Unit - II

Introduction to Quantum Mechanics

Free electron theory of Metals

Free e⁻ theory is developed in three stages :

→ ① classical free e⁻ theory :-

Drude & Lorentz developed this theory in 1900. According to this theory e⁻s obey laws of classical mechanics.

→ ② Quantum free e⁻ theory :-

Sommerfeld developed this theory in 1928. According to this theory e⁻s obey laws of quantum mechanics.

→ ③. Zone theory :-

Bloch developed this theory in 1928. According to this theory e⁻s move in periodic potential.

→ Classical free $e^{\ominus}$ theory:-

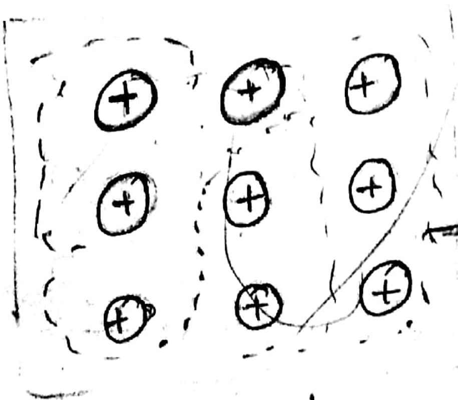
Drude & Lorentz developed this theory in 1900. This theory depends on the following postulates.

→ Metals consists atoms. with in this atom $e^{\ominus}$s are revolve around the nucleus.

→ All the valence $e^{\ominus}$s are free $e^{\ominus}$s. These $e^{\ominus}$s move freely throughout the volume of the metal.

→ These free $e^{\ominus}$s make collisions with positive metal ions but these collisions are elastic collisions..

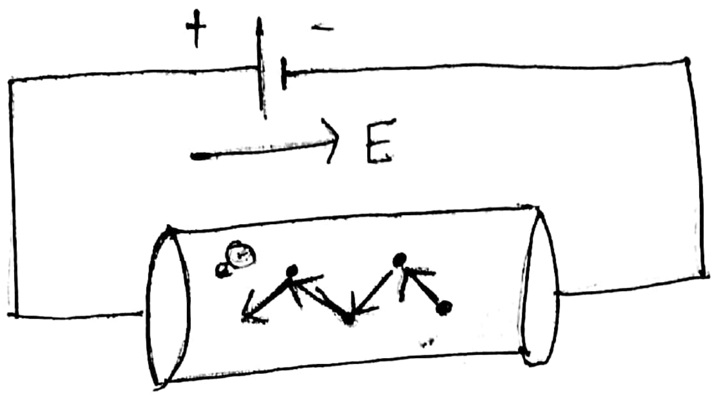
→ According to this theory $e^{\ominus}$s are moving in uniform potential field.



free $e^{\ominus}$ gas.

Fig:- metal.

when electric field(E) is applied on the metal, free $e^{\ominus}$s move in opposite direction to the applied electric field(E) as shown in the following figure:



According to Lorentz the force which is acting on the ~~free~~ $e^{\ominus}$s due to the applied field is $[\because F = qE]$

$$F_1 = -eE \quad — (1)$$

According to Newton's Law, the frictional force is

$$F_2 = ma$$

$$\therefore F_2 = \frac{m v_d}{\tau} \quad — (2) \qquad \because \left[a = \frac{v_d}{\tau}\right]$$

at steady state, $F_1 = F_2$
(At equilibrium)

$$\therefore \frac{mv_d}{\tau} = -eE$$

$$\boxed{v_d = \frac{-e\tau}{m} \cdot E} \quad \text{---} (4)$$

where $v_d \rightarrow$ drift velocity.

Drift velocity:-

In the presence of electrical field, in addition to the random velocity e⁻s gain an extra velocity due to applied electric field. This velocity is known as "drift velocity (v_d)".

current density (J):-

(The amount of charge crossing a unit area per unit time is called as current density (J) :)

charge ve

$$J = (-ne) \cdot v_d$$

$$= (-ne) \times \left(-\frac{e\tau}{m} E\right) \quad \because \left[\text{from eqn } (4)\right.$$

$$J = \frac{ne^2\tau}{m} E \quad \text{--- (5)}$$

$\because$

$$J \propto E$$

$$J = \sigma E \quad \text{--- (6)}$$

by comparing eqn (5) & (6), we can get Conductivity (σ) is

$$\boxed{\sigma = \frac{ne^2\tau}{m}}$$

Mobility (μ) :-

The steady state drift velocity per unit electrical field is known as mobility.

