Wave Mechanics: Part – II

• Schrodinger Wave Equation:

The idea of associating both wave and particle character with a massive particle like electron was first proposed by de Broglie. He associated a standing wave around the circumference of nth orbit of radius r having wavelength λ so that $2.\pi.r = n.\lambda$.
But according to Bohr's quantum condition for the privileged orbits, we have

$$I\omega = n\hbar \Rightarrow mr^2.\frac{v}{r} = n\hbar \Longrightarrow mvr = n\hbar$$

$$\therefore \frac{mvr}{2\pi r} = \frac{n\hbar}{n\lambda} \Longrightarrow \frac{mv}{2\pi} = \frac{h}{2\pi\lambda} \Longrightarrow \frac{h}{\lambda} = mv \Longrightarrow \lambda = \frac{h}{mv} = \frac{h}{p}$$

Let us represent a plane wave by the complex variable quantity $\Psi(x, t)$ which is called the wave function for the particle. Hence Ψ may be represented by –

$$\psi = ae^{-i\omega\left(t-\frac{x}{v}\right)} = ae^{-i\left(\omega t-\frac{\omega x}{v}\right)} = ae^{-i(\omega t-kx)} = ae^{i(kx-\omega t)}$$

$$where, k = \frac{\omega}{v} = \frac{2\pi\vartheta}{\vartheta\lambda} = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{p}{\hbar}$$

$$\therefore \psi = ae^{i\left(\frac{p}{\hbar}x-\omega t\right)} = ae^{i\left(\frac{p}{\hbar}x-\frac{E}{\hbar}t\right)}$$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2}ae^{i\left(\frac{p}{\hbar}x-\omega t\right)} = -\frac{p^2}{\hbar^2}\psi$$

Now, total energy = E = K.E. + P.E. = $\frac{p^2}{2m} + V.\ \therefore p^2 = 2m(E-V)$

$$\therefore \frac{\partial^2\psi}{\partial x^2} = -\frac{2m}{\hbar^2}(E-V)\psi$$

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

This is called **Schrodinger one dimensional time-independent wave equation**.

For a free particle, V = 0. So the Schrodinger equation reduces to:

$$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

Again, $\omega = 2\pi\vartheta = \frac{2\pi}{h}(h\vartheta) = \frac{E}{\hbar}$. $\quad \therefore \psi = ae^{i\left(kx-\frac{E}{\hbar}t\right)}$

$$\therefore \frac{\partial\psi}{\partial t} = -i\frac{E}{\hbar}ae^{i\left(kx-\frac{E}{\hbar}t\right)} = -i\frac{E}{\hbar}\psi$$

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

Substituting this result in time independent equation, we get:

$$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

This is known as **Schrodinger one dimensional time-dependent wave equation**.

For a free particle, V = 0.

$$\therefore -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}$$

Schrodinger Equation in the form HΨ = EΨ:

One dimensional time independent Schrodinger equation is:

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

$$\Rightarrow (-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V)\psi = E\psi$$

Now, $(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V)$ is called the Hamiltonian operator H_x for the one dimensional motion (say in x- direction). So, $H_x\Psi = E\Psi$

For three dimensional motion,

$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$ → **Schrodinger 3- Dimensional time - independent wave equation**

$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t}$ → **Schrodinger 3- Dimensional time - dependent wave equation**.

HΨ = EΨ → **Schrodinger Equation in the form HΨ = EΨ**

- ## Boundary conditions of Schrodinger Equation

  - As the operator is in the non-relativistic form, the equation is valid only in the non-relativistic domain.
  - The wave function must be single valued and finite everywhere.
  - If V is finite (continuous or not), Ψ and VΨ must be continuous.
  - For a surface having infinite potential, Ψ must be zero and the component of VΨ normal to the surface is undetermined.

