Quantum Mechanics

de-Broglie Hypothesis of Matter Waves :-

We know that light exhibits the phenomenon of interference, diffraction, polarization, photoelectric effect, Compton effect, emission and absorption of radiation. The phenomenon of interference, diffraction and polarization can only be explained on the basis of wave theory of light. These phenomenon show that light possesses wave nature. On the other hand the phenomenon of photoelectric effect, compton effect and emission and absorption of radiation can only be explained on the basis of quantum theory of light according to which light is propagate in small packets of energy $h\nu$ (called photon) and behave like particle. Thus these phenomenon indicate that light possess particle nature. Thus we can say that light possesses dual nature.

de-Broglie proposed that the idea of dual nature should be extended to all micro particle associated both wave and corpuscular (particle) characteristics with every particle.

According to de-Broglie "All material particles in motion have a wave character associated." Accordingly particle such as electron, proton, neutron have a wave associated in motion with them. These waves are called Matter Waves or de-Broglie Waves

The wavelength λ associated with any particle of momentum p is given by (2)

$$\boxed{\lambda = \frac{h}{p}}$$

where h - planck's constant

p - momentum of the particle

Expression of de-Broglie wavelength:- The λ of matter wave should be same as that of e.m. radiation.

A wave of frequency ν is associated with the photon of energy $h\nu$

$$E = h\nu \quad \text{——— (I)}$$

According to Einstein's mass energy relation

$$E = mc^2 \quad \text{——— (II)}$$

$$\therefore m = \frac{E}{c^2} = \frac{h\nu}{c^2} \quad (\text{from equ. (I)})$$

$\therefore$ corresponding momentum of photon:

$$p = mc$$
$$= \frac{h\nu}{c^2} \times c$$
$$= \frac{h\nu}{c}$$
$$= \frac{h}{\lambda} \qquad \because \nu = c/\lambda$$

$$\therefore \boxed{\lambda = \frac{h}{p}} \quad \text{——— (III)}$$

OR

$$\boxed{\lambda = \frac{h}{mv}} \quad \text{——— (IV)}$$

where v is the velocity of a moving particle.

$\Rightarrow$ A material particle of mass m moving with a velocity v has a wave associated with it of wavelength λ.

If E_K is the kinetic energy of the material particle, then in non-relativistic case (i.e. when $v \ll c$)

$$P = \sqrt{2mE_K}$$

$$\boxed{\lambda = \frac{h}{\sqrt{2mE_K}}} \quad \text{—— (v)}$$

If a charged particle carrying charge q is accelerated through a potential difference V volts, then

$$E_K = qV$$

$$\therefore \boxed{\lambda = \frac{h}{\sqrt{2mqV}}} \quad \text{—— (vi)}$$

When a material particle like neutron is in thermal equilibrium at tempr T, then they possess Maxwellian distribution of velocities and so their average kinetic energy is given by

$$E_K = \frac{1}{2}mv_{rms}^2 = \frac{3}{2}KT$$

$$\therefore \boxed{\lambda = \frac{h}{\sqrt{3mKT}}} \quad \text{—— (vii)}$$

where $K \rightarrow$ Boltzmann's const $= 1.38 \times 10^{-23}$ J/K

de-Broglie wavelength for accelerated electron:- Let an e^- be accelerated by potential V, then

$$\lambda = \frac{h}{\sqrt{2mqV}}$$

for e^- $m = 9.1 \times 10^{-31}$ kg, $h = 6.6 \times 10^{-34}$ J.sec

$q = e = 1.6 \times 10^{-16}$ Coul.

$$\therefore \boxed{\lambda = \frac{12.27}{\sqrt{V}}} \ A^0.$$

Relativistic expression for de-Broglie wavelength ($v \approx c$) (4)

$\because \lambda = h/p$ $\quad \lambda = \frac{h}{p} \times \frac{c}{c}$

$$\lambda = \frac{hc}{pc} \quad \text{——— (1)}$$

$$\because E^2 = p^2c^2 + m_o^2c^4$$

$$\therefore pc = \sqrt{E^2 - m_o^2c^4}$$

$$\therefore \lambda = \frac{hc}{\sqrt{E^2 - m_o^2c^4}} = \frac{hc}{\sqrt{(K + m_oc^2)^2 - m_o^2c^4}}$$

where E = total energy = Kinetic energy + Rest mass energy

$$= K + m_oc^2$$

$$\therefore \lambda = \frac{hc}{\sqrt{(K + m_oc^2)^2 - m_o^2c^4}}$$

$$\boxed{\lambda = \frac{hc}{\sqrt{K(K + 2m_oc^2)}}}$$

Characteristics ~~Properties~~ of Matter Waves:-

1. de-Broglie waves guide the particles.
2. They are not electromagnetic waves, (Because the e.m. waves are produced from an accelerated charge particle while de-Broglie waves are also associated with neutral particle moving without acceleration.
3. Wave nature and particle nature never appears simultaneously.
4. Matter waves cannot be observed in our daily life but observed only in microscopic world.
5. de-Broglie wavelength of a wave associated with

moving light particle is greater than that of heavier particle

6. Wavelength of a slow particle is greater than that fast moving particle.

7. The velocity of matter wave is not constant but depends upon the velocity of material ~~wave~~ particle.

8. The wave nature of matter introduces an uncertainty in the position of the particle because a wave cannot be exactly at this or that point.

9. de-Broglie waves are called probability waves. The amplitude of the wave reveals the probability of finding a particle in space at a particular point. A large wave amplitude means a large probability to find the particle at that position.