$$\boxed{\mu = \frac{\langle v_d \rangle}{E}}$$

$$\mu = \frac{\frac{e\tau}{m}\cancel{E}}{\cancel{E}} \quad \because \text{[from eq}^n \text{ (4)]}$$

$$\boxed{\mu = \frac{e\tau}{m}}$$

$$\therefore \sigma = \frac{ne^2\tau}{m}$$

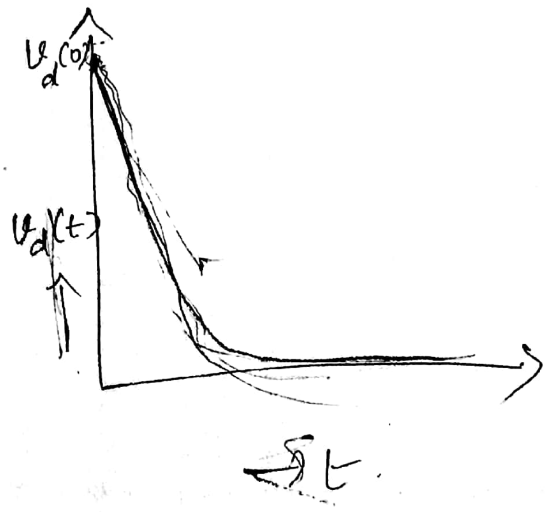
$$\sigma = ne \cdot \frac{e\tau}{m}$$

$$\boxed{\sigma = ne\mu}$$

Relaxation time (τ) :-

The time taken by the drift velocity to decrease '$\frac{1}{e}$' times of its initial value is known as "relaxation time" (τ).

$$\boxed{v_d(t) = v_d(0) \exp\left(\frac{-t}{\tau}\right)}$$



when $t = \tau$

$$v_d(t) = v_d(0) \exp\left(-\frac{t}{t}\right)$$

$$= v_d(0) \exp(-1)$$

$$\boxed{v_d(t) = \frac{v_d(0)}{e}}$$

Mean free path :-

The average distance travelled by the electron between two successive collisions is known as "mean free path (λ)".

Mean free time :-

The average time taken by the $e^{\ominus}$ ~~bet~~ for two successive collisions is known as mean free time.

At steady state relaxation time is equal to mean free time.

Success of classical Theory :-

→ 1). This theory verifies Ohm's Law.

→ 2). It explained thermal conductivity and electrical conductivity of metals.

3) It verifies Wiedemann-Franz law.

i.e. $\boxed{\frac{K}{\sigma T} = \text{constant}}$

where $K \rightarrow$ Thermal conductivity

$\sigma \rightarrow$ electrical conductivity

4) It explained optical properties of metals.

Drawbacks of classical Theory:-

Classical theory has the following drawback

1) The electrical properties of semiconductors and insulators not explained

2) Photo electric effect, compton effect and Black body radiation could not explained.

3). According to this theory, the specific heat of the metal is 4.5R. But the practical specific heat value is 3R. (where $R \rightarrow$ universal Gas constant)

→ 4) The theoretical value of paramagnetic susceptibility (χ) is greater than the experimental value.

→ 5) Ferromagnetism could not explained

II). Quantum free $e^{\ominus}$ theory :-

During 1928, Sommerfeld developed this theory.

→ According to this theory, $e^{\ominus}$s obey the quantum laws.

→ Free $e^{\ominus}$s are moving in uniform potential (field) in the lattice.

→ 3) According to quantum mechanics, energy is discontinuous. The eigen values are

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}}$$ where $n = 1, 2, \ldots$

→ 4) quantum theory (Sommerfeld theory): successfully explained the electrical properties of metals.

→ 5) It failed to explain the electrical properties of semiconductors and Insulators.

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Planck's Black body - Radiation

• In 1901, planck derived a theoritical expression for the energy distribution of Black body on the basis of quantum theory.

According to planck's theory, Energy is emitted in the form of packets. These energy packets are also called as "Quantas" or "photons".

The energy of photon is

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

where $h \rightarrow$ planck's constant

$\nu \rightarrow$ frequency of photon.

