MODULE- 2

QUANTUM MECHANICS

Dual nature of matter (de-Broglie Hypothesis)

Dual nature of light:

The concept of photoelectric effect and Compton Effect gives the evidence for particle nature of light. Where as in physical optics the phenomenon like interference, diffraction, superposition was explained by considering wave nature of light. This is wave particle duality of light.

Dual nature of matter:

On the basis of above concept (dual nature of light), in 1923, Louis de Broglie gave a hypothesis

"Since nature loves symmetry, if the radiation behaves as particles under certain conditions and as waves under certain conditions, then one can expect that, the entities which ordinarily behaves as particles (ex. Like electrons, protons, neutrons) must also exhibit properties attributable to waves under appropriate circumstances". This is known as **deBroglie hypothesis**

Matter is made up of discrete constituent particles like atoms, molecules, protons, neutrons and electrons, hence matter has particle nature. Wave nature of matter is experimentally observed by Davisson and Germer and G.P Thomson experiments. Hence matter also exhibit wave particle duality.

The waves associated with the moving particles are called de Broglie waves or matter waves or pilot waves.

Characteristics of matter waves:

1. Waves associated with moving particles are called matter waves. The wavelength 'λ' of a de-Broglie wave associated with particle of mass 'm' moving with velocity 'v' is
   $$\lambda = h/(mv)$$
2. Matter waves are not electromagnetic waves because the de Broglie wavelength is independent of charge of the moving particle.

3. The amplitude of the matter wave depends on the probability of finding the particle in that position.
4. The speed of matter waves depends on the mass and velocity of the particle associated with the wave.

Debroglie's Wavelength:

A particle of mass 'm' moving with velocity 'c' possess energy given by

$E = mc^2 \quad \rightarrow$ **(**Einstein's Equation) (1)

According to Planck's quantum theory the energy of quantum of frequency 'υ' is

$E = h\upsilon \quad \rightarrow (2)$

From (1) & (2)

$mc^2 = h\upsilon = hc/\lambda \qquad \text{since } \upsilon = c/\lambda$

$\lambda = hc/mc^2 = h/mc$

$\lambda = h/mv \qquad \text{since } v \approx c$

De Broglie wavelength of a free particle in terms of its kinetic energy

Consider a particle, since the particle is free, the total energy is same as

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Where 'm' is the mass, 'v' is the velocity and 'p' is the momentum of the particle.

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

The expression for de-Broglie wavelength is given by

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

Debroglie Wavelength of an Accelerated Electron:

If an electron accelerated with potential difference 'V' the work done on the 'eV', which is converted to kinetic energy.

Then

$$\frac{1}{2}mv^2 \quad \text{eV=} \rightarrow (1)$$

If 'p' is the momentum of the electron, then p=mv

Squaring on both sides, we have

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

$mv^2 = p^2/m$

Using in equation (1) we have

$eV = p^2/(2m)$

or $p = \sqrt{2meV}$

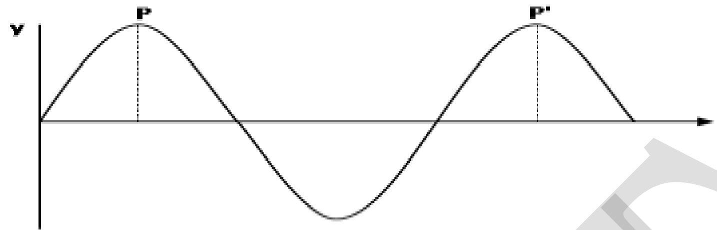
According to de-Broglie $\lambda = h/p$

Therefore $\lambda = \left[\frac{h}{\sqrt{2meV}}\right]$

$$\lambda = \frac{1}{\sqrt{V}}\left[\frac{6.626\times10^{-34}}{\sqrt{2\times9.11\times10^{-31}\times1.602\times10^{-19}}}\right] = \frac{1.226\times10^{-9}}{\sqrt{V}}\text{m}, \qquad \lambda = \frac{1.226}{\sqrt{V}}\text{nm}$$

Phase Velocity (V_{phase}) :

A progressive wave travelling along x-direction is represented by

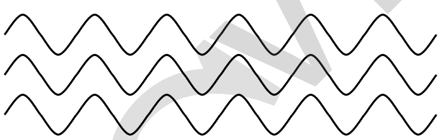


If 'p' is the point on a progressive wave, then it is the representative point for a particular phase of the wave, the velocity with which it is propagated owing to the motion of the wave is called *phase velocity.*

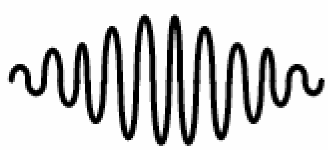
The phase velocity of a wave is given by $v_{phase} = (\omega\ /k)$.

