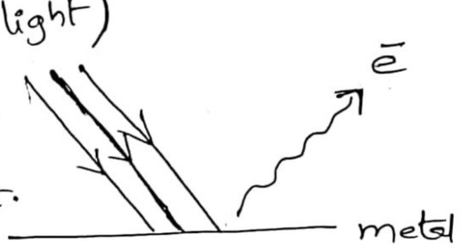
UNIT- IV Dual Nature of Matter and Radiation

photo electric effect: photo electric effect was discovered by Hertz and explained by Einstein.. when U.V light (or) monochromatic e.m radiation falls on the surface of metals like Li, Na, K etc, then the metal surface emits electrons. This phenomenon is known as P.E.E. The emitted electrons are called photo electrons and the metal that emits electrons is known as photo metal. The current constituted with the flow of these electrons is known as photo current.



Threshold frequency (ν_0): The minimum frequency of photo radiation at which a photo electron is emitted but no K.E is called Threshold frequency.

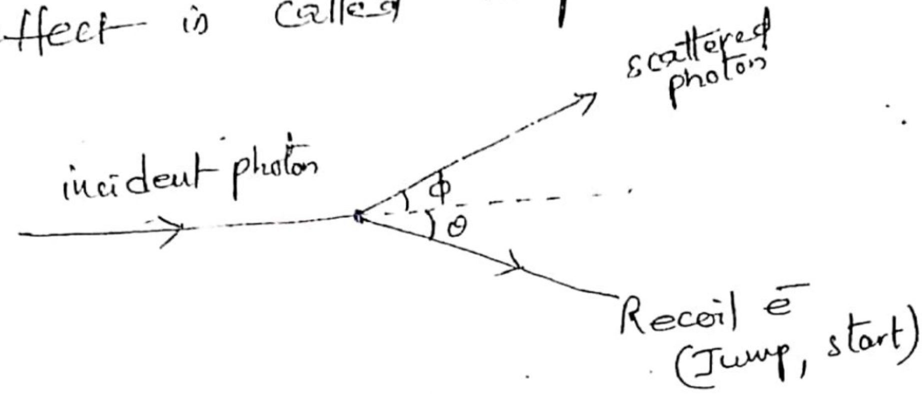
Threshold wave length (λ_0): The maximum possible value of wave length of incident radiation at which photoelectrons are emitted with no K.E is called threshold wave length.

Wave function (W): The minimum amount of light energy required to pull (or) remove an electron from the metal surface is called work function (W). It can be measured in electron Volt.

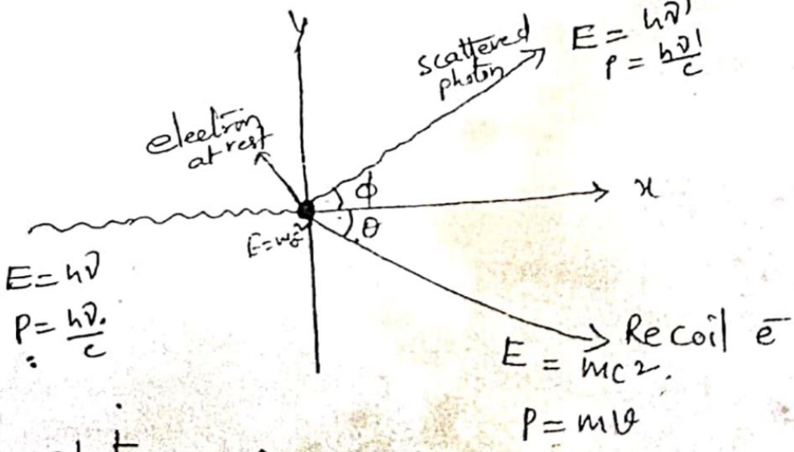
Compton effect :- When a monochromatic beam of x-rays is allowed to fall on certain substances of low atomic weight like Carbon, the x-ray beam is Scattered and it consists of two components.

1. The radiation having Same wavelengths as that of the incident radiation.
2. The other radiation with a higher wavelength Compared to the incident wavelengths.

The phenomenon of change in wave length of the scattered x-rays is called Compton shift. This effect is called Compton effect.