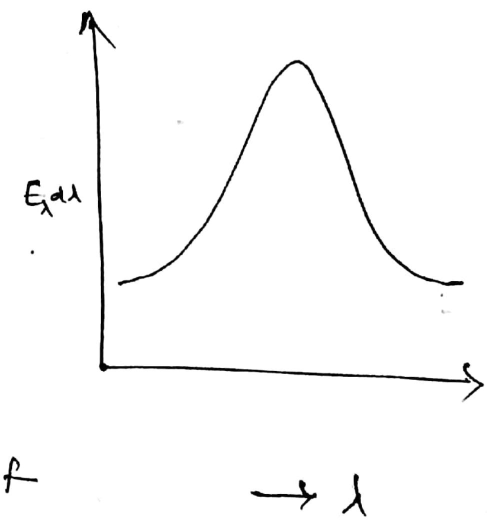
Assumptions:-

→ A Black body contains harmonic - oscillators of all possible frequencies.

→ The energy of each oscillator is quantised and it is given by

$E = nh\nu \quad \because (n = 0, 1, 2 \ldots$

→ The atomic oscillator can absorb or emit the energy in terms of $h\nu$ called quanta.



According to planck's, the equation for the energy - distribution of black body is

$$\boxed{E_\lambda \, d\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{1}{\exp\left(\frac{hc}{\lambda KT}\right) - 1} \, d\lambda}$$

This equation is valid for all range of wavelength of spectral distribution of black body Radiation.

Particle:- particle has mass and it is located at some point in the space. It can move from one place to another and it is discontinuous one.

A particle is specified by 1) mass (m), velocity (v), momentum (p) & energy ($K.E = \frac{1}{2}mv^2$).

Wave:- wave is continuous one and it spread out over a large region of space.

A wave is specified by its 1) wavelength (λ), 2) frequency (ν), 3) phase (ϕ) and 4) Amplitude (a) or Intensity ($I = a^2$).

de-Broglie Hypothesis - Matterwaves:-

In 1924, Louis de-Broglie made a suggestion that like radiation matter ~~wave~~ also exhibits dual nature. i.e; material particles like e^-s, protons and neutrons also exhibit wave properties.

A moving particle is associated with a wave is known as "Matterwave" and it's wavelength is given by

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

Derivation:-

According to planck's theory, the energy of photon is given by

$$E = h\nu = \frac{hc}{\lambda} \quad \text{--- (1)}$$

According to Einstein mass-Energy relation is

$$E = mc^2 \quad \text{--- (2)}$$

From eq^n 1 and 2,

$$mc^2 = \frac{hc}{\lambda}$$

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

- de Broglie applied this eq^n to material-particles. Thus, if a particle has a mass(m) and velocity (v), its momentum (p) is mv

∴ the wavelength of a particle is

$$\boxed{\lambda = \frac{h}{mv}} \quad (\text{or}) \quad \boxed{\lambda = \frac{h}{p}}$$

∴ This eq^n is called as de-Broglie's matter-wave equation.

→ <u>NOTE 1</u>: –

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

multiplying with 'm' on both sides.

$$mE = \frac{1}{2} m^2v^2$$

$$2mE = p^2$$

$$p = \sqrt{2mE}$$

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

$$\boxed{\lambda = \frac{h}{\sqrt{2mE}}}$$

Note (2) :-

If 'm_0' is rest mass and 'e' charge of the $e^{\ominus}$ and it is accelarated by 'V' potential or voltage then de-Broglie wave length eqn become

$$\lambda = \frac{h}{\sqrt{2m_0eV}}$$

$$\because \left\{ \begin{array}{l} E = qV \\ E = eV \end{array} \right.$$

$h = 6.625 \times 10^{-34}$, $e = 1.6 \times 10^{-19}$ c, $m_0 = 9.1 \times 10^{-31}$ kg.

Sub. these values in above eqn

$$\lambda = \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V}}$$

$$\boxed{\lambda = \frac{12.26}{\sqrt{V}} \, A^{\circ}}$$

Properties of Matter waves :-

→ ① Lighter particle consist large wave length

$$\lambda \propto \frac{1}{m}$$

→ ② Fast moving particle consist low-wave length

$$\lambda \propto \frac{1}{v}$$

if $v = \infty \Rightarrow \lambda = 0$.

→ ③ slow moving particle consist maximum wave length

if $v = 0 \Rightarrow \lambda = \infty$.

→ ④ These waves are not electromagnetic waves.

