Plausible arguments leading to Schrodingers equ^n :- By Schrodinger in 1926

- Classically mechanics of a particle is given by Newtons equ^n :-

$$m\frac{d^2x}{dt^2} = F \qquad F = -\frac{\partial V}{\partial x}.$$

$$\Rightarrow -\frac{\partial V}{\partial x} = m\frac{d^2x}{dt^2}$$

- Maxwells equ^n $\quad \frac{\partial E_x}{\partial x} = \rho(x)/\epsilon_0.$

- poynting equ^n :- energy flow per unit time per unit area.

$$W_{EM} = \frac{1}{2}\int\left(\epsilon_0 E^2 + \frac{B^2}{\mu_0}\right)d\tau$$

- The reasonable assumptions that should be maintained to derive Schrodinger equ^n are $\longrightarrow$

1. It must be consistent with the de Broglie-Einstein postulates, $\lambda = \frac{h}{p}$ & $\nu = E/h$

2. It must satisfy the non-relativistic energy conservation

$$E = \frac{p^2}{2m} + V \qquad \text{---(1)}$$

3. It must be linear in $\psi(x,t)$. That is if ψ_1 and ψ_2 are the two separate sol^n then $\psi = c_1\psi_1(x,t) + c_2\psi_2(x,t)$ is also a sol^n.

[any arbitrary linear combination]

ψ_i s have same first power

& c_1, c_2 can have any arbitrary values.

This assumption assures that we can add number of waves linearly to obtain wave packet. Interference & diff. already been checked by Davisson & Germer Expt.

4. The potential energy V is a func^n of x only for conservative cases and may be f^n of time also.

For free particle, $V = V_0$ $\therefore F = -\frac{\partial V}{\partial x}$ and free particle means $F = 0$. Schr. equ^n was derived for free particle.

Writing equ^n ① in term of postulate ①

$\lambda = \frac{h}{p}$ $\qquad \frac{h^2}{2m}\frac{1}{\lambda^2} + V(x,t) = h\nu$

$\nu = \frac{E}{h}$

$k = \frac{2\pi}{\lambda}$ $\qquad \frac{\hbar^2 k^2}{2m} + V(x,t) = \hbar\omega$ ——— ②

$E = \hbar\omega$ $\qquad \frac{\hbar^2 k^2}{2m} + V_0 = \hbar\omega$ —— (2i)

Now to follow the linear & homogeneity asks every term in the diff. equ^n be linear in $\psi(x,t)$. Also any derivative of $\psi(x,t)$ has the property.

Assumption 4.

wave sol^n → plane wave →

$$\psi(x,t) = \sin(kx - \omega t).$$

$$\alpha \frac{\partial^2 \psi}{\partial x^2} + V(x,t)\,\psi(x,t) = \beta \frac{\partial \psi}{\partial t} \quad —③$$

$$-\alpha k^2 \sin(kx-\omega t) + V_0 \sin(kx-\omega t) = -\beta\omega \cos(kx-\omega t) \quad —④$$

But the equ^n does not contain same $\psi(x,t)$.

So, let $\psi(x,t) = \cos(kx-\omega t) + \gamma \sin(kx-\omega t)$ —⑤

$$\therefore -\alpha k^2 \cos(kx-\omega t) - \alpha k^2 \gamma \sin(kx-\omega t) + V_0 \cos(kx-\omega t) + V_0 \gamma \sin(kx-\omega t)$$
$$= \beta\omega \sin(kx-\omega t) - \beta\omega\gamma\cos(kx-\omega t)$$

$$\Rightarrow \left[\alpha k^2 + \beta\omega\gamma + V_0\right]\cos(kx-\omega t) + \left[-\alpha k^2\gamma + V_0\gamma - \beta\omega\right]\sin(kx-\omega t) = 0$$

shows

$-\alpha k^2 + V_0 = -\beta\gamma\omega$ —(i)

$-\alpha k^2 \cancel{\gamma} + V_0 \cancel{\gamma} = \beta\omega/\gamma$ —(ii) $\therefore \frac{\beta\omega}{\gamma} = -\beta\omega\gamma$

$\Rightarrow \gamma = \frac{-1}{\gamma}$ $\qquad \Rightarrow \gamma^2 = -1$

$\Rightarrow \gamma = \pm i$

(i) → $\quad -\alpha k^2 + V_0 = \mp i\beta\omega$ —— ⑥

⑥ & ② $\quad \alpha = -\hbar^2/2m$

$\beta = \pm i\hbar$ (choose $\beta = i\hbar$.)

$\therefore$ ③ ⇒ $\boxed{-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x,t)\,\psi(x,t) = i\hbar\frac{\partial\psi}{\partial t}}$

Schroedinger equ^n :-

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} + V(x,t)\,\psi(x,t) = i\hbar\frac{\partial\psi(x,t)}{\partial t} \quad -(1)$$

Interpretation of ψ $\longrightarrow$ (Born's interpretation)

- We have seen the wave fn is complex. e.g. $e^{i(kx-\omega t)}$ is a plane wave that represents a free particle.
- the equ^n also carries a i term in the rt-hand-side and is because energy equ^n was followed and time derivative is done once.
- Presence of i in the wave fn shows that ψ has no physical interpretation. [Like water wave has a physical existence, ~~but~~ matter wave being represented by $\psi(x,t)$ has no physical existence.
- But wave fn has physical interest. Wave func^n has all the information of a particle which the uncertainty principle allows.
- Born defined a term called probability density $P(x,t)$ which gives the probability per unit length/volm of finding the particle near x and at time t.