Normalisability:

The quantity $|\Psi|^2$ is called the probability density. Therefore $|\Psi|^2 dv$ is the probability that the particle will be found in an element of volume dv. So the total probability that the particle may be found anywhere within the entire space must be unity. So, $\int |\psi|^2 dv = 1$ *i.e.* $\int \psi\psi^* dv = 1$.

Any wave function which satisfies this condition is called **Normalized wave function** or **Normalisable wave function.**

Orthogonality:

If Ψ_m and Ψ_n are any two normalized non degenerate eigen functions having different energy eigen values E_m and E_n respectively, then the condition of orthogonality is

$$\int \psi_m{}^* \psi_n \, dv = 1; for\ m = n$$
$$\int \psi_m{}^* \psi_n \, dv = 0; for\ m \neq n$$

So, we can say that for orthonormal wave function,

$$\int \psi_m \psi_n \, dv = 1; for\ m = n$$
$$\int \psi_m \psi_n \, dv = 0; for\ m \neq n$$

- ## Probability Current Density:

The state of motion of a particle in a one-dimensional system is specified by a normalized wave function Ψ. Therefore, the probability of finding the particle at an instant t in an unit volume is

$$\rho = \psi \psi^*$$

So the probability of finding the particle in an element of volume dv is

$$\rho dv = \psi \psi^* dv$$

So the probability of finding the particle in an convenient volume is

$$\int \rho dv = \int \psi \psi^* dv$$

As the total probability density over the entire space is unity that is constant, any decrease in the volume of ρ for an element of volume must be accompanied by an equal increase in the value of ρ in some other element of volume. Therefore, we can say that the probability flows from one region to another with time. This shift or flow of probability density may be considered as equivalent to the probability current density. Thus J represents the rate of decrease of the probability of finding the particle in the convenient volume.

$$\therefore \vec{J} = -\frac{\partial}{\partial t} \int \rho dv = -\frac{\partial}{\partial t} \int \psi \psi^* dv = -\int \frac{\partial}{\partial t} (\psi \psi^*) dv = -\int (\psi \frac{\partial \psi^*}{\partial t} + \psi^* \frac{\partial \psi}{\partial t}) dv$$

Three dimensional time dependent Schrodinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = i\hbar \frac{\partial \psi}{\partial t} \text{ -------------------------------------> (1)} \times \Psi^*$$

The complex conjugate equation of this is

$$-\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^* = i\hbar\frac{\partial\psi^*}{\partial t} \text{ ---------------------------------------> (2)} \times \Psi$$

Subtracting (2) from (1),

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

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

For one dimensional motion, this equation reduces to

$$\left(\frac{\partial\rho}{\partial t}\right)_x = \frac{i\hbar}{2m}\left(\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right) = \frac{i\hbar}{2m}\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$$

Now, $\vec{j} = -\frac{\partial}{\partial t}\int \rho dv = -\int\left(\frac{\partial\rho}{\partial t}\right) dv$

If j_x; j_y; j_z are the x, y, z components of $\vec{j}$ then we can write

$$j_x = -\int\left(\frac{\partial\rho}{\partial t}\right)_x dx = -\frac{i\hbar}{2m}\int\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)dx = -\frac{i\hbar}{2m}\int d\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$$

So, $j_x = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right)$.

Similarly, $j_y = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial y} - \psi\frac{\partial\psi^*}{\partial y}\right)$ and $j_z = -\frac{i\hbar}{2m}\left(\psi^*\frac{\partial\psi}{\partial z} - \psi\frac{\partial\psi^*}{\partial z}\right)$

Now, $\nabla.\vec{j} = \frac{\partial j_x}{\partial x} + \frac{\partial j_y}{\partial y} + \frac{\partial j_z}{\partial z} = -\frac{i\hbar}{2m}\left[\frac{\partial}{\partial x}\left(\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right) + \frac{\partial}{\partial y}\left(\psi^*\frac{\partial\psi}{\partial y} - \psi\frac{\partial\psi^*}{\partial y}\right) + \frac{\partial}{\partial z}\left(\psi^*\frac{\partial\psi}{\partial z} - \psi\frac{\partial\psi^*}{\partial z}\right)\right]$

$$\Rightarrow \nabla.\vec{j} = -\frac{i\hbar}{2m}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*)$$

$$\therefore \nabla.\vec{j} = -\frac{\partial\rho}{\partial t} \text{ i.e. } \frac{\partial\rho}{\partial t} + \nabla.\vec{j} = 0$$

This is known as conservation equation for continuity equation for probability

The states for which $\nabla.\vec{j} = 0$ i.e. $\frac{\partial\rho}{\partial t} = 0$ are called stationary States.