→ ⑤ Matter waves nature is depends on velocity of the particle.

→ ⑥ The wavelength of the matter waves ~~are~~ is independent of charge of the particle.

→ ⑦ Matter waves do not exhibit both properties (particle nature & wave nature) simultaneously.

→ ⑧. The wave velocity of matter wave can be greater than the velocity of light.

Davisson - Germer Experiment :- 1

In 1927, Davisson and Germer for the first time proved the wave nature of $e^{\ominus}s$.

Based on the concept of wave nature of matter. fast moving $e^{\ominus}s$ behave like waves. Hence accelerated $e^{\ominus}$ beam can be used for diffraction studies in crystals.

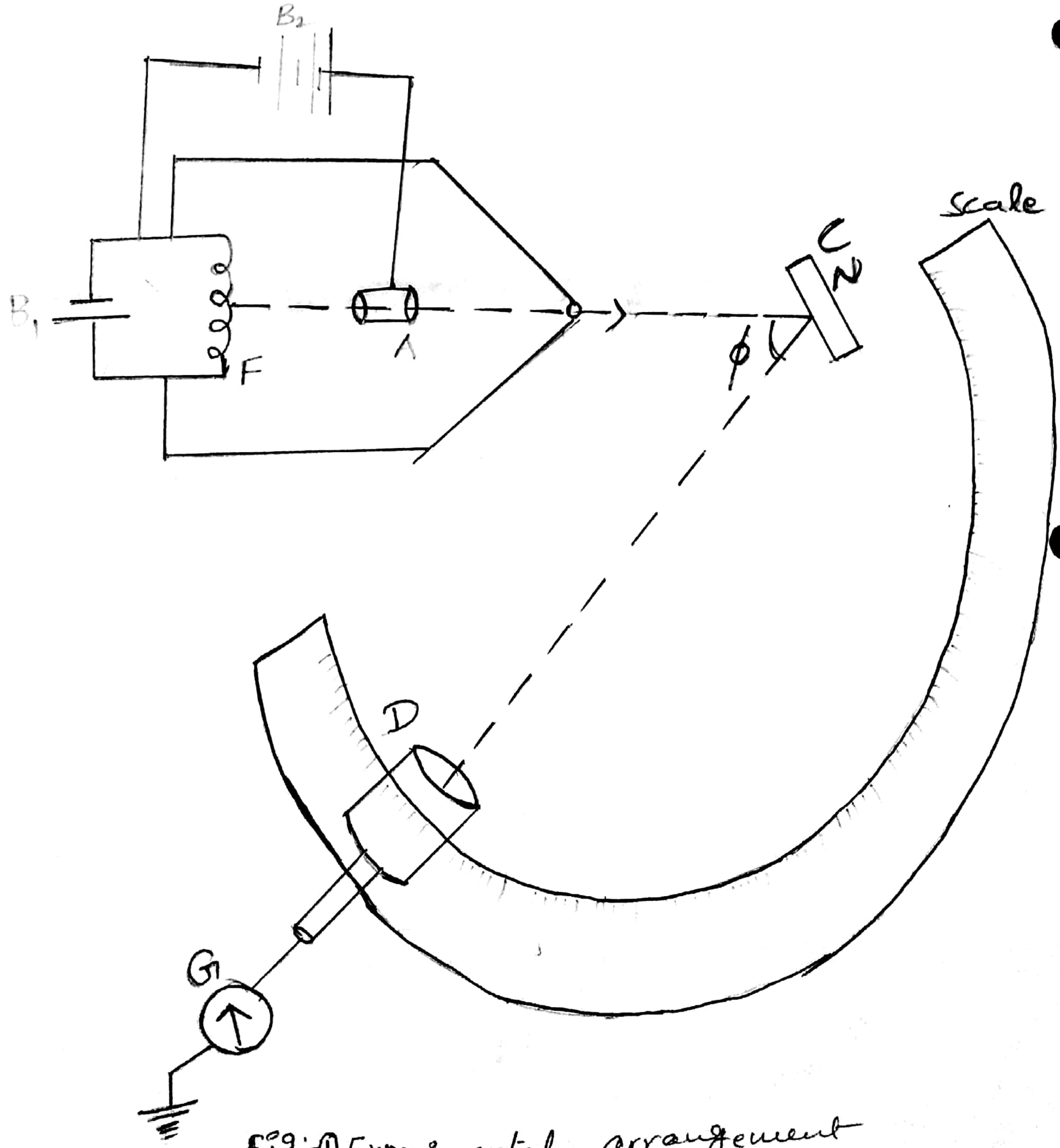


Fig:-①. Experimental arrangement

Fig①. shows the Davisson-Germer experimental arrangement. The $e^{\ominus}$s from a hot filament 'F' are accelerated through a suitable voltage. The narrow beam of $e^{\ominus}$s incident normally on the surface of a nickel crystal (N). The $e^{\ominus}$s are scattered in all directions by the atoms of Ni-crystal. The intensity of $e^{\ominus}$ beam is measured by the detector (D). This $e^{\ominus}$ detector is so arranged that it can be rotated around the Ni-crystal on the circular scale. The detector is connected to the galvanometer. The deflection of the galvanometer (G) is directly proportional to the intensity of beam entering the detector.

