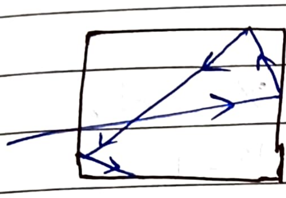
Module-4 Quantum Mechanics

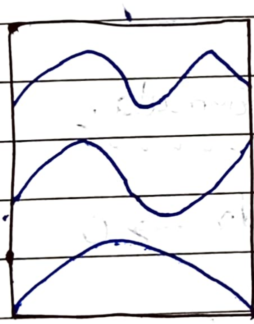
Black-body Radiation :-

Black-body: An Ideal body that can absorb and thus emit radiations of all frequencies incident upon it.

Experimental Realization :-



A hollow object with a very small cavity so that once a radiation enters the cavity, it gets trapped by reflection back and forth until it is absorbed. Such radiations which are constantly absorbed and emitted are called the black body radiation.



Density of standing wave in a cavity :-

$$G(\nu)\,d\nu = \frac{8\pi\nu^2\,d\nu}{c^3}$$

Rayleigh-Jeans Formula :-

$$U(\nu)d\nu = \frac{8\pi\nu^2}{c^3}KT\,d\nu = \frac{8\pi KT\nu^2\,d\nu}{c^3}$$

$U(\nu)d\nu$: Total energy per unit volume in the cavity between frequency interval ν to $\nu + d\nu$.

As $\nu \to \infty$
$U(\nu) \to \infty$
according to Rayleigh-Jeans Formula

However, in reality it is observed that as $\nu \to \infty$
$U(\nu)d\nu \to 0$.
This discrepancy is called the ultraviolet catastrophe in classical physics.

Planck's Radiation Law :-

not continuous — **Quantum oscillator** : $nh\nu$, $n = 0, 1, 2, \ldots$

Average energy per ν : $\dfrac{h\nu}{e^{h\nu/KT} - 1}$ [Bose-einstein's statistics]

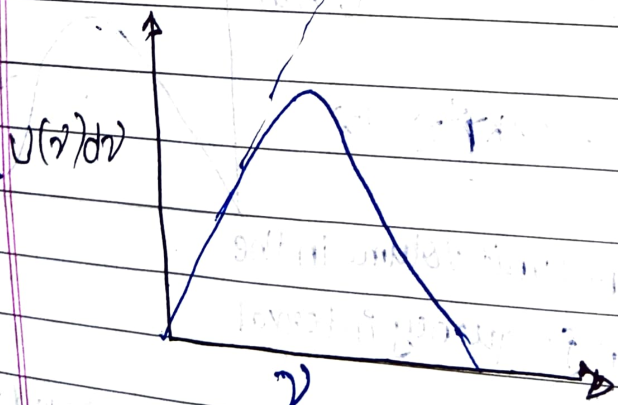
$$U(\nu)\,d\nu = \frac{8\pi\nu^2}{c^3}\,\frac{h\nu}{(e^{h\nu/KT} - 1)}\,d\nu$$

$$\boxed{U(\nu)\,d\nu = \frac{8\pi h\nu^3}{c^3}\,\frac{d\nu}{(e^{h\nu/KT} - 1)}}$$

Planck's radiation formula.

If $\nu \to \infty$, $U(\nu)\,d\nu \to 0$

If ν is small $\dfrac{h\nu}{KT} << 1$



$$\nu = \frac{\omega}{2\pi}$$

as ν is small, $e^{\frac{h\nu}{kT}} \approx 1 + \frac{h\nu}{kT} + \cdots$ $\left[\frac{h\nu}{kT} << 1\right]$

$$\boxed{U(\nu)d\nu = \frac{8\pi kT}{c^3}\nu^2 d\nu}$$

↳ Rayleigh-Jeans law.