- **Solution of Schrodinger equation**

One dimensional time dependent Schrodinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi = i\hbar\frac{\partial\psi}{\partial t}$$

In order to solve this equation by the method of separation of variables let us assume that

$\psi = \theta\phi$; where θ is a function of x only and ϕ is a function of t only.

$$\therefore \frac{\partial^2\psi}{\partial x^2} = \phi\frac{\partial^2\theta}{\partial x^2} \text{ and } \frac{\partial\psi}{\partial t} = \theta\frac{\partial\phi}{\partial t}$$

$$\therefore -\frac{\hbar^2}{2m}\phi\frac{\partial^2\theta}{\partial x^2} + V\theta\phi = i\hbar\theta\frac{\partial\phi}{\partial t} \;\; i.e. -\frac{\hbar^2}{2m}\frac{1}{\theta}\frac{\partial^2\theta}{\partial x^2} + V = i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t}$$

If V is independent of t, L.H.S. is a function of x only whereas R.H.S. is a function of t only.

Let, $-\frac{\hbar^2}{2m}\frac{1}{\theta}\frac{\partial^2\theta}{\partial x^2} + V = i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t} = E = constant$

$$\therefore -\frac{\hbar^2}{2m}\frac{1}{\theta}\frac{\partial^2\theta}{\partial x^2} + V = E \quad and \quad i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t} = E$$

$$Now, i\hbar\frac{1}{\phi}\frac{\partial\phi}{\partial t} = E \; or, \frac{\partial\phi}{\phi} = -\frac{i}{\hbar}Edt$$

$$or, \ln\phi = -\frac{i}{\hbar}Et + const. (\ln C_1, say)$$

$$or, \boldsymbol{\phi = C_1 e^{-\frac{i}{\hbar}Et}}$$

As it is a function of time, it must indicate the periodicity that is wave character. Hence E/ħ must correspond to the angular velocity or circular frequency of the wave.

Here $\omega = \frac{2\pi}{T} = 2\pi\vartheta$; where T and ϑ are the period and frequency of the wave.

And $\frac{E}{\hbar} = \omega$. $\quad \therefore E = \hbar\omega = \frac{h}{2\pi} \times 2\pi\vartheta = h\vartheta = Total\ Energy$

$$\therefore \boldsymbol{\phi = C_1 e^{-i\omega t}}$$

$$Again, -\frac{\hbar^2}{2m}\frac{1}{\theta}\frac{\partial^2\theta}{\partial x^2} + V = E \;\; or, \qquad \frac{\partial^2\theta}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\theta = 0$$

$$\frac{2m}{\hbar^2}(E - V) = \frac{2m}{\hbar^2}(K.E.) = \frac{2m}{\hbar^2}\left(\frac{1}{2}mv^2\right) = \left(\frac{mv}{\hbar}\right)^2 = \frac{p^2}{\hbar^2} = \frac{\left(h/_\lambda\right)^2}{\left(h/_{2\pi}\right)^2} = \left(\frac{2\pi}{\lambda}\right)^2 = K^2$$

$$\therefore \frac{\partial^2\theta}{\partial x^2} + K^2\theta = 0 \quad \therefore \theta = ae^{ikx} + be^{-ikx}; where\ a\ and\ b\ are\ constants.$$

$$\therefore \psi = \theta\phi = \left(ae^{ikx} + be^{-ikx}\right)C_1e^{-i\omega t} = Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)}$$

Hence in order to have a simple solution, ψ may be taken in the form

$$\boldsymbol{\psi = Ae^{i(kx-\omega t)} = Ae^{i(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t)}}$$

- **<u>Derivation of operators</u>**

1. **<u>Position ($\vec{r}$):</u>**

If a particle is at a distance r from some arbitrary origin and x, y, z are its components along three rectangular Axes then, the position operator r of the particle is given by:

$\vec{r} = i'x + j'y + k'z;$

i', j', k' being the unit vectors in the increasing directions of x, y, z respectively.