During the scattering process,
Compton assumed that incident photon collides with a free electron in the scattering material. The photon transfers some of its energy to the electron which recoils with this kinetic energy



Consider a photon of energy '$h\nu$' collides elastically with a free electron.

Energy before Collision | Energy after Collision

Energy of incident photon = $h\nu$

" of $\bar{e}$ at rest = m_0c^2

T.E before collision = $m_0c^2 + h\nu$

Energy of Scattered photon = $h\nu'$

" of recoil electron = mc^2

T.E after Collision = $mc^2 + h\nu'$

According to law of conservation of energy,

T.E before collision = T.E after collision

$$\boxed{h\nu + m_0c^2 = h\nu' + mc^2} \quad \text{--- (1)}$$

As the momentum is a Vector Quantity,

x and y components of momentum before and after collisions should be calculated.

Momentum before Collision

X-component

Momentum of photon = $\frac{h\nu}{c}$

" of electron = 0

T.M along x-axis = $\frac{h\nu}{c} + 0$

$= \frac{h\nu}{c}$

Y component

Momentum of photon = 0

" of $\bar{e}$ = 0

T.M along y-axis = 0.

Momentum after Collision

X-component

Momentum of Scattered photon = $\frac{h\nu'}{c}\cos\phi$

" of recoil $\bar{e}$ = $mv\cos\theta$

T.M along x-axis = $\frac{h\nu'}{c}\cos\phi + mv\cos\theta$

Y-component

Momentum of Scattered photon = $\frac{h\nu'}{c}\sin\phi$

" of recoil, $\bar{e}$ = $-mv\sin\theta$

T.M along y-axis = $\frac{h\nu'}{c}\sin\phi - mv\sin\theta$

Applying law of Conservation of momentum.

T.M before collision = T.M after collision

along x-axis, $\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\phi + m v \cos\theta$ — ②

along y-axis, $0 = \frac{h\nu'}{c}\sin\phi - m v \sin\theta$ — ③

multiplying ② with c, then $h\nu = h\nu'\cos\phi + mvc\cos\theta$

multiplying ③ with c, then $0 = h\nu'\sin\phi - mvc\sin\theta$

The above equations can be changed to

$$mvc\cos\theta = h\nu - h\nu'\cos\phi$$

$$mvc\sin\theta = h\nu'\sin\phi$$

Squaring and adding these two, we get

$$m^2v^2c^2 = [h\nu - h\nu'\cos\phi]^2 + h^2\nu'^2\sin^2\phi$$

$$m^2v^2c^2 = h^2\nu^2 + h^2\nu'^2\cos^2\phi - 2h^2\nu\nu'\cos\phi + h^2\nu'^2\sin^2\phi$$

$$\therefore m^2v^2c^2 = h^2\nu^2 + h^2\nu'^2 - 2h^2\nu\nu'\cos\phi \quad — ④$$

Consider ①, $h\nu + m_0c^2 = h\nu' + mc^2$

$$\Rightarrow mc^2 = (h\nu - h\nu') + m_0c^2$$

Squaring on both sides, $m^2c^4 = [(h\nu - h\nu') + m_0c^2]^2$

$$m^2c^4 = (h\nu - h\nu')^2 + m_0^2c^4 + 2(h\nu - h\nu')\cdot m_0c^2$$

$$m^2c^4 = h^2\nu^2 + h^2\nu'^2 - 2h^2\nu\nu' + m_0^2c^4 + 2(h\nu - h\nu')m_0c^2 \quad — ⑤$$

subtract (4) from (5)

$$m^2c^2\left[c^2-v^2\right] = -2h^2\nu\nu' + 2h^2\nu\nu'\cos\phi + 2(h\nu - h\nu')m_0c^2 + m_0^2c^4 \quad \text{--- (6)}$$

We know that from theory of relativity,

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} \Rightarrow \boxed{m_0^2c^2 = m^2(c^2-v^2)}$$

