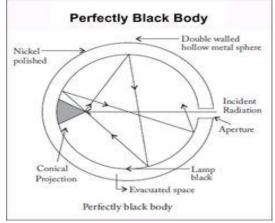
## Module IV.

## QUANTUM MECHANICS

#### **Blackbody Radiation:**

A Blackbody is one which absorbs all the light which is incident on it and re-radiates all those absorbed radiations when it is heated to incandescence (red hot).

#### Blackbody Radiation spectrum:



A Blackbody is one which absorbs the entire radiation incident on it and emits all the absorbed radiation when it is hotter. A true blackbody does not exist practically. Many Scientists tried to device an ideal blackbody, however, a blackbody designed by Wien has features very close to the true blackbody. A blackbody at a particular temperature found to emit a radiation of all possible wavelengths. The radiations emitted are analysed and is called blackbody radiation spectrum.

Nature of Blackbody radiation Spectrum: The radiations emitted is analysed and the intensity (or the energy density) of emitted radiation is plotted against the wavelength as shown in fig.

(i)At a constant temperature, radiations of different wavelengths are emitted out in different quantities. It is a continuous spectrum starting from certain minimum wavelength to maximum wavelength. There exist a particular wavelength (Called $\lambda_m$ ) for which intensity of emitted radiation is maximum.

(ii)There are different curves for different temperatures. The intensity emitted radiation increases with the increase of the temperature.

(iii) As the temperature of the body increases, the wavelength corresponding to maximum intensity  $(\lambda_m)$  shifts towards lower wavelength side.

(iv) The area under the curve gives the total radiant energy. The area under the curve is proportional to the

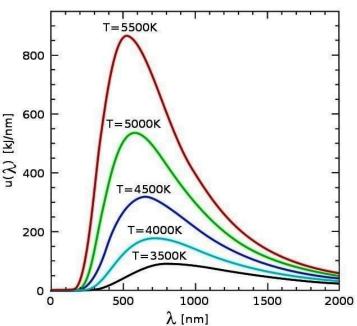
forth power of the absolute temperature. This is called Stefan's 4<sup>th</sup> power law [E  $\alpha$   $T^4$ ].

## Planck's Law:

In 1900, Max Plank explained the entire blackbody radiation spectrum by introducing the revolutionary idea of quantization of energy of the constituent atoms of the blackbody.

#### **Assumptions:**

i) A blackbody consists of large number of electrical oscillators whose energy is quantized. An oscillator may have any integral value for its energy given by E = nhv, where n is any positive integer, h is plank's constant, v is the frequency of oscillation.



ii) An oscillator may gain or lose energy by absorbing or emitting a radiation of frequency v respectively where  $v = \frac{\Delta E}{h}$ ,  $\Delta E$  is difference in energies of the oscillator before and after the emission or absorption take place.

With these assumptions Planck at an expression for distribution of energy of blackbody radiation as The energy radiated per unit volume from the surface of the blackbody in the wavelength interval  $\lambda$ and  $\lambda + d\lambda$  is  $E_{\lambda}d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{(\frac{hc}{hKT})} - 1}} d\lambda$  ------ (1)

**Note:** Plank's law signifies the particle nature of blackbody radiation. With the help of this, Einstein explained Photoelectric effect. Later Compton used the same idea to explain Compton Effect of the X rays. These two phenomena lead to assume dual nature for Electro Magnetic Radiation.

## **Matter waves**

#### De Broglie Hypothesis (Wave particle dualism)

Some of the Phenomena observed around 1900, like blackbody radiation, photoelectric effect etc, can be explained by assuming the particle nature. The phenomena like interference diffraction, polarization etc, can be explained only by assuming wave nature. Therefore it can be concluded that neither the wave theory nor the particle theory can be disputed and both are equally valid and light exhibit dual nature.

Nature manifest herself mainly in two forms, one is the energy and the other is matter. If light being a form of energy exhibit dual nature, then why cannot the matter? Based on these symmetry arguments, one can expect the matter also to exhibit dual nature.

Based on these symmetry arguments, in1923, Luis de Broglie argued that "every moving particle is associated with wave nature, whose wavelength is given by  $\lambda = \frac{h}{p} = \frac{h}{mv}$ , Where h is the Plank's constant, m is the mass, v is the velocity and p is the momentum of the moving particle". This statement (a logical argument without experimental proof) is called de Broglie hypothesis.