In 1926, Max Born put forward the rel^n bet^n $P(x,t)$ and the wave func^n as

$$P(x,t) = \psi^*(x,t)\psi(x,t).$$

$|\psi|^2 = \psi^*\psi$ is always real and positive.

Let
$$z = a+ib$$
$$z^* = a-ib$$
$$\therefore z^* z = a^2+b^2$$

but $\sqrt{a^2+b^2} = |\psi|$ is also real & +ve, but is not considered for probability density.

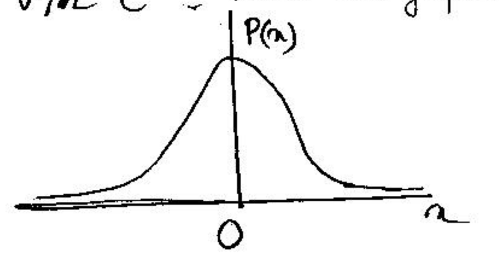
- It was with the analogy of intensity of e-m field or radiation is given by E^2 or B^2. In analogy with that $|\psi|^2$ is taken as the probability density.

Problem 1

Evaluate the probability density for the S.H. oscillator lowest energy state wave function given by

$$\psi(x,t) = A\, e^{-\left(\frac{\sqrt{cm}}{2\hbar}x^2\right)} e^{-(i/2)\sqrt{c/m}\, t}$$

. Draw the graph of probability density and x.



$$P = \psi^*\psi = A^2 e^{-\frac{\sqrt{cm}}{\hbar}x^2}$$

at $x = \pm\sqrt{2E/c}$, $P = A^2 e^{-\frac{\sqrt{cm}}{\hbar}\cdot\frac{2E}{c}}$

$$= A^2 e^{-\frac{2E}{\hbar}\sqrt{m/c}}$$

There is no limit on x beyond which the particle will not be found.

- Uncertainty principle provides the fundamental reason why quantum mechanics expresses itself in probabilities and not in certainties.
- Probability density is a real quantity and we can calculate it. But it does not tell any thing about $\psi(x,t)$.

Problems: [Assignment]

1. A particle is in motion along a line betn $x=0$ and $x=a$ with zero potential energy and at points $x<0$ and $x>a$, the potential energy is infinite. The wave function for the particle in the n^{th} state is given by

$$\psi_n = A \sin\frac{n\pi x}{a}$$

Find the probability density.

2. If $\psi_n(x) = \sqrt{2/a}\,\sin\frac{n\pi x}{a}$ is a given wave function show that the total probability of finding the particle is 1.

3. A particle moving along the +ve direction of the x-axis in a region of potential energy $V(x)$ is represented by a wave packet given by

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}}\int_{-\alpha}^{\alpha} A(p)\, e^{i/\hbar\,(px-Et)}\, dp$$

, by differentiating it and using expression for non-relativistic total energy expression obtain Schroedinger wave eqn.

Lecture 3

Constraints on Wave function :

In order to represent a physically observable system, the w. f^n must satisfy certain constraints:

1. Must be a solution of the Schrodinger equation.
2. Must be normalizable. This implies that the wavefunc^n approaches zero as $x \to \infty$.

Reason :- If ψ has finite value as $x \to \infty$, then the $\int_{-\infty}^{\infty} |\psi|^2 dx$ will blow off. Hence will become non-normalizable.

3. Must be finite and continuous f^n of x.
4. $\frac{\partial \psi}{\partial x}$ must also be continuous.

- to get physically observable quantities like x, p_x etc. as are got by operating ψ & $\frac{\partial \psi}{\partial x}$, hence ψ, $\frac{\partial \psi}{\partial x}$ must be finite.
- for $\frac{\partial \psi}{\partial x}$ to be finite, $\psi(x)$ must be continuous, as $\frac{\partial \psi}{\partial x}$ becomes infinite, as $\psi(x)$ is discontinuous.
- Again necessity for $\frac{d\psi}{dx}$ to be continuous felt as $\frac{d^2\psi}{dx^2}$ to be finite.

5. $\psi(x,t)$ must be single valued. As $\psi(x,t)$ is also probability amplitude which is proportional to probability of finding the particle, so probability at a place can not be multivalued.

Examples of physical wave f^n :-

$\psi(x,t) \longrightarrow e^{-\alpha x^2}$

$\longrightarrow e^{-\alpha|x|}$

$\longrightarrow \sin\frac{n\pi x}{a} \quad -a < x < a$

$\longrightarrow e^{i(kx-\omega t)}$ for some given limit.

