

Introduction to Quantum Mechanics

In the latter part of the 19th century, study of the emission of radiation from black body was carried out by Wilhelm Wein and Rayleigh Jeans to account for the energy emitted at different wavelengths. The equation given by Wein fitted to shorter wavelengths and Rayleigh formula fit the curve at longer wavelength side. Finally Max Plank worked out empirical equation that fitted the entire curve completely well.

Need of Quantum Mechanics: With this success, Plank analyzed how his equation could be interpreted and he realized that the energy of the emitted radiations are quantized. With this Plank's equation for energy density for blank body radiation was derived and his efforts laid the foundation for quantum mechanics.

Wave particle dualism

It is well known that light exhibits the phenomenon of interference, diffraction, and polarization. This phenomenon can be explained using wave theory of light. This phenomenon shows light behave as a wave, light has wave nature, but photoelectric effect, Compton Effect and black body radiation can be explained on the basis of quantum theory. According to which light propagates in small packets of energy $h \gamma$. These packets are called photons or quanta, which behaves like a particle. Thus light possesses waves as well as particles. It is referred to as wave-particle dualism or dual nature of light and matter. The wave associated with moving particles is called as matter wave. According to de-Broglie, a moving particle behaves sometimes as wave and sometimes as a particle.

De-Broglie hypothesis

According to de-Broglie, a moving particle behaves sometimes as wave and sometimes as a particle. The waves associated with moving material particle are called matter waves or de-Broglie waves.

Since nature loves symmetry, if the radiation behaves like a particle under certain circumstances and as waves under certain other circumstances. Then one can even expect that entities, which ordinarily behave as a particle to exhibit properties attributable to, only wave under appropriate circumstances.

$$\text{Therefore } p = \frac{h}{\lambda} \text{ or } \lambda = \frac{h}{p}$$

De-Broglie suggested that this equation applies as well to particle of mass 'm', moving with a velocity 'v'. Thus for a particle

$\mathbf{p=mv}$ λ is the wavelength of the waves associated with a particle of mass 'm' moving with a velocity 'v' de-Broglie called these waves as matter waves.

Thus wavelength of matter waves, $\lambda = \frac{h}{mv}$, [$\mathbf{p=mv}$] this result is known as *de-Broglie* equations

De-Broglie wavelength of an accelerated electron:

Consider an electron of mass 'm' accelerated through a potential difference of 'V'. The energy acquired by the electron is eV. The velocity acquired by the electron be v. Then,

$$eV = \frac{1}{2} mv^2.$$

$$p = mv$$

Squaring on both sides, we get,

$$p^2 = m^2 v^2$$

$$mv^2 = p^2/m$$

Substituting in Kinetic energy equation we get, $eV = p^2/2m$

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

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.602 \times 10^{-19} \times V}} = \frac{1.226 \times 10^{-9}}{\sqrt{V}} m$$

$$\boxed{\lambda = \frac{1.226 \times 10^{-9}}{\sqrt{V}} m}$$

Relation between Kinetic energy and de-Broglie wavelength of electron:

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

$$p = mv$$

Squaring on both sides, we get,

$$p^2 = m^2 v^2$$

$$mv^2 = p^2/m$$

Substituting in Kinetic energy equation we get, $eV = p^2/2m$

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

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

Phase Velocity (V_p)

Phase velocity is the speed at which a single wave's phase (like a crest or trough) travels. It is defined as the angular frequency (ω) divided by the wave number (k).

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

Group velocity (V_g)

The velocity of the wave packet's "envelope," which is the overall outline of the wave formed by the interference of multiple waves with slightly different frequencies. It is defined as the derivative of the angular frequency (ω) with respect to the wave number (k)

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

Group velocity and phase velocity are related by the equation

$$V_g = V_p + k \frac{dV_p}{dk}$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

According to classical mechanics, a particle can occupy a definite position and momentum at any instant of time. That is the trajectory of particle can be continuously traced. But, in atomic scale such notion does not work. According to quantum mechanics [wave mechanics] it is impossible to determine both position and momentum of particle simultaneously and accurately. If Δx is uncertainty (error) in the measurement of position and ΔP_x is the uncertainty in the measurement of momentum, then $\Delta x \Delta P_x \geq \frac{h}{4\pi}$ this is called Heisenberg uncertainty principle.