Such waves associated with moving particle are called as matter waves or de Broglie waves, and the wavelength  $\lambda = \frac{h}{p} = \frac{h}{mv}$  is called de Broglie wavelength.

#### **Properties of Matter waves**

- *1*) Matter waves are the waves associated only with the moving particle. The particles at rest cannot exhibit the wave nature.
- 2) Matter waves are called as pilot waves or guiding waves; they move with a velocity greater than the velocity of light leaving the particle behind.
- 3) Matter waves are also called as the probability waves; the amplitude of matter waves reveals the probability of finding the particle at a point in a given region of space.
- 4) Unlike EM waves, the matter waves of different wavelengths travel with different phase velocities.

#### de Broglie wavelength in different forms:

The de Broglie wavelength of a particle of mass 'm' moving with a velocity 'v' and momentum

'p'is given by 
$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Using the classical equation p = mv,

 $p^2 = m^2 v^2 = 2m \left(\frac{1}{2}mv^2\right) = 2m E_k$ We get  $p = \sqrt{2mE_k}$ 

Or

 $\therefore$  The de Broglie wavelength of a particle moving with a kinetic energy E<sub>k</sub> is

$$\lambda = rac{h}{\sqrt{2mE_k}}$$

For an electron accelerated by a potential difference of V volts, the kinetic energy is  $E_k = qV$ .

The de Broglie wavelength of an electron accelerated by a potential difference of V volts is given by

$$\lambda = rac{n}{\sqrt{2meV}}$$
 .

Note:  $\lambda = \frac{h}{\sqrt{2meV}} = \frac{1}{\sqrt{V}} \left[ \frac{6.625 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19}}} \right] = \frac{1.226 nm}{\sqrt{V}}$ 

The de Broglie wavelength of a particle which is in thermal equilibrium at a temperature T is •

$$\lambda = \frac{h}{\sqrt{3mKT}}$$

Where K is the Boltzmann's constant  $K = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ .

#### Note:

The velocity of the de Broglie waves calculated by classical approach exceeds the velocity of light. At that time, it was believed that the velocity light is the maximum attainable velocity. This contradictory was resolved by Max born by suggesting a moving particle can associate with number of de Broglie waves whose wavelength is likely to be in the neighbourhood of that predicted by de Broglie. According to Max Born, all such coherent waves will interfere constructively over a limited region of space where the particle is located (to form a wave packet) and interfere destructively elsewhere. The individual de Broglie waves move with a velocity greater than the velocity of light leaving the particle behind. This velocity is called 'Phase Velocity'. The wave packet enclosing the particle move with a different velocity called 'Group Velocity'.

According to Max Born, the particle can be located anywhere inside the wave packet. Hence there is an uncertainty regarding its position. Meanwhile if there exist no of de Broglie waves associated with the same particle, there is an uncertainty in its momentum (because =  $\frac{h}{n}$ ). This is known as uncertainty principle.

## Heisenberg's Uncertainty Principle:

Statement: "In any simultaneous measurement of position and momentum of a moving particle, the product of the corresponding uncertainties, which is inherently present in the measurement, is always greater than or equal to  $\left(\frac{h}{4\pi}\right)$ ".

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

Where  $\Delta x$  is the uncertainty regarding the position and  $\Delta p$  is the uncertainty regarding the momentum.

**Explanation:** If position is measured with great accuracy, then the simultaneous measurement of the momentum becomes less accurate, and vice versa. The product of the two corresponding uncertainties is always constant and greater than the limit  $\left(\frac{h}{4\pi}\right)$ .

