equation (1), we get

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

But
$$\omega=2\pi\nu$$

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

*i.e.* $$\frac{\omega}{u}=\frac{2\pi}{\lambda}. \qquad \ldots(5)$$

Also $$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}=\nabla^2\psi, \qquad \ldots(6)$$

$\nabla^2$ being Laplacian operator.

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

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

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

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

Substituting this in equation (7), we get

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

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

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

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

Substituting this in equation (9), we get

$$\nabla^2\psi+\frac{8\pi^2m}{h^2}(E-V)\psi=0 \qquad \ldots(10)$$

The above equation is called *Schroedinger time independent wave equation*. The quantity $\psi$ is usually referred as *wave function*.

Let us now substitute in equation (10),

$$\hbar=\frac{h}{2\pi}. \qquad \ldots(11)$$

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

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

**(ii) Schroedinger equation for a free particle.** For a free particle $V=0$ ; therefore if we put $V=0$ in equation (12), it will become the *Schroedinger equation for a free particle*, *i.e.*,

$$\nabla^2\psi+\frac{2mE}{\hbar^2}\psi=0. \qquad \ldots(13)$$

**(iii) Time-dependent Schroedinger Equation.**

Time-dependent Schroedinger equation may be obtained by eliminating $E$ from equation (12).

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

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

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

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

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

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

which gives
$$E\psi = i\hbar\, \frac{\partial \psi}{\partial t}. \qquad \text{...(14)}$$

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

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

Equation (15) may be written as

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V) \right) \psi = i\hbar\, \frac{\partial \psi}{\partial t}. \qquad \text{...(16)}$$

The operator $\left( \frac{\hbar^2}{2m} \nabla^2 + V \right)$ is called Hamiltonian and is represented by $H$ ; while operator $i\hbar\partial/\partial t$ operating on $\psi$, gives $E$ which may be seen from (14). Thus equation (16) may be written as
$$H\psi = E\psi. \qquad \text{...(17)}$$

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

## Normalised & Orthogonal Wave functions:

We know that $\psi\psi^* dv$ or $[\psi^2] dv$ represents the probability of finding the particle in the volm element $dv$.

In physical problem we come across the situations where the particle is bound by forces to a limited region. For examples: the electron in a atom, the particle in a box with impenetrable walls. In such the total probability of finding the particle in the entire space is a course, unity, i.e,

$$\int |\psi(r,t)|^2 dv = 1 \quad \text{--- (1)}$$

where integration extends over all space.

Equation (1) may be written as

$$\int \psi(r,t)\,\psi^*(r,t)\, dv = 1 \quad \text{--- (2)}$$

A wave function which satisfies above equation is said to be normalized to unity.

When the particle is bound to the limited regions the probability of finding the particle at infinity distance is zero, ie $\psi\psi^*$ at $x=\infty$ is zero.

Any solution of the wave equation may be normalized by multiplying or dividing by a constant and it can readily seen that the result is also a solution of the wave-function.

If $\psi_i$ & $\psi_j$ are two different wave functions, both being satisfactory solutions of wave equation for a given system, then these functions will be normalised if

$$\int \psi_i \psi_i^* dv = 1 \quad \& \quad \int \psi_j \psi_j^* dv = 1$$

If the two wave-functions $\psi_i$ & $\psi_j$ are such that the integral $\int \psi_i^* \psi_j dv$ or $\int \psi_j^* \psi_i dv$ vanishes over entire space, i.e,

$\int \psi_i^* \psi_j \, dv = 0$ or $\int \psi_j^* \psi_i \, dv = 0$, $i \neq j$

then the wave functions are said to be mutually orthogonal.

## Stationary State Solutions:

In a particular state if the probability distribution $\psi\psi^*$ is independent of time, then the state of the system is said to be stationary state.

Let us consider the probability distribution function $\psi\psi^*$ for a system in the state represented by the wave function

$$\psi(x,y,z,t) = \sum_{n=1}^{\infty} a_n \phi_n(x,y,z) e^{-iE_nt/\hbar} \quad \text{--- (1)}$$

Its conjugate is represented by

$$\psi^*(x,y,z,t) = \sum_{m=1}^{\infty} a_m^* \phi_m^*(x,y,z) e^{iE_mt/\hbar}$$

so that $\psi\psi^* = \left[\sum_{n=1}^{\infty} a_n \phi_n(x,y,z) e^{-iE_nt/\hbar}\right]\left[\sum_{m=1}^{\infty} a_m^* \phi_m^*(x,y,z) e^{iE_mt/\hbar}\right]$

$$= \sum a_n a_n^* \phi_n(x,y,z) \phi_n^*(x,y,z) + \sum_m \sum_n{}' a_n a_m^* \phi_n(x,y,z) \phi_m^*(x,y,z) e^{i(E_m - E_n)t/\hbar}$$

where the prime on the double summation indicates that the terms with $m=n$ are excluded. Clearly time enters in the probability function $\psi\psi^*$, hence $\psi$ expressed by equation (1) is not a stationary state solution. $\psi\psi^*$ will be independent of time $t$, only if $a_n$'s are zero for all values except for one value of $E_n$. In such a case the wave-function will contain only a single term & will be represented by

$$\psi_n(x,y,z,t) = \phi_n(x,y,z) e^{-iE_nt/\hbar} \quad \text{--- (2)}$$

The solution represented by equation (2) is stationary state solution, since $\psi\psi^* = \phi_n \phi_n^*$, which is independent of time.