Unphysical wave f^n :-

$\psi(x,t) \longrightarrow e^{\alpha|x|}$

$\longrightarrow \sinh kx$, $\cosh kx$ etc.

Schroedinger 3-D equ^n :-

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

<u>Time-independent</u> <u>schroendinger</u> <u>equ^n</u> :-

Let $\psi(x,t) = \phi(x)\,f(t)$. where V does not depend on time explicitly and total energy E is constant.

<u>Postulates</u> of <u>Quantum</u> <u>Mechanics</u> :

1. Associated with any particle moving in a conservative field of force is a wave fn which determines everything that can be known about the system.

2. With every physical observable q there is associated an operator Q which when operating upon the wave function associated with a definite value of that observable will yield that value times the wave function.

3. Any operator Q associated with a physically measurable property q will be Hamitian

4. The set of eigen func^{n}s of operator $\hat{Q}$ will form a complete set of linearly independent func^{n}s.

5. For a system described by a given wave fn, the expectation value of any property q can be found by performing the expectation value integral with r.t. that wave fn.

6. The time evolution of the w. fn is given by the TISE. Eq^n.

How to make a probabilistic phenomena a real one.

toss 2 $\rightarrow$ can you prove that prob. is $\frac{1}{2}$

If you toss a large no. of coin then on ~~toss~~ we can show the vality.

· Probability of finding the particle per unit length along x is $|\psi|^2$

$\therefore$ Total probability $= \int_{-\infty}^{\infty} |\psi|^2 dx = 1$ as the particle is somewhere along x-dirn.

in 3-D $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2 d\tau = 1$ where $d\tau = dx\,dy\,dz$.

This process is called normalization.

<u>Problem</u>

1. Normalize the wave function of linear harmonic oscillator at the ground state $\psi = A e^{-\left(\frac{\sqrt{cm}}{2\hbar}x^2\right)} \cdot e^{-i/2\sqrt{c/m}\,t}$ by determining the constant A.

$$A = \frac{(cm)^{1/8}}{(\pi\hbar)^{1/4}}$$

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

$$\Rightarrow 2\int_0^{\infty} A^2 e^{-\cancel{2}\left(\frac{\sqrt{cm}}{\cancel{2}\hbar}x^2\right)} dx = 1.$$

$$\Rightarrow A^2 \int_0^{\infty} e^{-\frac{\sqrt{cm}}{\hbar}x^2} dx = \frac{1}{2}$$

$$\Rightarrow A^2 \int_0^{\infty} e^{-z} \frac{\hbar}{\sqrt{cm}} x^{-1} \frac{\cancel{1}}{\cancel{2}} dz = \cancel{\frac{1}{2}}$$

$$\Rightarrow \frac{(cm)^{1/4}}{\hbar^{1/2}} A^2 \frac{\hbar}{\sqrt{cm}} \int e^{-z} z^{-1/2} dz = 1$$

$$\Rightarrow (cm)^{-1/4} \hbar^{1/2} A^2 \sqrt{\pi} = 1$$

$$\Rightarrow A^2 = \frac{(cm)^{1/4}}{(\pi\hbar)^{1/2}}$$

$$\Rightarrow \boxed{A = \frac{(cm)^{1/8}}{(\pi\hbar)^{1/4}}}$$

$$\frac{\sqrt{cm}}{\hbar} x^2 = z$$

$$\frac{\sqrt{cm}}{\hbar} 2x\,dx = dz$$

$$dx = \frac{\hbar}{2x\sqrt{cm}} dz$$

$$x^2 = \frac{z\hbar}{\sqrt{cm}}$$

$$x^{-2} = \frac{\sqrt{cm}}{z\hbar}$$

$$x^{-1} = \left(\frac{\sqrt{cm}}{z\hbar}\right)^{1/2} = \frac{(cm)^{1/4}}{\hbar^{1/2}} z^{-1/2}$$

$$\int_0^{\infty} e^{-x} x^{n-1} dx = \Gamma(n)$$

$\psi = A e^{-bx^2}$

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi = 2\int_0^{\infty} x A^2 e^{-2bx^2} dx$$

$$= 2A^2 \int_0^{\infty} x e^{-2bx^2} dx$$

$$= \frac{2A^2}{\sqrt{2b}} \int_0^{\infty} \cancel{z^{1/2}} e^{-z} \frac{dz\,\sqrt{2b}}{4b\,\cancel{z^{1/2}}}$$

$$= \frac{A^2}{2b}\int_0^{\infty} e^{-z} dz = \frac{A^2}{2b}\int_0 e^{-z} z^{1-1} dz.$$

$2bx^2 = z.$

$\therefore 4bx\,dx = dz$

$x = \left(\frac{z}{2b}\right)^{1/2}$

$dx = \frac{dz}{4b}\frac{1}{x} = \frac{dz}{4b}\frac{\sqrt{2b}}{z^{1/2}}$

We have $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

But wave funcⁿ must be consistant with Sch. wave equⁿ.

Now Sch. equⁿ shows that if $\psi(x,t)$ is a solⁿ, so too $A\psi(x,t)$

$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V(x,t)\psi = i\hbar\frac{\partial \psi}{\partial t}$ where A is any complex const.