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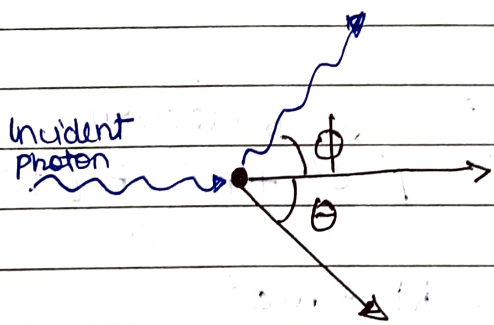
Compton Effect

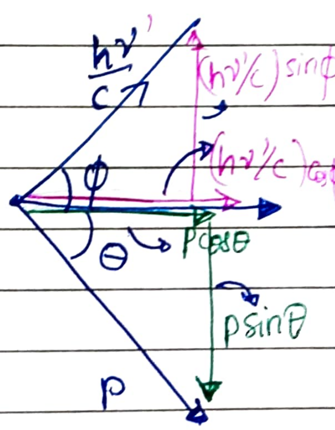
The scattering of a photon by an electron is called the Compton effect. Energy & momentum are conserved in such an event. And as a result, the scattered photon has less energy or longer wavelength than the incident photon.



Before collision

momentum of the photon $p_p^i = h\nu/c$

momentum of the electron $p_e^i = 0$



After collision

momentum of the photon $p_p^f = h\nu'/c$

momentum of the electron $p_e^f = p$.

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Momentum conservation :-

$$\frac{h\nu}{c} + 0 = \frac{h\nu'}{c}\cos\phi + p\cos\theta \quad — ①$$

$$0 = h\nu'\sin\phi - p\sin\theta \quad — ②$$

$$pc\cos\theta = h\nu - h\nu'\cos\phi \quad — ③ \quad [① \times c]$$

$$pc\sin\theta = h\nu'\sin\phi \quad — ④ \quad [② \times c]$$

Squaring and adding ③ & ④

$$\boxed{p^2c^2 = (h\nu)^2 - 2(h\nu)(h\nu')\cos\phi + (h\nu')^2}$$

— ⑤

$KE = h\nu - h\nu'$

Total energy of electron

$$E^2 = p^2c^2 + m^2c^4 \quad [\text{for any Particle}$$

— ⑥

$$E = KE + mc^2$$

$$E = (h\nu - h\nu') + mc^2 \quad — ⑦$$

Taking square of eqn ⑦ & comparing with eqn ⑥

$$\Rightarrow (h\nu - h\nu')^2 + \cancel{m^2c^4} + 2(h\nu - h\nu')mc^2 = p^2c^2 + \cancel{m^2c^4}$$

$$\Rightarrow p^2c^2 = (h\nu - h\nu')^2 + 2(h\nu - h\nu')mc^2 \quad (8)$$

comparing RHS of (5) & (8)

$$\Rightarrow \cancel{(h\nu)^2} - 2(h\nu)(h\nu')\cos\phi + \cancel{(h\nu')^2}$$

$$= \cancel{(h\nu)^2} + \cancel{(h\nu')^2} - 2(h\nu)(h\nu') + 2(h\nu - h\nu')mc^2$$

$$\Rightarrow 2(h\nu - h\nu')mc^2 = 2(h\nu)(h\nu')[1 - \cos\phi]$$

$$\Rightarrow c(\nu - \nu') = \frac{h\nu\nu'}{mc}(1 - \cos\phi).$$

$$c\left(\frac{1}{\nu'} - \frac{1}{\nu}\right) = \frac{h}{mc}(1 - \cos\phi)$$

$$\boxed{\lambda' - \lambda = \frac{h}{mc}(1 - \cos\phi)}$$ Compton Effect

By Arthur H. Compton in 1920

Compton wavelength

$\lambda_c = \frac{h}{mc}$ Compton wavelength of the scattering particle.

λ_c for electron $= 2.426 \times 10^{-12}$ m or 2.426 pm

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Compton Effect :-

$$\lambda' - \lambda = \lambda_c (1 - \cos\phi)$$

λ_c or compton wavelength gives the scale of the wavelength change of the incident photon.

The greatest or maximum wavelength change wi[ll] occur for $\phi = 180^\circ$

$$\boxed{\lambda' - \lambda = 2\lambda_c}$$

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Wave-particle Duality

De-Broglie hypothesis :-

Any moving material particle can be associated with the wave nature.