Group Velocity (V_{group}) :

When a group of two or more waves of slightly different wavelengths superimposed on each other, the resultant pattern is in the variation in amplitude, represents the wave group called wave packet. The velocity with which the wave packet is moving called group velocity of the waves and is given by $v_{group} = \frac{d\omega}{dk}$



Individual Waves



Wave Packet

Heisenberg's Uncertainty Principle:

According to classical mechanics a particle occupies a definite place in space and possesses a definite momentum. If the position and momentum of a particle is known at any instant of time, it is possible to calculate its position and momentum at any later instant of time. The path of the particle could be traced.

This concept breaks down in quantum mechanics leading to Heisenberg's Uncertainty Principle.

Heisenberg's Uncertainty Principle states that "It is impossible to measure simultaneously both the position and momentum of a particle accurately. If we make an effort to measure very accurately the position of a particle, it leads to large uncertainty in the measurement of momentum and vice versa".

If Δx and ΔP_x are the uncertainties in the measurement of position and momentum of the particle then the uncertainty can be written as

$$\Delta x \,.\, \Delta P_x \geq (h/4\pi)$$

In any simultaneous determination of the position and momentum of the particle, the product of the corresponding uncertainties inherently present in the measurement is equal to or greater than h/4π.

Similarly, 1) $\Delta E.\Delta t \geq h/4\pi$ 2) $\Delta L.\Delta\theta \geq h/4\pi$

Significance of Heisenberg's Uncertainty Principle:

Heisenberg's Uncertainty Principle asserts that it is impossible to measure simultaneously both the position and momentum of a particle accurately. If we make an effort to measure very accurately the position of a particle, it leads to large uncertainty in the measurement of momentum and vice versa. Therefore, one should think only of the probability of finding the particle at a certain position or of the probable value for the momentum of the particle.

Application of Uncertainty Principle:

Non-existence of electrons in the atomic nucleus:

The energy of a particle is given by

$$E=\frac{1}{2}mv^2 = \frac{p^2}{2m} \qquad (1)$$

Heisenberg's uncertainty principle states that

$$\Delta x \, . \Delta P_x \; \geq \; \frac{h}{4\pi} \rightarrow (4)$$

The diameter of the nucleus is of the order 10^{-14}m. If an electron is to exist inside the nucleus, the uncertainty in its position Δx must not exceed 10^{-14}m.

i.e. $\Delta x \leq 10^{-14}$m

The minimum uncertainty in the momentum

$$(\Delta P_x)_{\min} \; \geq \; \frac{h}{4\pi \; (\Delta x)_{\max}} \; \geq \; \frac{6.63 \times 10^{-34}}{4\pi \times 10^{-14}} \geq 0.527 \times 10^{-20} \text{ kg. m/s}$$

By considering minimum uncertainty in the momentum of the electron

i.e., $(\Delta P_x)_{\min} \geq 0.5 \times 10^{-20}$ kg.m/s = p → (2)

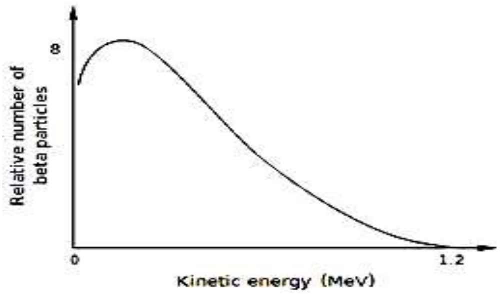
Consider eqn (1)

$$E = \frac{p^2}{2m} = \frac{(0.5 \times 10^{-20})^2}{2 \times 9.1 \times 10^{-31}} = 1.531 \times 10^{-11} = 95.68 \text{ MeV}$$

Where $m_o = 9.11 \times 10^{-31}$ kg

If an electron exists in the nucleus its energy must be greater than or equal to 95.68 MeV. It is experimentally measured that the beta particles ejected from the nucleus during beta decay have energies of about 3 to 4 MeV. This shows that electrons cannot exist in the nucleus.