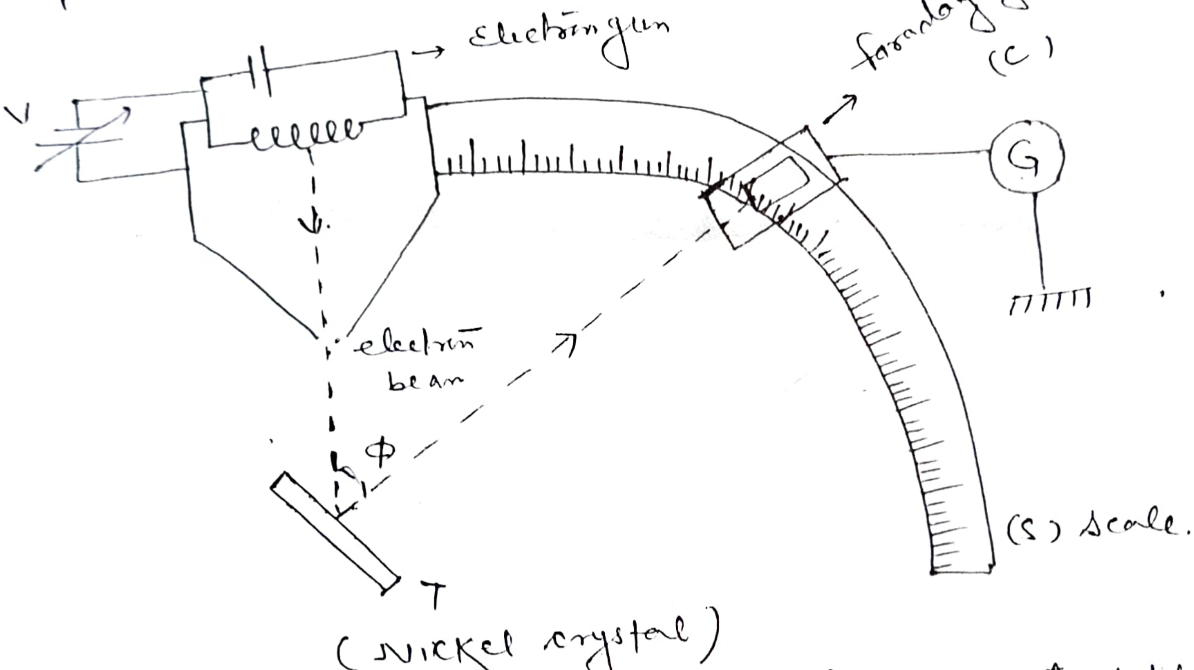
Matter waves cannot be observed. It is a wave model to describe and to study matter.

Davission & Germer's Experiment :-

The first proof of the existence of matter waves was obtained in 1927 by Davission and Germer the two American physicists. They also succeded in measuring the de-Broglie wavelength for moving particle.

Principle :- If material particles have a wave character associated. they are expected to show phenomenon such as interference, diffraction or polarization. In this experiment electrons beam suffers from the diffraction.

Experimental Arrangement and Working :- The filament in the electron gun is heated & electrons are emitted by thermionic emission and are accelerated by applying known potential difference. This beam comes out to electron gun in pencil form and made to fall on a Nickel crystal. The electrons are reflected from the crystal along different direction and the scattered electrons are collected in the faraday cylinder C. This cylinder is capable of rotating on a circular scale (S) to receive electrons in all directions. The cylinder is connected to the sensitive galvanometer. The current at each position in galvanometer is a measure of the electron intensity in the faraday cylinder at that position

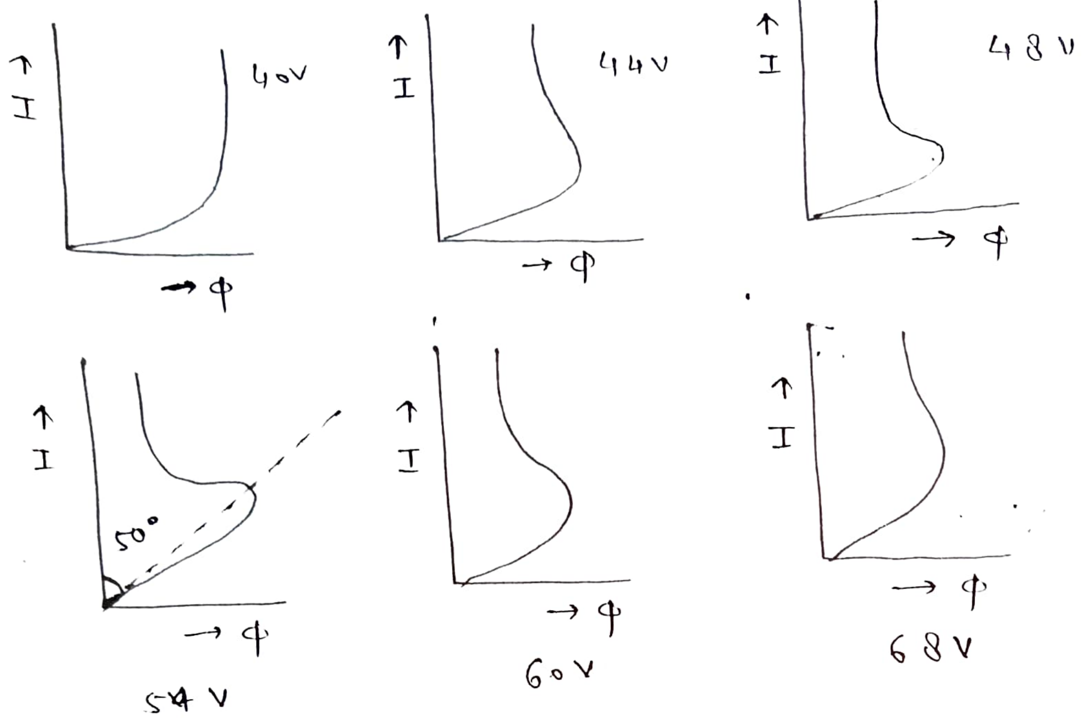


(Nickel crystal)

<u>Observations</u>:- Observations are taken for different potentials. The current is plotted against ϕ (angle between the incident beam and beam entering the cylinder). Instead of continuous variation, distinct maxima and minimas are observed. Bump begins to appear in the curve.

