de Broglie Waves and Wavelengths:

A light quantum or photon of energy E and frequency ν has the momentum

$$p = \frac{E}{c} = \frac{h\nu}{c} \quad [\because E = h\nu] \text{------} (1)$$

where h is Planck's constant and c is the velocity of light. In terms of wavelength λ, the momentum p is given by

$$p = \frac{h\nu}{c} = \frac{h\nu}{\nu\lambda} = \frac{h}{\lambda} \quad [\because c = \nu\lambda]$$

$$\therefore \boxed{\lambda = \frac{h}{p}} \text{------------} (2)$$

The wavelength λ of light quantum can thus be specified by its momentum.

de Broglie assumed that the equation (2) is generally valid and is applicable not only for photons but for material particles as well. He proposed: A material particle will have a matter wave associated with it, just as a light quantum has a light wave. That is, for a particle of mass m moving with speed v, the wavelength λ is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad \text{- - - - - - - - - - - -} (3)$$

This is referred to as the de Broglie wavelength of a particle in motion, the relation (3) is known as de Broglie relation.

The interpretation of the equation (3) are as:

(1) de Broglie, in fact was trying to understand the significance of Bohr's quantum Condition and seeking to fit into the Bohr orbit a whole number of standing waves, in analogy with such waves in a stretched string.

(2) The equation (3) may be rewritten in the following form:

$$p = \frac{h}{2\pi} K = \hbar K \quad (\hbar = h/2\pi)$$

where $K = 2\pi/\lambda$, the propagation Constant.

(3) Equation (3) expresses both the wave nature (λ) and the particle nature (momentum p): known as wave-particle dualism.

(4) In waves some quantity varies periodically. In sound wave it is the pressure, in lightwaves

The electric and magnetic fields. What quantity Then does vary in matter waves. It is Called The wavefunction ψ. But what indeed is ψ? The value of ψ associated with a moving body at (x, y, z) in space at time t is related to The likelihood or The probability of finding it There at The time t.

The ψ function has neither any direct physical significance nor can it be interpreted in terms of any experiment. The probability for an object to be at a certain place at a given time must lie within 0 and 1. But while The amplitude of a wave could be negative, a negative probability is meaningless. So ψ Cannot be an observable property. But $|\psi|^2$, square of The absolute value of ψ function, is free from above objection and is called The probability density. A high value of $|\psi|^2$ means strong probability of presence of The object, a very low $|\psi|^2$ implies a slight probability of The presence.

Heisenberg's Uncertainty Principle:

This principle states That it is fundamentally impossible to determine simultaneously

The position and the momentum of a particle to an accuracy better than one quantum of action.

Let us try to measure the position of an object with photons of wavelength λ. So the position can be best measured to an accuracy $\sim \lambda$. Thus the uncertainty in the measurement of position is

$$\Delta x \simeq \lambda$$

Let the object be detected by a single photon of momentum $p = h/\lambda$. On striking the object the photon transfer a part or whole of its momentum to the object. Thus the final momentum of the object is uncertain by an amount

$$\Delta p \simeq \frac{h}{\lambda}$$

The product of two uncertainties gives

$$\boxed{\Delta x \, \Delta p_x \geqslant h} \quad \text{-------------} (1)$$

The more exactly one determines the position, the smaller is Δx and consequently larger is Δp_x and vice versa. It is to be noted that uncertainties are not related to any way to the apparatus employed in measurement but in nature itself.

Energy - Time Uncertainty :

The energy of a particle is given by

$$E = \frac{p_x^2}{2m} \Rightarrow \Delta E = \frac{p_x}{m} \Delta p_x = v_x \Delta p_x$$

where v_x = velocity of the particle = $\frac{p_x}{m}$

$$\therefore \Delta E = \frac{\Delta x}{\Delta t} \cdot \Delta p_x$$

$$\Rightarrow \Delta E \cdot \Delta t = \Delta p_x \Delta x \geqslant h$$

$$\therefore \boxed{\Delta E \cdot \Delta t \geqslant h} \quad \text{- - - - - - - - - - - -} \quad (2)$$

This form of uncertainty relation implies that if a system maintains a particular state for a time Δt its energy is uncertain by at least a factor $h/\Delta t$.

Angular Momentum and Angular Position :

The energy of a particle in terms of moment of inertia and angular velocity is given by

$$E = \frac{1}{2} I \omega^2$$

$$\therefore \Delta E = \frac{1}{2} 2\omega \, \Delta(I\omega) = \omega \Delta L$$

where L = angular momentum $= I\omega$

But $\phi = \omega t \Rightarrow \Delta\phi = \omega \Delta t$

$$\therefore \Delta L \cdot \Delta\phi = \frac{\Delta E}{\omega} \times \omega \Delta t = \Delta E \cdot \Delta t \geqslant h$$

$$\therefore \boxed{\Delta L \cdot \Delta\phi \geqslant h} \quad \text{-------------} (3)$$

The equations (1), (2) and (3) are derived from de Broglie ideas. A more rigorous proof shows that the product of uncertainties may be reduced to at most $\hbar/2$ but we can not minimise it further. So the uncertainty relations are

$$\Delta x \cdot \Delta p_x \geqslant \hbar/2 \quad \text{-----------} (4)$$

$$\Delta E \cdot \Delta t \geqslant \hbar/2 \quad \text{-----------} (5)$$

and $$\Delta L \cdot \Delta\phi \geqslant \hbar/2 \quad \text{-----------} (6)$$

Statement : If Δx is the uncertainty of the position of a particle and the corresponding momentum uncertainty is Δp_x Then Heisenberg's uncertainty principle states That

$$\Delta x \cdot \Delta p_x \geqslant \hbar/2$$

Where $\hbar = h/2\pi$ and h is Planck's Constant.