The wavelength can be computed as $\lambda = \frac{h}{p} = \frac{h}{\gamma m v}$ $\Big| \; \gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$

m : mass of the Particle

v : velocity of the particle

Q. Find the de-Broglie wavelength of a golf ball of mass 46 gm moving with a velocity of 30 m/s

$$\lambda = \frac{h}{mv}\sqrt{1-\frac{v^2}{c^2}} = \frac{6.63 \times 10^{-34}}{46\times10^{-3} \times 30 \times \sqrt{1-\frac{30^2}{(3\times10^8)^2}}}$$

$$\lambda = 4.8 \times 10^{-34}\ m$$

Q. Determine the same for electrons moving with vel. 10^7 m/s

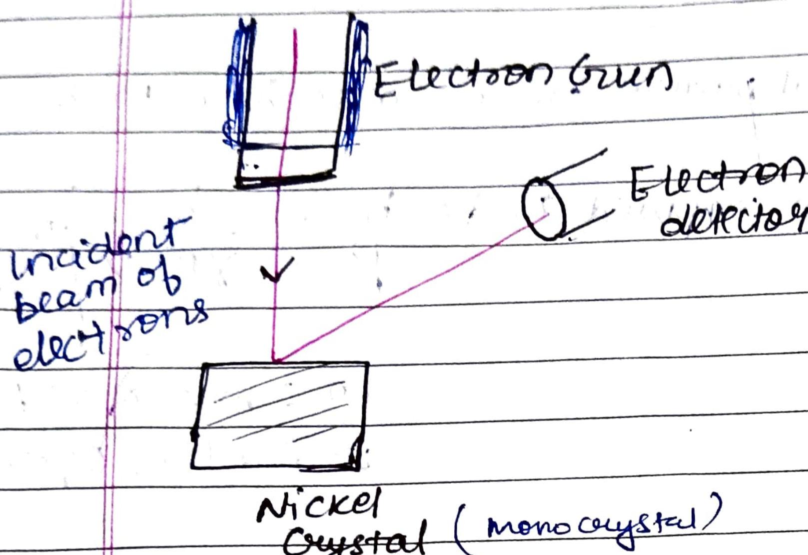
$$\lambda = \frac{6.63\times10^{-34}}{9.1\times10^{-31} \times 10^7 \sqrt{1-\frac{(10^7)^2}{(3\times10^8)^2}}}$$

$$\lambda_e = 7.3 \times 10^{-11}\ m$$

wave nature can be detected

G.P Thomson

Davisson - Germer Experiment :- (1927)



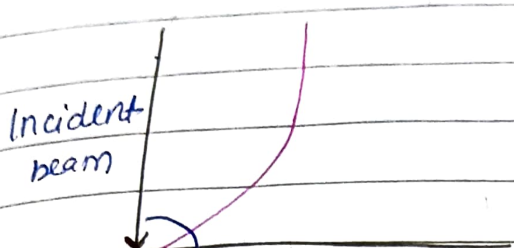
Independently done by G.P. Thomson (Son of J.J. Thompson)

The Davisson Germer experiment confirmed de-Broglie's hypothesis by showing that electron beams are deflected when they are scattered by the regular atomic arrays of crystals.

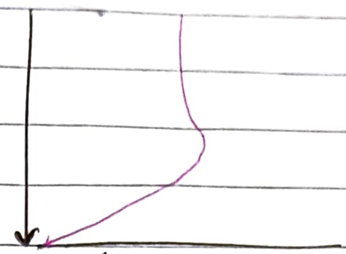
- The energy of the electrons in the primary beam, the angle at which they reach the target & the position of the detector could all be varied in the experiment.