Substitute this value in (6), we get

$$\cancel{m_0^2c^2} \cdot c^2 = -2h^2\nu\nu' + 2(h\nu - h\nu')m_0c^2 + \cancel{m_0^2c^4} + 2h^2\nu\nu'\cos\phi$$

$$\therefore\ 0 = -2h^2\nu\nu' + 2(h\nu - h\nu')m_0c^2 + 2h^2\nu\nu'\cos\phi$$

$$0 = -2h^2\nu\nu'(1-\cos\phi) + 2(h\nu - h\nu')m_0c^2$$

$$+\cancel{2}h^2\nu\nu'(1-\cos\phi) = +\cancel{2}(h\nu - h\nu')m_0c^2$$

$$h\frac{(1-\cos\phi)}{m_0c^2} = \frac{\nu-\nu'}{\nu\nu'} = \frac{1}{\nu'} - \frac{1}{\nu}$$

$$\therefore\ \frac{1}{\nu'} - \frac{1}{\nu} = h\frac{(1-\cos\phi)}{m_0c^2}$$

multiply with 'c', we get,

$$\frac{c}{\nu'} - \frac{c}{\nu} = \frac{hc}{m_0c^2}(1-\cos\phi)$$

$$\boxed{\lambda' - \lambda = \frac{h}{m_0c}\left[1-\cos\phi\right]}$$

This is Compton shift.

de-Broglie's hypothesis :

In 1924, de-Broglie extented dual nature to material particles like electrons, protons and neutrons. According to his hypothesis when particles are accelerated then those will be spread out like a wave with a certain wavelength. He gave simple mathematical equations to support his hypothesis as follows.

According to planck's theory, the energy of a photon whose frequency 'ν' can be expressed as $E = h\nu$

According to Einstein mass energy relation

$E = mc^2$, m – mass of a photon, c – velocity of a photon.

From these two $h\nu = mc^2$

ie $\frac{hc}{\lambda} = mc^2 \Rightarrow \lambda = \frac{h}{mc} = \frac{h}{mv} = \frac{h}{p}$

(PTO)

In the same way according to de-Broglie's hypothesis if an electron of charge 'e', mass 'm' is moving with a velocity in the presence of the potential 'V', then the wavelength associated with that electron can be expressed as $\lambda = \frac{h}{mv} = \frac{h}{p}$, which is called de-Broglie's wave equation.

The energy of electron interms of potential can be expressed as $E = eV$

The K.E of an electron $K.E = E = \frac{1}{2}mv^2$

$\therefore eV = \frac{1}{2}mv^2 \Rightarrow meV = \frac{m^2v^2}{2}$

$\therefore m^2v^2 = 2meV \Rightarrow p^2 = 2meV$

$\therefore p = \sqrt{2meV}$

Now de-Broglie wave equation becomes,

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

$\boxed{\therefore \lambda = \frac{12.27}{\sqrt{V}} \, \mathring{A}}$. This is the wavelength associated with an electron in presence of P.D.

<u>Matter waves</u>: According to de-Broglie's hypothesis, when the material particles like electrons are accelerated, then those will be spread out like waves called Matter waves

<u>properties</u>:— ① The motion of the particles generate matter waves.

② Lighter is the ~~velocity of the~~ particle greater will be the wavelength associated with it.

③ Smaller is the Velocity of the particle, greater will be the wavelength associated with it.

④ These waves are a new kind of waves. They are not electro magnetic waves.

⑤ The Velocity of matter waves depends on the Velocity of matter particles. ie it is not a constant.

⑥ The Velocity of matter waves is greater than the Velocity of light.

Wave function ψ :-

In Quantum Mechanics, the motion of an atomic particle is described by a Variable Quantity which is known as a wave function. It is represented by 'ψ'. It is a function of both position and time.

Physical Significance:-

① It relates the wave and particle nature.

② 'ψ' gives the information about the particle behaviour.

③ 'ψ' is a complex Quantity. So it can be expressed as $\psi = a+ib$. Hence its complex Conjugate can be represented by $\psi^* = a-ib$.

④ The product of ψ and ψ^* i.e. $|\psi\psi^*|$ (or) $|\psi|^2 = a^2+b^2$, is a real quantity and positive.

This $|\psi|^2$ represents the probability density, denoted by 'P'. This means that the probability of finding a particle at a particular position.

(5) The probability of finding a particle in a closed volume dv is represented by $P = \int |\psi|^2 dv$ (or) $\int (\psi \psi^*) dv$ where $dv = dx\,dy\,dz$

(6) If $P = 1$, then the condition is called normalisation property. ie $\int \psi \psi^* dx\,dy\,dz = 1$

i.e there is 100% chance of finding a particle with in the Volume.

