# Quantum Mechanics :-

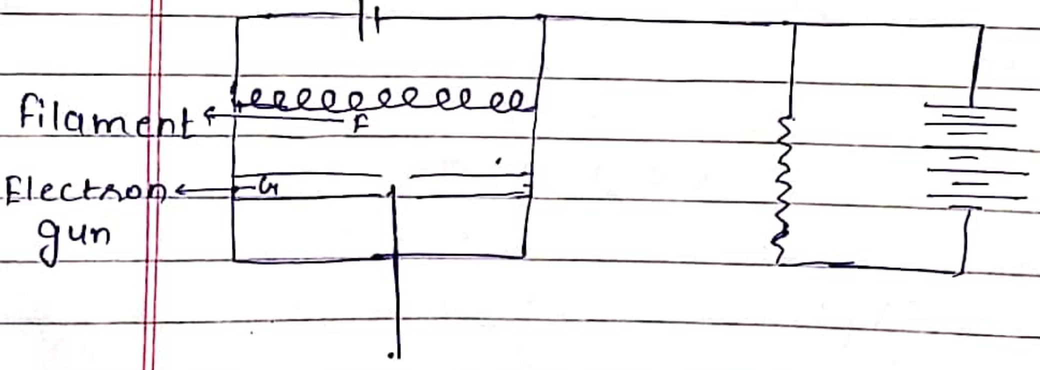
## Wave particle duality :-

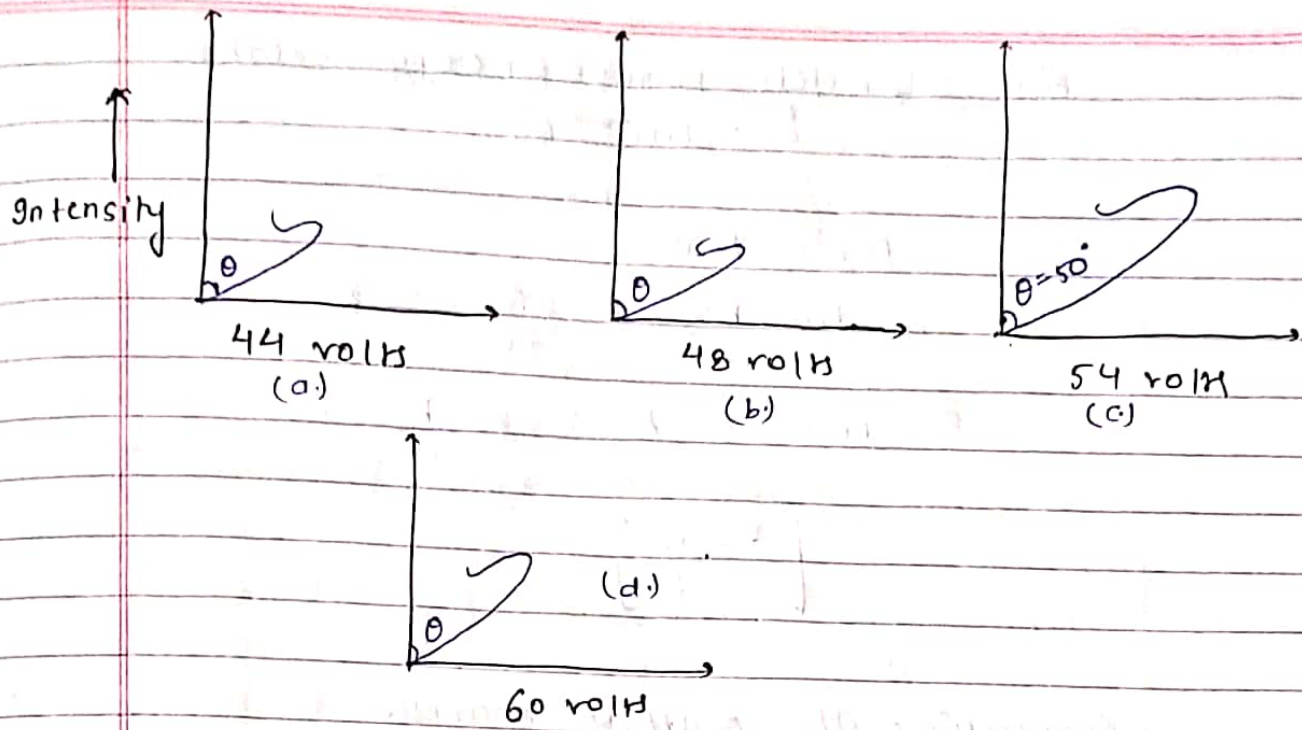
As we know that certain phenomenon such as Interference, diffraction and polarisation could be well explained by wave theory of light but certain other phenomenon like photoelectric effect, etc could not be explained by wave theory of light. These phenomenon could be explained by planck quantum theory. According to it-

"Light travels in the form of energy bundles known as quanta or photons having energy $h\nu$ that possess particle nature".

Therefore sometimes light obey wave theory and sometimes particle theory. This dual character of light is known as wave particle duality.

## Davisson Germer Experiment :-






$\lambda$ for $e^-$ $= \dfrac{12.27}{\sqrt{V_{(volt)}}} = \dfrac{12.27}{\sqrt{54}} = 1.67\,\text{Å}$

For diffraction:-

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

$d \rightarrow$ Interplanar surface dist $d = 0.91\,\text{Å}$

$\theta = 50^\circ$

$\lambda = 1.65\,\text{Å}$

## De-broglie wavelength :- (Matter waves).

According to Louis de-broglie a moving particle is always associated a wave around it which depends upon the mass and velocity of the particle. This a wave is known as de-broglie matter wave consider a photon whose energy is given by :-

$E = h\nu \longrightarrow ①$

Also Einstein mass Energy relation:-

$$E = mc^2 \rightarrow (2)$$

$$mc^2 = h\nu$$

$$m = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \rightarrow (3)$$

$$P = mc = \frac{h}{\lambda c} \cdot c = \frac{h}{\lambda}$$

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

**Properties of matter waves:-**

① If $v = 0$ $\lambda \Rightarrow \infty$ i.e. Indeterminate

$v \rightarrow \infty$ $\lambda = 0$. This assums that matter waves are generated only when the material particles are in motion.

② Expression of de-broglie wavelength

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

which is independent of charge. Hence matter waves are generated only by moving charge particle.