2. **<u>Momentum ($\vec{p}$):</u>**

Solution of one dimensional time dependent Schrodinger equation is

$$\boldsymbol{\psi = Ae^{i\left(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t\right)}}$$

$$\frac{\partial\psi}{\partial x} = i\frac{p_x}{\hbar}Ae^{i(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t)} = i\frac{p_x}{\hbar}\psi \quad i.e. -\boldsymbol{i}\hbar\frac{\boldsymbol{\partial\psi}}{\boldsymbol{\partial x}} = \boldsymbol{p_x\psi}$$

Here $\boldsymbol{p_x}$ is the eigenvalue of the operator $-\boldsymbol{i}\hbar\frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}}$ corresponding to the eigen-function $\boldsymbol{\psi}$. So, the operator for $\boldsymbol{p_x}$ is $-\boldsymbol{i}\hbar\frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}}$.

Hence in three dimensions, the operator for $\vec{\boldsymbol{p}}$ is - $-\boldsymbol{i}\hbar\left(\boldsymbol{i'}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial x}} + \boldsymbol{j'}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial y}} + \boldsymbol{z'}\frac{\boldsymbol{\partial}}{\boldsymbol{\partial z}}\right) = -\boldsymbol{i}\hbar\vec{\boldsymbol{\nabla}}$

3. **<u>Kinetic Energy (T):</u>**

$$\psi = Ae^{i\left(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t\right)}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2}Ae^{i\left(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t\right)} = -\frac{p_x^2}{\hbar^2}\psi; \quad i.e. -\hbar^2\frac{\partial^2\psi}{\partial x^2} = p_x^2\psi$$

$$\text{Now}, T_x = \frac{p_x^2}{2m}; \quad i.e. p_x^2 = 2mT_x; \quad i.e. -\hbar^2\frac{\partial^2\psi}{\partial x^2} = 2mT_x\psi$$

$$So, -\frac{\hbar^2}{\boldsymbol{2m}}\frac{\partial^2\psi}{\partial x^2} = T_x\psi$$

Here T_x is the eigenvalue of the operator $-\frac{\hbar^2}{\boldsymbol{2m}}\frac{\partial^2}{\partial x^2}$ corresponding to the eigenfunction ψ.

So the operator for T_x is $-\frac{\hbar^2}{\boldsymbol{2m}}\frac{\partial^2}{\partial x^2}$

Hence in three dimension the operator T is $-\frac{\hbar^2}{\boldsymbol{2m}}\boldsymbol{\nabla^2}$

4. **Total energy (E):**

Total energy of a particle for one dimensional motion is

E_x = K.E. + P.E. = T_x + V. i.e. $T_x = E_x - V$

Now, $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = T_x\psi = (E_x - V)\psi \;\; i.e. \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)\psi = E_x\psi$

Here E_x is the eigen value of the operator $\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)$ corresponding to the eigen function ψ.

So the operator for Ex is $\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V\right)$

Hence in three dimension, the operator for E is $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$

This operator is also called **Hamiltonian operator H.**

5. **Operator E or H as a function of time**

$$\psi = Ae^{i\left(\frac{p_x}{\hbar}x - \frac{E}{\hbar}t\right)}$$

$$\therefore \frac{\partial\psi}{\partial t} = -i\frac{E}{\hbar}ae^{i\left(kx - \frac{E}{\hbar}t\right)} = -i\frac{E}{\hbar}\psi$$

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

Here E is the eigenvalue of the operator corresponding to the eigen function $\hbar\frac{\partial}{\partial t}$. Therefore, the operator for E or H is $i\hbar\frac{\partial}{\partial t}$.