The graph drawn between scattering-angle (ϕ) and no. of scattered $e^{\ominus}$s is shown in following figure②.

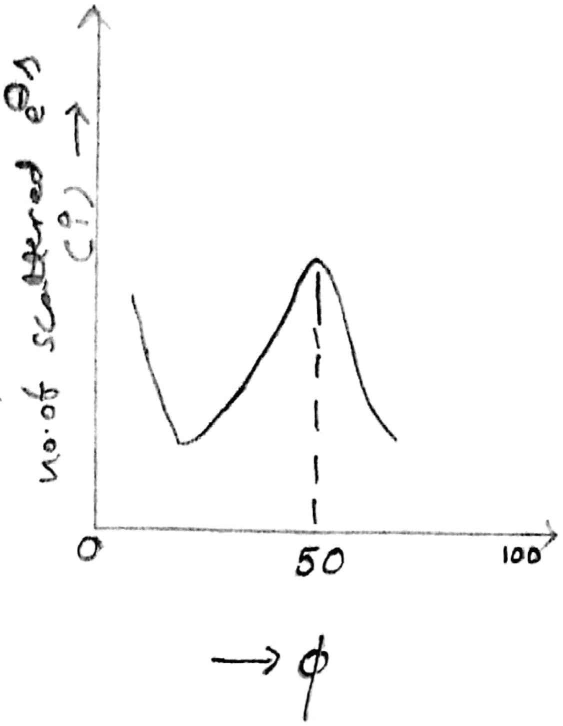


Fig ②. Scattering Curve.

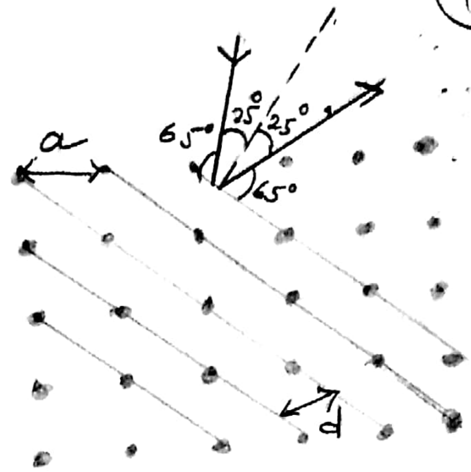


Fig ③ Determination of angle 'ϕ'.

The atomic rows of Ni-crystal act like the rulings of a diffraction grating. The crystal is producing the first order Bragg reflection at an angle $\theta = 90 - \phi/2$, $V = 54$ volt and $\phi = 50°$.

Applying Bragg's Law

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

for first order $n = 1$

for Ni-crystal $d = 0.909 \times 10^{-10}$ m.

$$\theta = 90 - \phi/2$$
$$= 90 - 50/2$$
$$\theta = 65°.$$

$$\lambda = 2 \times 0.909 \times 10^{-10} \times \sin 65^\circ$$

$$\lambda = 1.65 \times 10^{-10} m \Rightarrow \lambda = \underline{1.65 A^\circ}$$

According to de-Broglie theory,

$$\lambda = \frac{12.26}{\sqrt{V}}$$

$$\lambda = \frac{12.26}{\sqrt{54}}$$

$$\lambda = \underline{1.67 A^\circ}$$

Thus, there is an excellent agreement between the experimental value and theoretical value of wave length of $e^\ominus$ wave. This confirms the de-Broglie's concept of matter waves.