[**Beta decay:** In beta decay process, from the nucleus of an atom, when neutrons are converting into protons in releasing an electron (beta particle) and an antineutrino. When proton is converted into a neutron in releasing a positron (beta particle) and a neutrino. In both the processes energy sharing is statistical in nature. When beta particles carry maximum energy neutrino's carries minimum energy and vice-versa. In all other processes energy sharing is in between maximum and minimum energies. The maximum energy carried by the beta particle is called as the end point energy (E_{max}).



Principle of complementarity:

Statement: Principle of complementarity as stated by Bohr "In a situation where the wave aspect of the system is revealed, its particle aspect is concealed (hidden) and in a situation where the particle aspect is revealed its wave aspect is concealed (hidden). Revealing both simultaneously is impossible; the wave and aspects are complementary."

Note: Meaning of complementary: things are different from each other but make a good combination.

Explanation: If an experiment is designed to measure the particle nature of matter, during this experiment errors of measurement of both position and time is zero and hence and hence momentum, energy and the wave nature of the matter are completely unknown. and vice versa.

Correlation between Heisenberg's Uncertainty Principle, Debroglie wavelength and wave packet:

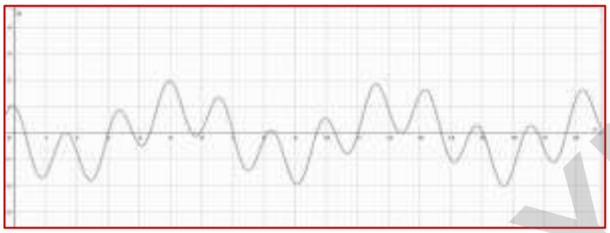
Although the uncertainty principle deals with many non-commute operators. if you certainly know the wavelength of the matter wave associated with the particle, you certainly know the momentum of the particle.

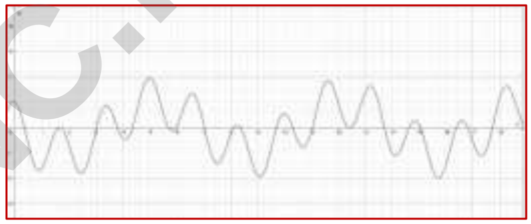
Given a wave function if you can tell its wavelength you will know the momentum but its position will be uncertain.

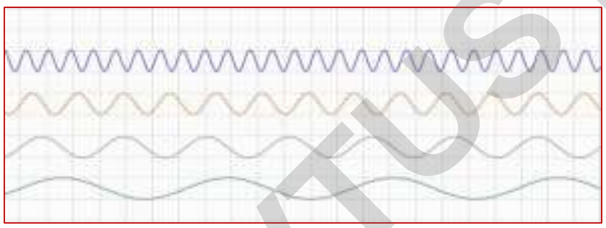
Note: In all the images only real part of the wave function is shown.

The wavelength of the following matter wave. The wavelength is the length of the red segment"

In this case you can certainly point out the wavelength; so you certainly know the momentum but you can't tell the position of the particle— it may be anywhere on the x-axis i.e the position uncertainty is very very high.







In any of the above three cases you cannot tell the wavelength of the matter wave.

For example, in the last case the wavelength uncertainty is large. This is in fact a superposition of many waves whose wavelength can be found. Such a wave packet is made up of many waves. So if you try to measure the wavelength of this wave packet you will get the wavelength of any of the waves shown above. Upon large number of observations, you will have many wavelengths and then calculate the standard deviation (the uncertainty). This will lead you to uncertainty in momentum which will of course be large (because you got a large number of wavelengths). But as you see the uncertainty in position will be comparatively smaller.

If the uncertainty in the de Broglie wavelength is large(small), the uncertainty in momentum is large(small) and consequently the uncertainty in position is small(large).

<u>Wave Function:</u>

A physical situation in quantum mechanics is represented by a function called wave function. It is denoted by 'ψ'. It accounts for the wave like properties of particles. Wave function is obtained by solving Schrodinger equation.