So we need to find the multiplicative constant A and that process is called normalization:

Now $\frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2 dx = \int_{-\infty}^{\infty}\frac{\partial}{\partial t}|\psi(x,t)|^2 dx.$

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}(\psi^*\psi) = \psi^*\frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t}\psi. \quad \text{--- (1)}$$

Now $\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\left[-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi\right]$

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

$\left(+\frac{1}{i\hbar}V\psi\right)$

$\frac{d\rho}{dt} = \frac{\partial}{\partial x}(J(x,t))$

$\rho(x)$

$\frac{\partial \rho}{\partial t} + \nabla\cdot J = 0.$

$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}J_x = 0.$

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

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

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

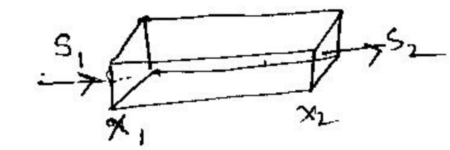
$$= \frac{\partial}{\partial x}\left[\frac{i\hbar}{2m}\left\{\psi^*\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right\}\right]$$

$$\therefore \frac{d}{dt}\int_{-\infty}^{\infty}|\psi|^2 dx = \frac{i\hbar}{2m}\left\{\psi^*\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right\}\Bigg|_{-\infty}^{\infty}$$

$$= 0.$$

probability current: $J_p = \frac{-i\hbar}{2m}\left[\psi^*\frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right]$

Probability current density



Let a particle of mass 'm' be moving in the +ve x dir^n from x_1 to x_2.

The wave fn $\psi(x,t)$ represents the particle.

$dA \rightarrow$ area of cross section of the region.

$\therefore$ Probability of finding the particle within the region is

$$\int_{x_1}^{x_2} P \, dx \, dA = \int_{x_1}^{x_2} |\psi|^2 \, dx \, dA \quad \text{---} (1)$$

As the particle moves along the +ve x-axis, the probability of finding the particle in the region decreases with time. The rate of decrease of probability in the region from x_1 to x_2 per unit area is called the probability current density out of the region.

$$S_2 - S_1 = -\frac{1}{dA}\left[\frac{d}{dt}\int_{x_1}^{x_2} |\psi|^2 \, dx \, dA\right]$$

Since x and t are independent variable.

$$= -\int_{x_1}^{x_2} \frac{\partial}{\partial t} |\psi|^2 \, dx \quad \text{---} (2)$$

not needed

$\therefore$ probability current density at x is

$$S = -\int \frac{\partial}{\partial t} |\psi|^2 dx = \cancel{\int \frac{\partial}{\partial t}(\psi^* \psi) \, dx}$$

$$= -\int \frac{\partial}{\partial t}(\psi^* \psi) \, dx$$

$$= \frac{-i\hbar}{2m}\left\{\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right\}.$$

Note $\therefore$ For particle in a box $\rightarrow$

Case I ψ is real.

$\therefore S = 0$. probability current density is zero. This shows that the ~~probability of decre~~ rate of decrease of probability within the box is zero or the particle is confined within the box.

Case II Show that the probability current density for a free particle is equal to the product of its probability density and its speed.

as $\psi^*\psi = A^2$. For a free particle $\psi(x,t) = Ae^{i(kx - \omega t)}$

$= Ae^{i/\hbar(px - Et)}$ — (1) $\quad p = \hbar k$, $E = \omega\hbar$.

$\pm i\hbar \nabla_x$

$$\therefore -i\hbar \frac{\partial \psi}{\partial x} = -i\hbar \cdot \frac{i}{\hbar} p_x \psi$$

$$\Rightarrow = p_x \psi. \quad \text{---} (2)$$

$\therefore \frac{\partial \psi}{\partial x} = i/\hbar \, p_x \psi$

$\frac{\partial \psi^*}{\partial x} = -i/\hbar \, p_x \psi^*$

Now $S = -\frac{i\hbar}{2m}\left[\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x}\psi\right] = -\frac{i\hbar}{2m}\left[\psi^* \frac{i}{\hbar} p_x \psi + \frac{i}{\hbar} p_x \psi^* \psi\right]$

$= \psi^* \psi \frac{p_x}{m} = |\psi|^2 v_x.$

Lecture – 3

Time-Independent Schroodinger equ^n:–

Let us consider $\psi(x,t) = \phi(x) f(t)$ and Total energy E is constant and V is fn of x only.