Heisenberg's Uncertainty principle :—

According to Heisenberg uncertainty principle, it is impossible to find out both the exact position & momentum of the particle at the same time.

The Heisenberg uncertainty principle states that in any simultaneous determination of a pair of physical quantities which describe the motion of the particle, the product of uncertainties is equal to :

$$\boxed{\Delta x \cdot \Delta p \geq \frac{h}{4\pi}}$$

$\Delta x \rightarrow$ uncertainty in the position value

$\Delta p \rightarrow$ " " " momentum value

Ily Heisenberg uncertainty principle concerns energy and time is

$$\boxed{\Delta E \cdot \Delta t \geq \frac{h}{4\pi}}$$

ΔE and Δt are the error in the measurement of energy & time respectively.

Schrodinger time-independent wave equation:-

The schroedinger wave equation is a fundamental eqn in quantum mechanics to explain the various phenomena associated with the atom and molecules.

Since, e⁻s exhibit wave nature, we can apply wave eqn to calculate all possible energy values.

According to de-Broglie, wavelength eqn of matter waves is

$$\lambda = \frac{h}{mv} \quad -(1).$$

According to classical mechanics, wave eqn is

$$\frac{\partial^2 \varphi}{\partial t^2} = v^2 \nabla^2 \varphi \quad -(2).$$

$$\because \left[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right.$$

∇^2 = Laplacian's operator

where φ = wave function.

$$\varphi = \varphi_0 \sin \omega t \quad -(3)$$

differentiate eqn (3) w.r. to. 't'

$$\frac{d\varphi}{dt} = \varphi_0 \cos\omega t \times \omega.$$

differentiate above eqn again w.r.t. 't'

$$\frac{d^2\varphi}{dt^2} = -\varphi_0 \sin\omega t \times \omega \times \omega$$

$$= -\omega^2 \underline{\varphi_0 \sin\omega t}$$

$$\frac{d^2\varphi}{dt^2} = -\omega^2\varphi \qquad \because [\text{from eq}^n \ (3)]$$

we know that

$$\omega = 2\pi\nu$$

$$\frac{d^2\varphi}{dt^2} = -4\pi^2\nu^2\varphi$$

$$\because \nu = \frac{v}{\lambda}$$

$$\frac{\partial^2\varphi}{\partial t^2} = -\frac{4\pi^2 v^2}{\lambda^2}\varphi \quad \text{--- (4)}$$

from eqn (2) & (4), we can get

$$\cancel{v^2}\nabla^2\varphi = -\frac{4\pi^2 \cancel{v^2}}{\lambda^2}\varphi$$

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0.$$

$$\nabla^2\psi + \frac{4\pi^2}{\left(\frac{h}{mv}\right)^2}\psi = 0 \qquad \because \left[\text{from eq}^n \ (1)\right]$$

$$\nabla^2\psi + \frac{4\pi^2 m^2 v^2}{h^2}\psi = 0$$

$\because$ Total Energy

$E = K.E + P.E$

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

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

$2(E-V) = mv^2$

$2m[E-V] = m^2v^2$

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

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

(or)

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

This is schrodinger time independent - wave eq^n for matter waves.

Note ①:-

for free particle $V=0$

$\therefore$ schrodinger time-independent wave eqn becomes

$$\boxed{\nabla^2\psi + \frac{2mE}{\hbar^2}\psi = 0}$$

Note ②:-

1-dimensional schrodinger time-independent wave eqn is

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

Physical significance of wave function:-

→ The wave function is represented with 'ψ'. It is a complex quantity

→ The wave function 'ψ' represents the variation of matter waves.

→ It connects the particle nature and its associated wave statistically.

→ $$\boxed{\int_{-\infty}^{\infty} \psi \cdot \psi^{*} \, dx\, dy\, dz = 1}$$

(or)