## 2·17. Expectation Values of Dynamical Quantities.

According to Born the wave-function $\psi$ has probabilistic interpretation, therefore it is essential to calculate the average or expectation value of any dynamical quantity defined by the wave-function. In physics such dynamical quantities are *space-co-ordinates, momenta* and *energy* of the system.

*The average or expectation value of a dynamical quantity is the mechanical expectation for the result of a single measurement.*

*Or*

*It may be defined as the average of the result af a large number of measurements on independent systems.*

The expectation value of any quantity $f(\mathbf{r})$ which depends upon position, for normalised wave-function may be written as

$$\langle f(\mathbf{r})\rangle=\int P(\mathbf{r}, t) f(\mathbf{r})\, d\tau$$

$$=\int \psi^*(\mathbf{r}, t) f(\mathbf{r}) \psi(\mathbf{r}, t)\, d\tau. \qquad \text{...(1)}$$

This is equivalent to the following three expressions :

$$\left.\begin{aligned}\langle x\rangle&=\int \psi^* x\psi\, d\tau\\ \langle y\rangle&=\int \psi^* y\psi\, d\tau\\ \langle z\rangle&=\int \psi^* z\psi\, d\tau\end{aligned}\right\} \qquad \text{...(3)}$$

where $\langle x\rangle$, $\langle y\rangle$ and $\langle z\rangle$ are the expectation values of the co-ordinates $x$, $y$ and $z$ of the particle respectively.

The expectation value of the potential energy, which is also the function of position, is written as

$$\langle V\rangle=\int V(\mathbf{r}, t) P(\mathbf{r}, t)\, d\tau$$

$$=\int \psi^*(\mathbf{r}, t) V(\mathbf{r}, t) \psi(\mathbf{r}, t)\, d\tau. \qquad \text{...(4)}$$

So far we have only considered the expectation values of the qaantities which depend upon position and no other quantities which are of dynamical interest, such as momentum and energy. The expectation value of these quantities may be found by using the corresponding differential operator.

One form of Schroedinger's equation is

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

so that the total energy can be represented by differential operator that acts on the wave-function $\psi$, *i.e.*

$$E = i\hbar \frac{\partial}{\partial t} \qquad \text{...(5)}$$

we have

total energy = kinetic energy + potential energy

*i.e.*
$$E = \frac{p^2}{2m} + V,$$

so that
$$\langle E \rangle = \langle \frac{p^2}{2m} \rangle + \langle V \rangle. \qquad \text{...(6)}$$

Also we have from eqn. (16) and (17) of section 2·2.

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

so that
$$\langle E \rangle = \langle -\frac{\hbar^2}{2m} \nabla^2 \rangle + \langle V \rangle. \qquad \text{...(7)}$$

Comparing (6) and (7), we get

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

so that
$$\mathbf{p} = \frac{\hbar}{i} \nabla = -i\hbar \nabla. \qquad \text{...(8)}$$

This eqn. suggests that the momentum can be represented by differential operator $(-i\hbar\nabla)$.

We can, now, write the expectation values of momentum and energy using the corresponding operators. The average value of energy, using eqn. (5), is written as

$$\langle E \rangle = \int \psi^* i\hbar \frac{\partial \psi}{\partial t} \, d\tau = i\hbar \int \psi^* \frac{\partial \psi}{\partial t} \, d\tau. \qquad \text{...(9)}$$

The average or expectation value of momentum, using eqn. (8) is written as

$$\langle \mathbf{p} \rangle = \int \psi^* (-i\hbar \nabla) \psi \, d\tau$$

$$= -i\hbar \int \psi^* \nabla \psi \, d\tau. \qquad \text{...(10)}$$

This equation is equivalent to three component equations given by

$$\left. \begin{aligned} \langle p_x \rangle &= -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, d\tau, \\ \langle p_y \rangle &= -i\hbar \int \psi^* \frac{\partial \psi}{\partial y} \, d\tau, \\ \text{and} \quad \langle p_z \rangle &= -i\hbar \int \psi^* \frac{\partial \psi}{\partial z} \, d\tau, \end{aligned} \right\} \qquad \text{...(11)}$$

where $\langle p_x \rangle$, $\langle p_y \rangle$, $\langle p_z \rangle$ are the expectation values of the components of the momentum along *X*, *Y* and *Z* axes respectively.

It is to noted that the *above formulae of expection values only hold if the wave-function $\psi$ is properly normalised*: otherwise we have the definition of expectation value of any quantity $f$ to be

$$\langle f \rangle = \frac{\int \psi^* f \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \ldots(12)$$

Therefore if the wave function is not normalised we have to use the definition given by eqn. (12) and the equations (1), (2), (3), (4), (9) and (11) will be modified accordingly.

*Moreover if the expectation values are to defined using operators, the integrand will consist of the operator operating on $\psi$; multiplied on the left by $\psi^*$.*