It shows that if position is measured with higher accuracy then measurement in momentum P will have lower accuracy and vice versa.

Statement of Heisenberg's uncertainty principle

"In any simultaneous determination of position and momentum of the particle, the product of the corresponding uncertainty inherently present in the measurement is equal to or greater than $\frac{h}{4\pi}$."

$$\Delta x \Delta P_x \geq \frac{h}{4\pi}$$

Heisenberg's uncertainty principle also be expressed as in terms of uncertainties involved in the measurement of physical variable pairs such as Energy and time, Angular displacement (θ) and angular momentum (L)

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

$$\Delta L \Delta \theta \geq \frac{h}{4\pi}$$

‘ Δ ’ is the minimum uncertainty involved in the measurement of the corresponding variable.

Physical significance of Heisenberg’s uncertainty principle

The physical significance is that one should not think of exact position, or an accurate value for momentum of a particle. Instead, one should think of probability of finding particle at certain position or probable value for momentum of particle. The estimates of such probability are made by means of certain mathematical function named as probability density function in quantum mechanics.

Application of Heisenberg’s uncertainty principle

Non-existence of an electron inside the nucleus:

The radius of the nucleus is found to be of the order of 0.5×10^{-14} m. If the electron exists within the nucleus of an atom it can be anywhere within the radius of the nucleus. The maximum uncertainty in the position of electron is equal to or less than the radius of the nuclei.
 $\Delta x = 0.5 \times 10^{-14}$ m.

From H U P, $\Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}$

Uncertainty in the momentum of the electron is

$$\Delta p_x \geq \frac{h}{4\pi\Delta x} \geq \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-15}}$$

$$\Delta p_x \geq 1.054 \times 10^{-20} \text{Ns},$$

which is the uncertainty of the momentum of the electron. Then the momentum of the electron must at least be equal to the uncertainty in momentum.

$$\therefore p_x = 1.1 \times 10^{-20} \text{Ns}$$

We know by theory of relativity

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$E^2 = \frac{m_0^2 c^6}{c^2 - v^2} \quad \text{_____ (1)}$$

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

$$p^2 = \frac{m_0^2 v^2 c^2}{c^2 - v^2}$$

Multiplying by c^2

$$p^2 c^2 = \frac{m_0^2 v^2 c^4}{c^2 - v^2} \quad \text{_____ (2)}$$

$$E^2 - p^2 c^2 = \frac{m_0^2 c^4 (c^2 - v^2)}{c^2 - v^2}$$

$$E^2 - p^2 c^2 = m_0^2 c^4$$

$$E^2 = p^2 c^2 + m_0^2 c^4$$

E = energy, c = velocity of light, m_0 = rest mass of electron, p = momentum of electron.

$$E^2 \geq (1.1 \times 10^{-20})^2 \times (3 \times 10^8)^2 + (9.1 \times 10^{-31})^2 \times (3 \times 10^8)^4$$

$$E \geq 3.3 \times 10^{-12} \text{ J} \Rightarrow E \geq \frac{3.3 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV}$$

$$E \geq 20.6 \text{ MeV}$$

This means that electron to exist inside the nucleus its energy must be greater than or equal to 20.6 MeV

But experimental investigations on β decay reveal that, the kinetic energy of β particles (which are same as electron) is the order of 3 to 4 MeV. This clearly indicates that electron cannot exist within the nucleus.