③ The wave or phase velocity $(v_p)$ of the matter wave is greater than the Electromagnetic waves that is Speed of light which can be shown as:-

$$E = h\nu \qquad E = mc^2$$

$$h\nu = mc^2 \qquad \nu = \frac{mc^2}{h}$$

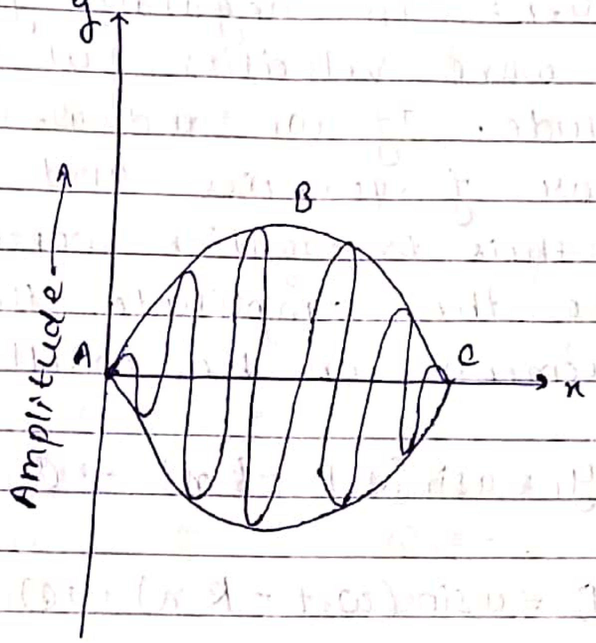
$$m = \frac{h\nu}{c^2} \qquad \lambda = \frac{h}{mv}$$

$$\lambda = \frac{c^2}{\nu v}$$

$$v_p = \nu\lambda$$

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

④ **Wave packet concept :-**




A wave packet is a bunch of wave corresponding to certain wavelength λ consisting group of no. of waves slightly different, phase, amplitude such that they interfere constructively over the small region of space somewhere ~~th~~ where which some particles can be located and outside the space they interfere d.

These wave packet move forward

The velocity with which wave packet moves forward known as group velocity ($v_g$).

**Expression for group velocity ($v_g$) :-**

Consider a wave packet having group of two waves slightly different in angular frequencies and wave velocities but of equal amplitude. If $\omega_1$ and $\omega_2$ are their angular frequencies and $k_1$ and $k_2$ are their propagation constants and a be the amplitude their seperate displacements can be written as :-

$$y_1 = a\sin(\omega_1 t - k_1 x) \rightarrow (1)$$

$$y_2 = a\sin(\omega_2 t - k_2 x) \rightarrow (2)$$

Now from the young's principle of interference :-

$$y = y_1 + y_2$$

$$y = a\sin(\omega_1 t - k_1 x) + a\sin(\omega_2 t - k_2 x)$$

$$\sin A + \sin B = 2\sin\left(\frac{A+B}{2}\right)\cos\left(\frac{A-B}{2}\right)$$

$$y = a\left[\sin\left(\frac{\omega_1 t - k_1 x + \omega_2 t - k_2 x}{2}\right).\cos\left(\frac{\omega_1 t - k_1 x - \omega_2 t + k_2 x}{2}\right)\right]$$

$$y = 2a\sin\left(\frac{(\omega_1+\omega_2)t}{2} - \frac{(k_1+k_2)x}{2}\right] \cdot \cos\left[\frac{(\omega_1-\omega_2)t}{2} - \frac{(k_1-k_2)x}{2}\right]$$

Substituting :-

$$\frac{\omega_1+\omega_2}{2} = \omega \qquad \frac{k_1+k_2}{2} = k$$

$$\omega_1-\omega_2 = \Delta\omega \quad , \quad k_1-k_2 = \Delta k$$

$$= 2a\sin\left[\omega t - kx\right]\cos\left[\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right]$$

$$y = \underbrace{2a\cos\left(\frac{\Delta\omega t}{2} - \frac{\Delta k x}{2}\right]}_{\text{amplitude}}\underbrace{\sin(\omega t - kx)}_{\text{phase}} \rightarrow (3)$$

Above eq (3) represents the resultant wave equation.

wherein the resultant amplitude of the wave is given by:-

$$A = 2a\cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right)$$

And resultant of phase of the wave is given by :-

$$\sin(\omega t - kx)$$

constant phase of the wave

$(\omega t - kx) =$ constant.

diff. above eq w.r.t $t$ we get :-

$$\omega - k\frac{dx}{dt} = 0$$

$$\frac{dx}{dt} = \frac{\omega}{k} = V_p$$

Scanned by CamScanner

$V_p$ is known as wave velocity.

const. amplitude of the wave gives

$$\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x = \text{const.}$$

diff. above eq. w.r.t $t$ we get.

$$\frac{\Delta\omega}{2} - \left(\frac{\Delta k}{2}\right)\frac{dx}{dt} = 0$$

$$\left[\frac{dx}{dt} = \frac{\Delta\omega}{\Delta k}\right] = V_g$$

$V_g$ is known as group velocity

when there are more waves:-

$$\left[V_g = \frac{d\omega}{dk}\right]$$

(most imp) Relation between group velocity and wave or ~~phaph to~~ phase velocity :-

of the individual wave with which the wave packet is constructed to have the wave velocity $V_p$ as :-

$$V_p = \frac{\omega}{k} \quad \text{or} \quad \omega = k.V_p \rightarrow ①$$

we know that general expression for group velocity is given by :-

$$V_g = \frac{d\omega}{dk} \rightarrow ②$$

from ① and ②

$$v_g = \frac{d}{dk}(k v_p)$$ $\left[k = \frac{2\pi}{\lambda}\right]$

$$= v_p + k\frac{dv_p}{dk} \rightarrow (3)$$

Where $k = \frac{2\pi}{\lambda}$.

Therefore $v_g = v_p + \frac{2\pi}{\lambda}\frac{dv_p}{d\left(\frac{2\pi}{\lambda}\right)}$

$$= v_p + \frac{1}{\lambda}\cdot\frac{dv_p}{d(1/\lambda)}$$

$$v_g = v_p - \frac{1}{\lambda}\cdot\lambda^2\cdot\frac{dv_p}{d\lambda}$$

$$v_g = v_p - \lambda\frac{dv_p}{d\lambda} \rightarrow (4)$$

Above eq. is req. relation b/w group velocity and wave velocity in dispersive medium where wave velocity is wavelength dependent.

From above eq. it is clear that in dispersive medium $v_g$ is always less that $v_p$.

