

# Engineering Physics

## Unit - II

### Quantum Mechanics

Introduction to quantum mechanics: →

→ Classical Mechanics: →

classical mechanics is concerned with the motion of particle under the influence of applied forces and based on Newton's three laws i.e. the law of inertia, the law of force and the law of action and reaction. It includes the concepts of absolute mass, absolute space and absolute time and the particle's position, mass, velocity & acceleration can be measured. It is less accurate and less reliable than the more recent mechanic field of quantum mechanics. There are some failures of classical mechanics which are as follows -

- (1) It could not explain the stability of atoms.
- (2) It could not explain the observed spectrum of black body radiations.
- (3) It could not explain some phenomena like photoelectric effect, Compton effect, Raman effect etc.

→ Quantum Mechanics: →

A new string of mechanics, quantum mechanics, was created by Planck, Bohr, Heisenberg, Einstein, Schrodinger and several other scientists in order to resolve the incompatibilities

of classical Mechanics. In Q.M. we give force on the motion of the basic constituent of matter such as  $e^-$ , atoms.

Quantum Mechanics describes light as both a wave and a particle, depending on the situation. Light exhibits interference and diffraction, both are associated to wave characteristics. However, there is also evidence that supports the particle theory of light that states e.m. waves consist of photon and bursts that have momentum and energy.

#### → Origin of quantum nature of light : →

Wave nature of light is capable of explaining many phenomenon like interference, diffraction, polarization etc but this wave theory is failed to explain the observed phenomenon of photo electric effect, Compton effect etc. This laid the scientist to develop a new theory of quantum nature of light. According to this theory light consists of a large number of oscillating particles or quanta emitted by the luminous body. Max Planck proposed this theory. The quantum has energy  $E = h\nu$ , where  $\nu$  is the freq. of the monochromatic radiation and  $h$  is the Planck's constant. These quanta are the basic units of energy and cannot be further divided. On basis of Planck's quantum theory of light, Einstein was able to explain photoelectric effect.

## Wave-particle duality :-

The wave theory of light successfully explained the phenomena such as interference, diffraction and polarization but it is failed to explain the photo-electric effect, Compton effect etc. However these phenomena have been explained by quantum theory of light.

According to quantum theory, light of frequency  $\nu$  is composed of tiny discrete packets or bundles of energy called photons, each having an energy  $h\nu$ . Photons behave almost exactly like a material particle. Thus light has a dual nature, i.e. it possess both particle and wave properties.

Note:- light never shows both characters simultaneously. when light (E.m. radiation) interacts with matter, It shows its particle character whereas when light interacts with light (e.m. radiation), it shows wave character.

## Matter waves :-

### (De-Broglie Hypothesis) :-

on the basis of the concept of dual nature of light Louis de Broglie in 1924 gave the hypothesis that -

" particles in motion possess a wave characteristic"

associated with them just like the radiant energy in the form of waves has particle properties associated with it."

Such wave associated with the material particles are known as "matter waves" or "de Broglie waves".

NOTE:- All the fundamental particles as  $e^-$ , photons, neutrons, atoms and molecules etc. have waves associated with them.

wave function is

### Introduction of wave mechanics:-

In Q.M. we assume dual nature of particles. De Broglie introduced the concept of matter waves. For understanding the behaviour of the fundamental particles of matter we associate a wave- $f^n$  with matter wave, known as wave mechanics. A mathematical formulation using a wave- $f^n$  wave-function  $\psi(x, y, z, t)$  was developed in 1926 by Schrodinger and it is known as wave mechanics or quantum mechanics.

### wave function:-

Schrodinger generalized the concept of matter waves and gave the eq<sup>n</sup> for describing the dynamics of quantum postulates. The eq<sup>n</sup> is known as the Schrodinger's equation. The idea of matter waves was used by Schrodinger to arrive at a wave eq<sup>n</sup> that describes quantum mechanical particles like e<sup>-</sup>, proton etc. As wave is a propagating disturbance, i.e. disturbance that varies periodically with position  $\vec{r}$  and time  $t$ , Schrodinger defined wave-function  $\psi(\vec{r}, t)$  which contains all the information about behaviour of the particle.

So A physical system is completely described by a wave-function  $\psi(x, y, z, t)$ . It is also known as quantum mechanical state of the system.