Alternate method

Non-existence of an electron inside the nucleus:

The diameter of the nucleus is found to be of the order of 10^{-14} m . If the electron exists within the nucleus of an atom it can be anywhere within the diameter of the nucleus. The maximum uncertainty in the position of electron is equal to or less than the diameter of the nuclei. $\Delta x = 10^{-14} \text{ m}$.

$$\text{From H U P, } \Delta x \cdot \Delta p_x \geq \frac{h}{4\pi}$$

Uncertainty in the momentum of the electron is

$$\Delta p_x \geq \frac{h}{4\pi\Delta x} \geq \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-15}}$$

$$\Delta p_x \geq 0.52 \times 10^{-20} \text{ Ns},$$

This is the uncertainty of the momentum of the electron. Then the momentum of the electron must at least be equal to the uncertainty in momentum.

$$\therefore p_x = 0.52 \times 10^{-20} \text{ Ns}$$

We know by theory of relativity

$$E = mc^2 = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$$E^2 = \frac{m_0^2 c^6}{c^2 - v^2} \quad \text{_____ (1)}$$

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

$$p^2 = \frac{m_0^2 v^2 c^2}{c^2 - v^2}$$

Multiplying by c^2

$$p^2 c^2 = \frac{m_0^2 v^2 c^4}{c^2 - v^2} \quad \text{_____ (2)}$$

$$E^2 - p^2 c^2 = \frac{m_0^2 c^4 (c^2 - v^2)}{c^2 - v^2}$$

$$E^2 - p^2 c^2 = m_0^2 c^4$$

$$E^2 = p^2 c^2 + m_0^2 c^4$$

E= energy, c= velocity of light, m_0 = rest mass of electron, p= momentum of electron.

$$E^2 \geq (1.1 \times 10^{-20})^2 \times (3 \times 10^8)^2 + (9.1 \times 10^{-31})^2 \times (3 \times 10^8)^4$$

$$E \geq 1.56 \times 10^{-12} \text{J} \Rightarrow E \geq \frac{1.53 \times 10^{-12}}{1.6 \times 10^{-19}} \text{eV}$$

$$E \geq 9.75 \text{MeV}$$

This means that electron to exist inside the nucleus its energy must be greater than or equal to 9.75 MeV

But experimental investigations on β decay reveal that, the kinetic energy of β particles (which are same as electron) is the order of 3 to 4 MeV. This clearly indicates that; electron cannot exist within the nucleus.

Wave function

The variable quantity characterizing the matter wave is called wave function. It is also called the state function. It is denoted by ψ . The value of the wave function associated with a moving body at particular point x, y, z in space at the time “ t ” is related to the wave function in quantum mechanics which accounts for the wave like properties of a particle. It is given by $\psi(x, y, z, t)$.

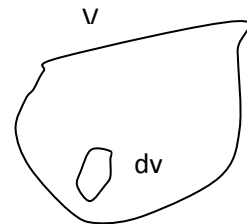
Wave function is a complex quantity.

A system is defined by its energy, momentum, position etc. once the wave function ψ corresponding to a system is known, the state of the system can be determined. A wave function corresponding to a system will change when system changes its states. In quantum mechanics it is postulated that the state of the system is completely characterized by a wave function.

Probability density

If we consider a single particle and ψ is the wave function associated with the particle then $|\psi|^2$ is the probability per unit volume that the particle will be found at the given point. It can also be stated in the following manner

Let V be a volume inside which a particle is known to be present, but where exactly the particle is situated inside V is not known. Then the probability of finding the particle in a certain element of volume dv of V is equal to $|\psi|^2 dv$. For this reason $|\psi|^2$ is called probability density.



Born interpretation states that the square of the magnitude of a wave function gives a probability density $|\psi|^2 = \psi^* \psi$

$\psi^* \psi$ is always positive and real quantity. ψ^* is complex conjugate of ψ . ψ^* and ψ may be complex. Probability of occurrence of an event is a real and positive quantity.

Normalization

If Ψ is a wave function associated with a particle, then $|\Psi|^2 dv$ is the probability of finding the particle in a volume dv .