- Davisson & Germer verified the predictions of the classical physics that the scattered electron will emerge in all direction with only a moderate dependence on there intensity, scattering angle & ~~on~~ energy of the primary electrons by using a block of nickel at target

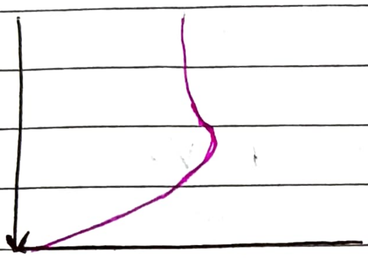
- However when the nickel block was heated in an oven the outcomes of the experiment where very different. A continuous variation of scattered electron intensity with angle was observed. Also distinct maxima & minima were observed whose positions were depended on the electron energy.



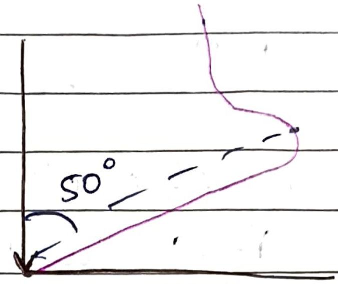
40V



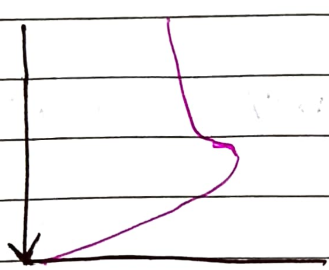
44V



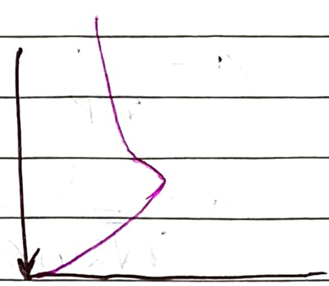
48V



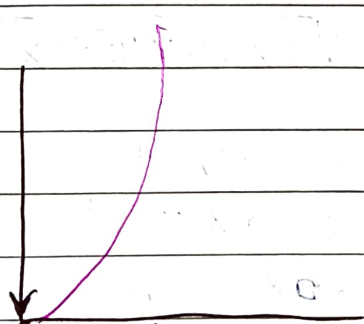
54V



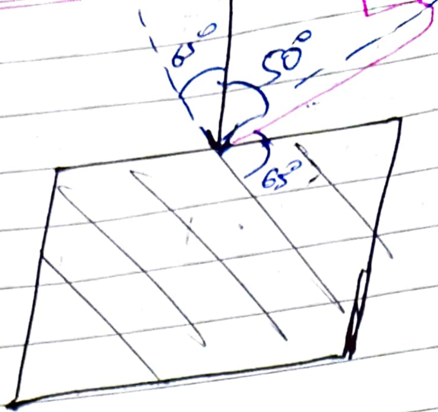
60V



64V



68V



X-ray diffraction

$n\lambda = 2d\sin\theta$

Bragg's eqn

$\lambda = 2d \sin 65^\circ$

$d = 0.091\,nm$ $\Rightarrow \lambda = 0.165\,nm$

Q. The KE of electrons is 54 eV.

$(\gamma = 1)$ Calculate de-Broglie wavelength

$$\lambda = \frac{h}{\gamma P} \qquad P = mv = \sqrt{2mKE}$$

$$\lambda = \frac{h}{\gamma\sqrt{2mKE}}$$

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 54 \times 1.6 \times 10^{-19}}}$$

$$= \frac{6.63 \times 10^{-34}}{3.96 \times 10^{-24}}$$

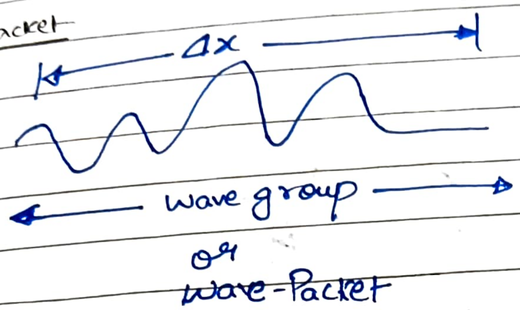
$\lambda = 1.66 \times 10^{-10}\,m$

$\lambda = 0.166\,nm$

Agrees well with the observed wavelength of 0.165nm

The Davisson - Germer experiment thus directly verifies the de Broglie's hypothesis of wave nature of moving objects