### Physical Interpretation of wave-fn. →

The wave function  $\psi(r, t)$  which is a solution of Schrödinger eq<sup>n</sup> provides a complete description of the behaviour of a particle in a potential field  $V(\vec{r}, t)$ .  $\psi(\vec{r}, t)$  is a complex fn, which itself has no physical meaning but it can be made related to the probability of finding the particle at the position  $\vec{r}$  at time  $t$ .

### (i) Schrödinger Interpretation:→

Schrödinger introduced the wave function  $\psi$  taking into account the wave-particle duality and accordingly assigned physical interpretation to  $\psi$ .

In case of E.M. waves, the intensity of an e.m. wave of amplitude  $E_0$  is  $I = \frac{1}{2} C \epsilon_0 E_0^2$  — (1)

whereas in quantum picture of photon beam, it is

$$I = N h \nu \quad \text{--- (2)}$$

where  $\epsilon_0$  is permittivity of free space and  $N$  is number of photons per unit volume.

From (1) + (2)

$$N = \frac{C \epsilon_0 E_0^2}{2 h \nu}$$

$$\text{or } N \propto E_0^2$$

i.e. intensity of photons or particles is proportional to square of the wave amplitude. According to Schrödinger, the square of the modulus of wave- $f^n$  measures particle density.

$$|\psi|^2 = \psi\psi^* = \text{particle density}$$

### Max Born's Interpretation: →

According to Max Born, the square of the modulus of wave- $f^n$  gives the probability density i.e., probability per unit volume.

$$|\psi|^2 = \text{probability density}$$

### Properties of wave-function: →

The acceptable wave- $f^n$  should have following properties.

- (1)  $\psi$  must be well behaved in the given region.  
i.e.  $\psi$  along with its derivatives must be single valued, continuous and finite everywhere.
- (2) The probability of finding a particle at certain location and at certain time i.e.  $\int |\psi|^2 dv$  remains constant wrt time. i.e.  $\psi$  must be normalized. i.e.

$$\int |\psi|^2 dx = 1$$

(3)  $\psi$  must obey superposition principle. i.e. If  $\psi_1$  and  $\psi_2$  are two independent solutions of the Schrödinger eq<sup>n</sup>, then  $(a_1\psi_1 + a_2\psi_2)$  will also be a sol<sup>n</sup> of Schrödinger eq<sup>n</sup>.

(4) The result of an experiment is the expectation value of given quat quantity  $Q$

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

where  $\psi$  is a normalized function.

orthogonal and normalized wave-function :-

Normalization of a wave-function :-

According to the physical meaning of wave-f<sup>n</sup> the probability of finding the particle in a volume element  $dV = dx dy dz$  is given by

$$\begin{aligned} P(\vec{r}, t) dV &= |\psi(\vec{r}, t)|^2 dV \\ &= \psi(\vec{r}, t) \cdot \psi^*(\vec{r}, t) dV \end{aligned}$$

As we know that the particle must exist somewhere in the whole universe, therefore the probability of finding a particle in the whole universe must be one hence

$$\int_{-\infty}^{\infty} |\psi(\vec{r}, t)|^2 dV = 1$$

If a wave-f<sup>n</sup>  $\psi(\vec{r}, t)$  is chosen s.t it satisfies the above condition, the wave-f<sup>n</sup> is said to be normalized and this property is called normalization of a wave-f<sup>n</sup>.

Note :-

$$\text{if } \int \psi \psi^* dV = N$$

$$\Rightarrow \frac{1}{N} \int \psi \psi^* dV = 1$$

$$\Rightarrow \int \left( \frac{\psi}{\sqrt{N}} \right) \left( \frac{\psi^*}{\sqrt{N}} \right) dv = 1$$

then  $\frac{\psi}{\sqrt{N}}$  is the normalized wave function and  $\frac{1}{\sqrt{N}}$  is the normalizing factor, which is a constant and independent of the coordinates  $x, y, z$ .

Orthogonal wave function: →

For a given quantum mechanical system, if two different wave-fns  $\psi_i$  and  $\psi_j$  represent possible solutions of same Schrodinger eqn and are such that

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j dv = 0 \quad \text{or} \quad \int_{-\infty}^{\infty} \psi_j^* \psi_i dv = 0 \quad \text{for } i \neq j$$

then these wave functions are called orthogonal wave-fns.

Eigen function and Eigen Values: →

If an operator  $O$  is operated on a wave function  $\psi$ , then

$$O\psi = \psi'$$

Here  $\psi'$  will be a function of same variables as wavefn  $\psi$ .