6. **Angular Momentum (L)**

$$\vec{L} = \vec{r} \times \vec{p} \quad where\ \vec{r} = position\ vector\ and\ \vec{p} = Linear\ Momentum$$

$$i.e. \vec{L} = -i\hbar\left(\vec{r} \times \vec{\nabla}\right)$$

If Lx, Ly and Lz are the x, y, z component of $\vec{L}$ then

$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$; $L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$; $L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$;

• Commutation relations among the different operators:

1. **[x, p]**

As x and p are two operators, their commutator i.e. [x, p] is also an operator. If this operator operates on and eigen function Ψ, then

$$[x,p]\psi = (xp - px)\psi = \left(-i\hbar x\frac{\partial}{\partial x} + i\hbar\frac{\partial}{\partial x}x\right)\psi = -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\frac{\partial}{\partial x}(x\psi)$$
$$= -i\hbar x\frac{\partial\psi}{\partial x} + i\hbar x\frac{\partial\psi}{\partial x} + i\hbar\psi = i\hbar\psi \quad \therefore \boldsymbol{[x,p] = i\hbar}. \text{ Similarly, } \boldsymbol{[p,x] = -i\hbar}$$

2. **[H, p]**

As H and p are two operators, their commutator i.e. [H, p] is also an operator. If this operator operates on and eigen function Ψ, then

$$[H,p]\psi = (Hp - pH)\psi = \left\{\left(i\hbar\frac{\partial}{\partial t}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)\left(i\hbar\frac{\partial}{\partial t}\right)\right\}\psi$$
$$= \left(\hbar^2\frac{\partial^2}{\partial t\partial x} - \hbar^2\frac{\partial^2}{\partial x\partial t}\right)\psi = \hbar^2\frac{\partial^2\psi}{\partial t\partial x} - \hbar^2\frac{\partial^2\psi}{\partial x\partial t} = 0$$
$$\therefore [H,p]\psi = 0.\psi \text{ } i.e. \text{ } \boldsymbol{[H,p] = 0} \text{ Similarly, } \boldsymbol{[p,H] = 0}$$

3. **[H, x]**

As H and x are two operators, their commutator i.e. [H, x] is also an operator. If this operator operates on and eigen function Ψ, then

$$[H,x]\psi = (Hx - xH)\psi = \left\{\left(i\hbar\frac{\partial}{\partial t}\right)x - x\left(i\hbar\frac{\partial}{\partial t}\right)\right\}\psi$$
$$= \left(i\hbar\frac{\partial}{\partial t}(x\psi) - i\hbar x\frac{\partial\psi}{\partial t}\right) = i\hbar x\frac{\partial\psi}{\partial t} + i\hbar\psi\frac{\partial x}{\partial t} - i\hbar x\frac{\partial\psi}{\partial t} = i\hbar\psi\frac{\partial x}{\partial t}$$

Now, p_x = mv = $m\frac{\partial x}{\partial t}$ $\quad \therefore \frac{\partial x}{\partial t} = \frac{p_x}{m}$

$$\therefore [H,p]\psi = i\hbar\frac{p_x}{m}\psi \text{ } i.e. \text{ } \boldsymbol{[H,p] = i\hbar\frac{p_x}{m}} \text{ Similarly, } \boldsymbol{[p,H] = -i\hbar\frac{p_x}{m}}$$