Note: Such pair of variable which cannot be measured simultaneously with great accuracy are called canonically conjugate variables. The above uncertainty relation is given for 1-D motion. For the 3-D motion the uncertainty relation is

$$\Delta x \cdot \Delta P_x \geq \frac{h}{4\pi}$$
$$\Delta y \cdot \Delta P_y \geq \frac{h}{4\pi}$$
$$\Delta z \cdot \Delta P_z \geq \frac{h}{4\pi}.$$

Such pair of variable which cannot be measured simultaneously with great accuracy are called canonically conjugate variables. The other examples of canonically conjugate variables are the angular momentum and angle as well as energy and time.

$$|\mathbf{e}. \qquad \Delta L \cdot \Delta \theta \geq \frac{h}{4\pi}$$

Where  $\Delta L$  is the uncertainty in the measurement of angular momentum And  $\Delta \theta$  is the uncertainty in the measurement of angular position

and 
$$\Delta E \, . \, \Delta t \, \geq \, rac{h}{4\pi}$$

Where  $\Delta E$  is the uncertainty in the measurement of energy And  $\Delta t$  is the uncertainty in the measurement of time

## Application of H U P: (To prove the nonexistence of electron inside the nucleus using HUP)

Consider that the electron is present inside the nucleus.

If an electron is present inside the nucleus, then the error in the determination of its position  $\Delta x \leq 1 \times 10^{-14} m.$ 

Then using HUP, 
$$\Delta p \ge \frac{h}{4\pi . \Delta x} = \frac{6.625 \times 10^{-34}}{4\pi (1 \times 10^{-14})} = 5.27 \times 10^{-21} \text{ kg} - \text{ms}^{-1}.$$

...

$$\Delta p \simeq p = 5.27 \text{ x } 10^{-21} \text{ NS}$$

The energy of the electron is given by classical equation  $E = \frac{p^2}{2m}$ 

$$E \ge \frac{(5.27 \times 10^{-21})^2}{(2 \times 9.1 \times 10^{-31})} = 1.5 \times 10^{-11} \text{ Joul.}$$
  
E \ge 95.37 x 10<sup>6</sup> eV \ge 95 MeV.

Or

I.e. If the electron resides inside the nucleus, it should have a minimum energy of 95Mev. But it has been experimentally verified that no electron of an atom do not possess that much of huge energy. Even the bête particles (which are most energetic electrons) possess a maximum energy of nearly 4Mev. This contradictory result proves the nonexistence of electron inside the nucleus.

## Wave function

Waves, in general, are associated with some quantity that varies periodically. For example, water waves involve the periodic variation of the height of water surface at a point. Similarly, sound waves are characterised by the periodic variation of pressure. The periodic variation of mutually perpendicular electric and magnetic vector characterises the electromagnetic waves. In the same way, 'the quantity that characterises the matter waves is called wave function'. It is always denoted by the Greek letter  $\Psi$ . The wave function contains all the information about the dynamical behaviour of the particle exhibiting the wave nature.

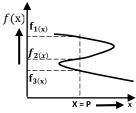
A wave function is also a solution Schrodinger's wave equation which describes the dynamical behaviour of a moving particle. As Schrodinger's wave equation is a second order differential equation, the wave function is complex in nature.

## Properties of Wave function:

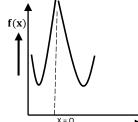
There may be a number of solutions for the Schrodinger's wave equation. Only the wave functions which satisfy the properties given bellow are called acceptable wave functions.

## 1) The wave function $\Psi$ should be single valued everywhere.

Consider an example f(x) as shown in figure. At X = P, the function f(x) has three different values. If f(x) were to be the wave function, the probability of finding the particle at X = P has three different values which is absurd. Hence the function f(x) cannot be the wave function.



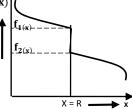
## 2) The wave function $\Psi$ must be finite everywhere.



Consider a function f(x) as shown in fi7gure. At X = Q, the  $f(x) = \infty$ . f(x) were to be the wave function, the probability of finding the particle at X = Q cannot be  $\infty$ . Therefore f(x) cannot be the wave function

3) The wave function  $\Psi$  and its first derivatives (both in space and time) must be continuous everywhere.

Consider a function f(x) as shown in figure. The function f(x) is not continuous at X = R, L.H.L.  $\neq R$ .H.L. The function f(x) may assume any value between f1(x) and f2(x) as it is not defined properly. In other words f(x) has a discontinuity at X = R. As f(x) is not continuous, its first derivatives cannot be finite. Therefore f(x) cannot be a wave function.



4) For the bound state, the wave function must vanish at infinity. If the wave function is complex, then the quantity  $\Psi^*\Psi dx$  must vanish at infinity.