According to statistical rule

$\int_0^V |\Psi|^2 dv = 1$. ----- (1) That means definite presence of particle in the particular region or space of volume V

If $\int_{-\infty}^{\infty} |\Psi|^2 dv = 0$. That means that particle does not exist.

$\int_{-\infty}^{\infty} |\Psi|^2 dv = 1$. That means the particle is there at somewhere in space.

A wave function that obeys equation (1) is said to be normalized.

Expectation value

The expectation value in quantum mechanics is the probabilistic average of a measurement's possible outcomes, calculated by weighting each outcome by its probability. It is a theoretical mean from many measurements on identical systems and is not necessarily the most probable result itself.

It is mathematically represented by the integral

$\langle A \rangle = \int \psi^*(x) \hat{A} \psi(x) dx$, $\hat{A}$ is operator and $\psi^*(x)$ is the complex conjugate of $\psi(x)$.

Properties of wave function:

Property (1) $\Rightarrow \Psi$ is single valued everywhere.

Property 2 $\Rightarrow \Psi$ is finite everywhere.

Property 3 $\Rightarrow \Psi$ and its first derivative with respect to its variable are continuous everywhere

Property 4 $\Rightarrow$ For bound states Ψ must vanish at infinity. If Ψ is a complex function, then $\Psi^* \Psi$ must vanish at infinity.

One –dimensional time independent Schrodinger's wave equation:

According to the de-Broglie theory for a particle of mass m , moving with a velocity of V , the wave length $\lambda = \frac{h}{p}$ ----- (1)

$P = m v$ = momentum of the particle

The wave equation for a de-Broglie wave considered traveling in positive x direction can be written in complex notation as

$$\psi = A e^{i(Kx - \omega t)} \text{-----}(2)$$

A =constant, ω =angular frequency of the wave, k =propagation constant

By differentiating equation (2) twice with respect to “ t ” we will get

$$\frac{d\psi}{dt} = A e^{i(Kx - \omega t)} (-i\omega)$$

$$\frac{d^2\psi}{dt^2} = A e^{i(kx - \omega t)} (-i\omega) (-i\omega)$$

$$\frac{d^2\psi}{dt^2} = -\omega^2 A e^{i(kx - \omega t)} = -\omega^2 \psi \quad \text{-----(3)}$$

The travelling wave equation is given by,

$$\frac{d^2 y}{dx^2} = \frac{1}{v^2} \frac{d^2 y}{dt^2}$$

$$\frac{d^2 \psi}{dx^2} = \frac{1}{v^2} \frac{d^2 \psi}{dt^2} \quad \text{-----(4)}$$

The above equation represents wave traveling with a velocity v , and ψ is the displacement at the instant t .

From equation (3) and (4), $\frac{d^2 \psi}{dx^2} = \left(\frac{-\omega^2}{v^2} \right) \psi$.

λ and γ are the wavelength and the frequency of the wave, then
 $\omega = 2\pi\gamma$ and $v = \gamma\lambda$, substituting for ω and v

$$\frac{d^2 \psi}{dx^2} = \frac{-4\pi^2 \psi}{\lambda^2}$$

Or, $\frac{1}{\lambda^2} = -\frac{1}{4\pi^2 \psi} \frac{d^2 \psi}{dx^2} \quad \text{-----(5)}$

For a particle of mass m moving with a velocity v ,

Kinetic energy = $\frac{1}{2} m v^2 = \frac{m^2 v^2}{2m} = \frac{p^2}{2m} \quad \text{-----(6)}$, But we know $p = \frac{h}{\lambda}$,

$$\therefore \text{Kinetic energy} = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{\lambda^2 2m} = \frac{h^2}{2m} \left(\frac{1}{\lambda^2} \right) = \frac{h^2}{2m} \left(-\frac{1}{4\pi^2 \psi} \frac{d^2 \psi}{dx^2} \right)$$

$$\therefore \text{Kinetic energy} = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} \quad \text{-----(8)}$$