$$\boxed{\int_{-\infty}^{\infty} |\psi|^{2} dx\, dy\, dz = 1}$$

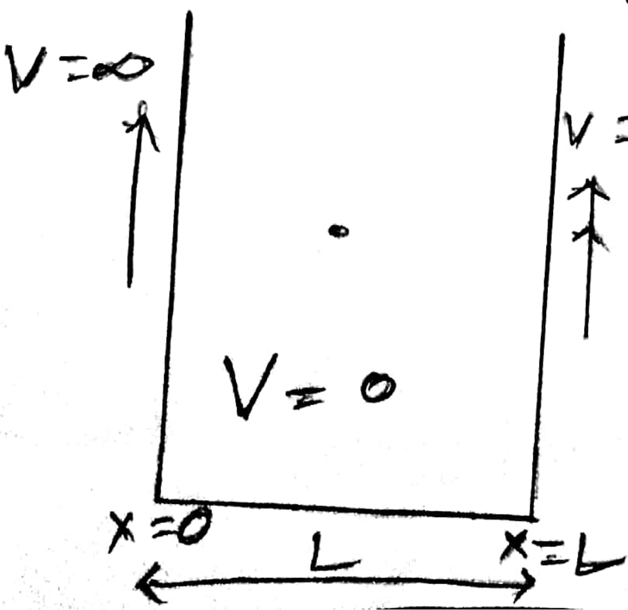
This function is known as normalization-function which gives the 100% probability to find out the particle.

→ So, $|\psi|^2$ gives the finding probability of a particle with in the space.

Particle in 1-Dimensional Potential Box :-

Consider a particle which is placed in an one-dimensional infinitely deep potential-box with finite width 'L'. We assume that the movement of the particle is restricted by the sides of the walls and when particle collides with the walls, there is no loss of energy of the particle and so the collisions are perfectly elastic.

Since the particle is moving freely inside the box its potential energy V=0. But the potential energy (V) is maximum at the walls and out side the box. Due to that the particle cannot escape from the box.



The one-dimensional wave eq^n is

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{2m(E-V)}{\hbar^2}\varphi = 0$$

with in the potential box $V = 0$

$\therefore$ above eq^n become

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{2mE}{\hbar^2}\varphi = 0.$$

Let $k^2 = \frac{2mE}{\hbar^2}$ = wave number

$$\frac{\partial^2\varphi}{\partial x^2} + k^2\varphi = 0$$

The general solution of above eq^n is

$$\varphi(x) = A\sin kx + B\cos kx \longleftarrow (1)$$

<u>Boundary</u> <u>conditions</u>:—

$\rightarrow$ $\varphi(x) = 0$ at $x = 0$

$\rightarrow$ $\varphi(x) = 0$ at $x = L$

By applying 1st boundary condition,
the eq^n (1) become

$$0 = A\sin k(0) + B\cos k(0)$$

$$0 = 0 + B(1)$$

$$\boxed{B = 0}$$

By substituting $B=0$ in eqn (1), we canget

$$\psi(x) = A\sin kx \quad -(2).$$

By applying 2nd boundary condition to eqn (2), we get

$$0 = A\sin kL$$

$\because A \neq 0$ then $\sin kL = 0$

$$kL = n\pi$$

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

finding probability of a particle is

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

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$$\int_0^L A^2 \sin^2 kx \, dx = 1 \quad \because [\text{from eq}^n \text{ ②}]$$

$$A^2 \int_0^L \sin^2 kx \, . \, dx = 1$$

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

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

$$\frac{A^2}{2} \left[x - \frac{\sin 2kx}{2k} \right]_0^L = 1$$

$$\frac{A^2}{2} L - \frac{\sin 2kL}{2k} = 1$$

$\left[\begin{array}{l} \sin 2kL \\ \sin 2 \times \frac{n\pi}{L} \times L \\ \sin 2n\pi = 0 \end{array} \right]$

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

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

Substitute 'K' & 'A' values in eq^n ②

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

This is the wave eq^n for the particle present in 1-dimensional potential Box.

Note ① Eigen values :-

We know that,

$$K^2 = \frac{2m}{\hbar^2} E \quad \text{--- ①}$$

and

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

$$K^2 = \frac{n^2\pi^2}{L^2} \quad \text{--- ②}$$

from eq^n ① & ②

$$\frac{2m}{\hbar^2} E = \frac{n^2\pi^2}{L^2}$$

$$E = \frac{n^2\pi^2}{L^2} \times \frac{\hbar^2}{2m} \qquad \because \hbar = \frac{h}{2\pi}, \quad \hbar^2 = \frac{h^2}{4\pi^2}$$

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

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

for $n=1$

$$E_1 = \frac{h^2}{8mL^2}$$

for $n=2$

$$E_2 = \frac{4h^2}{8mL^2}$$

for $n=3$

$$E_3 = \frac{9h^2}{8mL^2}$$

∴ These equations represent the energy values of the particle. These are also known as Eigen values of the particle.