For non-dispersive medium in which the wave velocity is independent of wavelength i.e. $v_p$ is constant. therefore :-

$$\frac{d(v_p)}{d\lambda} = 0$$

∴ Above eq (4) reduces to :-

$\boxed{v_g = v_p}$ for free space conditions

Therefore in a non-dispersive medium or in free space the group velocity equals to phase velocity.

## Wave velocity of de-broglie waves:-

$$\lambda = \frac{h}{p} = \frac{h}{mv} \rightarrow (1)$$

Also the propagation const :-

$$k = \frac{2\pi}{\lambda} = \frac{2\pi mv}{h} \rightarrow (2)$$

Energy of photon is given by :-

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

and $\omega = 2\pi\nu = 2\pi \frac{E}{h} \rightarrow (3)$

Also $E = mc^2$

$$\omega = \frac{2\pi mc^2}{h}$$

$$V_p = \frac{\omega}{k} = \frac{\frac{2\pi mc^2}{h}}{\frac{2\pi mv}{h}} = \frac{c^2}{V}$$

$$V_p = \frac{c^2}{V}$$

or $V_p \cdot V = c^2$

$$\boxed{V_p \cdot V_g = c^2}$$

because in free space $V = V_g$ particle move with same velocity of wave packet.

Relation between group velocity ($v_g$) and

consider a particle of mass $m_0$ is moving with velocity $v$ ($v<c$). Its ~~mass~~ total energy and momentum is given by :-

$$T.E\ (E) = mc^2 = \frac{m_0 c^2}{\sqrt{1-v^2/c^2}}$$

$$p = mv = \frac{m_0 v}{\sqrt{1-v^2/c^2}}$$

$$\omega = 2\pi\nu \qquad\qquad E = h\nu$$

$$= \frac{2\pi E}{h} \qquad\qquad \nu = \frac{E}{h}$$

$$= \frac{2\pi}{h} \cdot \frac{m_0 c^2}{\sqrt{1-v^2/c^2}}$$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi}{h/p} = \frac{2\pi}{h} \cdot p = \frac{2\pi}{h} \cdot \frac{m_0 v}{\sqrt{1-v^2/c^2}}$$

$$v_g = \frac{d\omega}{dk} = \frac{\frac{d\omega}{dv}}{\frac{dk}{dv}}$$

$$\frac{d\omega}{dv} = \frac{d}{dv}\left(\frac{2\pi}{h} m_0 c^2 \left(1-\frac{v^2}{c^2}\right)^{-1/2}\right)$$

$$= \frac{2\pi}{h} \cdot m_0 c^2 \times \frac{-1}{2}\left(1-\frac{v^2}{c^2}\right)^{-3/2} \cdot \frac{-2v}{c^2}$$

$$\frac{dk}{dv} = \frac{d}{dv}\left(\frac{2\pi}{h} m_0 v \left(1-\frac{v^2}{c^2}\right)^{-1/2}\right)$$

$$\cancel{= \frac{2\pi}{h} \cdot m_0} \quad v_g = \frac{\frac{d\omega}{dv}}{\frac{dk}{dv}} = v$$

# Heisenberg's uncertainity Principle :-

Simultaneous determination of exact position and momentum of a fast moving small particle is impossible.

If $\Delta x$ and $\Delta p$ are the errors or uncertainities in determining the position and momentum then according to uncertainity principle :-

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi} \text{ or } \hbar \quad \left(\hbar = \frac{h}{2\pi}\right)$$

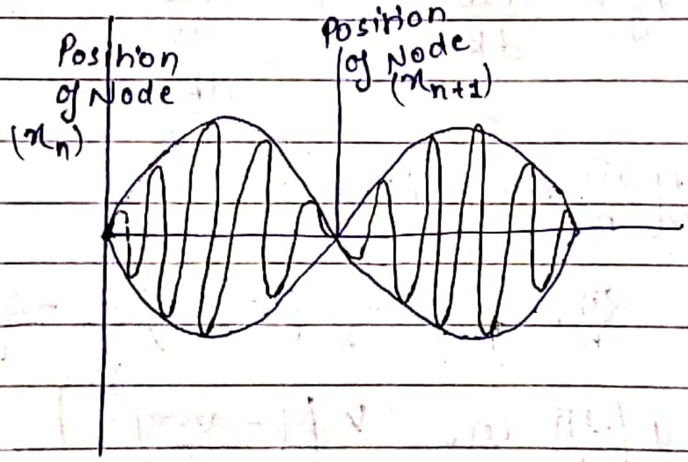
$$\Delta E \cdot \Delta t > h$$

$$\Delta J \cdot \Delta \theta \geq h$$

Angular momentum.

$$y = 2a\cos\left[\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right] \cdot \sin(\omega t - kx)$$

$$V_g = \frac{\Delta\omega}{\Delta k}$$




for the position of Nodes :-

$$2a\cos\left[\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right] = 0$$

Scanned by CamScanner

(A) $E^2 = p^2c^2 + m_0^2c^4$

$pc \gg m_0c^2$ Relativistic case.

$pc \ll m_0c^2$ Non. Relativistic case.

$2a \neq 0 \quad \therefore \cos\left(\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x\right) = 0$

$$\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x = (2n+1)\frac{\pi}{2}$$

$$\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x_n = (2n+1)\frac{\pi}{2} \rightarrow (A)$$

$$\left(\frac{\Delta\omega}{2}\right)t - \left(\frac{\Delta k}{2}\right)x_{n+1} = (2n+3)\frac{\pi}{2} \rightarrow (B)$$

Substract eq (A) from (B) :-

$$\left(\frac{\Delta k}{2}\right)\left(x_n - x_{n+1}\right) = \pi$$

$$\frac{\Delta k}{2} \cdot \Delta x = \pi$$

$$\Delta k \cdot \Delta x = 2\pi \qquad k = \frac{2\pi}{\lambda} = \frac{2\pi}{h} \cdot p$$

$$\frac{2\pi}{h} \Delta p \cdot \Delta x = 2\pi \qquad \Delta k = \frac{2\pi}{h} \cdot \Delta p$$

$$\therefore \boxed{\Delta x \cdot \Delta p = h}$$

$$\boxed{\Delta x \cdot \Delta p \geq h}$$

## Applications of Uncertainity Principle :-

### (1) Non existance of electron inside the Nucleus.

The typical size of the Nucleus is about $10^{-14}$ m. If any size of the particle is to exist into it then the uncertainity in the position is given by :-