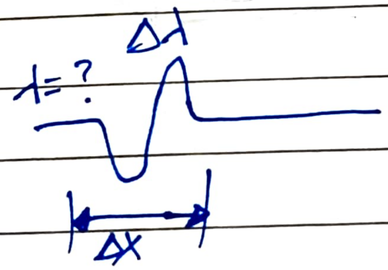
Wave packet



Uncertainty Principle

$$\boxed{\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}} \qquad \left[\hbar = h/2\pi\right]$$

The product of uncertainty in x i.e. Δx in the position of an object at some instant 't' & the uncertainty Δp in its momentum component in x direction at the same instant is equal to or greater than $h/4\pi$ or $\hbar/2$



Narrower its wave group more precisely particle position can be determined.

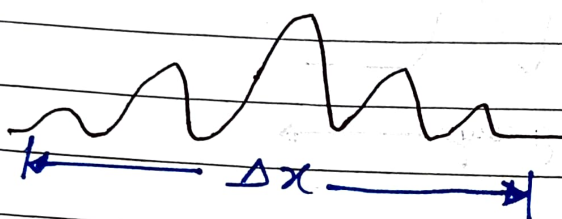
$\Delta x \rightarrow$ small

$\Delta \lambda \rightarrow$ large.

Since, $\lambda = \frac{h}{p}$

If $\Delta\lambda$ is not well defined
Δp is also not well defined

Larger Wave Packet



$\Delta x \rightarrow$ large
$\Delta\lambda \rightarrow$ small
$\Delta p \rightarrow$ small.

Alternate form

$$E = h\nu$$

$$\Delta E = h\Delta\nu$$

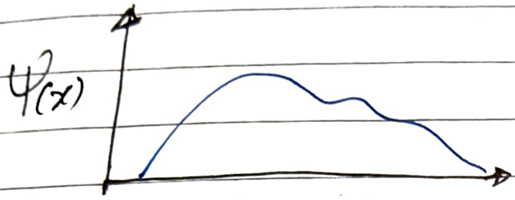
Now, $\Delta\nu \geq \frac{1}{\Delta t}$

$$\boxed{\Delta E \Delta t \geq \frac{\hbar}{2}}$$

$r \to 0$ to ∞
$\theta \to 0$ to π

Wave function

The wave associated with an object can be described by a function called wave function.



Properties

(I) Particle can exist only in the region where the wave fn $\psi(x)$ ~~is~~ is Non-zero.

(II) $\psi(x)$ itself has no physical interpretation or signification.

(III) $|\psi(x)|^2$ is known as the probability density. The probability of finding an object described by fn $\psi(x)$ at a pt 'x' at time 't' is proportional to the value of $|\psi(x)|^2$ at it.

(IV) If $|\psi(x)|^2$ is large, there is a greater chance of finding the particle at position x. While if $|\psi(x)|^2$ is small, the chance of finding the particle there is small. As long as $|\psi(x)|^2$ is not zero, there is a finite chance of finding a particle at that place.

(V) $\psi(x)$ is usually complex.

$\psi^*(x)$ is its complex conjugate.

$$\boxed{|\psi(x)|^2 = \psi^*(x)\,\psi(x)}$$

$$\psi(x) = A(x) + i\,B(x)$$

$$\psi^*(x)\,\psi(x) = A^2 + B^2 \quad [i^2 = -1]$$

$\psi^* \cdot \psi$ is always positive real quantity

The probability p of finding the particle b/w x + $x + dx$

$$P(x)\,dx = |\psi(x)|^2\,dx$$

The wave fn can be used to determine physical quantities like position, linear moment, angular momentum, energy etc.

Ex

Expectation value of position x

$$\boxed{\langle x \rangle = \frac{\int_{-\infty}^{\infty} x\,|\psi(x)|^2\,dx}{\int_{-\infty}^{\infty} |\psi(x)|^2\,dx}}$$

Normalisation

$$\int_{-\infty}^{\infty} |\psi|^2\,dV = 1 \quad \text{—— (A)}$$

$$\int_{-\infty}^{\infty} P\,dV = 1$$

If Eqn (A) is satisfying, wave function ψ is said to be normalized.

well-behaved wave function :-

1. ψ must be continuous & single-valued everywhere

2. $\frac{\partial \psi}{\partial x}$, $\frac{\partial \psi}{\partial y}$, $\frac{\partial \psi}{\partial z}$ must be finite, continuous & single valued everywhere.