(7) The wave function 'ψ' has no physical meaning where as the probability densi[ty] has a definite physical meaning.

Heisenberg uncertainty Principle :-

The product of uncertainties in determining the position and momentum of a particle is approximately equal to planck's constant.

If Δx is the uncertainty in determining the position of a particle and Δp is the uncertainty in determining the momentum. Then

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

The uncertainty principle can also be applicable to conjugate variables. ie $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$ and $\Delta J \cdot \Delta \theta \geq \frac{h}{4\pi}$, where $\Delta E, \Delta t$ are uncertainties in energy and time while ΔJ and $\Delta \theta$ are angular momentum and angle.

In classical mechanics, a moving particle at any instant has a fixed position in space and a definite momentum which can be determined if the initial values are known. In wave mechanics, the particle is described in terms of a wave packet.

When the wave packet is small (Localised), the position of a particle may be fixed but the wavelength 'λ' is not fixed and hence the momentum is not fixed. (Since $\lambda = \frac{h}{p}$). Because the wave is localised (or) finite and beyond the points A and B no wave is present & 'λ' is also keeps on changing and hence 'λ' is not fixed.

Small wave

('λ' keeps on changing)

On the other hand, when the wave packet is large. i.e the wave look like extended wave through out space. Hence the wave length 'λ' is fixed and hence momentum can be fixed. ($\because \lambda = \frac{h}{p}$)

Extended wave in space.

(λ is constant)

Because the wave is not a localised wave (or) it is extended wave in space and hence the position is not fixed (or) uncertainty.

There fore, it can be concluded that the certainty in momentum involves the uncertainty in position and the certainty in position involves uncertainty in momentum.

Applications:

(i) Non existance of electron in nucleus.

We know that the size of the nuclei is of the order of 10^{-15} m.

If an electron is present with in the nuclei, the uncertainty in its position should not exceed 10^{-15} m.

using Heisenberg uncertainty relation,

The uncertainty in momentum of electron is given by $\Delta P \geq \frac{h}{4\pi} \times \frac{1}{\Delta x}$

$$\therefore \Delta P \geq \frac{6.62 \times 10^{-34}}{4 \times \frac{22}{7} \times 10^{-15}}$$

$$\therefore \Delta P \geq 0.5266 \times 10^{-19} \text{ kgm/sec.}$$

This means that the momentum of the electron in the nucleus must be at least of the order of 0.5266×10^{-19} kgm/sec.

using relativistic formula, $E^2 = p^2c^2 + m_0^2c^4$

The energy of electron is given by $E^2 = p^2c^2 + m_0^2c^4$

$$\therefore E^2 = (0.5266 \times 10^{-19} \times 3 \times 10^8)^2 + \left[9.11 \times 10^{-31} \times (3 \times 10^8)^2\right]^2$$

$$\therefore E = 100 \text{ MeV}$$

This means that if the electron exists inside the nucleus, it should have the energy of the order of 100 MeV.

But the electrons emitted during Beta decay of radio active nuclei have energies less than 5 MeV. Hence it is evident that electrons do not exist in the nucleus.

② Finite width of Spectral lines:-

From Heisenberg uncertainty principle of energy and time relation, we have $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

Since the life time of electron in an excited state is finite ($\approx 10^{-8}$ sec), the energy levels of an atom is $\Delta E \geq \frac{h}{4\pi \cdot \Delta t}$,

Schrodinger's time independent wave equation:

Having got convinced with the de-Broglie's concept of matter waves, Schrodinger developed a wave equation for moving particles like electrons. Schrodinger equation is a fundamental equation in Quantum Mechanics, which describes the behaviour of matter waves.

Let a particle of mass 'm' moving with a velocity 'v', then it is associated with a wave.

Let 'ψ' be the wave function of the particle.

The equation for a simple harmonic wave travelling in x-direction is $y = A \sin(\omega t - kx)$

Similarly, the wave function 'ψ' associated with the moving particle be written as,

$$\psi(x,t) = \psi_0 \sin(\omega t - kx),$$

where $\psi_0 \rightarrow$ Amplitude

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

$K = \frac{2\pi}{\lambda}$, propagation vector.