$$\Delta x = 10^{-14} \text{ m}$$

$$\Delta x \cdot \Delta P_x \geq \hbar$$

$$\Delta P_x = \frac{h}{2\pi \cdot \Delta x}$$

$$\Delta P_x = \frac{6.6 \times 10^{-34}}{2\pi \times 10^{-14}}$$

$$= 10^{-20} \ kg\,ms^{-1}.$$

$$\Delta P_x = |\vec{P_x}| = P = 10^{-20} \ kg\,ms^{-1}$$

Now applying energy-momentum Relationship :-

$$E^2 = P^2c^2 + m_0^2c^4.$$

$$E = \sqrt{P^2c^2 + m_0^2 c^4}$$

$$= \sqrt{(10^{-20} \times 3 \times 10^8)^2 + (9.1 \times 10^{-31})^2 \times (3 \times 10^8)^4}$$

$$= 1.6 \times 10^{-12} \ J$$

$$= \underline{\underline{10 \ MeV}}.$$

Since the energy of the particles inside the Nucleus is ranging from 2 to 3 MeV. In case of electron the energy obtained through above calculated is 10 MeV which is much higher than the corresponding particles available inside the Nucleus. Hence electron cannot reside inside the Nucleus.

Imp

(2) <u>Radius of Bohr's first orbit</u> :-

We can determine the Radius of the Bohr's first orbit by making the use of uncertainity principle.

If $\Delta x$ and $\Delta p$ are the ~~the~~ uncertainity in position and momentum then :-

$$\Delta x . \Delta p \geq \hbar$$

$$\Delta p \geq \frac{\hbar}{\Delta x} \rightarrow (1)$$

The total energy of the $e^-$ is given by :-

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

$$= T + V \rightarrow (2)$$

$$\Delta E = \Delta T + \Delta V \rightarrow (3)$$

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

$$T = \frac{1}{2} \frac{m^2 v^2}{m} = \frac{p^2}{2m}$$

$$\Delta T = \frac{(\Delta p)^2}{2m} \rightarrow (4)$$

Now from eq (1) :-

$$\Delta T = \frac{\hbar^2}{(\Delta x)^2 . 2m} \rightarrow (5)$$

$$V = \frac{1}{4\pi\varepsilon_0} \frac{Ze(-e)}{x}$$

$$\Delta V = -\frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{\Delta x} \rightarrow (6)$$

Now from ~~p~~ eq. (3) :-

$$\Delta E = \frac{\hbar^2}{(\Delta x)^2 \cdot 2m} + \frac{1}{4\pi\varepsilon_0} \cdot \frac{ze^2}{\Delta x} \rightarrow (7)$$

This energy is minimum if :-

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

$$\frac{\hbar^2}{2m} \frac{-2}{(\Delta x)^3} + \frac{1}{4\pi\varepsilon_0} \cdot \frac{ze^2}{(\Delta x)^2} = 0$$

$$\frac{1}{4\pi\varepsilon_0} \cdot \frac{ze^2}{(\Delta x)^2} = \frac{\hbar^2}{m(\Delta x)^3}$$

$$\Delta x = \frac{\hbar^2}{m} \cdot \frac{4\pi\varepsilon_0}{ze^2}$$

$$= \frac{h^2}{4\pi^2} \cdot \frac{\cancel{4\pi}\varepsilon_0}{mze^2}$$

$$\Delta x = \frac{h^2}{\pi} \frac{\varepsilon_0}{mze^2}$$

**Ground state energy of linear harmonic Oscillator :-**

The total energy in case of linear harmonic oscillator is given by :-

$$E = K.E. + P.E. \rightarrow (1)$$

$$= \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

$$= \frac{p^2}{2m} + \frac{1}{2}kx^2 \rightarrow (2)$$

where $k \rightarrow$ force constant

$x \rightarrow$ position of displacement from mean position

Scanned by CamScanner

$$\Delta E = \frac{(\Delta P)^2}{2m} + \frac{1}{2}k(\Delta x)^2 \rightarrow (3)$$

Now let a particle of mass m executes the simple harmonic motion along x-direction. The uncertainity in its position will be $\Delta x$ then the uncertainity in momentum can be calculated as:-

$$\Delta P = \frac{\hbar}{2\Delta x} \rightarrow (4)$$

Now substituting:-

$$\Delta E = \frac{\hbar^2}{8m(\Delta x)^2} + \frac{1}{2}k(\Delta x)^2 \rightarrow (5)$$

Now energy will be minimum when $\frac{\partial(\Delta E)}{\partial(\Delta x)} = 0$

$$\frac{\hbar^2}{8m} \times \frac{-2}{(\Delta x)^3} + \frac{1}{2}k \times 2(\Delta x) = 0$$

$$\frac{\hbar^2}{4m(\Delta x)^3} = k(\Delta x)$$

$$(\Delta x)^4 = \frac{\hbar^2}{4mk}$$

$$\Delta x = \left(\frac{\hbar^2}{4mk}\right)^{1/4} \text{ put in } (5)$$

$$\Delta E_{min} = \frac{\hbar^2}{8m\left(\frac{\hbar^2}{4mk}\right)^{1/2}} + \frac{1}{2}k\left(\frac{\hbar^2}{4mk}\right)^{1/2}$$

$$= \frac{\hbar^2}{8m}\left(\frac{4mk}{\hbar^2}\right)^{1/2} + \frac{1}{2}k\left(\frac{\hbar^2}{4mk}\right)^{1/2}$$

$$= \frac{\hbar}{4}\left(\frac{k}{m}\right)^{1/2} + \frac{1}{4}\left(\frac{k\hbar^2}{m}\right)^{1/2}$$

$$= \left(\frac{k}{m}\right)^{1/2}\left(\frac{\hbar}{2}\right)$$

Scanned by CamScanner

$$= \frac{\hbar}{2}\sqrt{\frac{K}{m}} \qquad \boxed{\omega = \sqrt{\frac{K}{m}}}$$

$$= \frac{\hbar}{2}\omega$$

$$= \frac{h}{2\pi} \times \frac{\omega}{2}$$

$$= \frac{h}{4\pi} \times 2\pi\nu$$

$$\boxed{\Delta E_{min} = \frac{1}{2}h\nu}$$

Physical significance and Interpretation of wave function ($\psi$) :-

The quantity with which the quantum mechanics is concerned is wave function ($\psi$) of a particle. While $\psi$ independent has no meaning. It absolute magnitude square

$|\psi|^2$ or $\psi\psi^*$ if $\psi$ is complex

gives the probability density of finding a particle at particular point in particular time. It has certain characteristic properties:-

(i) The wave function $\psi(\vec{r}, t)$ gives the behaviour of a particle at a given position $\vec{r}$ and at a given time $t$.