The total energy E is the sum of K.E + potential energy

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

$$\text{Potential energy} = V$$

Therefore $E = -\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} + V \quad \text{-----(9)}$

$$\text{Or } -\frac{h^2}{8\pi^2 m} \frac{d^2 \psi}{dx^2} = (E - V) \psi \quad \text{-----(10)}$$

$$\frac{d^2 \psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E - V) \psi$$

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

This is the time independent Schrodinger's equation in one dimension

Eigen values and Eigen function:

We have Schrodinger wave equation given by,

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

In order to determine the wave function Ψ , the Schrodinger equation has to be solved. SWE is a second order differential equation; there are many solutions.

All of them may not be acceptable to our conditions. Hence, that wave function which would be corresponding meaningfully to a physical system must be selected. To be an acceptable a wave function

- (1) Wave function must be a single valued.
- (2) Wave function must be finite everywhere.
- (3) Wave function and its first derivative must be continuous everywhere.
- (4) Wave function must vanish at infinite for bound state.

Such acceptable wave functions are named in quantum mechanics as **Eigen functions**.

Definition: "Eigen functions are those wave functions of quantum mechanics which possess the properties that are single valued, finite everywhere and also their first derivatives with respect to their variable are continuous everywhere".

Eigen values:

When Eigen functions are known, quantum mechanical operators are used to evaluate physical quantities. There is only a restricted set of Eigen function; there is also restricted set of energy values. These values are called **Eigen values**. The wave function must be such that the operator operating on it must reproduce the wave function multiplied by a constant. This constant value is the Eigen value.

Application of Schrodinger wave equation:

Particle in one-dimensional potential well of infinite height (Particle in a box):

Consider a particle of mass “m” which is free to move in the x-direction only in the region from $x=0$ to $x=a$. Outside this region, the potential V is taken to be infinite and within this region it is zero (which mean that the particle is bound within the limits $x=0$ to $x=a$) such a type of potential in space is called infinite potential well. A particle found within such an infinite potential is referred to as particle in a box.

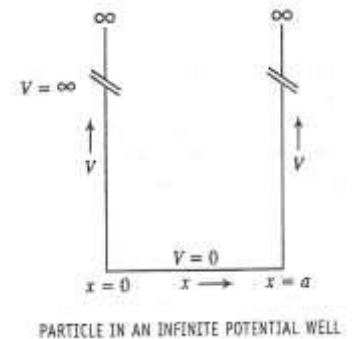
The Schrodinger equation is,

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

Outside the well the Schrodinger equation is,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E-\infty) \psi=0 \quad \text{-----(1)} \quad (\text{since } V=\infty)$$

This equation holds good if $\psi=0$ for all points outside the well, $|\psi|^2=0$, which means that the particle cannot be found at all outside the well.



Inside the well the Schrodinger, s equation is given by,

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

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E)\psi=0 \quad \text{-----(2)} \quad (\text{since } V=0)$$

In the equation (2) we have to put $\frac{8\pi^2m}{h^2} E = k^2$,

$$\text{We have, } \frac{d^2\psi}{dx^2} + k^2\psi=0 \quad \text{-----(3)}$$

Discussion of the solutions;

The solution of the above equation (3) is given by

$$\psi = C \cos(kx) + D \sin(kx) \quad \text{-----(4)}$$

But $\psi = 0$ at $x=0$, $\therefore$ equation (4) becomes, $0 = C \cos(k \cdot 0) + D \sin(k \cdot 0)$.

Therefore, $C=0$ ----- (5)

Also $\psi = 0$ at $x=a$, $\therefore$ equation (4) becomes $0 = C \cos(ka) + D \sin(ka)$.