3. ψ must be normalizable which means that ψ must go to zero as x tends to $\pm \infty$, $y \to \pm \infty$, $z \to \pm \infty$. as to have $\int_{-\infty}^{\infty} |\psi|^2 dV$ = finite

$\psi \to 0$, $x \to \pm \infty$, $y \to \pm \infty$, $z \to \pm \infty$

$$\int_{-\infty}^{\infty} |\psi|^2 dV = \text{finite}$$

Time-dependent Schrodinger's Equation in one Dimension

For a particle moving freely in +ve X-direction

$$\boxed{\Psi = A e^{i\omega\left(t - \frac{x}{v}\right)}} \longrightarrow (1)$$

$$\omega = 2\pi\nu \quad , \quad v = \nu\lambda$$

$$\boxed{\Psi = A e^{-2\pi i\left(\nu t - \frac{x}{\lambda}\right)}}$$

$$E = h\nu = 2\pi\hbar\nu$$

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

$$\Psi = A e^{-\frac{i}{\hbar}(Et - px)} \quad \text{— (2)}$$

wave-function for a free particle.

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{+ip}{\hbar}\right)^2 \psi = \frac{-p^2}{\hbar^2}\Psi$$

$$\Rightarrow p^2 \psi = -\hbar^2 \frac{\partial^2 \psi}{\partial x^2} \quad \text{— (3)}$$

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

$$\Rightarrow \boxed{\frac{\partial \Psi}{\partial t} = \frac{E}{i\hbar}\Psi} \quad \text{— (4)}$$

Total Energy of the Particle :

$$E = \frac{p^2}{2m} + U(x,t)$$

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

$$\Rightarrow \boxed{i\hbar \frac{\partial \psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi} \quad (5)$$

$\Rightarrow$ Time dependent Schrodinger's Equation in One-Dimension.

Linearity & Superposition

(1) Schrodinger's eqn is linear in ψ

(2) If ψ_1 & ψ_2 are two soln of Schrodinger's eqn then linear combination of ψ_1 & ψ_2 is also a soln.

$$\boxed{\Psi = a\Psi_1 + b\Psi_2}$$

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Schrodinger's Equation : steady state form :-

$$\Psi = A e^{-\frac{i}{\hbar}(Et - px)}$$ [free Particle]

when potential energy of a particle does not depend on time, schrodinger's eqn can be simplified :-

$$\Psi = \psi e^{-\frac{iEt}{\hbar}} \quad \text{— (6)}$$

where ψ is a position dependent function

Substitute (6) in the time-dependent form of schrodinger's equation :-

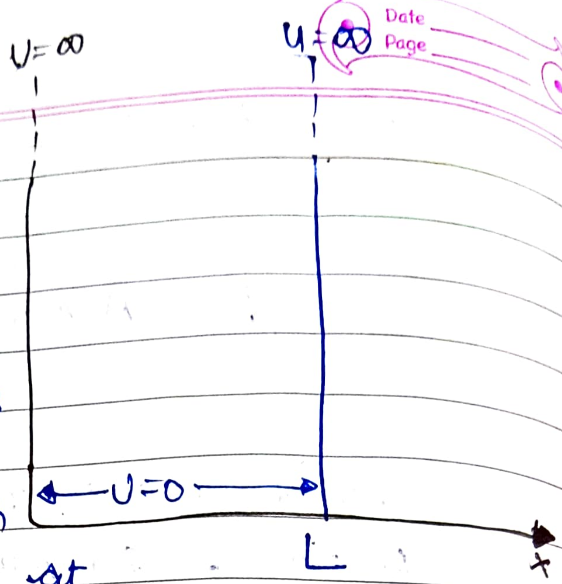
$$i\hbar\left(-\frac{iE}{\hbar}\right) e^{-\frac{iEt}{\hbar}} = -\frac{\hbar^2}{2m} e^{-\frac{iEt}{\hbar}} \frac{\partial^2\psi}{\partial x^2} + V e^{-\frac{iEt}{\hbar}}$$

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0} \quad \text{— (7)}$$

Steady-state form of the schrodinger's eqn.