(ii) It is a measure of probability

density. Therefore $\psi$ cannot be infinite.

(iii) $\psi$ must be single value because probobility is a single value quantity.

(iv) $\psi$ must be continous so that it could be differentiate and its first derivative should exist everywhere.

(v) The total probability over the whole space is given by :-

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

$$\Rightarrow \int_{-\infty}^{\infty} |\psi|^2 dv = 1$$

This is also known as condition of Normalization.

## Equation of motion of matter waves :-

Imp (a.) **Schrodinger's time Independent wave Equation**

In many situations it has been observed that the force acting upon a particle does not depends upon time but vary with the position of the particle. The differential Equation describing the situation is known as schrondinger's time Independent wave Equation or Steady state Schrondingers Eqn.

According to de-broglie theory a particle of mass m moving with a velocity v is always associated with a wave whose wavelength is given by :-

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

If the particle has wave properties then it is ~~ex~~ expected that there must be some kind of wave eqn. which describes the behaviour of the particle

Consider a system of stationary waves associated with the particle

Let $(x, y, z, t)$ be the space-time coordinates of the particle and $\psi$ be the wave function for the de-broglie wave at any time t then the classical diff. eqn. of the wave motion is given by :-

$$\frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2} = \nabla^2 \psi \rightarrow (1)$$

where $\nabla^2$ being the laplasian ~~operator~~. operator. Solution of eq (1) may be of the form

$$\psi(x, y, z, t) = \psi_0(x, y, z)\, e^{-i\omega t} \rightarrow (2)$$

or.

$$\psi(\vec{r}, t) = \psi_0(\vec{r})\, e^{-i\omega t} \rightarrow (2)$$

$$i = \sqrt{-1}$$

$$\frac{\partial \psi}{\partial t} = (-i\omega)\, \psi_0(\vec{r})\, e^{-i\omega t}$$

$$\frac{\partial^2 \omega}{\partial t^2} = (-i\omega)(-i\omega)\, \psi_0(\vec{r})\, e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi \rightarrow (11)$$

put in (1)

$$\frac{1}{v^2}(-\omega^2 \psi) = \nabla^2 \psi$$

$$-\frac{\omega^2}{v^2}\psi = \nabla^2 \psi \qquad \omega = 2\pi\nu = \frac{2\pi v}{\lambda}$$

$$-\left(\frac{2\pi}{\lambda}\right)^2 \psi = \nabla^2 \psi \qquad \frac{\omega}{v} = \left(\frac{2\pi}{\lambda}\right)$$

$$\nabla^2 \psi + \left(\frac{2\pi}{\lambda}\right)^2 \psi = 0$$

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

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

Total Energy $(E)$ = K.E + P.E $= \frac{1}{2}mv^2 + V$

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

$$2m(E-V) = m^2 v^2 \rightarrow (5)$$

put (5) in (A)

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

$$\nabla^2 \psi + \frac{1}{\hbar^2} 2m(E-V)\psi = 0$$

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

In case of free particle P.E $V = 0$

$$\therefore \nabla^2 \psi + \frac{2m}{\hbar^2} E\psi = 0$$

## Schrodinger's time dependent Equation:-

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

$$\frac{\partial \psi}{\partial t} = \psi_0(\vec{r}) \cdot e^{-i\omega t} \cdot (-i\omega)$$

$$= -i\omega\psi$$

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

$$= \left(-i \times 2\pi \times \frac{E}{h}\right) \cdot \psi$$

$$= \cancel{(-i \times 2\pi \times E} \left(\frac{-i \times i}{-i} \times \frac{2\pi \times E}{h}\right) \psi$$

$$= \left(\frac{2\pi E}{i \times h}\right) \psi$$

$$E\psi = \left(\frac{i \times h}{2\pi}\right) \cdot \frac{\partial \omega}{\partial t} = (i\hbar)\frac{\partial \omega}{\partial t}$$

from general equation:-

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

multiply by $\frac{\hbar^2}{2m}$ :-

$$\frac{\hbar^2}{2m}\nabla^2\psi + i\hbar\frac{\partial \omega}{\partial t} - V\psi = 0$$

$$\frac{\hbar^2}{2m}\nabla^2\psi + i\hbar\frac{\partial \omega}{\partial t} - V\psi = 0$$

Now Rearranging above eq :-

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

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

Scanned by CamScanner

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

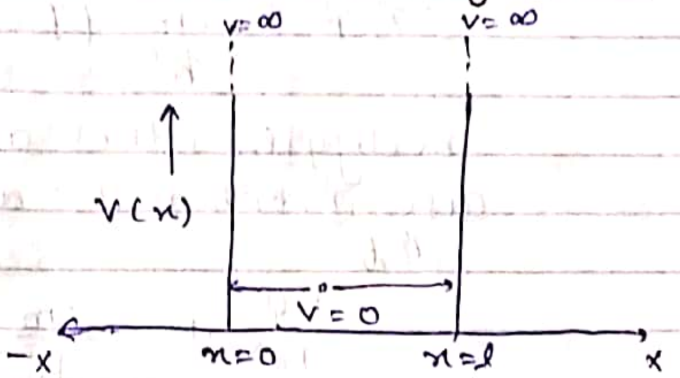
$$E = i\hbar \frac{\partial \psi}{\partial t}$$

where H and E are operators.
H depends upon the space coordinates and E depends upon the time coordinates. Both are known as Energy operators.

most Imp

## Applications of Schrodinger's wave Equation

(i) **Particle in a box: motion along one-dimension:-**




Let us consider a case in which a particle is trapped in a rectangular potential box as shown in fig. The particle has mass m and is restricted to move along a straight line in x-direction in the range $x=0$ to $x=l$. Suppose the walls of the box are infinitely hard so that particle does not loose energy while deflected back from the walls and the velocity is too low that we can ignore the relativistic effect. Suppose the potential energy V of the particle is 0 inside the box and becomes $\infty$ outside the box.

$$V = 0 \qquad 0 < x < l$$

$$V = \infty \qquad l < x < 0$$

Under these conditions the particle is restricted to move in an infinitely long potential box. The general form of the Schrodinger's time independent wave is given by:

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E-V)\psi = 0 \rightarrow (1)$$

modifying the above eq. for the case mentioned above:-

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \cdot E\psi = 0 \rightarrow (A).$$