Mathematically it is given by

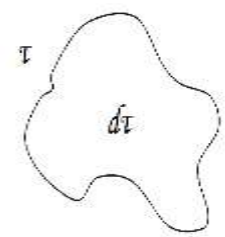
$$\psi = Ae^{i(kx-\omega t)}$$

<u>Physical significance of wave function:</u>

The wave function itself has no physical significance, the physical significance is given by a function called probability density or probability function.

<u>Probability density:</u>

If ψ is the wave function associated with a particle, then $|\psi|^2$ is the probability of finding a particle in unit volume. If 'τ' is the volume in which the particle is present but where it is exactly present is not known. Then the probability of finding a particle in certain elemental volume dτ is given by $|\psi|^2 d\tau$. Thus $|\psi|^2$ is called probability density. The probability of finding an event is real and positive quantity. In the case of complex wave functions, the probability density is $|\psi|^2 = \psi^* \psi$, where ψ* is Complex conjugate of ψ.



<u>Max Born interpretation of wave function:</u>

We know $\psi = Ae^{i(kx-\omega t)}$

Complex conjugate of ψ is given by $\Psi^* = Ae^{-i(kx-\omega t)}$

probability density is $|\psi|^2 = \psi \psi^* = A^2$, Where A = Square of amplitude.

According to max born interpretation, as square of the amplitude A^2 for electromagnetic waves represent Intensity of the wave. In quantum mechanics square of the amplitude A^2 represent the probability of finding the particle in certain position.

Normalization:

The probability of finding a particle having wave function 'ψ' in a volume 'dτ' is '$|\psi|^2 d\tau$'. If it is certain that the particle is present in finite volume 'τ', then

$$\int_0^{\tau} |\psi|^2 d\tau = 1$$

If we are not certain that the particle is present in finite volume, then

$$\int_{-\infty}^{\infty} |\psi|^2 d\tau = 1$$

In some cases $\int |\psi|^2 d\tau \neq 1$ and involves constant.

The process of integrating the square of the wave function within a suitable limits and equating it to unity the value of the constant involved in the wave function is estimated. The constant value is substituted in the wave function. This process is called as normalization.

The wave function with constant value included is called as the normalized wave function and the value of constant is called normalization factor.

Expectation value:

In Quantum mechanics, the expectation value is the probabilistic expected value of the result (measurement) of an experiment, Can be thought of as an average of all the possible outcomes of a measurement.

Expectation value as such is not the most probable value of the measurement.

Explanation: The result of measurement of the position x isa continuous random variable. Consider a wave function ψ(x). The $|\psi|^2$ value is the probability density for the position and $|\psi|^2 dx$ is the probability of finding the particle between x and x+dx. If the measurement is repeated many times, many possible outcomes are possible and the expectation value of these out comes can be expressed as

$$< x >= \int_{-\infty}^{\infty} |\psi|^2 \, dx$$

Time independent Schrodinger wave equation

Consider a particle of mass 'm' moving with velocity 'v'. The de-Broglie wavelength 'λ' is

$$\lambda = \frac{h}{m\mathrm{v}} = \frac{h}{P} \rightarrow (1)$$

Where 'mv' is the momentum of the particle.

The wave eqn is

$$\psi = Ae^{i(kx-\omega t)} \rightarrow (2)$$

Where 'A' is a constant and 'ω' is the angular frequency of the wave.

Differentiating equation (2) with respect to 't' twice

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

The equation of a travelling wave is

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

Where 'y' is the displacement and 'v' is the velocity.

Similarly, for the de-Broglie wave associated with the particle

$$\frac{d^2\psi}{dx^2} = \frac{1}{\mathrm{v}^2}\frac{d^2\psi}{dt^2} \rightarrow (4)$$

where 'ψ' is the displacement at time 't'.

From eqns (3) & (4)

$$\frac{d^2\psi}{dx^2} = -\frac{\omega^2}{\mathrm{v}^2}\psi$$

But ω = 2πυ and v =υ λ where 'υ' is the frequency and 'λ' is the wavelength.