Diff. this equation w.r.to 'x',

$$\frac{d\psi}{dx} = (-K)\psi_0 \cos(\omega t - kx)$$

$$d^2\psi/dx^2 = (-K)(-k)\psi_0 [-\sin(\omega t - kx)]$$

$$\therefore \frac{d^2\psi}{dx^2} = -k^2 \psi_0 \sin(\omega t - kx)$$
$$= -k^2\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi \text{ and hence } \boxed{\frac{d^2\psi}{dx^2} + k^2\psi = 0}$$

$$\therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \left(\frac{2\pi}{\lambda}\right)^2\psi = 0 \qquad \left(\because k = 2\pi/\lambda\right)$$

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \quad \text{— (1)}$$

But from de-Broglie's hypothesis $\lambda = \frac{h}{mv}$

then $\lambda^2 = \frac{h^2}{m^2v^2}$ — (2)

put (2) in (1), we get $\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\left(\frac{h^2}{m^2v^2}\right)}\psi = 0$

$$\therefore \frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}(m^2v^2)\psi = 0 \quad \text{— (3)}$$

The total energy of the particle $E = K.E + P.E$

for moving particle $K.E = \frac{1}{2}mv^2$ and

let $V(r)$ be the potential energy of electron.

then $E = K.E + P.E \Rightarrow E = \frac{1}{2}mv^2 + V(r)$

$$\Rightarrow \frac{1}{2}mv^2 = E - V(r)$$

$$mv^2 = 2\left[E - V(r)\right]$$

$$\Rightarrow m^2v^2 = 2m\left[E - V(r)\right] \quad \text{— (4)}$$

put ④ in ③, we get $\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2} 2m[E-V(r)]\psi = 0$

ie $\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2} 2m[E-V(r)]\psi = 0$

$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}[E-V(r)]\psi = 0$ — ⑤

In Quantum mechanics, most frequently $h/2\pi$ occurs as $\hbar$. ie $\hbar = \frac{h}{2\pi}$, $\Rightarrow h = \hbar \times 2\pi$

Hence $h^2 = \hbar^2 \times 4\pi^2$ — ⑥

put ⑥ in ⑤, we get $\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2 \times 4\pi^2}[E-V(r)]\psi = 0$

$$\Rightarrow \boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E-V(r)]\psi = 0}$$

This is the one dimensional Schrodinger's time independent wave equation.

This equation can be extended in 3-Dimensional

ie $\left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}\right) + \frac{2m}{\hbar^2}[E-V(r)]\psi = 0$

ie $\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\psi + \frac{2m}{\hbar^2}[E-V(r)]\psi = 0$

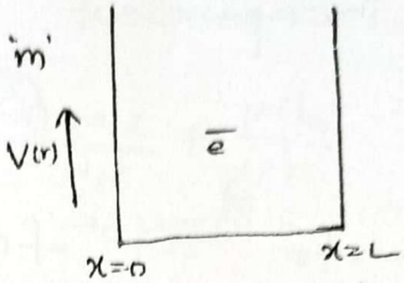
$\Rightarrow \boxed{\nabla^2\psi + \frac{2m}{\hbar^2}[E-V(r)]\psi = 0}$, where $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

In this equation as the time factor does not appear and hence it is called time independent.

Scanned with CamScanner

Particle in a potential Box:-

Suppose an electron of mass 'm' moves back and forth in a one dimensional crystal of length 'L' parallel to x- direction.



At the two ends of the crystal ie at $x=0$ and at $x=L$ two potential walls of infinite height exist, so that the particle may not penetrate the walls. Assume that the P.E of the crystal is constant. Let us assume the P.E of the electron inside the crystal is zero.

As the particle is inside the potential box, the probability of the particle inside the crystal is equal to one. ie $|\psi\psi^*|$ (or) $|\psi|^2=1$ and out side the potential box, the probability $P=|\psi|^2=0$, Hence $\psi(x)=0$ for $0 \geq x \geq L$.

This study will show Quantum nos., discrete values of energy, the wave function associated with particle

Consider one dimensional Schrodinger time independent wave equation ie

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

for a free particle, $V(r) = 0$.

$$\therefore \frac{d^2\psi}{dx^2} + \frac{2mE\psi}{\hbar^2} = 0$$

Let $\frac{2m}{\hbar^2}E = k^2$, — ①

$\therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0$ This is a second order differential equation in terms of 'ψ'.