In several function  $\psi'$  will be quite different from  $\psi$ , in some cases, it may be observed

$$O\psi = \lambda \psi$$

where  $\lambda$  is some constant.

In all such cases function  $\psi$  is called an eigenfn of the operator  $O$  and  $\lambda$  is called the eigen value of the given fn  $\psi$ .

Schrodinger's equation:- Schrodinger defined wave-f"  $\psi(r, t)$  which contains all the information about the behaviour of the particle. Since matter waves are not real waves, the wave-function is expected to be complex in general and can be written as -

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

here angular frequency  $\omega = 2\pi\nu = 2\pi v \cdot h = \frac{E}{\hbar/2\pi} = E/\hbar$

and wave vector  $K = \frac{2\pi}{\lambda} = \frac{2\pi \cdot h}{\lambda \cdot h} = \frac{h}{\lambda} \cdot \frac{1}{\hbar/2\pi} = P/\hbar$

Time Dependent Schrodinger's wave equation:-

Let a particle of mass  $m$  is moving along  $x$ -dir in conservative force field. If the potential energy, momentum and total energy of the particle is  $U$ ,  $p_x$  (along  $x$ -dir) and  $E$  respectively then the wave-f" for the moving particle can be given as -

$$\psi(x, t) = A \exp \left\{ \frac{i}{\hbar} (p_x - Et) \right\} \quad \text{--- (1)}$$

on differentiating eq" (1) w.r.t. time, we get

$$\frac{\partial \psi(x, t)}{\partial t} = -\frac{iE}{\hbar} A \exp \left\{ \frac{i}{\hbar} (p_x - Et) \right\}$$

$$\text{or } \frac{\partial \psi(x, t)}{\partial t} = -\frac{iE}{\hbar} \psi(x, t)$$

$$E \psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad \text{--- (2)}$$

here  $E \rightarrow i\hbar \frac{\partial}{\partial t}$  is known as total energy operator.

on differentiating eq" (1) ~~w.r.t. x~~, we have -

$$\frac{\partial \psi(x, t)}{\partial x} = \frac{ip}{\hbar} \psi(x, t)$$

$$\Rightarrow P\psi(x,t) = \frac{i}{\hbar} \frac{\partial \psi(x,t)}{\partial x} = -i\hbar \frac{\partial \psi(x,t)}{\partial t}$$

here  $P \rightarrow -i\hbar \frac{\partial}{\partial x}$  is known as momentum operator in  $x$ -dir.

again differentiating it -

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = -\frac{P^2}{\hbar^2} \psi(x,t) \quad \text{--- (3)}$$

$$\text{or } P^2 \psi(x,t) = -\frac{\hbar^2}{m} \frac{\partial^2 \psi(x,t)}{\partial x^2} \quad \text{--- (4)}$$

By means of the principle of conservation of energy in non-relativistic mechanics, we have -

$$\text{Total energy} = K.E. + P.E.$$

In general, P.E. is f' of  $x$  and  $t$  so -

$$E = \frac{P^2}{2m} + U(x,t) \quad \text{--- (5)}$$

on multiplying eq (5) by  $\psi(x,t)$  from left, on the both sides

$$E\psi(x,t) = \frac{P^2}{2m} \psi(x,t) + U\psi(x,t) \quad \text{--- (6)}$$

using eq (2) + (4) in eq (6), we get

$$\boxed{i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + U\psi(x,t)} \quad \text{--- (7)}$$

Eq (7) is known as Schrodinger 1-D time dependent wave eq.  
for free particle  $U=0$

$$\text{So } i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2}$$

This is Schrodinger's 1-D time dependent wave eq for free particle.

In 3-D, Schrodinger eq' Shall have a form

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi$$

$$\boxed{i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + U\psi} \quad \text{3-D eq'} \quad \textcircled{8}$$

where  $\nabla^2$  = Laplacian operator  $= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Hamiltonian (Total energy operator) :-

from eq'  $\textcircled{8}$

$$i\hbar \frac{\partial \psi}{\partial t} = \left( -\frac{\hbar^2}{2m} \nabla^2 + U \right) \psi \quad \text{--- } \textcircled{9}$$

$$\text{or} \quad E\psi = H\psi \quad \text{--- } \textcircled{10}$$

Comparing eq'  $\textcircled{9}$  &  $\textcircled{10}$

$$H = \left[ -\frac{\hbar^2}{2m} \nabla^2 + U \right] \rightarrow \text{Hamiltonian operator}$$

or Total energy operator.