4. **[x, $\boldsymbol{\frac{\partial}{\partial x}}$]**

As x and $\frac{\partial}{\partial x}$ are two operators, their commutator i.e. [x, $\frac{\partial}{\partial x}$] is also an operator. If this operator operates on and eigen function Ψ, then

$$\left[x,\frac{\partial}{\partial x}\right]\psi = \left(x\frac{\partial}{\partial x} - \frac{\partial}{\partial x}x\right)\psi = x\frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x}(x\psi) = x\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial x} - \psi = -\psi$$

$$\therefore \left[x,\frac{\partial}{\partial x}\right]\psi = -1.\psi \text{ } i.e. \text{ } \boldsymbol{\left[x,\frac{\partial}{\partial x}\right] = -1} \text{ Similarly, } \boldsymbol{\left[\frac{\partial}{\partial x},x\right] = 1}$$

5. **[p, $\frac{\partial}{\partial x}$]**

As p and $\frac{\partial}{\partial x}$ are two operators, their commutator i.e. [p, $\frac{\partial}{\partial x}$] is also an operator. If this operator operates on and eigen function Ψ, then

$$\left[p, \frac{\partial}{\partial x}\right]\psi = \left(\left(-i\hbar\frac{\partial}{\partial x}\right)\frac{\partial}{\partial x} - \frac{\partial}{\partial x}\left(-i\hbar\frac{\partial}{\partial x}\right)\right)\psi = -i\hbar\frac{\partial^2\psi}{\partial x^2} + i\hbar\frac{\partial^2\psi}{\partial x^2} = 0$$

$$\therefore \left[p, \frac{\partial}{\partial x}\right]\psi = 0.\psi \ i.e.\ \left[\mathbf{p}, \boldsymbol{\frac{\partial}{\partial x}}\right] = \mathbf{0} \text{ Similarly, } \left[\boldsymbol{\frac{\partial}{\partial x}}, \boldsymbol{p}\right] = \mathbf{0}$$

6. **[H, $\frac{\partial}{\partial x}$]**

As H and $\frac{\partial}{\partial x}$ are two operators, their commutator i.e. [H, $\frac{\partial}{\partial x}$] is also an operator. If this operator operates on and eigen function Ψ, then

$$\left[H, \frac{\partial}{\partial x}\right]\psi = \left(\left(i\hbar\frac{\partial}{\partial t}\right)\frac{\partial}{\partial x} - \frac{\partial}{\partial x}\left(i\hbar\frac{\partial}{\partial t}\right)\right)\psi = -i\hbar\frac{\partial^2\psi}{\partial t\partial x} + i\hbar\frac{\partial^2\psi}{\partial x\partial t} = 0$$

$$\therefore \left[H, \frac{\partial}{\partial x}\right]\psi = 0.\psi \ i.e.\ \left[\mathbf{H}, \boldsymbol{\frac{\partial}{\partial x}}\right] = \mathbf{0} \text{ Similarly, } \left[\boldsymbol{\frac{\partial}{\partial x}}, \boldsymbol{H}\right] = \mathbf{0}$$

Q. Show that the Eigen values of a Hermitian operator are real. (3)

Ans: If Ψ(x) is an Eigen function of a Hermitian operator $\hat{\alpha}$ belonging to the Eigen value 'a', then we can write

$$\hat{\alpha}\psi = a\psi$$

Taking the complex conjugate, we get,

$$\hat{\alpha}^*\psi^* = a^*\psi^*$$

So, we have

$$\int \psi^*\hat{\alpha}\psi dx = \int \psi^* a\psi dx = a\int \psi^*\psi dx \ ----\rightarrow (1)$$

$$\int \psi\hat{\alpha}^*\psi^* dx = \int \psi a^*\psi^* dx = a^*\int \psi\psi^* dx \ ----\rightarrow (2)$$

Since the integrals on the left hand side of the above two equations are equal in view of

$$\int \psi^*\hat{\alpha}\psi dx = \int \psi\hat{\alpha}^*\psi^* dx;\ \ [for\ real\ expectation\ value, \langle\alpha\rangle = \langle\alpha\rangle^*]$$

We have, $a\int \psi^*\psi dx = a^*\int \psi^*\psi dx$. Which gives $a = a^*$. So the Eigen values are real in nature.