Sol^n in this form exist when potential energy do not depend on time explicitly so that $V(x)$ can be written for P.E.

$$\frac{\partial^2 \psi}{\partial x^2} = f(t) \frac{\partial^2 \phi(x)}{\partial x^2}$$

$$\frac{\partial \psi}{\partial t} = \phi(x) \frac{\partial f}{\partial t}$$

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

$$\Rightarrow \frac{-\hbar^2}{2m} f(t) \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi f = i\hbar\, \phi(x) \frac{\partial f}{\partial t}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{1}{\phi} \frac{\partial^2 \phi}{\partial x^2} + V(x) = i\hbar \frac{1}{f} \frac{\partial f}{\partial t} = E \text{ (Constant)}$$

$$\therefore -\frac{\hbar^2}{2m} \frac{1}{\phi} \frac{\partial^2 \phi}{\partial x^2} + V(x) = E$$

$$\Rightarrow \boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi = E\phi} \quad \text{—— (1)}$$

$$i\hbar \frac{1}{f} \frac{\partial f}{\partial t} = E$$

$$\Rightarrow \int \frac{\partial f}{f} = \frac{1}{i\hbar} \int E\, \partial t \Rightarrow \ln f(t) = -i/\hbar\, E t + \ln C$$

$$f(t) = C e^{-i/\hbar\, E t}.$$

$$\Rightarrow f(t) = C e^{-i/\hbar\, E t}$$

$$\therefore \psi(x,t) = C\phi(x)\, e^{-i/\hbar\, E t}.$$

Equ^n (1) is time independent Sch. equ^n for a particle subjected to a conservative potential field and having constant energy E

$\phi(x) \rightarrow$ eigen function.

$\psi(x,t) \rightarrow$ wave func^n.

Sch. equ^n. $-\frac{\hbar^2}{2m} \frac{\partial^2 \phi}{\partial x^2} + V(x)\phi = E\phi$. is the time-independent

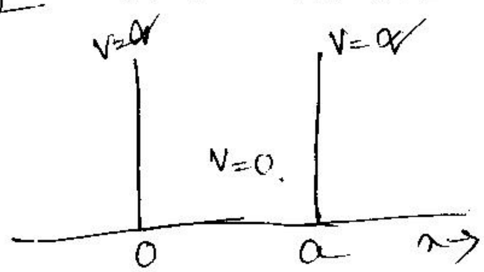
ϕ is the eigen func^n.

Now energy in case of bound situation are discrete and every possible energy has ~~every~~ a corresponding eigen func^n.

In general,

$$\boxed{\psi(x,t) = \sum_{n=1}^{\infty} c_n \phi_n(x)\, e^{-i/\hbar\, E_n t}} \quad \text{—— (1)}$$

eg. Particle in an infinite potential well — (Particle in a box)



$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} = E\phi \qquad k^2 = \frac{2mE}{\hbar^2}$$

$$\Rightarrow \frac{d^2\phi}{dx^2} + \frac{2mE}{\hbar^2}\phi = 0.$$

$$\Rightarrow \frac{d^2\phi}{dx^2} + k^2\phi = 0.$$

$\therefore \phi(x) = A\sin kx + B\cos kx$

Now, $\phi(x) = 0$ at $x=0$ & at $x=a$. | Wave f^n must be continuous at the boundary.

$\therefore B = 0.$

and $\phi(x) = A\sin kx$

at $x=a$, $0 = A\sin ka$

$\therefore ka = n\pi$

$\therefore k = \frac{n\pi}{a}$ $\quad n = 1, 2, 3 \text{ - - - -}$

$\therefore \phi(x) = A\sin\frac{n\pi x}{a}$ | $n=0$, $\phi=0$. $\therefore$ trivial sol^n. particle does not exist, so discarded.

So particle with $E=0$ can not be present inside a box.

$n=0$
$\Rightarrow k=0$
$\Rightarrow E=0.$

$$\therefore E_n = \frac{k^2\hbar^2}{2m}$$

$$= \frac{n^2\pi^2\hbar^2}{2a^2m} = \frac{n^2h^2}{8ma^2}$$

Thus, E_1, E_2 - - - etc. are all possible energies for a free particle confined within a box. Hence ϕ_1, ϕ_2 ---- etc. are possible eigen func^{n}s.

Thus soln (i) gives the general form of the wave func^n.

Lecture - 4

Basis vectors

- A set of vectors in a vector space V is called a basis or a set of basis vectors, if the vectors are linearly independent every vector in the vector space is linear combination of this set whose coeff. are refered to as vector coordinates.

For example,

$$\bar{V} = 3\hat{i} + 2\hat{j} + 8\hat{k}$$

$\therefore \bar{V} = (3, 2, 8) \longrightarrow$ is the co-ordinates.

$\hat{i}, \hat{j}, \hat{k}$ are $(1,0,0)$, $(0,1,0)$, $(0,0,1)$

But special quality is they are orthogonal.

- But a vector space can have several distinct sets of basis vectors.

- Thus a basis of a vector space is a linearly independent subset of V that spans V.

(1) A basis $B = \{v_1, \cdots v_n\}$ if.

$$a_1v_1 + a_2v_2 + \cdots + a_nv_n = 0 \quad , \text{ then necessarily } a_1 = \cdots a_n = 0$$

and

(2) for every x in V, $x = b_1v_1 + b_2v_2 + \cdots b_nv_n$.

where b_i are the co-ordinates of the vector x.

Change of basis :

e.g. In two Dim^n vector space R^2

simple basis $e_1 = (1,0)$; $e_2 = (0,1)$

Let $V = (a,b)$ is a vector in R^2

$\therefore V = a(1,0) + b(0,1)$

For any two linearly independent vectors, like $(1,1)$ and $(-1,2)$, will also form a basis R^2.

