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C9T (Elements of Modern Physics) , Topic :- Schrödinger's Equation (Unit 2)

- **Wave Function :** According to Milllikon, the wave function ψ is an auxilliary mathematical quantity introduced to facilitate computations relative to experimental results. Originally , ψ has four interpretations –

(a) Particle density : In any electromagnetic wave system, the energy per unit volume = Square of amplitude of wave (A^2).

Number of the photons per unit volume = $\frac{Energy\ per\ unit\ volume}{Energy\ of\ one\ photon}$

i.e. Photon density = $\frac{A}{h\nu}$

i.e. Photon density $\propto A^2$

For a matter wave , if ψ be the amplitude of matter wave the particle density $\propto |\psi|^2$.

Here, square of absolute value of ψ is a measure of particle density.

(b) Charge density : If the particle density is multiplied by the charge of the particle then charge density is obtained. Then charge density $\propto |\psi|^2$. Hence square of absolute value of ψ is a measure of charge particle.

(c) Probability interpretation : - We see that $|\psi|^2$ is proportional to particle density. But there are certain cases in which ψ refers only to single particle. Naturally , there is s question – where the particle is in wave packet?

To explain it - Max. Born suggest a new idea about the physical significance of ψ.

According to Max. Born $|\psi|^2$does not measure the particle density at any point but gives the probability of finding the particle at that point at any given point.

(d) Normalization condition : The value of square of ψ may be real or imaginary depending upon the value of ψ. Since the probability of finding a particle at a given point in space must be real, thus it is taken as $\psi\psi^*$ or $|\psi|^2$.

Thus probability of finding the particle in volume dv = $|\psi|^2\ dv$.

Total probability of finding the particle somewhere must be unity i.e. $\iiint |\psi|^2\ dv = 1$. This is the normalization condition.

❖ **Limitations of $\boldsymbol{\psi}$:** The most important limitations of ψ are following –

- **(i)** ψ must be finite for all values of *x,y,z* .
- **(ii)** ψ must be single valued.
- **(iii)** ψ must be continuous everywhere expect where potential energy is zero.
- **(iv)** ψ is analytical i.e. it passes continuous first order derivative.
- **(v)** ψ vanishes at the boundaries.

❖ **Schrödinger Time- Independent Equation :-**

Let us consider a group of waves associated with a moving particle. Let $\psi(r,t)$ represents the displacement of these waves at a site *r* at any instant *t* .

The wave motion can be represented by the classical wave equation

$$\nabla^2\psi = \frac{1}{v^2}\frac{\partial^2\psi}{\partial t^2} \qquad \ldots\ldots\ldots\ldots\ldots(1)$$ Where v is the velocity

To find the solution of the above equation, let us take trial solution

$$\psi(r,t) = \psi(r).e^{-i\omega t}$$

$$\therefore \frac{\partial^2\psi}{\partial t^2} = -\omega^2\,\psi \ \ldots\ldots\ldots(2)$$

Putting in equation (1), we get

$$\nabla^2\psi = -\frac{\omega^2}{v^2}\psi$$

$$= -\frac{(2\pi\nu)^2}{(\lambda\nu)^2}\psi$$

$$= -\frac{4\pi^2}{\lambda^2}\psi$$

$$= -(\frac{p}{\hbar})^2\psi \quad \text{as } \lambda = \frac{h}{p}$$

$$= -(\frac{mv}{\hbar})^2\psi \;\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

If E and V be the total energy and the potential energy of the particle respectively, then,

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

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

$$or, mv = \sqrt{2}m(E-V)$$

Putting in equation (3) $\nabla^2\psi = -\frac{2m(E-V)}{\hbar^2}\psi$

$$\boldsymbol{\nabla^2\psi + \frac{2m(E-V)}{\hbar^2}\psi = 0}$$

This is known as Schrödinger time- independent equation.