Particle in a box

we consider the particle is trapped in a box with infinitely hardwalls



A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.

i) The particle is restricted to travelling along x-axis. b/w x=0 & x=L by infinitely hard walls.

ii) The particle does not lose energy when it collides with such wall so its total energy remains constant

iii) The potential energy (V) of particle is ∞ (infinite) in both ends of the box. it is considered to be zero (0)

iv) As the particle cannot have infinite energy it can't exist outside the box.

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Inside the box. (time Independent) Schrodinger's Equation can be written as ;

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar}E\psi = 0} \quad [U=0]$$

eq. $\frac{d^2y}{dx^2} + \alpha y = 0$

$y = ce^{mx}$

$m^2 + \alpha = 0$

$m = \pm i\sqrt{\alpha}$

$y = c_1 e^{i\sqrt{\alpha}x} + c_2 e^{-i\sqrt{\alpha}x}$

$y = c_1[\cos(\sqrt{\alpha}x) + i\sin(\sqrt{\alpha}x)] + c_2[\cos(\sqrt{\alpha}x) + i\sin(\sqrt{\alpha}x)]$

$y = A\cos(\sqrt{\alpha}x) + B\sin(\sqrt{\alpha}x)$

$$\boxed{\psi = A\sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x + B\cos\left(\frac{\sqrt{2mE}}{\hbar}\right)x}$$

$\psi = 0$ at $x = 0 \Rightarrow B = 0$

$\psi = 0$; at $x = L$

$A\sin\left\{\left(\frac{\sqrt{2mE}}{\hbar}\right)L\right\} = 0$

$\frac{\sqrt{2mE}}{\hbar} L = n\pi$, $n = 0, 1, 2, \ldots$

$$\boxed{E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}} \qquad n = 1, 2, 3, \ldots$$

Particle can have only above energy values inside a box

$$\psi = A \sin\left(\frac{\sqrt{2mE}}{\hbar} x\right)$$

substituting E from (9)

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

for each n, ψ & $\frac{\partial \psi}{\partial x}$ is single valued & continuous fn of x.

$$\int_0^L |\psi|^2 \, dx = 1$$

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

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

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

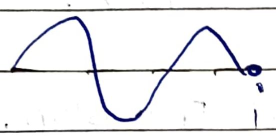
$$\frac{A^2}{2} L = 1$$

$$\boxed{A = \sqrt{\frac{2}{L}}}$$

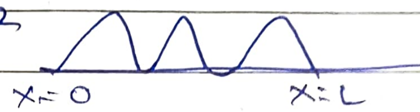
$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \ldots$$

Adding n to distinguish different states.

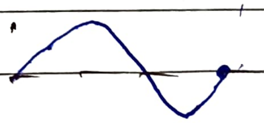
$n = 3$ ψ_3



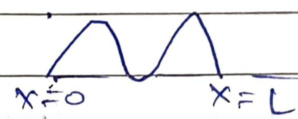
$|\psi_3|^2$



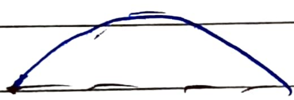
$n = 2$ ψ_2



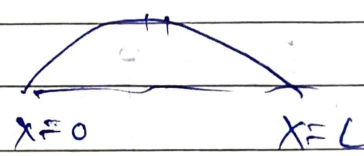
$|\psi_2|^2$



$n = 1$ ψ_1



$|\psi_1|^2$



ψ_n & $|\psi_n|^2$ are both zero at $x = 0$ & $x = L$

A particle in the lowest energy level of $n = 1$ is most likely to be in the middle of the box.
However a particle in next higher state $n = 2$ is never there.