<u>Result</u>:- The most prominent of bump plot at $\phi = 50^\circ$ & $V = 54\ V$ shows association of wave nature with fast moving electron. This gives an evidence

that electrons are diffracted by the crystal & verifies
the existence of electron wave



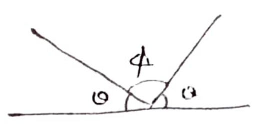
The wave length associated with an electron

$$\lambda = \frac{12.27}{\sqrt{V}} = \frac{12.27}{\sqrt{54}} = 1.67\,A^{0} \quad \text{—— (I)}$$

In this case nickel crystal acts as a plane diffraction grating with lattice spacing $0.91\,A^{0}$. Atoms ~~are~~ in the crystal are ~~arrangement~~ arranged in a regular manner.

Applying Bragg's diffraction equation

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



$$n = 1$$

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

$$2\theta + 50 = 180°$$

$$= 2 \times 0.91 \sin 65°$$

$$\theta = 65°$$

$$\lambda = 1.65\,A^{0} \quad \text{—— (II)}$$

The wavelength calculated by Bragg's equation is showing excellent agreement with wavelength calculated by de-Broglie hypothesis.

Conclusion:- The Davission - Germer experiment is an experimental evidence of matter wave where electrons are showing association of wave character.

Concept of a Wave Packet:-

According to de-Broglie hypothesis a material particle in motion is associated with a wave of wave length $\lambda = \frac{h}{mv}$. If E is the energy of the particle and ν the frequency of the wave then

$$E = h\nu$$

$$\text{or} \quad \nu = \frac{E}{h} \quad \text{—} (1)$$

according to Einstein's mass energy relation

$$E = mc^2$$

$$\nu = \cancel{\frac{E}{h}} \cdot \frac{mc^2}{h}$$

The de-Broglie wave velocity u is given by

$$u = \nu\lambda$$

$$= \frac{\cancel{m}c^2}{\cancel{h}} \cdot \frac{\cancel{h}}{\cancel{m}v}$$

$$\boxed{u = \frac{c^2}{v}}$$

where $v \to$ velocity of particle

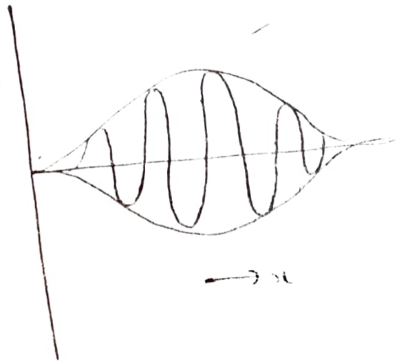
$v < c$

$u > c$

$\therefore u > c$

$\Rightarrow$ de-Broglie wave velocity must be greater than c ie speed of light. This is an unexpected result. According to this result, the de-Broglie wave associated with the particle would travel faster than the particle itself, thus leaving the particle far behind. Thus, it is clear that a material particle cannot be equivalent to a single wave train. Since we know that by theory of relativity, the speed of light is maximum speed that can be attained by a particle in nature. This difficulty was resolved by Schroodinger by postulating that a material particle in motion is equivalent to a wave packet rather than a single wave.

Wave Packet:- A wave packet is a group of waves, each with slightly different velocity and wavelength, with phases and amplitudes so chosen that they interface constructively over only a small region of space where the particle can be located, outside of which they produce destructive interference so that the amplitudes reduces to zero rapidly.



The velocity with which the wave packet moves forward in the medium is called group velocity (v_g)

$$\boxed{v_g = \frac{d\omega}{dK}}$$

The average velocity of an individual wave in the medium with which the wave packet is constructed is called phase velocity (or wave velocity) (v_p)

$$\boxed{v_p = \frac{\omega}{K}}$$

$u = \nu\lambda = 2\pi\nu \cdot \left(\frac{\lambda}{2\pi}\right) = \omega/k$.

Relation between Group velocity & particle velocity:-

de-Broglie assumption that the equation $E = \hbar\omega$ is valid for matter as well as for radiation, may be made plausible by computing the group velocity of a wave packet that represents a non-relativistic particle whose energy and momentum are connected by the relation

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

$E = \hbar\omega$

$E = p^2/2m$

$\frac{dE}{dp} = \frac{\cancel{2}p}{\cancel{2}m} \Rightarrow \frac{dE}{dp} = \frac{p}{m} = v$ — (I)

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

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

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

$p = \hbar \cdot k$

$\because E = \hbar\omega$ & $p = \hbar k$

$dE = \hbar\, d\omega$ $dp = \hbar\, dk$

$\therefore \frac{dE}{dp} = \frac{d\omega}{dk} = v_g$ — (II)

from eqn. (I) & (II)

$$\boxed{v_g = v}$$

ie group velocity of wave packet = velocity of a particle

For relativistic Particle –

$m_0 c \to$ Const

$$E^2 = p^2c^2 + m_0^2c^4$$

$$\cancel{2}E\, dE = \cancel{2}pc^2\, dp$$

$$\frac{dE}{dp} = \frac{pc^2}{E} \quad \text{— (1)}$$

$E = mc^2$ $p = mv$

$$\because E = \frac{m_0c^2}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \& \quad p = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$$