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

$$K.E = \frac{1}{2}m\text{v}^2 = \frac{m^2\text{v}^2}{2m} = \frac{P^2}{2m} \rightarrow (6)$$

$$= \frac{h^2}{2m\lambda^2} \rightarrow (7)$$

Using eqn (5)

$$K.E = \frac{h^2}{2m}\left(-\frac{1}{4\pi^2\psi}\right)\frac{d^2\psi}{dx^2} = -\frac{h^2}{8\pi^2 m\psi}\frac{d^2\psi}{dx^2} \rightarrow (8)$$

Total Energy E = K.E + P.E

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

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

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

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

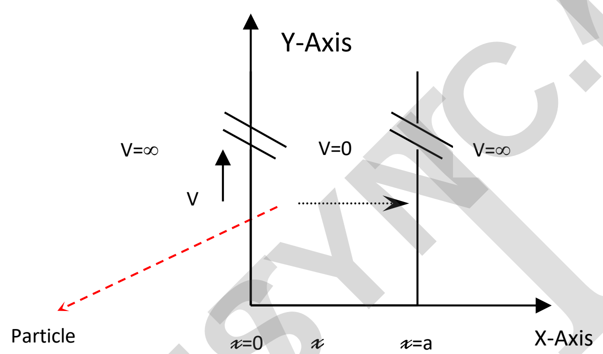
This is the time independent Schrodinger wave equation for one dimensional case.

For three dimensional case it can be eritten as follows.

$$\boxed{[\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}] + \frac{8\pi^2 m}{h^2}(E-V)\psi(x,y,z) = 0}$$

Application of Schrodinger wave equation:

Energy Eigen values of a particle in one dimensional, infinite potential well (potential well of infinite depth) or of a particle in a box



Consider a particle of a mass 'm' free to move in one dimension along positive x-direction between x=0 to x=a. The potential energy outside this region is infinite and within the region is zero. The particle is in bound state. Such a configuration of potential in space is called infinite potential well. It is also called particle in a box. The Schrödinger equation outside the well is

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

For outside, the equation holds good if ψ = 0 & $|\psi|^2 = 0$. That is particle cannot be found outside the well and also at the walls

The Schrodinger's equation inside the well is:

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

Let $\frac{8\pi^2 m}{h^2}E = k^2 \quad \rightarrow (3)$

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

The solution of above equation is:

$\psi = C \cos kx + D \sin kx \rightarrow (4)$

at $x = 0 \rightarrow \psi = 0$

$0 = C \cos 0 + D \sin 0$

$\therefore C = 0$

Also $x = a \rightarrow \psi = 0$

$0 = C \cos ka + D \sin ka$

But C = 0

$\therefore D \sin ka = 0 \longrightarrow (5)$

$D \neq 0$ (because the wave concept vanishes)

i.e. $ka = n\pi$ where $n = 0, 1, 2, 3, 4\ldots$ (Quantum number)

$k = \frac{n\pi}{a} \rightarrow (6)$

sub eqn (5) and (6) in (4)

$$\psi_n = D \sin \frac{n\pi}{a} x \rightarrow (7)$$

This gives permitted wave functions.

The Energy Eigen value given by

Substitute equation (6) in (3)

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

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

This is the expression for energy Eigen value.

For n = 0 is not acceptable inside the well because $\psi_n = 0$. It means that the electron is not present inside the well which is not true. Thus the lowest energy value for $n = 1$ is called zero point energy value or ground state energy.

i.e. $E_{zero\text{-}point} = \frac{h^2}{8ma^2}$

The states for which n >1 are called exited states.

To find out the value of D, normalization of the wave function is to be done.

i.e. $\int_0^a |\psi_n^2| dx = 1 \rightarrow (8)$

using the values of ψ_n from eqn (7)

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

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

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

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

$$\frac{D^2}{2}[a-0] = 1$$

$$\frac{D^2}{2}a = 1$$

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

Substitute D in equation (7)

the normalized wave functions of a particle in one dimensional infinite potential well is:

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x \rightarrow (9)$$

Eigen functions:

Eigen functions are those wave functions in Quantum mechanics which possesses the following properties:

1. They are single valued.

2. Finite everywhere and

3. The wave functions and their first derivatives with respect to their variables are continuous.

Eigne values:

If the wave function is operated by a quantum mechanical operator such that we get back the wavefunction back multiplied by some constant is called as Eigne value.

$\hat{H}(\psi) = \lambda(\psi)$

Where λ = Constant → is called as eigen value

If the quantum mechanical operator is Energy operator, then λ is termed as energy eigen value.