## Physical Significance of wave function - Born's Interpretation (Probability density):

In Quantum Mechanics, it is postulated that the wave function contain all the information about the moving particle exhibiting wave nature. As the wave function is complex in nature, the quantity ' $\Psi$ ' has no direct physical significance. However, when it is multiplied with its complex conjugate  $\Psi^*$ , it would yield a real meaning. The quantity  $\Psi^*\Psi = |\Psi|^2$  is called the probability density. The probability density is a measure of probability of finding the particle at point in a given region of space.

The probability of finding the particle over an interval dx is given by  $\Psi^*\Psi dx = |\Psi|^2 dx$ 

The probability of finding the particle over entire space (1D) is given by

$$\int_{-\infty}^{\infty} \Psi^* \Psi \, dx = \int_{-\infty}^{\infty} |\Psi|^2 \, dx$$

## Normalization:

For a single particle system, the probability density should be always unity. Consider an example that we are trying to calculate the probability of finding an electron at a point on the Bohr's orbit. If the electron is observed only six times out of ten trials, the probability of finding the electron is 0.6. It is not true if we say only 60% of the electron is observed all the time. Then one has to make the probability of finding the electron to be equal to unity by multiplying the wave function with an appropriate constant.

"The process of making the probability density to be equal to unity is called normalization and the constant of multiplication is called normalization constant". The above explanation can be expressed in terms of equations as

Let 
$$\int_{-\infty}^{\infty} \Psi^* \Psi \, dx = N$$
  
Then  $\frac{1}{N} \int_{-\infty}^{\infty} \Psi^* \Psi \, dx = 1$   
Or  $\int_{-\infty}^{\infty} \frac{1}{\sqrt{N}} \Psi^* \cdot \frac{1}{\sqrt{N}} \Psi \, dx = 1$  ------ (i)  
Where  $\left(\frac{1}{\sqrt{N}}\right)$  the normalization constant and the wave function is  $\frac{1}{\sqrt{N}} \Psi$  is called normalized wave function. If we denote  $\frac{1}{\sqrt{N}} \Psi$  by new wave function  $\psi$  equation (i) becomes

$$\int_{-\infty}^{\infty} \Psi^* \Psi \, dx = 1 \qquad \qquad \text{(ii)}$$

This is the condition for normalization. Any wave function satisfying above equation is said to be normalized.

## Setting up of 1-D time independent Schrodinger's Wave Equation

Consider a particle of mass m, moving with a velocity v and a momentum p along +ve X-axis. The de Broglie waves associated with the moving particle have a wavelength in the neighbourhood of

$$\lambda = \frac{h}{p} \quad \dots \quad (1)$$

The wave function representing those de Broglie waves is of the form

$$\Psi = A \ e^{i(\omega t - kx)} \quad \dots \quad (2)$$

Where  $\omega$  is the angular frequency and *K* is the Wave number.

Differentiating the above equation twice partially w.r.t. x, we get

We know that the wave number  $k = \frac{2\pi}{\lambda} \implies K^2 = \frac{4\pi^2}{\lambda^2}$   $\therefore \quad \frac{d^2\Psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\Psi = 0$ From equation (1), we have  $\lambda^2 = \frac{h^2}{p^2} \implies \frac{1}{\lambda^2} = \frac{p^2}{h^2}$  $\therefore \quad \frac{d^2\Psi}{dx^2} + \frac{4\pi^2p^2}{h^2}\Psi = 0$  ------(4)

The total energy  $E = E_K + V \implies E - V = E_K$ 

This is the time independent Schrodinger's wave equation in 1-D.

#### Note:

(i) For a free particle V = 0.

 $\therefore$  1-D time independent Schrodinger's wave equation for a free particle is

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 mE}{h^2} \Psi = 0$$

(ii) The time independent Schrodinger's wae equation for three dimensions is

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

## **Eigen Value equation - Eigen values and Eigen functions:** On rearranging S. W. E.

$$\left[-\frac{h^2}{8\pi^2 m} + V\right]\Psi = \mathbf{E}\Psi$$

Ie.  $\widehat{H} \Psi = E \Psi$  Where  $\left[-\frac{\hbar^2}{8\pi^2 m} + V\right] = \widehat{H}$  where  $\widehat{H}$  is called Hamiltonian Operator. Above equation is called Eigen value equation. Any wave function satisfying this equation is called eigen function.

