Lecture-07

Hamiltonim Operator:-

1

To prove Schrodinger equation, we have used

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,t) = \frac{\hbar^2 k^2}{2m}\int e^{i(kx-\omega t)} f(k)\, d^3k$$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2 = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

$\because \psi(x,t) = \int e^{i(kx-\omega t)} f(k)\, d^3k$

$$\Rightarrow -\frac{\hbar^2}{\cancel{2m}}\nabla^2 = \frac{p^2}{\cancel{2m}}$$

$\because p = \hbar \cdot k$ &

$$\Rightarrow p^2 = -\hbar^2\nabla^2$$

$E = \hbar\cdot\omega$

$$\Rightarrow p = \left(\frac{\hbar}{i}\right)\nabla$$

$= \frac{h}{2\pi}\cdot 2\pi\nu$

Also

$= h\nu$

To prove Schrodinger equation, we have used :-

$$i\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\int e^{i(kx-\omega t)} f(k)\, d^3k$$

$$i\hbar\frac{\partial}{\partial t} = E \qquad \because E = \hbar\omega$$

$$\Rightarrow E = i\hbar\frac{\partial}{\partial t}$$

Now we define Hamiltonian Operator

$$H = -\frac{\hbar^2}{2m}\nabla^2$$

This operator is in form of r & P.
(as $P = m\cdot v = m\cdot\frac{dr}{dt}$, so H depends on P & p depends on r)

Schrodinger equation is basic equation for wave mechanics. let's we write Schrodinger equation in transparent & clear form; as

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$$

$H\Psi = E\Psi$, so

$\left\{ \because H = -\frac{\hbar^2}{2m}\nabla^2\Psi \right.$

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

$\because H(p) = \frac{p^2}{2m}$

$H(p) \rightarrow H\left(\frac{\hbar}{i}\nabla\right)$

we get Hamiltonian op

by further extending the Schrodinger equation to the case of particle moving in potential, so H

By further substitution:-

$H(r, p) \rightarrow H\left(r, \frac{\hbar}{i}\nabla\right)$

That is if there is present potential energy denoted by $V(r)$

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\Psi$$

so new Schrodinger equation becomes:-

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

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It specifies, how the wave packet describing the particle develops in the time while interacting with given potential field.

Schrodinger's Equation (Time Independent):

We have studied Schrodinger equation in which wave packet of particles are develops with time. Now we form time independent wave fn. We use method of seperation of variables.

$$\psi(r,t) = \psi(r).\phi(t)$$

Schroedinger wave equation is

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

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

Dividing by $\psi(r)\phi(t)$, we get

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

$$\frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = \frac{1}{\phi(t)}\, i\hbar\frac{\partial\phi}{\partial t}$$

as variables are seperated, so each let set each side equal to a constant (say E).

$\Rightarrow$ L.H.S:-

$$\frac{1}{\psi(r)}\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\psi(r)=E$$

$$\Rightarrow\left[-\frac{\hbar^2}{2m}\nabla^2+V(r)\right]\psi(r)=E\psi(r) \quad \text{—(1)}$$

R.H.S:-

$$\frac{1}{\phi(t)}\,i\hbar\frac{\partial\phi}{\partial t}=E \Rightarrow E\,dt=i\hbar\frac{\partial(\phi(t))}{\phi(t)}$$

$$\Rightarrow \frac{E\,dt}{i\hbar}=\frac{\partial(\phi(t))}{\phi(t)} \quad \text{—(2)}$$

(2) $\Rightarrow$ Taking integration; as

$$\Rightarrow \int\frac{1}{\phi(t)}\partial\phi(t)=\frac{1}{i\hbar}\int E\,dt$$

$$\ln|\phi(t)|=\frac{1}{i\hbar}Et+\ln|c|$$

$$\phi(t)=e^{Et/i\hbar+c}=e^{Et/i\hbar}\cdot e^{c}=ce^{Et/i\hbar}$$

$$\phi(t)=ce^{Et/i\hbar}$$

$$\phi(t)=ce^{-iEt/\hbar}$$

$$\because \frac{Et}{i\hbar}=\frac{-iEt}{-i(i\hbar)}=\frac{-iEt}{\hbar}$$

so time in-dependent eq^n

$$\psi(r,t)=\psi(r)\cdot\phi(t)$$

$$=c\psi(r)e^{-iEt/\hbar} \rightarrow \text{Time seperated.}$$

Schwarz Inequality:-

let ψ & ϕ be two wave fn, then

$$\left|\int \phi^* \psi\, d^3r\right|^2 \le \left(\int |\phi|^2 d^3r\right)\left(\int |\psi|^2 d^3r\right)$$