Now substituting $\hbar = \frac{h}{2\pi}$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} \cdot E\psi = 0$$

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

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

$E = \frac{k^2h^2}{8\pi^2 m}$ $\rightarrow (B)$

the soln. of eq (3) may be of the form:-

$\psi(x) = A\sin kx + B\cos kx \rightarrow (4)$

where A and B are constants to be evaluated using boundary condition-s. As the particle cannot have infinite energy. Therefore it has to move inside the box $x=0$, to $x=l$

$\therefore \quad \psi = 0$, at $x=0$ and $x=l$

Applying in eq (4) at $x=0$ we get :-

$$\boxed{B=0}$$

Applying in eq (4) at $x=l$ :-

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

$$0 = A\sin kl$$

$$A \neq 0 \Rightarrow \sin kl = 0$$

$$kl = n\pi$$

$$k = \frac{n\pi}{l} \quad \text{where } n = 1, 2, 3, \ldots$$

substituting value of k in eq (B) we get:-

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

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

$$\frac{n^2}{l^2} = \frac{8mE}{h^2}$$

$$\left[E_n = \frac{n^2h^2}{8ml^2}\right] \rightarrow (5) \quad \text{where } n = 1, 2, 3, \ldots$$

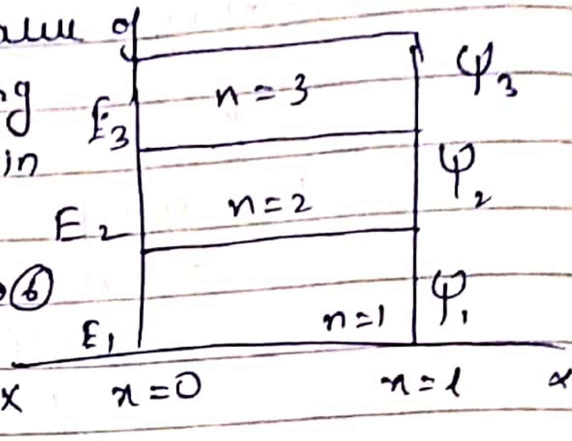
From eq (5) It is clear that inside the box particle cannot have arbitrary energy but can have certain dist discrete energy corresponding to $n = 1, 2, 3, \ldots$

~~each~~

Energy permitted energy is called Eigen value of the particle. & constitutes the energy level of system, the integer 'n' specifies energy level $E_n$ is called quantum no.. as shown in the figure.

Now to find Eigen value of the particle putting $V=0$ and $K = \frac{n\pi}{l}$ in eq. (4) :-

$$\psi_{(x)} = A\sin\left(\frac{n\pi}{l}\right).x \rightarrow (6)$$




Now from the Normalisation condition :-

$$\int_{-\infty}^{\infty} \psi\psi^* \text{ or } |\psi|^2 dV = 1$$

from eq (6) :-

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

after solving :-

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

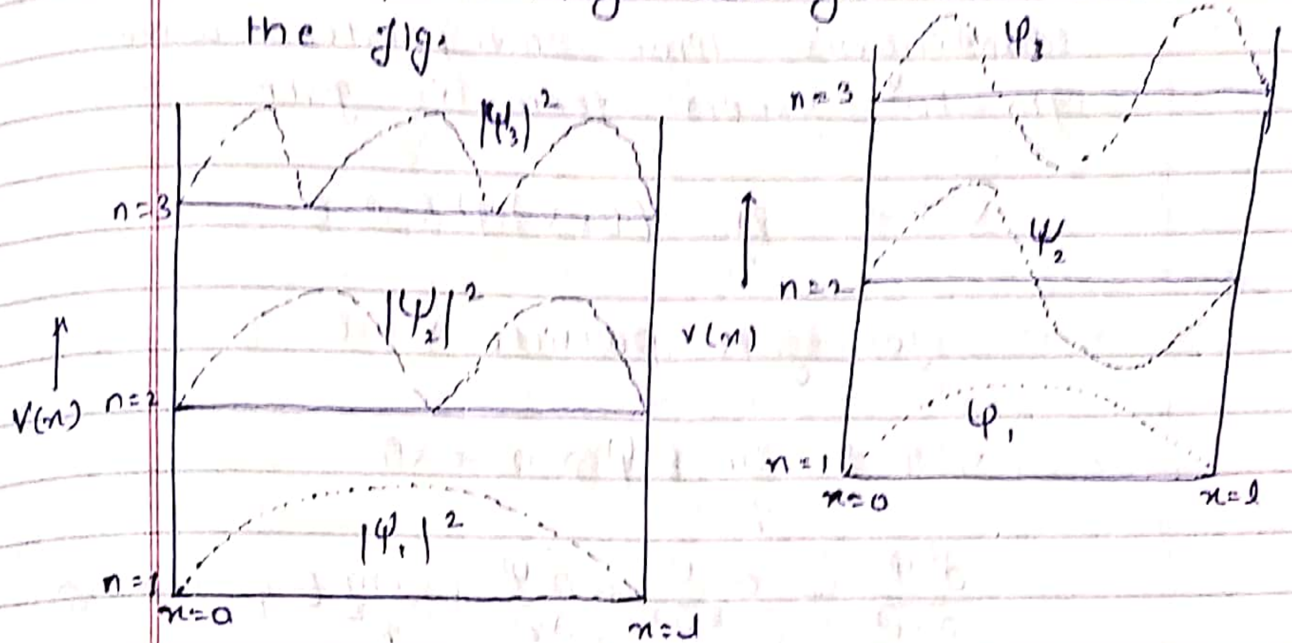
$$\psi_n = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi}{l}\right).x \quad ; n = 1, 2, 3, \ldots$$

Although $\psi_n$ may be -ve or +ve but $|\psi_n|^2$ is always +ve.

$\therefore$ $\psi_n$ is Normalised.

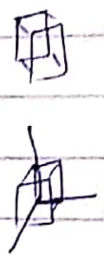
Its value at given $x$ gives the probability of finding the particle there.

First three Eigen functions together with probability density are shown in the fig.




Further at a particular point the probability of finding the particle is diff. in diff. energy states.

ex:- A particle in lower Energy state say $n=1$ is not likely to be in the middle of the box while the particle in the next energy state $n=2$ is never there.