Time-dependent Schrödinger Equation:

The wavelength of matter wave is given by de Broglie's equation

$$\lambda = \frac{h}{p} \Rightarrow \vec{p} = \frac{h}{\lambda} = \vec{K}\hbar \text{ - - - - - (1)}$$

The energy of The particle is related to The frequency by

$$E = h\nu = \frac{h}{2\pi} \cdot 2\pi\nu = \hbar\omega \text{ - - - - - - (2)}$$

The state of a particle in motion is described by The wavefunction $\Psi(\vec{r},t)$ and to study its motion in a general way, we need an equation to be satisfied by Ψ, subject however to The relations expressed in (1) and (2).

Such an equation was provided by Erwin Schrödinger in 1926 which is basic to quantum mechanics just as Newton's equation is basic to classical mechanics.

Free Particle Wavefunction:

A free particle i.e not subjected to any force moving along x-direction with a definite momentum is given by the infinite plane wave

$$\psi(x,t) = A e^{i(K_x x - \omega t)}$$

$$\Rightarrow \psi(x,t) = A e^{\frac{i}{\hbar}(p_x x - Et)} \quad \text{-------- (3)}$$

replacing K_x by $p_x/\hbar$ and ω by $E/\hbar$

Differentiating (3) w.r.to t, we have

$$i\hbar \frac{\partial \psi}{\partial t} = E\psi(x,t) \quad \text{--------- (4)}$$

Now by successive differentiation of (3) w.r.to x

$$-i\hbar \frac{\partial \psi}{\partial x} = p_x \psi \quad \text{---------- (5)}$$

and
$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = \frac{p_x^2}{2m}\psi(x,t) \quad \text{------ (6)}$$

Classically, for a free non-relativistic one-dimensional particle $E = p_x^2/2m$. So from equations (4) and (6) we have

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2}} \quad \text{--------(7)}$$

The equation (7) is the required one-dimensional time-dependent Schrödinger equation for a free particle

In Three dimensions: $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi \cdots (8)$

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

We may rewrite equations (4) and (5) in the following form:

$$\left(i\hbar \frac{\partial}{\partial t}\right)\psi = E\psi \text{ and } \left(-i\hbar \frac{\partial}{\partial x}\right)\psi = p_x\psi$$

which suggest that the energy and the momentum may be considered as differential operators

$$\boxed{\hat{E} = i\hbar \frac{\partial}{\partial t} \text{ and } \hat{p}_x = -i\hbar \frac{\partial}{\partial x}}$$

In Three dimensions:

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \text{ and } \hat{\vec{p}} = -i\hbar\vec{\nabla}$$

General Wave Equation:

Classically, The energy E also known as Hamiltonian of a particle in a potential $V(\vec{r},t)$ is given by

$$E = \frac{p^2}{2m} + V(\vec{r},t) \text{ -------- } (9)$$

Schrödinger assumed $\hat{r}$ to be The operator for The position Coordinate r and t That for time. So The operator for The potential is $\hat{V}(\vec{r},t)$. We now substitute The operators for E and $\vec{p}$ and $V(\vec{r},t)$ in equation (9) and allow The resulting operator equation to operate on The wave function $\Psi(\vec{r},t)$

$$\therefore\ i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r},t)\right]\Psi(\vec{r},t) \text{ ---- } (10)$$

The equation (10) is The time-dependent Schrödinger equation for a particle moving in a potential $V(\vec{r},t)$.

Thus the operator for the Hamiltonian H of the system is

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{r},t)} \text{ - - - - - - - (11)}$$

Putting this $\hat{H}$ in equation (10) we get

$$i\hbar\frac{\partial \psi(\vec{r},t)}{\partial t} = \hat{H}\psi(\vec{r},t) \text{ - - - - - - - (12)}$$

This is reduced form of the time-dependent Schrödinger equation.

