Quantum Mechanics

1) Rev. of de-Broglie's hypothesis.
2) Rev. of Prop. of matter waves.

Wave function ψ:

(1) A quantity ψ represents de-Broglie's waves as electric field vector represents light waves.

(2) The quantity ψ is called wavef^n $\psi(x,y,z,t)$ is a f^n of space and time.

(3) ψ represents position of particle, However it is not possible to locate position of particle exactly. There is only a prob. of finding particle

(4) ψ is a complex quantity

$$\psi = A+iB \quad \text{and} \quad \psi^* = A-iB$$
$$|\psi|^2 = \psi\psi^* = A^2+B^2 \Rightarrow \text{prob. of finding}$$

particle.

(5) The prob. of finding particle in vol. dv $= dx\,dy\,dz$ is given by

$$|\psi|^2\,dx\,dy\,dz$$

Requirements of acceptable wave f^n

(1) ψ must be finite
(2) ψ must be single valued
(3) ψ and its first derivative must be continuous.

(1) Limitations of CM
(2) Scope of QM
(3) De-broglie's hypo.
(4) Davisson Germer expt.
(5) Uncertainty principle
(6) v_g / v_p ; Matter waves, wave function, probability, Amplitude Normalization Uncer
(7) Schrodinger's eq^n TDSE → TISE. Particle in a box problem (1D infinite potential well - bc's
(8) Energy - momentum quantization 3D Eq^n + Degeneracy

Time dependent Schrödinger equation :

The 1D wave eq^n is

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 y}{\partial t^2}$$

and sol^n of this eq^n is

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

- $\parallel$'ly for matter waves

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2} \longrightarrow (1)$$

and sol^n $\psi(x,t) = A e^{i(kx-\omega t)} \longrightarrow (2)$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{p}{\hbar}$$

$$\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar}$$

$$\psi(x,t) = A e^{i\left[\frac{p}{\hbar}x - \frac{E}{\hbar}t\right]}$$

$$\psi(x,t) = A e^{-i/\hbar\,[Et - px]} \longrightarrow (3)$$

$$TE = KE + PE$$

$$E = \frac{p^2}{2m} + V \longrightarrow (4)$$

$$E\psi = \frac{p^2}{2m}\psi + V\psi$$

$$\psi = A e^{-i/\hbar\,[Et - px]} \longrightarrow (3)$$

Diff^n eq^n (3) w.r.t x, we get

$$\frac{\partial \psi}{\partial x} = \left[A e^{-i/\hbar\,[Et-px]}\right]\left[(-i/\hbar)(-p)\right]$$

$$\frac{\partial^2 \psi}{\partial x^2} = \underbrace{\left[A e^{-i/\hbar\,[Et-px)}\right]}_{\psi}\underbrace{\left[(-i/\hbar)(-p)(-i/\hbar)(-p)\right]}_{\frac{i^2}{\hbar^2}p^2 = \frac{-p^2}{\hbar^2}}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-p^2}{\hbar^2}\psi$$

$$p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \longrightarrow (5)$$

Diff^n eq^n (3) w.r.t t, we get

$$\frac{\partial \psi}{\partial t} = \underbrace{\left[A e^{-i/\hbar(Et-px)}\right]}_{\psi}\left[(-i/\hbar)(E)\right]\frac{i}{i}$$

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

$$E\psi = i\hbar \frac{\partial \psi}{\partial t} \longrightarrow (6)$$

from eq^n (4) (5) & (6)

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

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

Reduction to TISE

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

$\because \psi(x,t)=\phi(x)\,\phi(t)$

$$\therefore -\left(\frac{\hbar^2}{2m}\right)\phi(t)\frac{d^2\phi(x)}{dx^2}+V\phi(x)\phi(t)=i\hbar\,\phi(x)\frac{d\phi(t)}{dt}$$

dividing by $\phi(x)\,\phi(t)$, we get

$$\underbrace{-\left(\frac{\hbar^2}{2m}\right)\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+V}_{f^n \text{ of } x}=\underbrace{\frac{i\hbar}{\phi(t)}\frac{d\phi(t)}{dt}}_{f^n \text{ of } t}$$

correct only if LHS and RHS are equal to constant. let RHS $=E$ (Constant)

$$\therefore -\left(\frac{\hbar^2}{2m}\right)\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2}+V=E$$

$$\boxed{-\left(\frac{\hbar^2}{2m}\right)\frac{d^2\psi(x)}{dx^2}+V\psi(x)=E\psi(x)} \Rightarrow -\left(\frac{\hbar^2}{2m}\right)\nabla^2\psi+V\psi=E\psi$$

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

$$\boxed{H\psi=E\psi}$$

Free particle :