It has a solution of $\psi(x) = A\sin kx + B\cos kx$

To find A and B, apply boundary conditions

① $\psi(x) = 0$ at $x=0$ ② $\psi(x) = 0$ at $x = L$

Applying boundary condition ①, we get

$$0 = B \Rightarrow \boxed{B=0}$$

Applying boundary condition ②, we get

$$A \sin kL = 0 \Rightarrow kL = n\pi$$

$$\therefore k = \frac{n\pi}{L} \Rightarrow k^2 = \frac{n^2\pi^2}{L^2} \quad \text{— ②}$$

from ① & ②

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

$$\therefore \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2\pi^2 \times h^2}{4\pi^2 \times 2mL^2} = \frac{n^2h^2}{8mL^2}$$

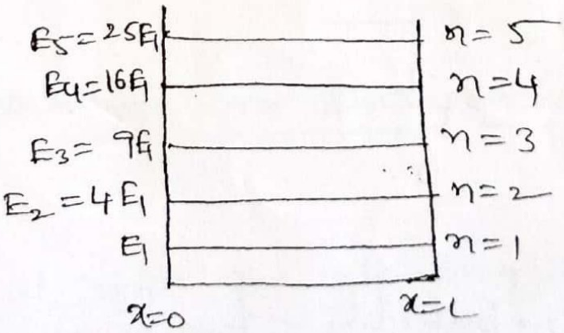
$$\therefore \quad \boxed{E_n = \frac{n^2h^2}{8mL^2}} \quad \text{--- (3)}$$

Equation (3) indicates that a particle in the box can take discrete values of energy for $n = 1, 2, 3, \ldots$ ie energy is Quantised.

These discrete values of energy are called Eigen values of energy (or) allowed energy states.

The no. 'n' is called Quantum no.

From equation (3), the energy is inversely proportional to mass of the particle and square of the length of the potential box.



Wave function ψ:

wave function $\psi = A \sin kx$

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

To find 'A', apply normalisation property,

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

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

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

$\therefore A^2 \left[\frac{1}{2}\left[x\right]_0^L + 0\right] = 1 \Rightarrow A^2 = \frac{2}{L}$

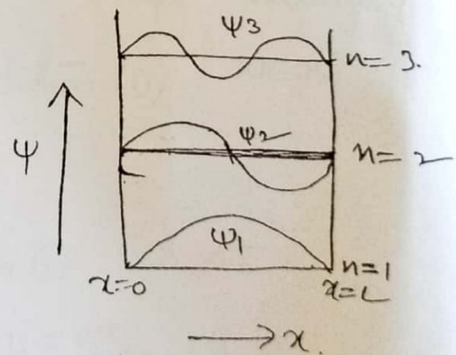
$\Rightarrow A = \sqrt{\frac{2}{L}}$.

$\therefore$ wave function $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}\right)x$.

for $n=1$, ψ_1 has two nodes at $x=0$ and at $x=L$

for $n=2$, ψ_2 has 3 nodes at $x=0, L/2, L$

for $n=3$, ψ_3 has 4 nodes at $x=0, \frac{L}{3}, \frac{2L}{3}, L$



Probability density :-

We know that $P = \frac{2}{L} \sin^2\left(\frac{n\pi}{L}\right)x$

This is maximum when $\left(\frac{n\pi}{L}\right)x$ is $\frac{n\pi}{2}$, for $n=1,3,5$

$\therefore \frac{n\pi}{L}x = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2} \ldots$