Hamiltonian operator depends on position only and  
E is called energy operator which depends on  
time only.

Time independent Schrodinger's eq<sup>n</sup>: →

We know from eq<sup>n</sup> ①

$$\Psi(x, t) = A e^{\frac{i p x}{\hbar}} \cdot e^{-\frac{i E t}{\hbar}} \quad \text{--- (11)}$$

In most of the physical system the potential energy doesn't depend on the time but depends only on the position of the particle i.e.  $V(x, t) = V(x)$ . For such a system, the wave f<sup>n</sup>  $\Psi(x, t)$  can be separated into time independent and time dependent part as

$$\Psi(x, t) = \psi(x) e^{-\frac{i E t}{\hbar}} \quad \text{--- (12)}$$

We know that time dependent Schrodinger eq<sup>n</sup> is

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V\Psi(x, t) \quad \text{--- (13)}$$

putting eq<sup>n</sup> ② in eq<sup>n</sup> ⑬

$$i\hbar \frac{\partial}{\partial t} [\psi(x) e^{-\frac{i E t}{\hbar}}] = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} [\psi(x) e^{-\frac{i E t}{\hbar}}] + V\psi(x) e^{-\frac{i E t}{\hbar}}$$

or

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

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

or

$$\boxed{\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0} \quad \text{--- (14)}$$

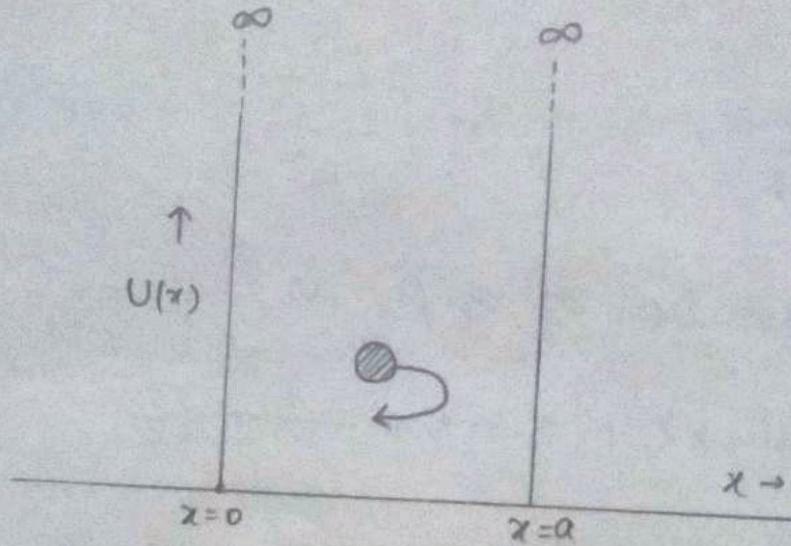
This is time independent 1-D Schrodinger's eq<sup>n</sup>.

Similarly in 3-D Case

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

Application of Schrodinger wave equation:-

Free particle in 1-D box:-



One dimensional infinite potential box

Consider a particle restricted to move from  $x=0$  to  $x=a$  as shown in figure. We say that the particle is confined in 1-D infinite potential well because the potential energy is zero within the box and infinite at the walls. This means particle is free within the well and can't be found outside the well. This sets the boundary conditions on wave-f: i.e.,

$$\psi = 0 \text{ for } x \leq 0 \text{ and } x \geq a \quad \text{--- (1)}$$

The potential energy  $U(x)$  of the particle can be defined as

$$U(x) = \begin{cases} 0, & \text{for } 0 < x < a \\ \infty, & \text{for } x \leq 0 \text{ and } x \geq a \end{cases}$$

Schrodinger's time independent eq" describing the quantum mechanical motion of a particle within the box is -

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

or

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2me}{\hbar^2} K^2 \psi = 0 \quad \dots \textcircled{2}$$

where  $K^2 = \frac{2me}{\hbar^2}$  or  $K = \sqrt{\frac{2me}{\hbar^2}}$   $\dots \textcircled{3}$

The general solution of eq"  $\textcircled{2}$  is -

$$\psi(x) = A \sin Kx + B \cos Kx \quad \dots \textcircled{4}$$

Determination of Constants A & B :-

The values of A & B can be determined by using boundary conditions in eq"  $\textcircled{1}$