An operator operating on a wave function gives constant

times the same wave function. The constant thus obtained is called Eigen value of the operator. Eigen value of an operator refers to the expectation value (most probable value) of the dynamical variable represented by that particular operator.

The commonly used operators and the corresponding dynamical variables are listed below.

#### **Operators in Quantum Mechanics:**

Operator is a mathematical rule which yield the expectation value of a dynamical variable.

Eg. Consider the function  $y = \sin 2x$ , if  $\left(\frac{d}{dx}\right)$  is the operator then  $\frac{d}{dx}(Sin 2x) = 2$ . Cos 2x which implies Sin 2x is not the Eigen function of the operator  $\left(\frac{d}{dx}\right)$ . Now consider the operator  $\left(\frac{d^2}{dx^2}\right)$ , then  $\frac{d^2}{dx^2}(Sin 2x) = -4 \sin 2x$  which implies Sin 2x is the Eigen function of the operator  $\left(\frac{d^2}{dx^2}\right)$  and -4 is the eigen value of  $\left(\frac{d^2}{dx^2}\right)$ .

## PARTICLE IN A POTENTIAL WELL OF INFINITE HEIGHT AND FINITE WIDTH:

#### The Wave Function and Energy Eigen Values:

Consider a moving free particle trapped between imaginary walls of infinite height at x=0 and x = a. The potential acting on the particle inside the well is zero. The potential outside the well is  $\infty$ . The dynamical behaviour of the particle is studied by solving the time independent Schrodinger's wave equation.

For the region I and III, S.W.E can be written as

 $\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - \infty) \Psi = 0 \qquad (1)$ The only possible solution for the above equation is  $\Psi = 0$ ,

i.e. the particle cannot enter in to the region I and III.

For the region II, S.W.E can be written as

Put Then  $\frac{d^2\Psi}{dr^2} + K^2 \Psi = 0$ 

The solution to the above equation is of the form  $\Psi = C \cos Kx + D \sin Kx$  ------ (3)

The behaviour of the particle at the walls forms the boundary conditions. As it is continuously in motion in region II, the particle cannot stick on to the walls.

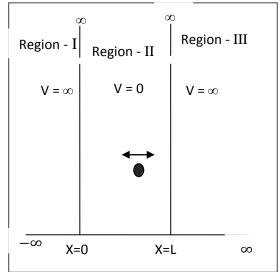
: The boundary conditions are (i)  $\Psi=0$  at x = 0 and (ii)  $\Psi=0$  at x = a.

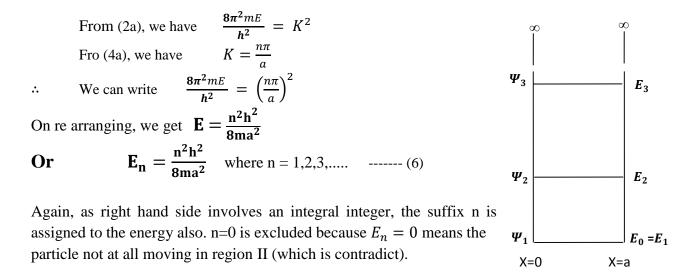
From the1<sup>st</sup> boundary condition  $\Psi_{x=0} = C \cos K x_{x=0} + D \sin K x_{x=0}$ 0 = C + 0 $\Rightarrow C = 0$ The wave function becomes  $\Psi = D \sin Kx$  ------ (4)

From the 2<sup>nd</sup> boundary condition 
$$\Psi_{x=a} = D$$
 Sin Ka  
 $0 = D \sin Ka$   
Since  $D \neq 0$ ,  $\sin Ka = 0$   
 $\Rightarrow Ka = \sin^{-1}(0)$   
 $\therefore Ka = n\pi$ , where  $n = 0, 1, 2, 3, ....$   
And  $K = \frac{n\pi}{a}$  ------ (4a)

Therefore the wave function becomes  $\Psi_n = D \sin\left(\frac{n\pi x}{a}\right)$  where n = 1,2,3,.... (5) As right hand side involves an integral integer, the suffix n is assigned to the wave function also.n=0

is excluded because  $\Psi_n = 0$  means the particle is nowhere present in region II(which is a contradict).