- **For Free Particle :**

  Force on free particle = 0 , or, $\frac{dv}{dx} = 0$. Conventionally , we take V = 0

  Thus time-independent Schrödinger equation for free particle,

$$\boldsymbol{\nabla^2\psi + \frac{2mE}{\hbar^2}\psi = 0}$$

❖ **Schrödinger time- dependent equation from time-independent equation :**

Schrödinger time independent equation,

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

$$\text{Or, } \nabla^2\psi - \frac{2mV}{\hbar^2}\psi = -\frac{2mE}{\hbar^2}\psi$$

$$\text{Or, } -\frac{\hbar^2}{2m}\left(\nabla^2\psi - \frac{2m}{\hbar^2}V\psi\right) = E\,\psi \;\ldots\ldots\ldots(1)$$

Let the trial solution , $\psi(r,t) = \psi(r).e^{-i\omega t}$

$$\text{Or, } \frac{\partial\psi}{\partial t} = -i\omega t$$

$$\text{Or, } i\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\psi = E\,\psi \qquad \ldots(2)$$

From equation (1) and (2)

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

This is known as Schrödinger time dependent equation.

- The operator $\boldsymbol{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right) = \hat{H}}$, called Halmiltonian operator.
- The operator $\boldsymbol{i\hbar\frac{\partial}{\partial t} = \hat{E}}$ **,** called Energy operator.

$$\hat{H}\,\boldsymbol{\psi} = \hat{E}\,\boldsymbol{\psi}$$

- **Probability Density :** For a particle in a state $\psi(x,t)$, probability density is defined as the product of $\psi(r,t)$ and its complex conjugate $\psi^*(x,t)$.
  Probability density $\rho = \psi^*(x,t).\,\psi(r,t)$
  (1) 1 D case – The probability density of finding particle in a distance *dx* is given by
  $\rho dx = \psi\psi^* dx$
- **Normalisation :** If we consider a small element of volume dv defined by the coordinates $(x, x+dx)$; $(y, y+dy)$; and $(z, z+dz)$ then
  Prob. Of finding the particle within volume dv is given by
  $$\rho dv = \psi\psi^* dxdydz$$
  Prob. Of finding the particle within a finite volume *v*
  $$\int_v \rho dv = \iiint_v \psi\psi^* dxdydz$$
  The process of integration over all possible locations is unity. This is called normalization.
  $$\boldsymbol{i.e.\iiint \psi\psi^* dxdydz = 1} \qquad \text{for all space}$$
  N.B. For 1-D case : $\int_{-\infty}^{+\infty} \boldsymbol{\psi\psi^* dx = 1}$
- **Stationary State :** The state of a wave function is called stationary state if probability density of the state does not change with time.
  $$i.e. \frac{\partial \rho}{\partial t} = 0$$
  Criterion of stationary state –
  (i) $\frac{\partial \rho}{\partial t} = 0$ i.e. $\frac{\partial}{\partial t}(\psi\psi^*) = 0$
  (ii) $\frac{\partial \rho}{\partial t} + \vec{\nabla}.\vec{j} = 0$ i.e. $\vec{\nabla}.\vec{j} = 0$ (where $\frac{\partial \rho}{\partial t} = 0$)
  i.e Current density vector is solenoidal in nature.

❖ <u>Probability current density : Probability interpretation of ψ</u>

➢ Probability interpretation of ψ :

Statistical interpretation of wave function ψ says that $\psi\psi^*$ or $|\psi|^2$ is a measure of probability of finding the particles in a certain region. Now the statement is true for all time, since the particle will certainly be found within whole space i.e. total probability must be conserved i.e. $\psi\psi^*$ must be conserved.

➢ <u>Probability current density</u> :

Probability density of a wave function ψ, $\rho = \psi\psi^*$

Probability current density $\vec{J} = \frac{\partial\rho}{\partial t} = \frac{\partial}{\partial t}(\psi\psi^*) = \frac{\partial\psi}{\partial t}\psi^* + \frac{\partial\psi^*}{\partial t}\psi$

According to equation of continuity, $\vec{\nabla}.\vec{j} + \frac{\partial\rho}{\partial t} = 0$ …………(1)

Now Schördinger time dependent equation,

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

Its complex conjugate, $\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi^* = -i\hbar\frac{\partial\psi^*}{\partial t}$ ……….(3)

Multiplying equation (2) on left by ψ^* and equation (3) by ψ

We get –

$$-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V\psi\psi^* = i\hbar\psi^*\frac{\partial\psi}{\partial t} \qquad \text{……………(4)}$$

$$-\frac{\hbar^2}{2m}\psi\nabla^2\psi^* + V\psi^*\psi = -i\hbar\psi\frac{\partial\psi^*}{\partial t} \qquad \text{………(5)}$$