- If v, w are linearly independent, then

$av + bw = 0$, (a, b are scalars)

$\therefore a = 0$

$b = 0$.

$v \to (1,1)$.

$w = (-1,2)$.

$a(1,1) + b(-1,2) = (0,0)$

$av + bw = 0$

$a - b = 0$

$a + 2b = 0$.

$a(1,1) + b(-1,2) = 0$.

$\Rightarrow b = 0$, hence $a = 0$.

$a - b = 0$.

$a + 2b = 0$.

$\therefore (1,1)$ & $(-1,2)$ also form a basis

$\Rightarrow b = 0$

$a = 0$

2 To prove that these two vectors generate R^2, we have to let (a,b) be an arbitrary element of R^2,

$$r(1,1) + s(-1,2) = (a,b)$$

$r - s = a$

$r + 2s = b$

Subtracting, $3s = b - a$

$$s = \frac{b-a}{3}$$

$r = s + a$

$$= \frac{b-a}{3} + a = \frac{b+2a}{3}$$

Class-4

Normalization of eigen f^n :-

$\because \quad \psi(x,t) = \sum_{n=1} \boxed{C_n \phi_n(x)} e^{-i/\hbar E_n t}$.

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

$$\Rightarrow |C_n|^2 \int_{-\infty}^{\infty} \phi_n^* \phi_n \, dx = 1$$

$\rightarrow$ Normalization of eigen func^n.

Orthogonality of eigen f^n :-

Time independent sch. equ^n $\longrightarrow$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_m}{dx^2} + V(x)\psi_m = E_m \psi_m \quad \text{--- (1)}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} + V(x)\psi_n = E_n \psi_n \quad \text{--- (2)}.$$

$(1)^*$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_m^*}{dx} + V(x)\psi_m^* = E_m \psi_m^* \quad \text{--- (3)}$$

$\therefore \quad \psi_m^* \times (2)$ & $\psi_n \times (3)$

$$-\frac{\hbar^2}{2m}\psi_m^*\frac{d^2\psi_n}{dx^2} + V(x)\psi_m^*\psi_n = E_n \psi_m^* \psi_n \quad \text{--- (4)}$$

$$-\frac{\hbar^2}{2m}\psi_n\frac{d^2\psi_m^*}{dx} + V(x)\psi_n\psi_m^* = E_m \psi_m^* \psi_n. \quad \text{--- (5)}$$

(5) $-$ (4)

$$+\frac{\hbar^2}{2m}\left[\psi_m^*\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\psi_m^*}{dx^2}\right] = (E_m - E_n)\psi_m^*\psi_n.$$

$$\Rightarrow \frac{\hbar^2}{2m}\left[\frac{d}{dx}\left(\psi_m^*\frac{d\psi_n}{dx}\right) - \frac{d}{dx}\left(\psi_n\frac{d\psi_m}{dx}\right)\right] = (E_m - E_n)\psi_m^*\psi_n$$

$$\Rightarrow \frac{d}{dx}\left[\left(\psi_m^*\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_m}{dx}\right)\right] = \frac{2m}{\hbar^2}(E_m - E_n)\psi_m^*\psi_n$$

on $\int_{-\infty}^{\infty}$.

$$0 = \frac{2m}{\hbar^2}(E_m - E_n)\int_{-\infty}^{\infty}\psi_m^*\psi_n \, dx. \quad \therefore \int_{-\infty}^{\infty}\psi_m^*\psi_n \, dx = 0.$$

$$\therefore \int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = 1 \quad \text{for } m = n$$
$$= 0 \quad \text{for } m \neq n.$$

Ortho normal set of basis vectors.

$$\psi_n(x,t) = \sum_n c_n \phi_n(x)\, e^{-i/\hbar E_n t}$$
$$\psi_m^*(x,t) = \sum_m c_m^* \phi_m^*(x)\, e^{i/\hbar E_m t}.$$

$$\int_{-\infty}^{\infty} \psi_m^* \psi_n \, dx = \int_{-\infty}^{\infty} \left[c_1^* \phi_1^*(x)\, e^{i/\hbar E_1 t} + c_2^* \phi_2^*(x)\, e^{i/\hbar E_2 t} + \cdots \right] \times \left[c_1 \phi_1 e^{-i/\hbar E_1 t} + c_2 \phi_2 e^{-i/\hbar E_2 t} + \cdots \right] dx$$

$$= \int_{-\infty}^{\infty} |c_1|^2 \phi_1^* \phi_1 \, dx + |c_2|^2 \phi_2^* \phi_2 \, dx + \cdots$$
$$+ \int_{-\infty}^{\infty} c_1^* c_2^* \phi_1^*(x) \phi_2(x)\, e^{i/\hbar (E_1 - E_2) t} + \cdots$$

$$= \sum_n |c_n|^2 = 1$$

$$|c_1|^2 + |c_2|^2 + \cdots |c_n|^2 = 1$$

eg (1) A superposed state of a quantum particle is given by $\psi(x) = c_1 \psi_1(x) + c_2 \psi_2(x)$ where $\psi_1(x)$ and $\psi_2(x)$ are orthonormal states, show that $c_1^2 + c_2^2 = 1$