But $A=0$ from equation (5), hence $D \sin(ka)=0$, here $D \neq 0$

$\therefore \sin(ka)=0$ or $ka = n\pi$, where $n = 1, 2, 3, \dots$ n is called quantum number which is either zero or positive integer.

$$\therefore k = \frac{n\pi}{a} \text{----- (6)}$$

Substituting for “C” and “k” from equation (5) and (6) in the equation (4) .

$$\psi = 0 \cos\left(\frac{n\pi}{a}x\right) + D \sin\left(\frac{n\pi}{a}x\right)$$

$$\psi_n = D \sin\left(\frac{n\pi}{a}x\right) \text{----- (7)}$$

Energy Eigen value:

$$\frac{8\pi^2 m}{h^2} E = k^2, \text{ since } k = \frac{n\pi}{a}$$

$$\frac{n^2 \pi^2}{a^2} = \frac{8\pi^2 m}{h^2} E$$

$$E = \frac{\frac{n^2 \pi^2}{a^2}}{\frac{8\pi^2 m}{h^2}} = \frac{n^2 \pi^2 h^2}{8\pi^2 m a^2} = \frac{n^2 h^2}{8ma^2}$$

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

This is **Energy Eigen value equation**.

When $n=0$, $E=0$, value zero for n is not acceptable.

Because when $n=0$, $\psi_n=0$

For $n=1$, $E_1 = \frac{h^2}{8ma^2} = \text{ground state energy} = \text{zero point energy}$

For $n=2$, $E_2 = \frac{4h^2}{8ma^2} = 4E_1$

Thus the energy in the **first excited state** is 4 times the zero point energy.

For $n=3$, $E_3 = \frac{9h^2}{8ma^2} = 9E_1$

Thus the energy in the **second excited state** is 9 times the zero point energy.

Thus $n=1$, E_1 - Ground state energy or zero point energy.

$n=2$, E_2 - First excited state energy

$n=3$, E_3 - Second excited state energy.

Normalization

The integral of the wave function over the entire space in the well must be unity because, there is only one particle is present inside the well somewhere else.

$$\int_0^a |\psi_n|^2 dx = 1 \text{-----} (8)$$

Substituting for ψ_n from equation (7), we will get,

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

$$\text{But we know that } \sin^2 \theta = \frac{1}{2} (1 - \cos 2\theta).$$

$$\int_0^a D^2 \frac{1}{2} \{1 - \cos(2\frac{n\pi x}{a})\} dx = 1$$

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

$$\text{Or } \frac{D^2}{2} \left[x \right]_0^a - \frac{D^2}{2} \left[\frac{\sin\left(\frac{2n\pi x}{a}\right)}{\frac{2n\pi}{a}} \right]_0^a = 1.$$

$$\text{Or, } \frac{D^2}{2} (a - 0) - \frac{D^2}{2} \frac{a}{2n\pi} [\sin\left(\frac{2n\pi a}{a}\right) - \sin\left(\frac{2n\pi 0}{a}\right)]$$

$$\text{Or, } \frac{D^2 a}{2} = 1, \text{ [since, } \sin(2n\pi) = 0, \sin(0) = 0]$$

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

Thus the normalized wave function of a particle in one-dimensional potential well is

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \text{-----} (9)$$

This is the **Eigen function**.

Wave functions, probability densities and Energy levels for particle in an infinite potential well

The most probable location of the particle in the well and its energies are to be evaluated for the different permitted states.

We can write the eigen functions ψ_1, ψ_2, ψ_3 . For a particle in the well by considering $n=1,2,3$ respectively in the equation.

Let us consider the first 3 cases.

Case (i): $n=1$:

This is the ground state and the particle is normally found in this state.

For $n=1$, the eigen function is,

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right), \text{ from equation (9)}$$

$\psi_1=0$, for both $x=0$ and $x=a$.

But ψ_1 has maximum value for $x = \left(\frac{a}{2}\right)$.

Thus a plot of ψ_1 versus “ x ” will be shown in figure

And a plot of $|\psi_1|^2$, the probability density versus “ x ” is also shown below.