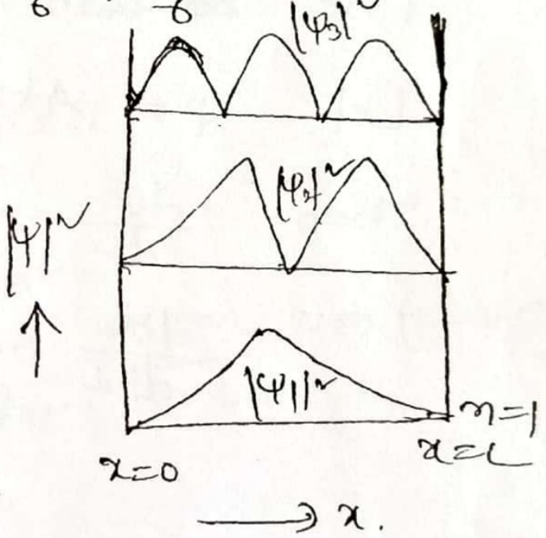
$x = \frac{L}{2n}, \frac{3L}{2n}, \frac{5L}{2n} \ldots$

for $n=1$, the most probable position of the particle is at $x = L/2$

for $n=2$, the most probable position of the particle is at $x = \frac{L}{4}, \frac{3L}{4}$

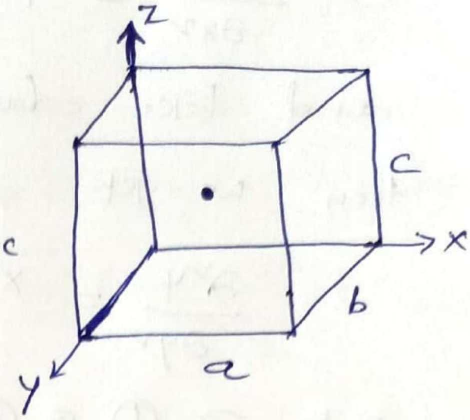
for $n=3$, the most probable position of the particle is at $x = \frac{L}{6}, \frac{3L}{6}, \frac{5L}{6}$.

These are as shown.



Particle in 3-Dimensional Potential box :

Let us consider a particle of mass 'm' moving in a 3-dimensional rectangular box having sides a, b, c along x, y and z-axes as shown in figure.



The P.E of the particle inside the box will be zero. The P.E of the particle out side the box be '∞'.

The Schrodinger time independent wave equation for a particle moving inside the box is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad \text{—} \text{ (1)}$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi + \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$\Rightarrow \boxed{\nabla^2 \psi + \frac{8\pi^2 m}{h^2} E\psi = 0}, \quad \text{where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

This is Second order diff. equation, where the wave function ψ is a function of co-ordinates (x, y, z)

$\Rightarrow$ $\psi(x, y, z)$ is a product of 3-function each depending on just one-coordinate

$$\therefore \psi(x, y, z) = X_x Y_y Z_z \quad \text{—} \text{ (2)}$$

Take double derivative w.r.to 'x' ones.

$$\frac{\partial^2 \psi}{\partial x^2} = yz \frac{d^2 x}{dx^2} \quad — ⓐ$$

and take double derivative w.r.to y and z again, then we get

$$\frac{\partial^2 \psi}{\partial y^2} = xz \frac{d^2 y}{dy^2} \quad — ⓑ \qquad \frac{\partial^2 \psi}{\partial z^2} = xy \frac{d^2 z}{\partial z^2} \quad — ⓒ$$

put ⓐ, ⓑ & ⓒ in equation ①,

$$yz \frac{d^2 x}{dx^2} + xz \frac{d^2 y}{dy^2} + xy \frac{d^2 z}{dz^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

$$yz \frac{d^2 x}{dx^2} + xz \frac{d^2 y}{dy^2} + xy \frac{d^2 z}{dz^2} + \frac{8\pi^2 m}{h^2} E\, xyz = 0$$

Dividing through out by xyz, we get

$$\frac{1}{x} \frac{d^2 x}{dx^2} + \frac{1}{y} \frac{d^2 y}{dy^2} + \frac{1}{z} \frac{d^2 z}{dz^2} + \frac{8\pi^2 m}{h^2} E = 0$$

$$\frac{1}{x} \frac{d^2 x}{dx^2} + \frac{1}{y} \frac{d^2 y}{dy^2} + \frac{1}{z} \frac{d^2 z}{dz^2} = -\frac{8\pi^2 m E}{h^2}$$

(cont.)