The more explicit form of equation (10) is

$$\frac{ih}{2\pi}\frac{\partial \psi}{\partial t} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi$$

Physical Interpretation of wavefunction ψ:

According to statistical interpretation, the quantity $\psi^*\psi = |\psi|^2$ gives the probability of finding the system or particle at $\vec{r}$ at time t, ψ^* being the complex conjugate of ψ. $|\psi|^2$ is never negative. The quantity $|\psi|^2$ is known as the probability density $\rho(\vec{r},t)$

$$\therefore P(\vec{r},t) = |\psi|^2 \quad \text{------------(13)}$$

The probability of finding the system in a volume element dV ($= dx\,dy\,dz$) is then $|\psi|^2 dV$. If then this quantity be integrated from $-\infty$ to $+\infty$ we get the total probability which is unity

$$\therefore \int_{-\infty}^{\infty} |\psi|^2 dV = 1 \quad \text{----------(14)}$$

A wavefunction ψ satisfying the equation (14) is called a normalised wavefunction and the equation (14) is the normalisation condition. If however $\psi(\vec{r},t)$ is not normalised the above equation (14) may be utilised to normalise the wavefunction. On multiplying the wavefunction by a constant N and from (14) we have

$$|N|^2 \int_{-\infty}^{\infty} |\psi|^2 dV = 1$$

$$\therefore |N|^2 = \frac{1}{\int_{-\infty}^{\infty} |\psi|^2 dV} \quad \text{--------(15)}$$

where N is the normalisation constant.

Probability Current Density : Conservation

The probabilistic interpretation of wavefunction ψ leads to another important parameter— The probability current density.

The time-dependent Schrödinger equation and its Complex Conjugate form are respectively

$$i\hbar \frac{\partial \psi}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi \text{ ------- (16)}$$

and

$$-i\hbar \frac{\partial \psi^*}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi^* \text{ ------ (17)}$$

where it is assumed That $V(\vec{r})$ is real.

Multiplying (16) by ψ^* and (17) by ψ and on subtraction we have

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

$$\Rightarrow \frac{\partial}{\partial t} (\psi^* \psi) = \frac{i\hbar}{2m} \vec{\nabla} \cdot \left(\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right)$$

$$\text{----- (18)}$$

We now define a vector

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

$$\text{----- (19)}$$

So That from (18) we have

$$\frac{\partial}{\partial t}(\psi^*\psi) + \vec{\nabla}\cdot\vec{j}(\vec{r},t) = 0 \quad \text{-------} (20)$$

or, $$\frac{\partial \rho}{\partial t} + \vec{\nabla}\cdot\vec{j}(\vec{r},t) = 0 \quad \text{---------} (21)$$

The equation (21) is known as equation of Continuity. Since $\psi^*\psi$ is The probability density ρ, $\vec{j}(\vec{r},t)$ is to be interpretated as probability current density. It is The flow of probability across unit area per unit time.

Integrating (20) over a volume and using Gauss's divergence Theorem we have

$$\frac{\partial}{\partial t}\int_V (\psi^*\psi)\, dV = -\int (\vec{\nabla}\cdot\vec{j})\, dV = -\oint \vec{j}(\vec{r},t)\cdot d\vec{s} \quad \text{----} (22)$$

From equation (22) any decrease or increase in probability within a particular region is attended with inflow or outflow of probability across its surface implying That any increase in probability with time in some region would decrease The probability of finding it outside That region by an equal amount. Thus The equation (22) expresses The Conservation of probability density and may be termed quantum mechanical probability Conservation equation.

Time-independent Schrödinger Equation:

In many situations, The system does not change with time (The steady state) and potential is a function of Co-ordinate only. We can separate The variables in time-dependent Schrödinger equation to get two equations: (1) One dependent on t and (2) The other dependent on $\vec{r}$. Then

$$\Psi(\vec{r},t) = \phi(t)\psi(\vec{r}) \quad ------(1)$$

The Schrödinger time-dependent equation is given by

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

Putting The equation (1) into (2) we get

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

$$\Rightarrow i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = \frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) \quad --(3)$$

dividing Throughout by $\phi(t)\psi(\vec{r})$

Now The L.H.S of equation (3) is a function of t only and The R.H.S is a function of Co ordinate only. So each side must be equal to a Constant

E say

$$\therefore i\hbar \frac{d\phi(t)}{dt} = E\phi(t) \text{ - - - - - - - - - } (4)$$

and $$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r}) \text{ - - - - } (5)$$

The equation (5) is called time-independent Schrödinger equation or simply Schrödinger equation. Generally it is written in the following form:

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0} \text{ - - - - - } (6)$$

In equation (4) $i\hbar\frac{d}{dt}$ is the energy operator that operates on $\phi(t)$ to give a constant E. E is the energy of the system.

Now $$\frac{d\phi(t)}{\phi(t)} = -\frac{iE}{\hbar}dt$$

Integrating

$$\ln\phi(t) = -\frac{iE}{\hbar}t$$

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

$$\therefore \text{Wave function } \Psi(\vec{r},t) = \phi(t)\psi(\vec{r})$$
$$= \psi(\vec{r})\, e^{-\frac{iE}{\hbar}t} \text{ - - - - } (7)$$

In most situations, The equation has a set of solutions so That The equation (7) is written as

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-\frac{iE_n}{\hbar}t} \quad \ldots\ldots\ldots (8)$$

If The system is in any eigenstate given by (8) The probability density is

$$\Psi_n^*(\vec{r},t)\,\Psi_n(\vec{r},t) = |\psi_n(\vec{r})|^2 \quad ------ (9)$$

and is independent of time. Such states for which The probability density is Constant in time are Called stationary states.