Subsitute the values of E & p in eqn.(1)

$$\frac{dE}{dp} = \frac{\cancel{m_0} v \cancel{c^2}}{\cancel{m_0}\cancel{c^2}} = v$$

$$\because v_g = \frac{dE}{dp} = v$$

$$\therefore \boxed{v_g = v}$$

Relation between 'c', v_g & v_p:-

$v_p = \omega/k$ — (1)

$\because \omega = 2\pi\nu = \frac{2\pi E}{h}$ & $k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$

$$v_p = \frac{E}{p} = \frac{mc^2}{m\,v_{particle}} = \frac{c^2}{v_{particle}}$$

$\because v_{particle} = v_g$

$$\therefore v_p = \frac{c^2}{v_g}$$

$$\therefore \boxed{v_g v_p = c^2}$$

(Non-Relativistic free Particle) Relation between v_g, v_p :-

$$\because \lambda = \frac{h}{m v_g}$$

$$\because E = \frac{1}{2} m v_g^2$$

$$E = h\nu \quad \Rightarrow \nu = \frac{E}{h} = \frac{\frac{1}{2} m v_g^2}{h}$$

$\therefore$ phase velocity is given by $v_p = \nu\lambda$

$$= \frac{\frac{1}{2}\cancel{m} v_g^{\cancel{2}}}{\cancel{h}} \times \frac{\cancel{h}}{\cancel{m} v_g}$$

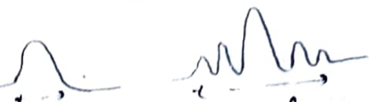
$$\boxed{v_p = \frac{v_g}{2}}$$

phase velocity $= \frac{1}{2}$ (group velocity)

Heisenberg's Uncertainty Principle :- This principle is a direct consequence of the dual nature of matter. According to classical Mechanics a moving particle has a definite momentum and occupies a definite position in space and it is possible to determine both its Position and velocity (or momentum), but it does not describe satisfactorily the behaviour of the particle of atomic dimensions.

In quantum mechanics a moving particle is describe

by a wave packet and moves with velocity. Particle (12)
may be found anywhere within the wave packet.
If we consider a small wave-packet, the position of the particle becomes almost certain, but the velocity of the particle become quite uncertain. On the other hand, if we consider a very large wave-packet, the position becomes uncertain and velocity (or momentum) of the particle become certain.



Hence, it is impossible to determine simultaneously both the position and momentum (or velocity) of a particle with accuracy."

" The product of uncertainties in determining the position and momentum of a particle at the same instant is of the order of $\hbar$."

$$\boxed{\Delta x . \Delta p \geq \hbar}$$

where $\hbar = h/2\pi$

Δx — uncertainty in position

Δp — " " momentum.

Similarly, Uncertainty relation for energy and time

$$\boxed{\Delta E . \Delta t \geq \hbar}$$

ΔE – Uncertainty in energy. Δt → Uncertainty in time.

for angular position and angular momentum

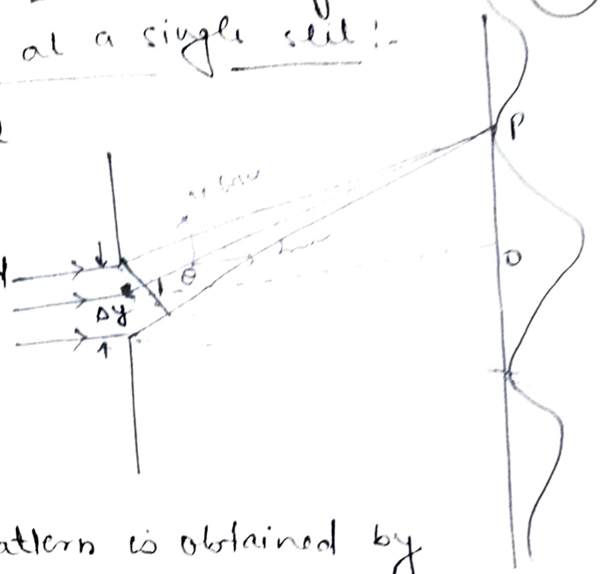
$$\boxed{\Delta \phi . \Delta J \geq \hbar}$$

$\Delta \phi$ → Uncertainty in angular position

ΔJ → " " " momentum.

Experimental Illustration of Uncertainty Principle

Diffraction of electron beam at a single slit :-



A parallel beam of $\bar{e}$s fall normally on a single slit of width Δy. Electrons get diffracted after passing through the slit & a diffraction pattern is obtained on the screen.

The first minima of the pattern is obtained by

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

$$\Delta y \sin\theta = \lambda$$

$$\therefore \Delta y = \lambda / \sin\theta \quad \text{—— (1)}$$

Initially the electrons are moving along x-axis & has zero momentum along y-axis. After passing through the slit electron deviate from their original path the acquire an additional component of momentum along y-axis ($P\sin\theta$). As the electron may be anywhere within the pattern from angle $-\theta$ to $+\theta$. So the uncertainty in the y-component of momentum of the electron.

$$\Delta P_y = P\sin\theta - (-P\sin\theta)$$

$$= 2P\sin\theta$$

$$= 2\frac{h}{\lambda}\sin\theta \quad \text{—— (11)}$$

$$\therefore \Delta y \cdot \Delta P_y = \frac{\cancel{\lambda}}{\cancel{\sin\theta}} \cdot \frac{2h}{\cancel{\lambda}} \cdot \cancel{\sin\theta}$$

$$= 2h / 4\pi$$

$$\boxed{\Delta y \cdot \Delta P_y \geq \hbar}$$

i.e. the product of uncertainty in determining in position and the momentum simultaneously is always > $\hbar$, which is Heisenberg's Uncertainty Principle.