$\psi = 0$  at  $x=0$ , we have

$$\begin{aligned} 0 &= A \sin 0 + B \cos 0 \\ &\Rightarrow B = 0 \end{aligned}$$

Now eq"  $\textcircled{4}$  becomes

$$\psi(x) = A \sin Kx \quad \dots \textcircled{5}$$

again  $\psi = 0$  at  $x=a$

$$0 = A \sin Ka$$

$$\sin Ka = 0 = \sin n\pi$$

$$Ka = n\pi \quad \dots \textcircled{6}$$

$$n = 1, 2, 3, \dots$$

To determine Constant  $n$ , let us apply the normalization condition of the wave-f"

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

$$\begin{aligned} & \therefore \int_0^a A^2 \sin^2 Kx dx = 1 & \text{from eq } ⑥ K = \frac{n\pi}{a} \\ & \Rightarrow \frac{A^2}{2} \cdot \frac{1}{2} \int_0^a (1 - \cos 2Kx) dx = 1 & \because \cos 2\theta = 1 - 2\sin^2 \theta \\ & \Rightarrow \frac{A^2}{2} \int_0^a \left[ 1 - \cos \frac{2n\pi x}{a} \right] dx = 1 \\ & \Rightarrow \frac{A^2}{2} \cdot a = 1 \quad \Rightarrow A = \sqrt{\frac{2}{a}} \end{aligned}$$

Eigenfunctions and eigen values:-

on putting the value of A, K in eq<sup>n</sup> ⑤

$$\boxed{\psi = \sqrt{\frac{2}{a}} \sin \left( \frac{n\pi}{a} \cdot x \right)} \rightarrow \text{Eigenfunctions}$$

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

The wave f" corresponding to eigen value  $E_n$  is called as eigen function and

Now from eq ⑤ + ⑥

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

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

or

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

$n=1, 2, 3 \dots$

Energy eigen values.

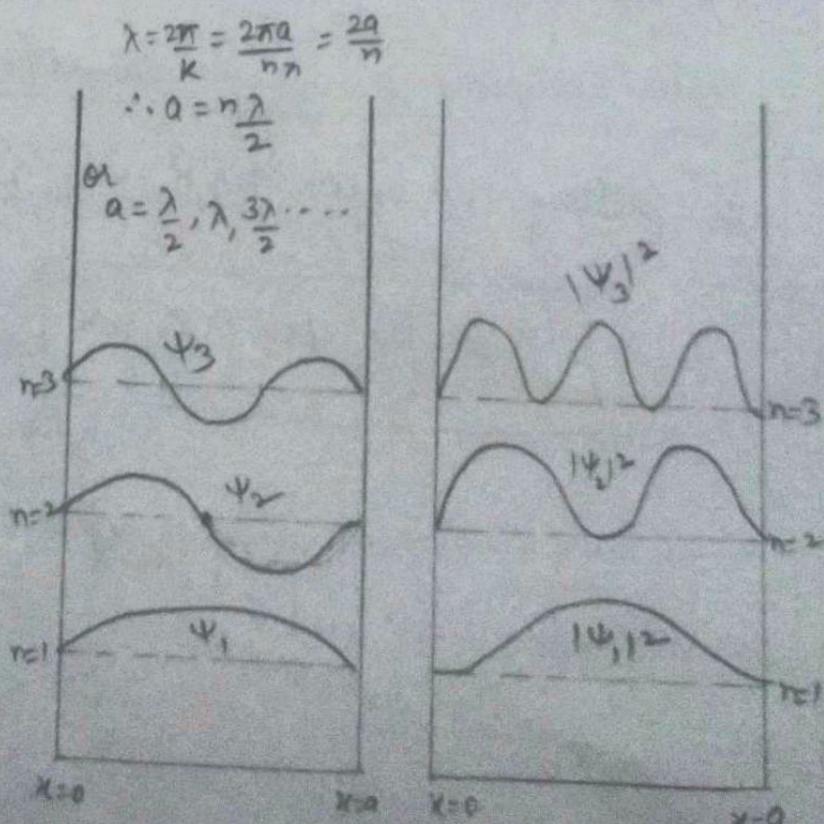
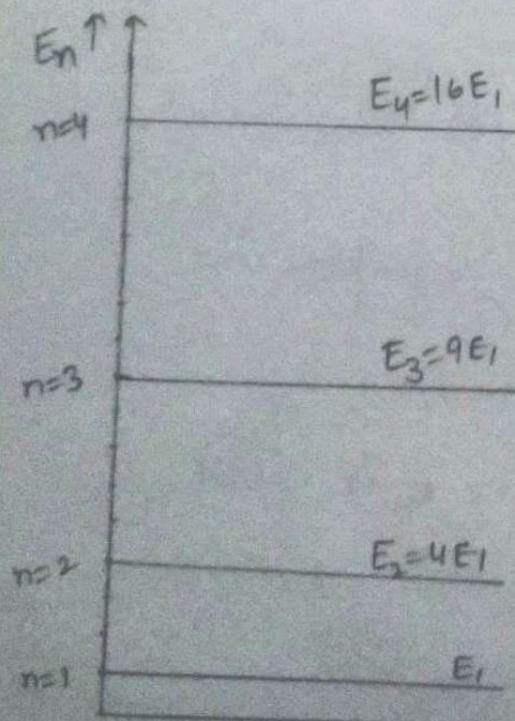
⑧