The least possible energy of the particle inside the potential well is called **Zero point energy** or ground state energy. All other possible energies ( $E_2$ ,  $E_3$ , and so on, called excited states) are the integral multiple of this ground state energy. Therefore the energy of the particle confined in a potential well is said to be quantized. All the characteristic energy levels are represented by appropriate wave functions, called eigen functions. The figure shows the energy eigen values and corresponding eigen functions of the particle confined in an infinite potential well and finite width.

#### Normalization of the wave function:

We know that the condition for normalization is  $\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$  (7)

But, we know that the wave function  $\Psi_n$  is zero in region I and region III and is real only in region II. Therefore, the condition for normalization reduces to  $\int_0^a \Psi_n^* \Psi_n dx = 1$  ------ (8)

Where 
$$\Psi_n = D \sin\left(\frac{n\pi x}{a}\right)$$
;  $\Psi_n^* = D^* \sin\left(\frac{n\pi x}{a}\right)$   

$$\therefore \int_0^a \Psi_n^* \Psi_n \, dx = \int_0^a D^* \sin\left(\frac{n\pi x}{a}\right) \cdot D \sin\left(\frac{n\pi x}{a}\right) \, dx = 1$$

$$D^* \cdot D \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) \, dx = 1$$

$$|D|^2 \cdot \frac{1}{2} \int_0^a \left[1 - \cos\left(\frac{2n\pi x}{a}\right)\right] \, dx = 1$$

$$|D|^2 \cdot \frac{1}{2} \left\{ [a - 0] - [o - o] \right\} = 1$$

$$\therefore \quad |D|^2 \cdot \frac{a}{2} = 1$$

$$Or \quad |D|^2 \cdot \frac{a}{2} = 1$$

$$Or \quad D = \sqrt{\frac{2}{a}}$$

Therefore the normalized wave function for the particle confined in an infinite potential well and finite width is  $\Psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$  ------ (9)

# +Eigen functions, probability densities and energy levels for particle in an infinite potential well:

The wave function and the particle confined in an infinite potential well and finite width is

$$\Psi_n = \sqrt{\frac{2}{a}} \quad \sin\left(\frac{n\pi x}{a}\right) \quad \dots \dots \quad (a)$$

and

<u>Case I  $\rightarrow$  n=1:</u> The energy corresponding to n=1 is the lowest possible energy, called zero point energy (Ground state energy), denoted by E<sub>0</sub>. This energy level is represented by the wave function

$$\Psi_1 = \sqrt{\frac{2}{a}} \quad \sin\left(\frac{\pi x}{a}\right)$$

 $\Psi_1 = 0$  for  $\mathcal{X} = 0$  and  $\mathcal{X} = a$  and  $\Psi_1$  is maximum when  $\mathcal{X} = a/2$ .

 $E_n = \frac{n^2 h^2}{9ma^2} = n^2 E_0$  where n = 1,2,3,.... (b)

The wave function  $\Psi_1$  and the probability density  $|\Psi_1|^2$  can be represented as shown in figure.

<u>Case II  $\rightarrow$  n=2:</u> The energy corresponding to n = 2 is E<sub>2</sub> = 4E<sub>0</sub> called the 1<sup>st</sup> excited state. This energy level is represented by the wave function  $\Psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$ 

$$\Psi_2 = 0$$
 for  $x = 0$ ,  $a/2$  and  $a$ .

 $\Psi_2 = \sqrt{\frac{2}{a}}$  for x = a/4 and  $\Psi_2 = -\sqrt{\frac{2}{a}}$  for x = 3a/4.

The wave function  $\Psi_2$  and the probability density  $|\Psi_2|^2$  can be represented as shown in figure.

<u>Case III  $\rightarrow$  n=3:</u> The energy corresponding to n = 3 is E<sub>3</sub> = 9E<sub>0</sub> called the 2<sup>nd</sup> excited state. This energy level is represented by the wave function  $\Psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right)$ 

 $\Psi_3 = 0$  for x = 0, a/3 and 2a/3.

$$\Psi_3 = \sqrt{\frac{2}{a}}$$
 for x = a/6 & 5a/6 and  $\Psi_3 = -\sqrt{\frac{2}{a}}$  for x = a/2.

The wave function  $\Psi_3$  and the probability density  $|\Psi_3|^2$  can be represented as shown in figure given bellow.