Application of Uncertainty Principle :-

(i) The non-existence of the electrons in the nucleus :-

The radius of the nucleus of any atom is $\simeq 10^{-14}$ m

So, if an e^- is confined within nucleus, the uncertainty in its position must be greater than $\Delta q = 2 \times 10^{-14}$ m

According to uncertainty Principle

$$\Delta q \Delta p \simeq \hbar$$

$$\Delta p \simeq \hbar / \Delta q = \frac{1.055 \times 10^{-34}}{2 \times 10^{-14}}$$

$$= 5.275 \times 10^{-21} \text{ kg.m/sec.}$$

this is uncertainty in momentum of the $\bar{e}$ the momentum of $\bar{e}$ must be at least Comparable with its magnitude.

The K.E of the $\bar{e}$ of mass m is given by

$$K.E = P^2/2m = \frac{(5.275 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31}} \text{ J}$$

$$= 97 \text{ MeV}$$

If the electrons exist inside the nucleus, their K.E. must be of the order of 97 MeV. But experimental observations show that no e^- in the atom Possesses energy greater than 4 MeV. Clearly the interference is that the electrons donot exists in the nucleus.

(ii) Radius of Bohr's first orbit $r = \dfrac{h^2 \epsilon_0}{m Z e^2 \pi}$

(iii) Ground state Energy of H-atom

$$E_n = \frac{-Rhc}{n^2}$$

Do your self

(i) Minimum energy of a harmonic Oscillator :-

Let a particle of mass m execute simple harmonic motion along x-axis.

The total energy of the particle

$$E = K.E + P.E$$

$$E = \frac{P^2}{2m} + \frac{1}{2}Kx^2 \quad \text{— (1)}$$

The uncertainty in position of particle $= \Delta x$.

" " momentum " $= \Delta P$

from Heisenberg's Uncertainty Principle

$$\Delta x . \Delta P \simeq \hbar/2$$

$$\therefore \Delta P = \frac{\hbar}{2\Delta x}$$

$$E = \left(\frac{\hbar}{2\Delta x}\right)^2 \frac{1}{2m} + \frac{1}{2}K(\Delta x)^2$$

$$= \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}K(\Delta x)^2 \quad \text{— (ii)}$$

for minimum energy $\frac{\partial E}{\partial(\Delta x)} = 0$

$$\frac{\hbar^2}{8m}(-2)(\Delta x)^{-3} + K(\Delta x) = 0$$

$$-\frac{\hbar^2}{4m(\Delta x)^3} + K(\Delta x) = 0$$

$$\Delta x = \left(\frac{\hbar^2}{4mK}\right)^{1/4}$$

Substitute this value in equ. (ii)

$$E = \frac{\hbar^2}{8m}\left(\frac{4mK}{\hbar^2}\right)^{1/2} + \frac{1}{2}K\left(\frac{\hbar^2}{4mK}\right)^{1/2}$$

$$= \frac{\hbar}{4}\sqrt{\frac{K}{m}} + \frac{\hbar}{4}\sqrt{\frac{K}{m}}.$$

$$E = \frac{1}{2} \hbar \sqrt{\frac{K}{m}}$$

$\therefore \sqrt{\frac{K}{m}} = \omega$ = angular frequency

$$\therefore \boxed{E_{min} = \frac{1}{2} \hbar \omega}$$

*** The wave function ψ itself has no physical significance. ψ cannot be determined experimentally. This represents the probability, meaning something must lie between 0 & 1. In between probability for ex. 0.1 or 0.2 means there is 10% or 20% chance of finding the object. But the amplitude of a wave function can be negative as well as positive. But negative probability has no meaning.

Ex. Write two examples of wave functions which are (a) acceptable (b) not acceptable.

Solu. (a) Acceptable - $\sin x$, $\cos x$. because these are continuous wave-functions and their values lie between +1 and -1

(b) Not acceptable.-

$\frac{1}{x}$, x^n.

$\therefore$ at $x \rightarrow$ $\frac{1}{x} \rightarrow \infty$

& $x^n \longrightarrow \pm\infty$ for $x = \pm\infty$.

Wave function ψ

If a moving particle has wave properties, there should be a wave equation to describe the motion of the particle. Schrodinger gave a equation for this which is the fundamental equation of wave mechanics. The wave function $\psi(x,t)$ which is a solution to the Schrodiger equation undergoes periodic changes and give information about the particle within the wave packet at position $\vec{x}$ and at time t. Schrodinger himself attempted the physical interpretation of ψ in terms of charge density.

"If ψ is amplitude of the matter wave at any point in space, then the no. of material particles per unit volume i.e particle density must be $\propto \psi^2$. The square of absolute value of ψ i.e $|\psi|^2$ is a measure of particle density." Usually $\psi^* \psi$ is written instead of $|\psi|^2$ where ψ^* is a complex conjugate of ψ.

$|\psi|^2 \rightarrow$ represents the probability density of the particle in the state ψ. ***

Normalized Wave function :- The particle is certainly some where in the space, hence the total probability of finding the particle in the whole space is unity

i.e $$\int_{-\infty}^{\infty} |\psi|^2 \, d\tau = 1$$

wave function obeying this equation is called normalized wave function.