It also tells us that particle takes only discrete values or eigen values. Another significant aspect is that trapped particle doesn't have zero energy. The min. energy allowed is called as zero point energy and is given by -

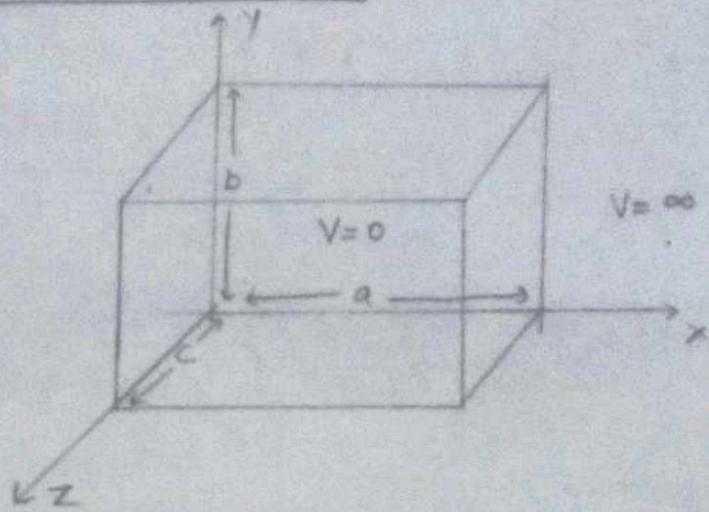
$$E_0 = \frac{\pi^2\hbar^2}{2ma^2} = \frac{\hbar^2}{8ma^2} \quad \text{for } n=1$$

The state corresponding to this energy is called as ground state.

Discrete energy levels, Eigen wave-f" and probability density curves



Free particle in a 3-D box : →



Let us consider the motion of a free particle in a 3-D potential box of length  $a$ , breadth  $b$  and height  $c$ . The potential inside the box is  $V(x, y, z) = 0$  and outside infinite. The Schrödinger eq" becomes -

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad \text{--- (1)}$$

where  $m$  is the mass of the particle and  $E$  is its total energy.

for solving the eq" ①

Let  $\psi(x, y, z) = X(x) Y(y) Z(z)$  --- (2)

( $\because$  the three variables  $x, y + z$  are independent, the method of separation of variables can be employed.)

Substituting eq ③ in eq ①, and then we get

$$ye \frac{\partial^2 X}{\partial x^2} + xe \frac{\partial^2 Y}{\partial y^2} + xy \frac{\partial^2 Z}{\partial z^2} = -\frac{2me}{h^2} XYZ$$

Dividing by  $XYZ$ , we have

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -\frac{2me}{h^2} \quad \text{--- } ④$$

as the three terms on L.H.S. are independent to each other, so that each term can be put equal to some constant. So

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -k_x^2 \Rightarrow \frac{\partial^2 X}{\partial x^2} + k_x^2 X = 0 \quad \text{--- } ⑤$$

$$\frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} = -k_y^2 \Rightarrow \frac{\partial^2 Y}{\partial y^2} + k_y^2 Y = 0 \quad \text{--- } ⑥$$

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -k_z^2 \Rightarrow \frac{\partial^2 Z}{\partial z^2} + k_z^2 Z = 0 \quad \text{--- } ⑦$$