ie $$\frac{1}{x} \frac{d^2 x}{dx^2} = -\frac{8\pi^2 m E_x}{h^2} \quad — ⓐ'$$

$$\frac{1}{y} \frac{d^2 y}{dy^2} = -\frac{8\pi^2 m E_y}{h^2} \quad — ⓑ'$$

$$\frac{1}{z} \frac{d^2 z}{dz^2} = -\frac{8\pi^2 m E_z}{h^2} \quad — ⓒ'$$

Re-arrange ⓐ', ⓑ' and ⓒ'

$$\frac{d^2 x}{dx^2} + \frac{8\pi^2 m}{h^2} E_x . x = 0. \quad \text{and} \quad \frac{d^2 z}{dz^2} + \frac{8\pi^2 m}{h^2} E_z . z = 0$$

$$\frac{d^2 y}{dy^2} + \frac{8\pi^2 m}{h^2} E_y . y = 0$$

Total energy of a particle in all 3-directions

$$E = E_x + E_y + E_z \quad \text{--- (3)}$$

we already know that equations for 1-D box.

$$X = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a}\right)x, \quad Y = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b}\right)y \quad \text{and}$$

$$Z = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi}{c}\right)z$$

and $E_x = \dfrac{n_x^2 h^2}{8ma^2}, \quad E_y = \dfrac{n_y^2 h^2}{8mb^2}, \quad E_z = \dfrac{n_z^2 h^2}{8mc^2}$

The wave function in 3-D box becomes,

$$\psi = XYZ$$

$$\therefore \psi = \sqrt{\frac{2}{a}} \cdot \sin\left(\frac{n_x \pi}{a}\right)x \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b}\right)y \cdot \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi}{c}\right)z$$

$$\therefore \boxed{\psi = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right)}$$

This is the expression for wave function.

The expression for energy $E = E_x + E_y + E_z$.

$$\therefore E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_y^2 h^2}{8mc^2}$$

$$\therefore \boxed{E = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]}$$

This is the expression for energy of a particle in 3-D potential box.

postulates of Quantum Mechanics

The relation ship between quantum mechanics and operators has helped to present the concepts in the form of some postulates.

They are

① The state of a system in Q.M is described by a wave function $\psi(x,y,z,t)$ where $x,y,z \rightarrow$ are 3 - co-ordinates, $t \rightarrow$ time

For a wave function 'ψ' to describe any physical system, the following boundary conditions must be satisfied.

(a) $\psi(x)$ as well as $\frac{d\psi}{dx}$ must be finite

(b) $\psi(x)$ as well as $\frac{d\psi}{dx}$ must be continuous.

(c) $\psi(x)$ as well as $\frac{d\psi}{dx}$ must be single valued

(d) $\psi(x)$ must satisfies Born's condition.

ie, The probability of finding a particle in a given volume element $dx\,dy\,dz$ is given by $|\psi|^2 dx\,dy\,dz$ (or) $\psi\psi^* dx\,dy\,dz$

If the particle is some where in the space then the probability be equal to 1.

i.e $\therefore \int \psi \psi^* \, dx\,dy\,dz = 1$

This is called Normalisation property.

② Every observable physical property of a system can be characterized by a linear operator. For example, The position (A) is characterised by an operator ($\hat{A}$). When this operator operates on a wave function 'ψ', then the result is $\hat{A}\psi = a\psi$, where 'a' is observable Quantity known as eigen Value of operator.

The following table shows some quantum mechanics operators corresponding to different classical observable quantities.

Classical Quantity	Quantum Mechanical Operator
Cartesian components of position x, y, z →	$\hat{x}, \hat{y}, \hat{z}$
position Vector r →	$\hat{r}$
momentum P →	$-i\hbar\nabla$
Cartesian components of linear momentum P_x, P_y, P_z →	$-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}$
Total energy E →	$i\hbar\frac{\partial}{\partial t}$

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③ When an operator $\hat{A}$ is operated on a wave function 'ψ', an average result obtained is given by

$$\langle A \rangle = \frac{\int \psi^* A \psi \, dx dy dz}{\int \psi \psi^* \, dx dy dz}$$

If the wave function 'ψ' is normalized to unity, then the denominator is equal to 1.

Then $\langle A \rangle = \int \psi^* A \psi \, dx dy dz$

For example, $\langle P_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, dx dy dz$

$$\langle P_y \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial y} \, dx dy dz$$

$$\langle P_z \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial z} \, dx dy dz$$

$$\langle E \rangle = i\hbar \int \psi \psi^* \frac{\partial \psi}{\partial t} \, dx dy dz$$