Orthogonal wave function :- If the two wave functions ψ_m and ψ_n are such that $\int \psi_m^* \psi_n \, d\tau = 0$

or $\int \psi_n^* \psi_m \, d\tau = 0 \qquad m \neq n.$

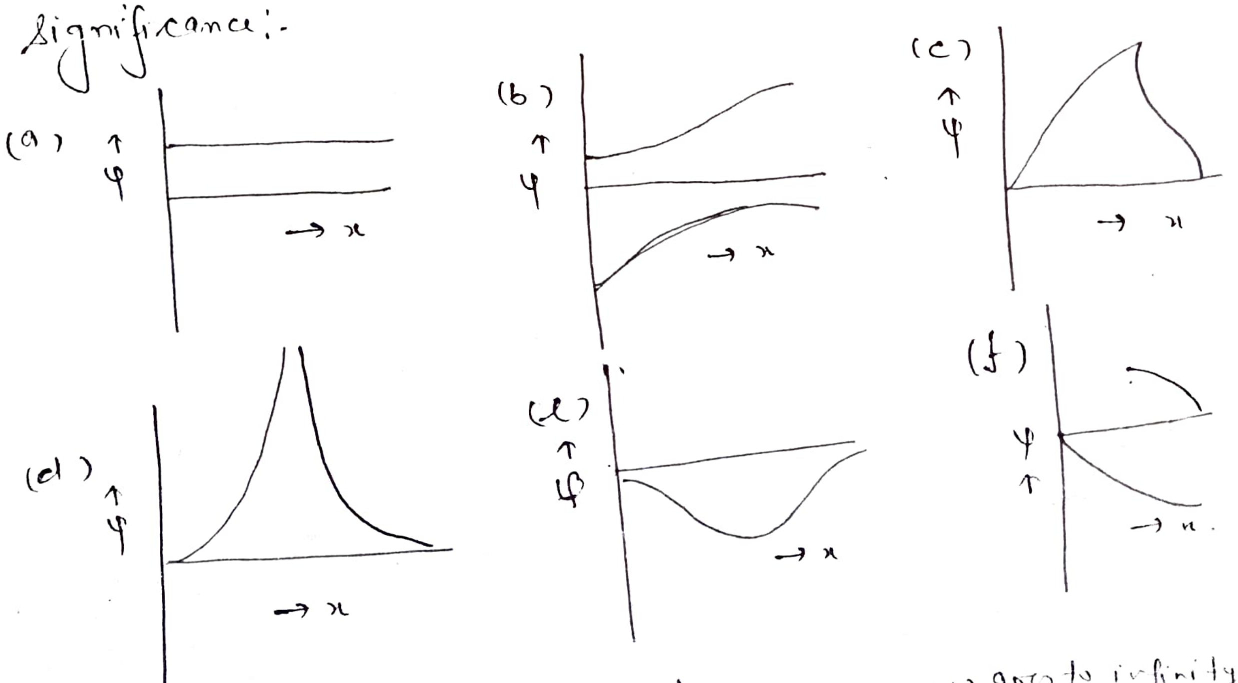
then the wave function ψ_m & ψ_n are said to be orthogonal to each other represents the orthogonality condition.

Properties of wave function

1. It must be normalized
2. It must be finite everywhere because if ψ is infinite than means infinite probability of finding the particle which is impossible
3. It must be single-valued because if ψ has more than one value means more than one probability of finding the particle, which is impossible
4. It must be continuous and have a continuous first derivative everywhere.

These requirements must be satisfied by an acceptable wave function.

Q. which of the wave functions cannot have physical significance:-



Ans. (b) double values (c) discontinuous derivative (d) goes to infinity (f) discontinuity

Schrodinger Wave Equation:-

In wave mechanics a material particle is equivalent to a wave packet. To locate the position of the particle within the wave packet. Schrodinger gave an equation which we shall derive.

(1) Time independent Schrodinger Equation:-

Consider a system of stationary waves associated with a moving particle. Let $\psi(\vec{r}, t)$ be wave displacement for the de-Broglie wave at any location $\vec{r}$ at time t.

Then the differential equation of the wave motion in 3-D in accordance with Maxwell's wave equation can be written as

$$\nabla^2 \psi = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2}$$

$$\text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2} \qquad \text{—— (1)}$$

where $u \rightarrow$ wave velocity.

The solution of equ. (1)

$$\psi(\vec{r}, t) = \psi_0 e^{-i\omega t} \qquad \text{—— (11)}$$

where ψ_0 is the amplitude at the point considered. It is a function of position $\vec{r}$ and not of time 't'

Diff. w.r.t 't'

$$\frac{\partial \psi}{\partial t} = -i\omega \psi(\vec{r}, t)$$

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

from equ. (1) $\quad \frac{\partial^2 \psi}{\partial x^2} + \cancel{\frac{\partial^2 \psi}{\partial y^2}} + \cancel{\frac{\partial^2 \psi}{\partial z^2}} = -\frac{\omega^2}{u^2} \psi(\vec{r}, t)$

$$\because \quad \omega = 2\pi\nu = \frac{2\pi u}{\lambda}$$

$$\frac{\omega}{u} = \frac{2\pi}{\lambda}$$

$$\frac{\partial^2\psi}{\partial x^2} + \cancel{\frac{\partial^2\psi}{\partial y^2}} + \cancel{\frac{\partial^2\psi}{\partial z^2}} = -\frac{4\pi^2}{\lambda^2}\psi$$

or

$$\nabla^2\psi = -\frac{4\pi^2}{\lambda^2}\psi \quad \text{—— (III)}$$

for introducing the concept of wave mechanics.