So eq ④ becomes

$$k_x^2 + k_y^2 + k_z^2 = \frac{2me}{h^2} \quad \text{--- } ⑧$$

The solution of eq ⑤ is given by

$$X(x) = A \sin k_x x + B \cos k_x x \quad \text{--- } ⑨$$

where  $A$  &  $B$  are constants. For a box, at  $x=0$  and  $x=a$ , the potential  $V$  is infinite. Hence the wave functions  $X(x)$  at these positions must be zero. i.e.

$$X(x)=0 \quad \text{at } x=0$$

from ⑨  $0 = A \sin k_x 0 + B \cos k_x 0$

$$\text{or} \quad B=0$$

$$\text{So} \quad X(x) = A \sin k_x x$$

again  $X(x) = 0$  at  $x=a$

$$\text{i.e. } 0 = A \sin K_x a$$

$$\rightarrow \sin K_x a = 0 = \sin n_x \pi$$

$$K_x a = n_x \pi \Rightarrow K_x = \frac{n_x \pi}{a} \quad \text{--- (9)}$$

where  $n_x = 1, 2, 3, \dots$  positive integer

$$\therefore X(x) = A \sin\left(\frac{n_x \pi}{a} x\right) \quad \text{--- (10)}$$

To determine  $A$ , applying normalization condition  
b/w  $x=0$  and  $x=a$ , we have -

$$\int_0^a |X|^2 dx = 1 \Rightarrow \int_0^a X(x) \overline{X(x)} dx = 1$$

$$\text{or } A^2 \int_0^a \sin^2\left(\frac{n_x \pi}{a} x\right) dx = 1$$

$$\Rightarrow A^2 \cdot \frac{a}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

Therefore

$$X(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi}{a} x\right) \quad \text{--- (11)}$$

Similarly the solutions of eqn (5) + (6) are -

$$Y(y) = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi}{b} y\right) \quad \text{--- (12)}$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi}{c} z\right) \quad \text{--- (13)}$$

Thus total wave function of a free particle in a 3-D box will be

$$\boxed{\Psi(x,y,z) = \sqrt{8/abc} \sin\left(\frac{n_x \pi}{a}\right)x \sin\left(\frac{n_y \pi}{b}\right)y \sin\left(\frac{n_z \pi}{c}\right)z} \quad (14)$$

From eq (7)

$$\left(\frac{n_x \pi}{a}\right)^2 + \left(\frac{n_y \pi}{b}\right)^2 + \left(\frac{n_z \pi}{c}\right)^2 = \frac{2mE}{\hbar^2}$$

Hence allowed values of total energy  $E$  are given by

$$E = \frac{\pi^2 \hbar^2}{2m} \left[ \left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2 \right] \quad (15)$$

When a box is cubical, i.e.  $a=b=c$  the wave function is given by

$$\boxed{\Psi(x,y,z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a}\right)x \sin\left(\frac{n_y \pi}{a}\right)y \sin\left(\frac{n_z \pi}{a}\right)z} \quad (16)$$

and allowed values of total energy  $E$

$$E = \frac{\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\boxed{E = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)} \quad (17)$$

### Concept of degeneracy :-

A quantum state is called degenerate when there is more than one wave function for a given energy.

The different set of quantum numbers ( $n_x, n_y, n_z$ ) corresponds to different wave functions but may have same energy. Such thus the number of different sets of quantum numbers or wave f" associated with the particle of a given energy value is called order of degeneracy. It is denoted by "g".

Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of potential energy can remove the degeneracy.