For free particle, $V = 0$

Consider an electron freely propagating along x-axis and not acted by any force.

$$-\frac{\hbar^2}{2m} \cdot \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\because V = 0$$

$$-\left(\frac{\hbar^2}{2m}\right) \frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2}\right)\psi = 0$$

$$K^2 = \frac{2mE}{\hbar^2} \longrightarrow (1)$$

$$\frac{d^2\psi}{dx^2} + K^2\psi = 0 \longrightarrow (2)$$

The general sol^n is

$$\psi = Ae^{iKx} + Be^{-iKx} \longrightarrow (3)$$

$A, B \Rightarrow$ constant

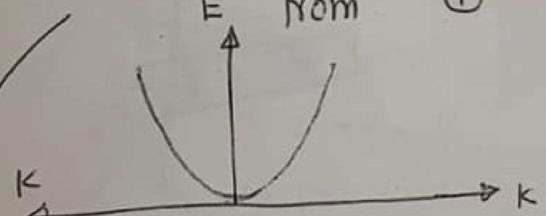
$\because$ wave is propagating only along x-axis

we can write $\boxed{\psi = Ae^{i(Kx - \omega t)}} \longrightarrow (4)$

As particle is free, no boundary condition can be applied ie no restriction on K

from (1) $E = \frac{\hbar^2 K^2}{2m} = \frac{h^2 K^2}{8m\pi^2}$

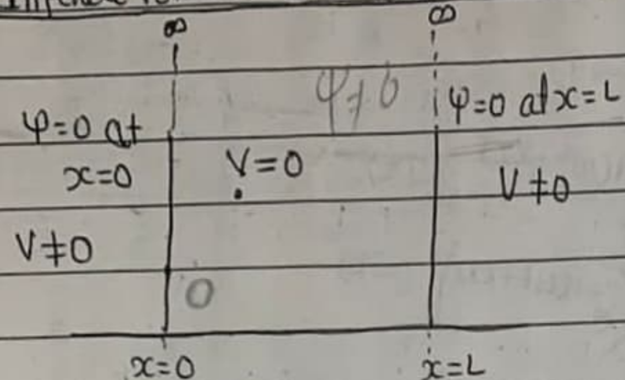
$E \propto K^2$



The particle is permitted to have any values of E

Energy is not quantized i.e a freely moving particle possesses a continuous energy spectrum.

Infinite Potential well (Particle in box)



TISE, $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \longrightarrow (1)$$

$V = 0$ when $0 < x < L$

$V \neq 0$ when $x \leq 0$ and $x \geq L$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$$

$$\hbar = \left(\frac{h}{2\pi}\right)$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{h^2}4\pi^2 E\psi = 0$$

$x = 0;\ \psi(x) = 0$

$x = L;\ \psi(x) = 0$

$$\frac{d^2\psi}{dx^2} + \left(\frac{8m\pi^2 E}{h^2}\right)\psi = 0 \longrightarrow (2)$$

let $k^2 = \frac{8\pi^2 m E}{h^2}$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \longrightarrow (3)$$

The sol^n is

$$\psi = Ae^{ikx} + Be^{-ikx} \longrightarrow (4)$$

when $x=0, \ \psi = 0$

$$0 = A + B$$

$$\therefore B = -A$$

from (4)

$$\psi = A\left(e^{ikx} - e^{-ikx}\right)\frac{2i}{2i}$$

$$\because \sin\theta = \left(\frac{e^{i\theta} - e^{-i\theta}}{2i}\right)$$

$$\psi = (2iA)\sin Kx \longrightarrow (5)$$

when $x = L$, $\psi = 0$

$$\cancel{0 = 2iA\sin KL}$$

$KL = 0$; $KL = n\pi$

$$\Rightarrow KL = n\pi$$

$$K = \left(\frac{n\pi}{L}\right) \longrightarrow (6)$$

from (5) & (6),

$$\psi = (2iA)\sin\left(\frac{n\pi x}{L}\right)$$

or, $\boxed{\psi_n = (2iA)\sin\left(\frac{n\pi x}{L}\right)} \longrightarrow (7)$