$$\lambda = \frac{h}{mv}$$

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0 \quad \text{—— (IV)}$$

If E & V are the total and Potential energies of the particle respectively, then

$$K.E = E - V$$

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

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

$$\therefore \quad \nabla^2\psi + \frac{4\pi^2}{h^2}\cdot 2m(E-V)\psi = 0$$

$$\boxed{\nabla^2\psi + \frac{8m\pi^2}{h^2}(E-V)\psi = 0} \quad \text{—— (V)}$$

This is the time independent Schrodinger wave equation.

$$\because \quad \hbar = \frac{h}{2\pi}$$

$$\therefore \quad \boxed{\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0} \quad \text{—— (VI)}$$

For a free particle, $V = 0$

$$\boxed{\nabla^2 \psi + \frac{2m}{\hbar^2} E\psi = 0} \quad \text{——— (VII)}$$

(II) Time dependent Schrodinger Equation :-

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

$$= -i(2\pi\nu)\psi$$

$$= -2\pi\nu i \psi$$

$$= \frac{-2\pi E i}{h}\psi \times \frac{i}{i}$$

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

$$\therefore E\psi = i\hbar\frac{\partial \psi}{\partial t} \quad \text{——— (VIII)}$$

Substitute this value in eqn (VI)

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial \psi}{\partial t} - V\psi\right] = 0$$

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

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

$$\boxed{\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial \psi}{\partial t}} \quad \text{——— (IX)}$$

or $\boxed{H\psi = E\psi}$ ——— (X)

where $H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right) \rightarrow$ hamiltonian operator.

$E = i\hbar\, \partial/\partial t \longrightarrow$ Energy operator.

This form describe the motion of a non-relativistic material particle.

Operator:- An operator is a rule by means of which a given function is changed into another function.

The measurable quantities like energy, momentum, position etc are called observable. Each observable has a definite operator associated with each.

1. <u>Energy operator:-</u>

$$\therefore H\psi = E\psi$$

$$\therefore E_{op} = i\hbar\,\partial/\partial t$$

$$H\psi = E\psi$$

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

2. <u>Momentum operator:-</u>

$$H = E = K.E. + P.E.$$

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

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

$$p^2 = \frac{\hbar^2}{i^2}\nabla^2$$

$$\boxed{P_{op} = \frac{\hbar}{i}\nabla}$$

$$(P_x)_{op} = \frac{\hbar}{i}\,\partial/\partial x$$

$$(P_y)_{op} = \frac{\hbar}{i}\,\partial/\partial y$$

$$(P_z)_{op} = \frac{\hbar}{i}\,\partial/\partial z$$

3. <u>Kinetic Energy Operator</u> -

$$K.E. = -\frac{\hbar^2}{2m}\nabla^2$$

$$(T)_{op} = -\frac{\hbar^2}{2m}\nabla^2$$

4. Velocity Operator :-

$$K.E = -\frac{\hbar^2}{2m}\nabla^2 = \frac{1}{2}mv^2$$

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

$$v_{op}^2 = +\frac{\hbar^2}{i^2 m^2}\nabla^2$$

$$\therefore \boxed{V_{op} = \frac{\hbar}{im}\nabla}$$

Postulates of Quantum Mechanics :-

The mathematical formulation of Quantum mechanics is based on the following postulates -

1. There is a wavefunction associated with every physical state of the system. The wave function is a function of all position coordinates & time and contains information about the properties of the system.

2. The Superposition principle is valid for functions representing physical states as

$$\psi = \sum_i c_i\psi_i = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + \cdots c_i\psi_i.$$

where $c_i \rightarrow$ expansion co-efficients.

3. Every physical observable is associated with an operator that may be energy, momentum, position etc.

4. The measurements of an observable can provide the values (λ) given by the equation

$$\hat{P}\psi = \lambda\psi$$

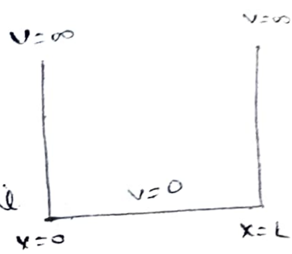
This is called eigen value equation and the values 'λ' are called eigen values.

5. If an experiment is performed which is capable of determining wether one or more alternative is actually taken the probability of an event is the sum of the probability for alternative $P = P_1 + P_2$

Application of Schrodinger Equation :-

Schrodinger Eqn. is useful for investigating various quantum mechanical problems. With the help of this equation and boundary conditions, the expression for ~~expression for~~ the wavefunction is obtained. Then the probability of finding the particle is calculated by using the wave function.

1. Particle in a Box :-



Consider a particle within a 1-D box extending from $x=0$ to $x=L$, then Potential function is

$$V=0 \quad \text{for} \quad 0<x<L$$
$$V=\infty \quad \text{for} \quad x<0 \ \& \ x>L$$

The particle is trapped in a box with infinitely hard box walls means the particle does not loose energy when it collides with walls, i.e its total energy remains constant.

Schrodinger equation for the particle inside the box can be written as-

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + K^2 \psi = 0 \quad \text{———— (i)}$$

where $K^2 = \frac{8\pi^2 m}{h^2} E$

The general solution of this equation is

$$\psi(x) = A \sin Kx + B \cos Kx \quad \text{—— (ii)}$$

where A & B are constant.