### Degeneracy of energy levels in cubical box:-

In a cubical box,  $a=b=c$

so

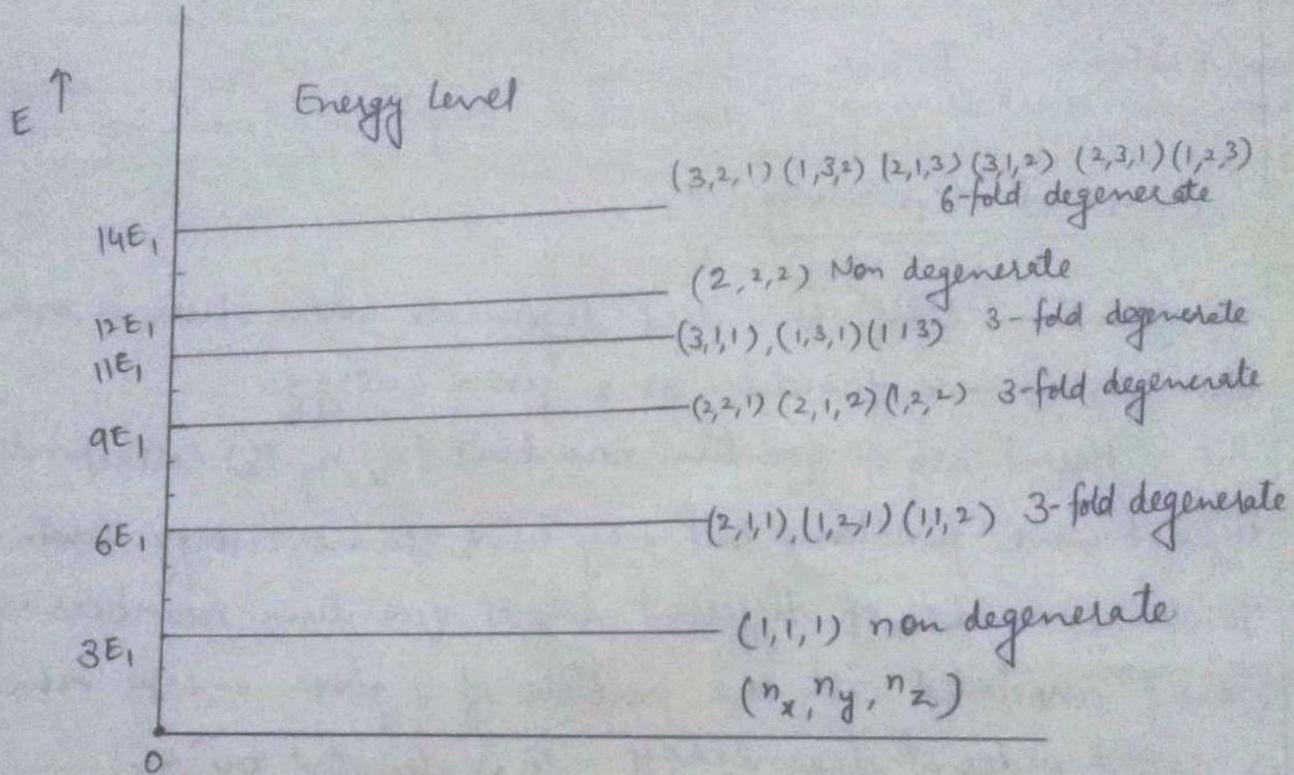
$$\psi(x, y, z) = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{n_x \pi}{a}\right) x \cdot \sin\left(\frac{n_y \pi}{a}\right) y \cdot \sin\left(\frac{n_z \pi}{a}\right) z \quad (1)$$

and

$$E = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\text{Let } \frac{\hbar^2}{8ma^2} = E_1$$

$$\text{so } E = E_1 (n_x^2 + n_y^2 + n_z^2) \quad \text{--- (2)}$$



(1.)  $(1,1,1)$  and  $(2,2,2)$  and so on states are non-degenerate.

So lowest energy of non-degenerate state is

$$E_{(1,1,1)} = 3 \cdot \frac{\hbar^2}{8ma^2}$$

(2.) Doubly degenerate :-

Doubly degenerate is unavailable. So there is no value of energy.

(3) Triply degenerate: →

Eg. if  $(n_x, n_y, n_z) = (1, 1, 2)$

Then  $E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = 6E_1 = \frac{6\hbar^2}{8\pi^2 a^2}$

But

$$\Psi_{1,1,2} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{2\pi}{a}z\right)$$

$$\Psi_{1,2,1} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{\pi}{a}x\right) \sin\left(\frac{2\pi}{a}y\right) \sin\left(\frac{\pi}{a}z\right)$$

$$\Psi_{2,1,1} = \left(\frac{2}{a}\right)^{3/2} \sin\left(\frac{2\pi}{a}x\right) \sin\left(\frac{\pi}{a}y\right) \sin\left(\frac{\pi}{a}z\right)$$

i.e. a single energy eigen value corresponds to three eigen functions, then case is said to be degenerate and order of degeneracy is 3.

Similarly  $(n_x, n_y, n_z) = (1, 2, 2)$

is also 3-fold degenerate.

(4) Six fold degenerate: →

$(n_x, n_y, n_z) = (1, 2, 3)$  is 6-fold degenerate.