From normalized condⁿ

$$\int_0^L |\psi_n|^2 dx = 1$$

$$\int_0^L (2iA)^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$\sin^2\theta = \frac{1-\cos 2\theta}{2}$$

$$\therefore \frac{(2iA)^2}{2}\int_0^L \left[1-\cos\frac{2n\pi x}{L}\right]dx = 1$$

$$\frac{(2iA)^2}{2}\left[L-\left(\frac{\sin 2n\pi x/L}{2n\pi/L}\right)_0^L\right]=1$$

$$\frac{(2iA)^2}{2}\left[L-\left(\frac{\sin 2n\pi \frac{L}{L}}{2n\pi/L}\right)-0\right]=1$$

$$\downarrow$$

$$0$$

$$(2iA)^2\left(\frac{L}{2}\right)=1$$

$$2iA=\sqrt{\left(\frac{2}{L}\right)} \longrightarrow (8)$$

From eqn (7) & (8)

$$\boxed{\psi_n=\sqrt{\left(\frac{2}{L}\right)}\sin\left(\frac{n\pi x}{L}\right)} \longrightarrow (9)$$

$$\boxed{|\psi_n|^2 = \left(\frac{2}{L}\right)\sin^2\left(\frac{n\pi x}{L}\right)} \longrightarrow (10)$$

also $\because K = \frac{n\pi}{L}$

$$k^2 = \frac{n^2\pi^2}{L^2}$$

$$\therefore k^2 = \frac{8\pi^2 mE}{h^2}$$

$$\frac{8\cancel{\pi^2} mE}{h^2} = \frac{n^2\cancel{\pi^2}}{L^2}$$

$$E = \left(\frac{n^2h^2}{8mL^2}\right)$$

$$\boxed{E_n = \left(\frac{n^2h^2}{8mL^2}\right)} \longrightarrow (11)$$

$$\frac{2mE}{\hbar} = k^2$$

$$E = \frac{\hbar^2 k^2}{2m}$$

$$= \frac{h^2}{4\cancel{\pi^2}}\cdot\frac{n^2\cancel{\pi^2}}{L^2\,2m}$$

$$E = \frac{n^2h^2}{8mL^2}$$

$E \propto n^2$

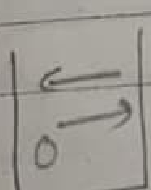
$E \propto \frac{1}{L^2}$

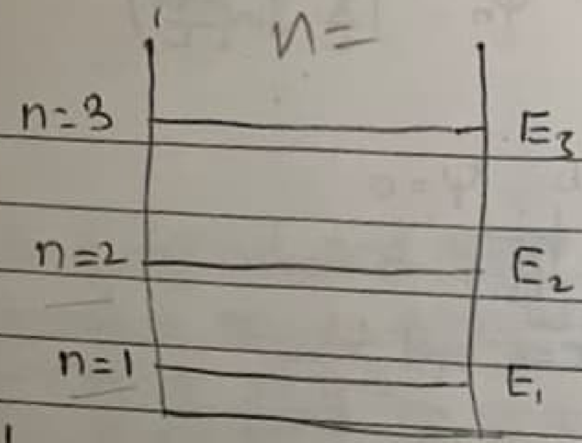
$\therefore$ Energy is quantized and depend on (n) & (L).

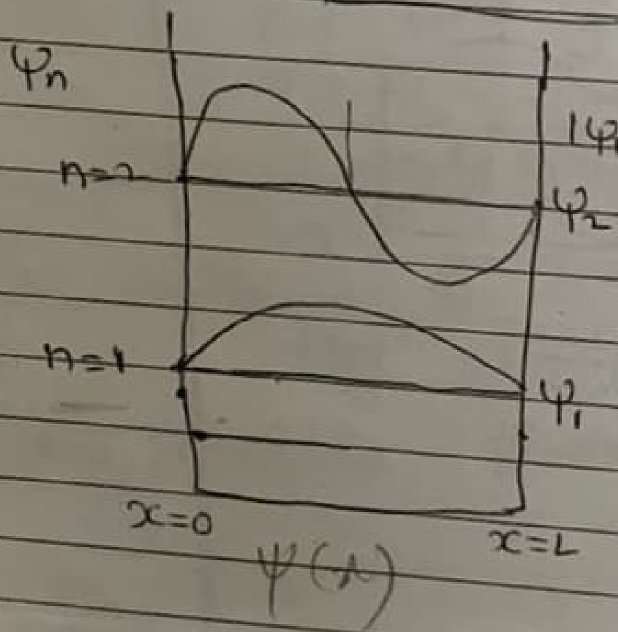
$n=1$ $\Rightarrow$ zero point energy

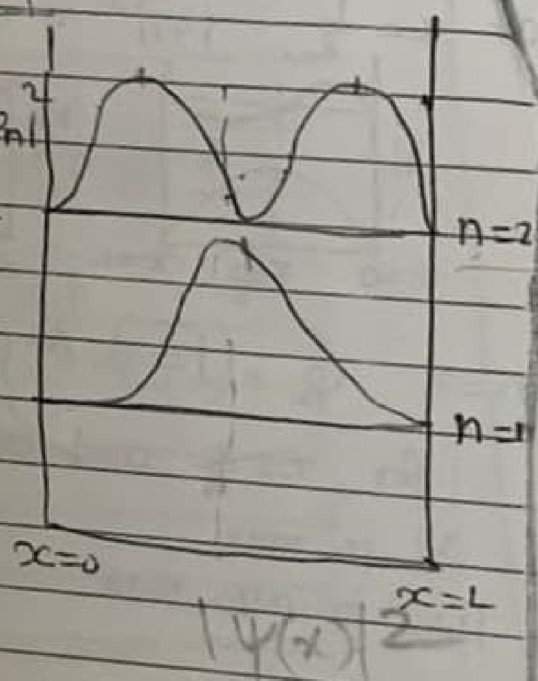
$n=2$: First exc state

$n=3$ Second " "