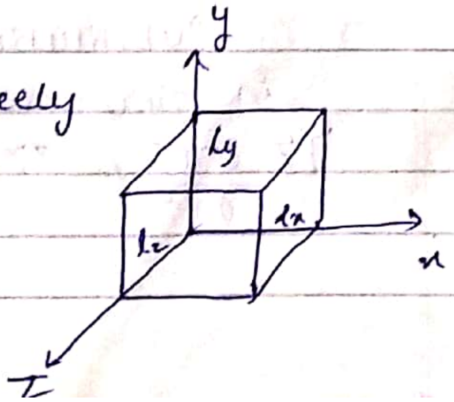
## Particle in a box: (Motion along three Dimension) :-

Particle can move freely within the region.

$0 < x < l_x$

$0 < y < l_y$

$0 < z < l_z$



where $V = 0$

$$\left.\begin{array}{l} 0 > x > l_x \\ 0 > y > l_y \\ 0 > z > l_z \end{array}\right\} \quad V \to \infty$$

Schrodinger's time independent wave eqn. in general form is given by :-

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

for free particle $V = 0$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} E \psi = 0 \rightarrow ①$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} E \psi = 0 \rightarrow ①$$

eq. ① is the diff. eqn. for three independent variable $x, y$ and $z$. This can be solved by the method of seperation of variable.

The soln. of eq ① can be written as :-

$$\psi_{(x,y,z)} = X_{(x)} Y_{(y)} Z_{(z)} = XYZ \rightarrow ②$$

where $X_{(x)}\, Y_{(y)}\, Z_{(z)}$ are the functions of their respective coordinates.

$\because$ eq ② is the soln. of eq ① then it has to satisfy eq ①.

$\therefore$ Substituting the value of $\psi$ from eq ② in eq ① we get :-

$$YZ\frac{\partial^2 X}{\partial x^2} + XZ\frac{\partial^2 Y}{\partial y^2} + XY\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2} E XYZ = 0$$

$\div$ by $XYZ$

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2}E = 0 \rightarrow (3)$$

Rearranging eq (3) we get :-

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E \rightarrow (4)$$

In eq. (4) LHS is func. of $x$ alone whereas RHS is func. of $y, z$. and some constants. Both the sides of eq. (4) can only be equal if they are seperately equal to some common constants.

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = k_x \rightarrow (5)$$

$$-\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E = k_x \rightarrow (6)$$

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = k_y \rightarrow (8) \qquad \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E - k_x \rightarrow (7)$$

$$-\frac{1}{X}\frac{\partial^2 X}{\partial x^2} - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2m}{\hbar^2}E = k_y .$$

$$-k_x - \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} - \frac{2mE}{\hbar^2} = k_y \rightarrow (9)$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -k_x - k_y - \frac{2mE}{\hbar^2} \rightarrow (10)$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = k_z \rightarrow (11)$$

$$-\frac{2mE}{\hbar^2} = k_z + k_x + k_y \rightarrow (12)$$

For simplification :-

$\because E = E_x + E_y + E_z$

$$k_x + k_y + k_z = -\frac{2m}{\hbar^2} E = -\frac{2m}{\hbar^2}(E_x + E_y + E_z) \rightarrow (12)$$

$$k_x = -\frac{2m}{\hbar^2} E_x \qquad k_y = -\frac{2mE_y}{\hbar^2} \qquad k_z = -\frac{2mE_z}{\hbar^2}$$

Now substituting the values of $k_x$, $k_y$ and $k_z$ in eq. (B) (8) and (11) (10) (11)

we get:-

$$\frac{\partial^2 X}{\partial x^2} + \frac{2m}{\hbar^2}(E_x) X = 0 \rightarrow (13)$$

$$\frac{\partial^2 Y}{\partial y^2} + \frac{2m}{\hbar^2}(E_y) Y = 0 \rightarrow (14)$$

$$\frac{\partial^2 Z}{\partial z^2} + \frac{2m}{\hbar^2}(E_z) Z = 0 \rightarrow (15)$$

gen. soln. of eq (13) can be of the form:-

$$X(x) = A\sin(Bx + C) \rightarrow (16)$$

A, B, C are constants which can be obtained from boundary values.

As we know that $|X(x)|^2$ give the probability of finding the particle at any point along x-axis wherein probability of finding particles at walls of box is 0 because potential energy is $\infty$ over there. Therefore particle has to move inside the box within the limits $x=0$, $x=l_x$

$\therefore$ we have $|X(x)|^2 = 0$ at $x=0$ & $x=l_x$

$$|X(x)| = 0$$

Now applying these boundary conditions in eq. 16 we get

$\sin C = 0$ & $\sin(Bl_x + C) = 0$

$\therefore C = 0$

$Bl_x + 0 = n_x \pi$

$B = \dfrac{n_x \pi}{l_x}$

Now substituting these values this gives:-

$$X(x) = A \sin\left(\frac{n_x \pi}{l_x} \cdot x\right) \rightarrow 17$$

Now applying the condition of Normalisation

$$\int_0^{l_x} |X(x)|^2 dx = 1$$

$$A = \sqrt{\frac{2}{l_x}} \rightarrow 18$$

The normalised wave function is given by:-

$$X(x) = \sqrt{\frac{2}{l_x}} \sin\left(\frac{n_x \pi x}{l_x}\right) \rightarrow 19$$

$$\frac{\partial X(x)}{\partial x} = \sqrt{\frac{2}{l_x}} \cos\left(\frac{n_x \pi x}{l_x}\right) \times \frac{n_x \pi}{l_x}$$

$$\frac{\partial^2 X(x)}{\partial x^2} = -\sqrt{\frac{2}{l_x}} \cdot \sin\left(\frac{n_x \pi x}{l_x}\right) \times \left(\frac{n_x \pi}{l_x}\right)^2$$

$$\frac{\partial^2 X}{\partial x^2} = -X(x) \left(\frac{n_x \pi}{l_x}\right)^2 \rightarrow 20$$

Now substitute $\dfrac{\partial^2 X(x)}{\partial x^2}$ in eq 13 we get:-

$$-\left(\frac{n_x \pi}{l_x}\right)^2 X(x) + \frac{2m}{\hbar^2} E_x X(x) = 0$$

$$\frac{2m}{\hbar^2} E_x = \left(\frac{n_x \pi}{l_x}\right)^2$$

or $$E_x = \frac{\hbar^2}{2m} \frac{n_x^2 \pi^2}{l_x^2}$$

$$= \frac{1}{2} \frac{n_x^2 h^2}{4 m l_x^2}$$

$$= \frac{n_x^2 h^2}{8 m l_x^2} \rightarrow (21)$$

$$E_y = \frac{n_y^2 h^2}{8 m l_y^2}, \quad E_z = \frac{n_z^2 h^2}{8 m l_z^2}$$

where $n = 1, 2, 3$

Total energy $E = E_x + E_y + E_z$

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right]$$

∴ The total wave function becomes :-

$$\psi(x, y, z) = 2\sqrt{\frac{2}{l_x l_y l_z}} \sin\left(\frac{n_x \pi x}{l_x}\right) \cdot \sin\left(\frac{n_y \pi y}{l_y}\right) \sin\left(\frac{n_z \pi z}{l_z}\right).$$

## Postulates of quantum mechanics :-

We have seen that schrodinger formulation of quantum mechanics there exists a wave function $\psi$ which represents a wave associated with a moving particle. On the basis of earlier discussion we have the following postulates as given here under :-

(i) For a system consisting of a particle moving under the influence of conservative force. A wave function $\psi(x, y, z)$ is being associated which represents the behaviour of the system in consistent with the uncertainity principle.