(2) If $c_1 = \frac{1}{\sqrt{2}}$, find $c_2 = ?$

~~Orthogonality of eigen func^n:~~

Operators in Quantum Mechanics

Let e^{mx}, operator $\frac{d}{dx}$

$$\therefore \frac{d}{dx} e^{mx} = m e^{mx}$$

$$\boxed{\hat{A}\psi = a\psi} \leftarrow \text{eigen value equ}^n.$$

(1) $\psi = e^{\frac{i}{\hbar}(p_x x - Et)}$ —(1) $p_x = \hbar k_x$, $E = \hbar\omega$

$$\therefore \frac{\partial}{\partial x}\psi = i/\hbar \, p_x \psi$$

$$\therefore -i\hbar \frac{\partial}{\partial x}\psi = -i i\hbar . \frac{1}{\hbar} p_x \psi .$$

$$-i\hbar\frac{\partial}{\partial x}\psi = p_x \psi .$$

$$\therefore \boxed{\hat{p}_x = -i\hbar\frac{\partial}{\partial x}} \leftarrow \text{momentum operator for}$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}$$

(2) $\hat{E} = i\hbar\frac{\partial}{\partial t}$

(3) Total energy operator $\rightarrow$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \hat{V}$$

$$\hat{H}\psi = E\psi .$$

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

$\hookrightarrow$ energy eigenvalue equ^n

(2a) K.E operator :-

$$\hat{K} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$$

$$K.E = \frac{p^2}{2m}$$

$$\therefore \frac{1}{2m}\frac{\partial^2\psi}{\partial x^2} = \left(\frac{i}{\hbar}\right)^2 p_x^2$$

$$= -\frac{1}{\hbar^2}\frac{p_x^2}{2m}\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = \frac{p_x^2}{2m}\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = \frac{p_x^2}{2m}\psi .$$

Angular momentum operators:

$$\bar{L} = \bar{r} \times \bar{p}$$

$$= \begin{vmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{i}\left(yp_z - zp_y\right) + \hat{j}\left(zp_x - xp_z\right) + \hat{k}\left(xp_y - yp_x\right)$$

$$\therefore L_x = yp_z - zp_y$$

$$\hat{L}_x = \hat{y}\hat{p}_z - z\hat{p}_y$$

$$= -i\hbar\left[\hat{y}\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right]$$

$$\hat{L}_y = -i\hbar\left[\hat{z}\frac{\partial}{\partial x} - \hat{x}\frac{\partial}{\partial z}\right]$$

$$\hat{L}_z = -i\hbar\left[x\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right]$$

Expectation values:-

Prob. that the electron will be within x & $x+dx$

$$= \frac{\text{no. of electrons in the position bet}^n\ x \text{ and } x+dx}{N}$$

but prob bet^n x & $x+dx$ = $\psi^*(x)\psi(x)\,dx$

$\therefore$ No. of electrons in the position bet^n x and $x+dx$ = $N\,\psi^*(x)\,\psi(x)\,dx$

Sum of all the measured values of $x_1, x_2 \cdots\cdots x_N$

$$x_1 + x_2 + x_3 + \cdots + x_N = \int x\, N\, \psi^*(x)\psi(x)\,dx.$$

$$\therefore \langle x\rangle = \frac{x_1 + x_2 + \cdots + x_N}{N} = \int_{-\infty}^{\infty} \psi^*(x)\, x\, \psi(x)\,dx$$

$$= \int_{-\infty}^{\infty} \psi^*(x)\, \hat{x}\, \psi(x)\,dx$$

$$\hat{x}\hat{p}_x\psi = \hat{x}\left(-i\hbar\frac{\partial}{\partial x}\psi\right) = -i\hbar\, x\frac{\partial\psi}{\partial x}.$$

$$\hat{p}_x\hat{x}\psi = -i\hbar\frac{\partial}{\partial x}(x\psi)$$

$$= -i\hbar\left[x\frac{\partial\psi}{\partial x} + \psi\right]$$

Lecture - 5

(1) Expectation value in quantum mechanics

In Q.M, the expectation value is the probabilistic expected value of the result of an experiment. It is not the most probable value of a measurement, indeed the expectation value may have zero probability of occuring.

Let in an experiment we have position results as $x_1, x_2 \cdots x_N$

So av. of x is defined as $\langle x \rangle = \dfrac{x_1 + x_2 + \cdots + x_N}{N}$

In quantum Mechanics,

Prob. that a particles position will be betn x & $x+dx$ is

$$\psi^*(x)\,\psi(x)\,dx = \frac{\text{no. of electrons in position bet}^n\ x\ \&\ x+dx}{N}$$

$\therefore$ No. of particles in the position betn x and $x+dx$ $= N\psi^*(x)\psi(x)\,dx$.