Applying the boundary condition $\psi(x)=0$ at $x=0$, which means the probability of finding particle at the wall $x=0$ is zero. we obtained

$$A \sin 0 + B \cos 0 = 0$$

$$\Rightarrow B = 0$$

$$\therefore \psi(x) = A \sin kx.$$

at $x = L$, $\psi(x) = 0$

$$0 = A \sin kL$$

Sin nπ = A sin kL

$$kL = n\pi$$

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

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

$$\therefore \psi(x) = A \sin \frac{n\pi}{L} \cdot x$$

using normalized condition

$$\int_0^L |\psi(x)|^2 dx = 1$$

$$\int_0^L \left| A \sin \frac{n\pi}{L} x \right|^2 dx = 1$$

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

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

$2\sin^2 x = 1 - \cos 2x$

$$\frac{A^2}{2} \int_0^L dx = 1$$

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

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

$$\boxed{\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x}$$

$$\because \cancel{k^2 = \frac{2m}{\hbar^2}E \because \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}} \qquad \because k^2 = \frac{8\pi^2 m}{h^2}E$$

or
$$\frac{8\pi^2 m E}{h^2} = \frac{n^2\pi^2}{L^2}$$

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

where $n = 1, 2, 3 \ldots$

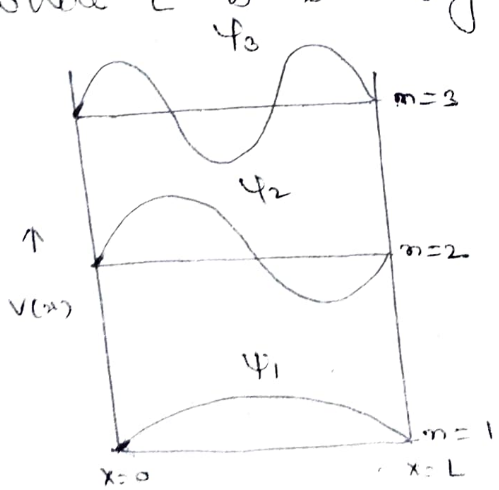
$$\therefore \boxed{E_n = \frac{n^2 h^2}{8mL^2}}$$

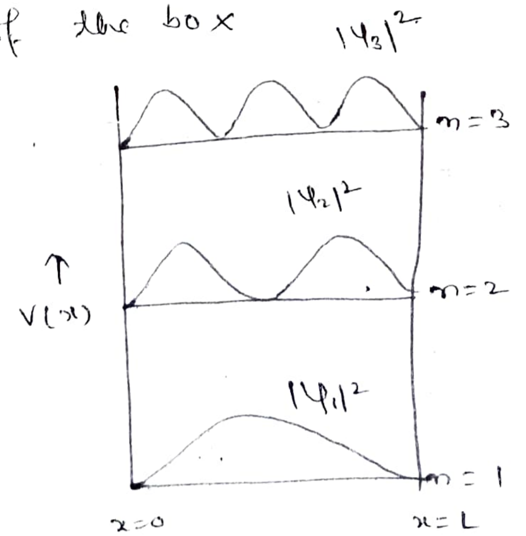
Thus, it can be concluded that in an infinite potential well the particle cannot have an arbitrary energy. but can take only certain discrete energy values corresponding $n = 1, 2, 3, \ldots$ These are called the eigen values of the particle in the well. The corresponding wave function ψ to each eigen values are called Eigen functions.

The normalised wave function for 1D.

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x.$$

where L is the length of the box





A particle in the lowest energy level ($n=1$) is most likely to be in the middle of the box while a particle in the next higher state ($n=2$) is never there. (14)

Zero Point Energy :- The quantum state with lowest ($n=1$) is called ground state while states with higher n ($=2,3,\dots$) are called excited states.

For a particle in 1-D box of length 'L', the energy is given by $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$

If $n=1$ then $E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$

This is the energy of the ground state as well as the minimum energy of the particle. or we can say, even when the temperature of the box is reduced to 0K the total energy will still be E_1 and not be zero, so, it is called zero point energy of the particle

If the energy of the particle is zero, then it cannot exist in the box, as we know that-

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n x \pi}{L} \quad \text{for } 0<x<L$$

$$E_n(x) = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

If $E=0$, then $n=0 \Rightarrow \psi_0(x) = 0$ for all values of x means probability of finding the particle which is $|\psi(x)|^2$ will also be zero. This means particle does not exist anywhere in the box, which is not true. Hence $n=0$ state is not allowed.

Expectation values : It is average of results of a large no. of measurements on systems.

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

If wave function is normalized, then $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

expectation value $\langle x \rangle = \int_{-\infty}^{\infty} x|\psi|^2 dx$

The expectation values of quantities involving operators.

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

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

$$\langle E \rangle = \int_{-\infty}^{\infty} \psi^* (i\hbar) \frac{\partial \psi}{\partial t} \, dx$$

Ex. Find expectation value of $\hat{p}$ for the wave function $\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi x}{L}$ $\quad 0 < x < L$

$\psi(x) = 0 \quad x > L$

$$\langle p \rangle = \int \psi^* \hat{p} \psi \, dx$$

$$\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$\langle p \rangle = \int \psi^* \frac{\hbar}{i} \frac{\partial \psi}{\partial x} dx$$

$$= \int \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi x}{L} \left\{ \frac{\hbar}{i} \frac{\partial}{\partial x} \left(\frac{2}{L}\right)^{1/2} \sin\frac{\pi x}{L} \right\} dx$$

$$= \left(\frac{2}{L}\right) \frac{\hbar}{i} \cdot \frac{\pi}{L} \int_0^L \sin\frac{\pi x}{L} \cos\frac{\pi x}{L} dx.$$

$$= \frac{\hbar \pi}{i L^2} \int_0^L \sin\frac{2\pi x}{L} dx$$

$$= \frac{\hbar \cancel{\pi}}{i L^{\cancel{2}}} \left[\frac{\cos\frac{2\pi x}{L}}{\frac{2\cancel{\pi}}{\cancel{L}}} \right]_0^L$$

$$= -\frac{\hbar}{i L 2} \left[\cos 2\pi - \cos 0 \right]$$

$\langle P \rangle = 0$