n=
n=3
E3
n=2
E2
n=1
E1


ψn
n=2
ψ2
n=1
ψ1
x=0
x=L
ψ(x)


|ψn|2
n=2
n=1
x=0
x=L
|ψ(x)|2

(14)

(1) For $n = 1$ $\qquad \because \psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

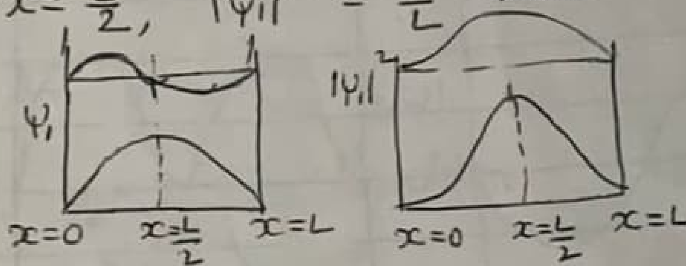
$\psi_1 = \sqrt{\left(\frac{2}{L}\right)} \sin\left(\frac{\pi x}{L}\right)$

at $x = 0$ and $x = L$, $\psi = 0$

$x = \frac{L}{2}$ $\quad \psi_1 = \sqrt{\left(\frac{2}{L}\right)} \Rightarrow$ max

$|\psi_1|^2$ is zero at $x = 0$ and $x = L$

at $x = \frac{L}{2}$, $|\psi_1|^2 = \frac{2}{L} \Rightarrow$ max

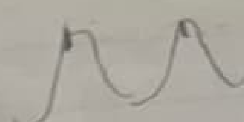


(2) for $n = 2$, $\psi_2 = \left(\sqrt{\frac{2}{L}}\right) \sin\left(\frac{2\pi x}{L}\right)$

for $x = \frac{L}{4}$ and $x = \frac{3L}{4}$

ψ_2 is max

$|\psi_2|^2$ is also max



(1) Energy is quantized and depend on principal quantum no. (n) and width (L).

(2) Energy cannot be zero

if $E = 0$

$\Rightarrow p = 0$

$\lambda = \infty$

$\therefore$ particle cannot trapped in box.

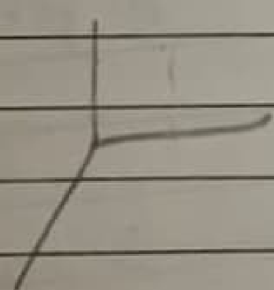
(3) ψ_n can be -ve or +ve but

$|\psi|^2$ is only +ve

for $n=1$

(4) ~~Max probability at centre.~~

1-D



Thus first excited state is three - fold degenerate

Eigen values and Eigen functions for particle in box.

$$E_n = \frac{n^2 h^2}{8mL^2}$$

and $\psi_n = \sqrt{\left(\frac{2}{L}\right)} \sin\left(\frac{n\pi x}{L}\right)$

The possible values of E are called eigen values and the corresponding ψ are called eigen function.

Degeneracy:

For different combination of quantum numbers we may have same energy value but wave f^n are different.

Such quantum states having same energy are called degenerate.

for example: $a=b=c \Rightarrow (a)(b)(c)=a^3$

$$\psi_{112} = \sqrt{\frac{8}{abc}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{b} \sin\frac{2\pi z}{c}$$

$$\psi_{121} = \sqrt{\frac{8}{abc}} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{b} \sin\frac{\pi z}{c}$$

$$\psi_{211} = \sqrt{\frac{8}{abc}} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{b} \sin\frac{\pi z}{c}$$

are different, but corresponding energies are same.

for first ψ_{112}, $n_x = 1$ $n_y = 1$ $n_z = 2$

$$n^2 = n_x^2 + n_y^2 + n_z^2 = 6$$

$$E_{112} = \frac{6h^2}{8ma^2}$$

for other two, $E_{121} = E_{211} = \frac{6h^2}{8ma^2}$

The number of different states with a certain value of energy is known as degree of degeneracy.

Thus first excited state is three-fold degenerate