(ii) For every dynamical quantity there exists an operator in quantum mechanics.

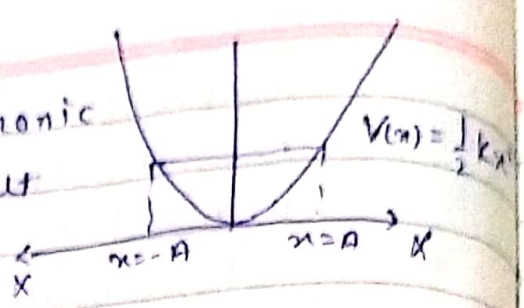
| Dynamic variables | Symbol | Quantum mechanical operator. |
|---|---|---|
| position | $x, y, z$ | $x, y, z$ |
| momentum | $P_x, P_y, P_z$ | $\frac{\hbar}{i}\frac{\partial}{\partial x}, \frac{\hbar}{i}\frac{\partial}{\partial y}$ $\frac{\hbar}{i}\frac{\partial}{\partial z}$ |
| Total Energy | $E$ | $i\hbar\frac{\partial}{\partial t}$ |
| K.E | $K$ | $\frac{-\hbar}{2m}\nabla^2 + V$ |
| P.E. | $V(x,y,z)$ | $V(x,y,z)$ |

(iii) $\psi$ and its derivatives must be continous, single valued, finite and its partial derivatives must exist for all values of $x, y, z, t$.

(iv) Condition of Normalisation is given by:-
$$\int_{-\infty}^{\infty} \psi\psi^* \text{ or } |\psi|^2 dV = 1$$

**One dimensional harmonic Oscillator**
(or)
**Parabolic Potential Wall:-**

One dimensional harmonic Oscillator is nothing but simply the particle undergoing simple harmonic motion under the influence of restoring force.




$$f = -kx \rightarrow (1)$$

where $k$ = force constant and $x$ is the displacement from mean position since

$f = -kx$ $\quad V_x$ = potential Energy

$$V_x = -\int_0^x f(x)\,dx$$

or

$$k\int_0^x x\,dx = \frac{1}{2}kx^2 \rightarrow (2)$$

Now substituting the value of potential energy in schrodinger's time independent 1-D equation.

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

changing in 1-Dimensional

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \rightarrow (3)$$

Soln. of eq (3) may be of the form

$$\psi(x) = Ae^{-bx^2} \rightarrow (4)$$

$$\frac{d\psi}{dx} = Ae^{-bx^2}(-b)2x$$

$$= -2Ab\left[xe^{-bx^2}\right]$$

$$\frac{d^2\psi}{dx^2} = -2Ab\left[e^{-bx^2} + xe^{-bx^2}(-b)2x\right]$$

Scanned by CamScanner

$$= -2Abe^{-bx^2}[1 - 2x^2 b]$$

$$\frac{d^2\psi}{dx^2} = 2Ab[2bx^2 - 1]e^{-bx^2}$$

$$2Ab[2bx^2 - 1]e^{-bx^2} + \frac{2m}{\hbar^2}[E - \tfrac{1}{2}kx^2]Ae^{-bx^2} = 0$$

$$4b^2x^2 - 2b + \frac{2mE}{\hbar^2} - \frac{mk}{\hbar^2}x^2 = 0$$

$$\left(4b^2 - \frac{mk}{\hbar^2}\right)x^2 + \frac{2mE}{\hbar^2} - 2b = 0 \rightarrow (6)$$

eq. (6) is an identity.
∴ the terms of various powers of $x = 0$
∴ we get

$$4b^2 - \frac{mk}{\hbar^2} = 0 \rightarrow (7)\ (A)$$

$$\frac{2mE}{\hbar^2} = 2b \rightarrow (7)\ (B)$$

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

Substituting the value of b in eq. (7) (A) we get

$$\frac{4m^2E^2}{\hbar^4} = \frac{mk}{\hbar^2}$$

$$\frac{4mE^2}{\hbar^2} = k$$

$$E^2 = \frac{k\hbar^2}{4m} \qquad \hbar = \frac{h}{2\pi}$$

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

$$E = \frac{\hbar}{2}\omega = \frac{h}{2\pi} \times \frac{1}{2} \times 2\pi\nu = \frac{h\nu}{2}$$

## Numericals:-

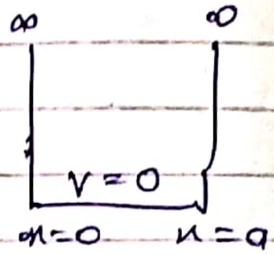
(1) Find the energy of an $e^-$ moving in 1-Dimension in an $\infty$ high potential box of width 1.0 Å mass of $e^- = 9.1 \times 10^{-31}$ kg
$h = 6.6 \times 10^{-34}$

$\Rightarrow$
$$E = \frac{n^2 h^2}{8 m l^2}$$

Imp (2) A particle is in motion along a line between $x = 0$ and $x = a$ with 0 potential energy. At points for which $x < 0$ and $x > a$ the P.E $= \infty$. The wave function for the particle in $n^{th}$ state is given by
$$\varphi_n = A \sin\left(\frac{n\pi x}{a}\right).$$

Find the expression for normalised wave function. (soln. in notes).

$\Rightarrow$
$$\int_0^a |\varphi_n|^2 dx = 1$$




(3) The speed of $e^-$ is measured to be $5 \times 10^3\ ms^{-1}$ to an accuracy of 0.003 %. Find the uncertainity in determining the position of $e^-$

$\Rightarrow$
$$\Delta v = 5 \times 10^3 \times \frac{0.003}{100}$$

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$