$\therefore$ Sum of all the positions $x_1, x_2 \cdots x_N$

$$= \int_{-\infty}^{\infty} x\, N\, \psi^*(x)\,\psi(x)\,dx$$

$$\therefore \frac{x_1 + x_2 + \cdots x_N}{N} = \langle x \rangle = \int_{-\infty}^{\infty} x\, \psi^*(x)\,\psi(x)\,dx$$

$$= \int_{-\infty}^{\infty} \psi^*\, \hat{x}(\psi(x))\,dx.$$

$$\therefore \langle x \rangle = \int_{-\infty}^{\infty} \psi^*\,\hat{x}\,\psi\,dx.$$

---

(2) $\langle p \rangle = \dfrac{d\langle x \rangle}{dt} = \dfrac{d}{dt}\displaystyle\int_{-\infty}^{\infty} x\,\psi^*\psi\,dx.$

$$= \int_{-\infty}^{\infty} x\,\frac{\partial}{\partial t}|\psi|^2\,dx$$

$$= \frac{i\hbar}{2m}\int_{-\infty}^{\infty} x\,\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right]dx$$

on integration by parts, & under limit the first part goes to zero.

$$= -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left[\psi^*\frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right]dx$$

$$\frac{d\langle x\rangle}{dt} = -\frac{i\hbar}{2m}\int_{-\infty}^{\infty} \psi^*\frac{\partial\psi}{\partial x} - \left[\frac{\partial}{\partial x}(\psi^*\psi) - \psi^*\frac{\partial\psi}{\partial x}\right] dx$$

$$= -\frac{i\hbar}{m}\int_{-\infty}^{\infty} \psi^*\frac{\partial\psi}{\partial x}\, dx \quad \Big| \text{ as } \int_{-\infty}^{\infty}\frac{\partial}{\partial x}(\psi^*\psi)\,dx = 0 \text{ at the boundary.}$$

$$\langle p\rangle = m\frac{d\langle x\rangle}{dt}$$

$$= -i\hbar\int_{-\infty}^{\infty}\psi^*\frac{\partial}{\partial x}\psi\, dx$$

$$= \int_{-\infty}^{\infty}\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\, dx.$$

$$\boxed{\langle p\rangle = \int_{-\infty}^{\infty}\psi^*\hat{p}_x\psi\, dx.}$$

∴ In general, all expectation value of the observables be given by $\langle A\rangle = \int_{-\infty}^{\infty}\psi^*\hat{A}\psi\, dx.$ where ψ is normalised eigen state.

Example :-

For particle in one dimensional box →

$$\psi_1 = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \quad 0 < x < a$$

$$\therefore \langle x\rangle = \frac{2}{a}\int_0^a x\sin^2\frac{n\pi x}{a}\, dx.$$

$$= \frac{2}{a}\int_0^a x\frac{1}{2}\left(1-\cos\frac{2n\pi x}{a}\right) dx$$

$$= \frac{2}{a}\int_0^a x\,dx - \frac{2}{a}\int_0^a x\cos\left(\frac{2\pi n x}{a}\right) dx$$

$$= \frac{2}{a}\cdot\frac{a^2}{2\cdot 2} - \frac{2}{a}\left[x\frac{a}{2\pi n}\sin\left(\frac{2\pi n x}{a}\right)\Big|_0^a - \frac{a}{2\pi n}\int_0^a \sin\frac{2\pi n x}{a}\, dx\right]$$

$$\therefore \boxed{\langle x\rangle = \frac{a}{2}}$$

$$\langle p_x \rangle = \int_0^a \psi^* \left(-i\hbar \frac{\partial \psi}{\partial x}\right) dx$$

$$= -i\hbar \int_0^a \psi^* \frac{\partial}{\partial x}\left[\sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a}\right] dx$$

$$= -i\hbar \frac{2}{a} \cdot \frac{n\pi}{a} \int_0^a \sin\frac{n\pi x}{a} \cos\frac{n\pi x}{a} \, dx$$

$$= 0.$$

Prob. to be given →

$$\langle x^2 \rangle = \frac{2}{a}\int_0^a x^2 \sin^2\frac{n\pi x}{a}$$

$$= \frac{2}{a}\left(\frac{a^3}{6} - \frac{a^3}{4\pi^2 n^2}\right)$$

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2$$

obtain Δx.

Quantum Mechanical Operators are Harmitian operators:

In mathematics we write the eigen value equ^n is

$$AX = \lambda X \quad \text{—} \; (1)$$

where A is an $(n \times n)$ matrix.

& X is a column vector or a matrix of $(n \times 1)$

Now, A is an operator $\hat{A}$ which acting on X a vector creates a vector multiple i.e. a vector having same Dir^n & of different magnitude.

$\therefore \quad \hat{P}_x \psi = p_x \psi$ — (2) then (2) is an eigen value equ^n and the eigen value the observable momentum.

- A matrix is called Harmitian, when taken a transposed & complex conjugate we get the same matrix A.

e.g. $\quad A = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$

$$A^T = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \quad \& \quad \overline{A^T} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = A.$$

$\therefore$ A is Harmitian.

$\therefore \quad A^{T^*} = A \Rightarrow$ Harmitian matrix