It indicates the probability of the finding the particle at different location inside the well.

$|\psi_1|^2$ is 0 both at $x=0$, and at $x=a$.

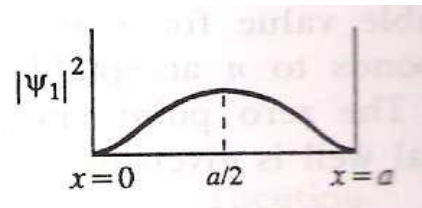
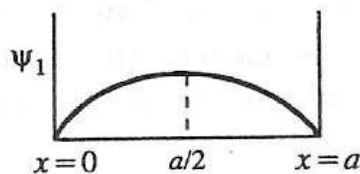
ψ is maximum at $x = \left(\frac{a}{2}\right)$ it says that the particle is cannot be found at all at the walls of the well,

and the probability of finding the particle is maximum at the central region.

If $n=1$

$$E_1 = \frac{h^2}{8ma^2} = \text{-----} \quad (10)$$

This is **ground state energy** or **zero point energy**.



Case (ii): $n=2$:

This is the first excited state i.e. the next immediate higher state permitted for the particle after the ground state.

The eigen function for this state is

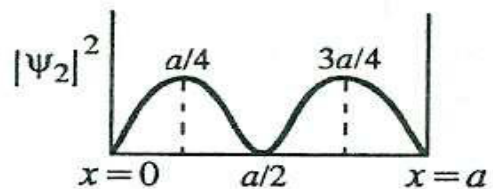
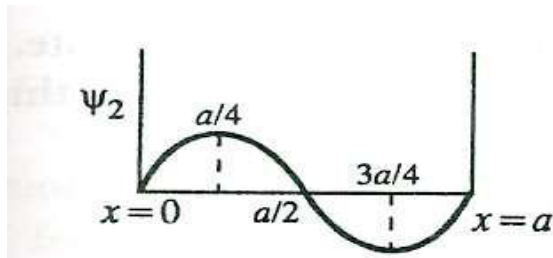
$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right)$$

Now $\psi_2 = 0$ for the values $x=0$, $\frac{a}{2}$, and a , also ψ_2 is maximum for $x=(\frac{a}{4})$ and $(\frac{3a}{4})$.

The plot of $|\psi_2|^2$ versus x in this figure $|\psi_2|^2 = 0$ at $x=0$, $\frac{a}{2}$ and a .

It means that in the first excited state the particle cannot be observed either at the walls, or at the center. If $n=2$, energy equation $E_2 = 4E_1$, **First excited state**.

Thus the energy in the first excited state is 4 times the zero point energy.



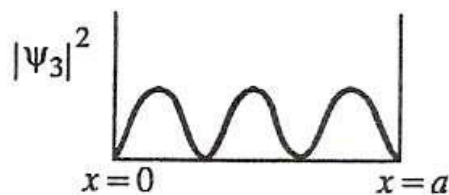
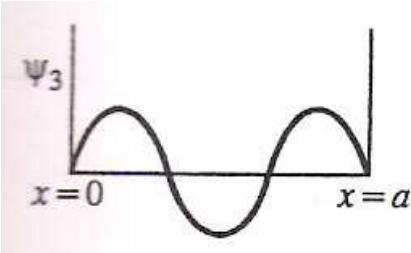
Case (iii), $n=3$:

The Eigen function for the second excited state as,

$$\psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right), \quad \psi_3 = 0, \text{ for } x=0, \frac{a}{3}, \frac{2a}{3} \text{ and } a.$$

ψ_3 will be a maximum value for $x=\frac{a}{6}, \frac{a}{2}$ and $\frac{5a}{6}$.

The plot of ψ_3 versus x and $|\psi|^2$ versus x is as shown bellow.



$$\text{For } n=3, E_3 = \frac{9h^2}{8ma^2} = 9E_1$$

Thus the energy in the **second excited state** is 9 times the zero point energy.