Subtracting Equation (4) – (5) we get

$$-\frac{\hbar^2}{2m}\left[\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\right] = i\hbar\left[\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right] \qquad \text{…………(6)}$$

Again, $\vec{\nabla}.\left(\psi\vec{\nabla}\psi^*\right) = \vec{\nabla}\psi.\vec{\nabla}\psi^* + \psi\nabla^2\psi^*$ ……….(7)

$\vec{\nabla}.\left(\psi^*\vec{\nabla}\psi\right) = \vec{\nabla}\psi^*.\vec{\nabla}\psi + \psi^*\nabla^2\psi$ ………..(8)

Subtracting, equation (7) – (8)

$\vec{\nabla}.\left(\psi\vec{\nabla}\psi^*\right) - \vec{\nabla}.\left(\psi^*\vec{\nabla}\psi\right) = \psi\nabla^2\psi^* - \psi^*\nabla^2\psi$ ………(9)

From equation (6) and (9)

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

$$or, \frac{\partial\psi}{\partial t}\psi^* + \frac{\partial\psi^*}{\partial t}\psi = -\frac{\hbar^2}{2m}\frac{1}{i\hbar}\left[\vec{\nabla}.\left(\psi\vec{\nabla}\psi^*\right) - \vec{\nabla}.\left(\psi^*\vec{\nabla}\psi\right)\right]$$

$$or, \frac{\partial\rho}{\partial t} = \frac{i\hbar}{2m}\left[\vec{\nabla}.\left(\psi\vec{\nabla}\psi^*\right) - \vec{\nabla}.\left(\psi^*\vec{\nabla}\psi\right)\right] \quad \text{………………} (10)$$

From equation (1) and (10)

$$\vec{\nabla}.\vec{j} + \frac{i\hbar}{2m}\left[\vec{\nabla}.\left(\psi\vec{\nabla}\psi^*\right) - \vec{\nabla}.\left(\psi^*\vec{\nabla}\psi\right)\right] = 0$$

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

$$\boldsymbol{or, \vec{j} = \frac{i\hbar}{2m}\left(\psi\vec{\nabla}\psi^* - \psi^*\vec{\nabla}\psi\right)}$$

We get ***Probability current density***.

- **Operator :** An operator is a mathematical term which operating on a function transferred to another function. If $\hat{P}$ is an operator operated to a function *u(x)* then it is changed into another function *v(x).*

  i.e. $\hat{P}\, u(x) = v(x)$

  Such as : $\frac{d}{dx}(Sin\alpha x) = \alpha Cos\alpha x$

- **Momentum Operator :** If ψ be an eigen function of an operator with eigen value as linear momentum then the operator is called linear momentum operator.

  Let $\psi = Ae^{i(\vec{k}.\vec{r}-\omega t)}$

  $\therefore \vec{\nabla}\psi = ikAe^{i(\vec{k}.\vec{r}-\omega t)}$

  Or, $\vec{\nabla}\psi = ik\,\psi$ Since $P = \hbar k$ or, $k = \frac{P}{\hbar}$

  Or, $\vec{\nabla}\psi = i\frac{P}{\hbar}\psi$

  Or, $-i\hbar\vec{\nabla}\psi = P\,\psi$

  $\therefore$ $\boxed{\hat{\boldsymbol{P}} = -\boldsymbol{i\hbar}\vec{\boldsymbol{\nabla}}}$ Linear momentum operator.

  $p_x = -i\hbar\frac{\partial}{\partial x}$; $p_y = -i\hbar\frac{\partial}{\partial y}$; and $p_z = -i\hbar\frac{\partial}{\partial z}$

- **Expression of angular momentum operator :**

We know , Angular momentum , $\vec{L} = \vec{r}\times\vec{p} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$

$$or, \vec{L} = \hat{\imath}(yp_z - zp_y) + \hat{\jmath}(zp_x - xp_z) + \hat{k}(xp_y - yp_x)$$

Equating, $L_x = yp_z - zp_y$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

Similarly, In operator form,

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

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

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