Proof:-

let α be a complex constant

Then we take

$$\int |\phi + \alpha\psi|^2 d^3r = \int (\phi + \alpha\psi)(\phi^* + \alpha^*\psi^*)\, d^3r$$

$\bar{z} = z^* =$ conjug

$z \cdot z^* = |z|^2$

$z + z^* = 2\mathrm{Re}(z)$

$(z^*)^* = z$

$$= \int \left[|\phi|^2 + \phi\alpha^*\psi^* + \alpha\psi\phi^* + |\alpha|^2|\psi|^2\right] d^3r$$

$$= \int \left[|\phi|^2 + (\phi^*\alpha\psi)^* + \alpha\psi\phi^* + |\alpha|^2|\psi|^2\right] d^3r$$

$$= \int \left[|\phi|^2 + \underbrace{\alpha\psi\phi^*}_{z} + \underbrace{(\alpha\psi\phi^*)^*}_{z^*} + |\alpha|^2|\psi|^2\right] d^3r$$

$$= \int \left[|\phi|^2 + 2\mathrm{Re}(\alpha\phi^*\psi) + |\alpha|^2|\psi|^2\right] d^3r \ge 0$$

Here (Re) denotes real part

To make $\int \alpha\phi^*\psi\, d^3r$ be real

let u is phase of $\int \phi^*\psi\, d^3r$ i.e

$u =$ phase of $\int \phi^*\psi\, d^3r$ & let

$$\underbrace{\alpha = d e^{iu} \Rightarrow |\alpha| = d}_{\text{now}}$$

6

$\because z = x + iy = r\cos\varphi + r\,i\sin\varphi$

$\Rightarrow \quad = r[\cos\varphi + i\sin\varphi] = re^{i\varphi}$

$= d\,e^{i\mu}$ &

as $\alpha = d\,e^{-i\mu}$

$|\alpha| = \sqrt{d^2 (\cos(-\mu) + i\sin(-\mu))}$

$= d\sqrt{\cos^2(\mu) + \sin^2(\mu)}$

$= d(1) = d$

$\Rightarrow |\alpha| = d$

right hand side should be non-neg. as. we take quadratic form & its root must be imaginary or real. & Discriminent must be less then or equal to zero. we take; as

$a = \int |\varphi|^2 d^3r, \; b = 2\alpha\int \varphi^* \psi \, d^3r, \; c = |\alpha|^2 \int |\psi|^2 d^3r$

$D = \cancel{B^2}\; b^2 - 4ac \le 0$

$D = |2\alpha\int \varphi^*\psi\, d^3r|^2 - 4\left[\int|\varphi|^2 d^3r\right]\left[|\alpha|^2 \int|\psi|^2 d^3r\right]$

$= 4|\alpha|^2 \int \varphi^*\psi\, d^3r - 4|\alpha|^2 \left(\int|\varphi|^2 d^3r\right)\left(\int|\psi|^2 d^3r\right)$

$\because |\alpha| = d \Rightarrow |\alpha|^2 = d^2$

$= 4d^2 \left\{ |\int \varphi^*\psi\, d^3r|^2 - \left(\int|\varphi|^2 d^3r\right)\left(\int|\psi|^2 d^3r\right)\right\} \le 0$

$\Rightarrow |\int \varphi^*\psi\, d^3r|^2 \le \left(\int|\varphi|^2 d^3r\right)\left(\int|\psi|^2 d^3r\right)$

$\Rightarrow$ Schwarz Inequality.

Schwarz-Inequality for finite sum :-

Integral form of Schwarz Inequality :-

$$\left|\int \phi^{*} \psi \, d^3\underline{r}\right|^2 \le \left(\int |\phi|^2 d^3\underline{r}\right)\left(\int |\psi|^2 d^3\underline{r}\right)$$

$\int$ = sums

$\sum_n$ = sums

Schwarz Inequality for finite sums Takes the form:-

$$\left|\sum a_n b_n\right|^2 \le \left(\sum_n |a_n|^2\right)\left(\sum_n |b_n|^2\right)$$

Equality is obtained when ϕ is parallel to ψ. i.e $\phi = c\psi$

L.H.S:-

$$\left|\int (c\psi)^{*} \psi \, d^3\underline{r}\right|^2 = |c|^2 \left|\int |\psi|^2 d^3\underline{r}\right|^2$$

R.H.S:-

$$\left[\int |c\psi|^2 d^3\underline{r}\right]\left[\int |\psi|^2 d^3\underline{r}\right]$$

$$|c|^2 \left|\int |\psi|^2 d^3\underline{r}\right|^2$$

$\Rightarrow$ L.H.S = R.H.S

$\Rightarrow$ Equality holds