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

Let us consider the most probable location of the particle in the well and its energies for first three cases.

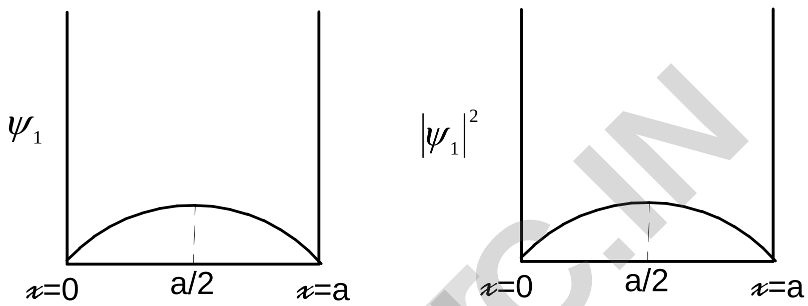
Case I → n=1 It is the ground state and the particle is normally present in this state.

The Eigen function is

$\psi_1 = \sqrt{\frac{2}{a}} Sin \frac{\pi}{a} x$ ∵from eqn (7)

$\psi_1 = 0$ for $x = 0$ and $x = a$

But ψ_1 is maximum when $x = a/2$.



The plots of ψ_1 versus x and $|\psi_1|^2$ verses x are shown in the above figure.

$|\psi_1|^2 = 0$ for $x = 0$ and $x = a$ and it is maximum for $x = a/2$. i.e. in ground state the particle cannot be found at the walls, but the probability of finding it is maximum in the middle.

The energy of the particle at the ground state is

$$E_1 = \frac{h^2}{8ma^2} = E_0$$

<u>Case II → n=2</u>

In the first excited state the Eigen function of this state is

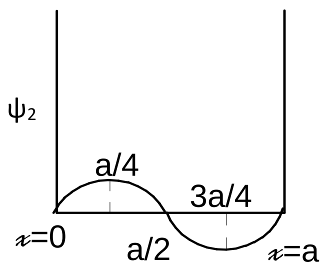
$$\psi_2 = \sqrt{\frac{2}{a}} Sin \frac{2\pi}{a} x$$

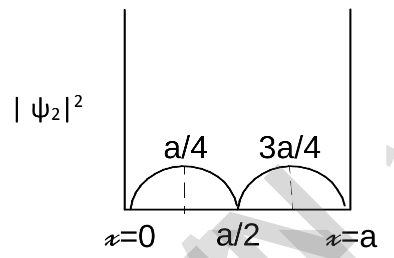
$\psi_2 = 0$ for the values $x = 0, a/2, a$.

Also ψ_2 is maximum for the values $x = a/4$ and $3a/4$.

These are represented in the graphs.

$|\psi_2|^2 = 0$ at $x = 0, a/2, a$, i.e. particle cannot be found either at the walls or at the centre. $|\psi_2|^2 = \text{maximum} \;\; for \; x = \dfrac{a}{4}, \; x = \dfrac{3a}{4}$





The energy of the particle in the first excited state is $E_2 = 4E_0$.

Case III → n=3

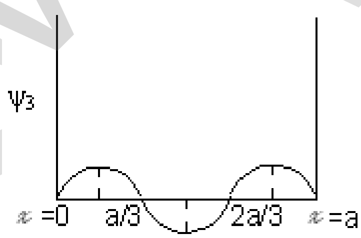
In the second excited state,

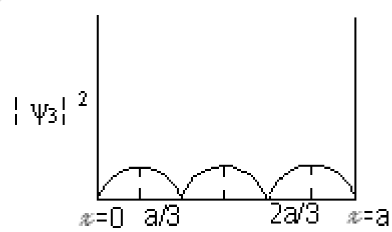
$$\psi_3 = \sqrt{\frac{2}{a}} Sin \frac{3\pi}{a} x$$

$\psi_3 = 0$, for $x = 0, a/3, 2a/3$ and a.

ψ_3 is maximum for $x = a/6, a/2, 5a/6$.

These are represented in the graphs.





$|\psi_3|^2 = 0$ for $x = 0, a/3, 2a/3$ and a. $|\psi_3|^2 = \text{maximum} \;\; for \; x = \dfrac{a}{6}, x = \dfrac{a}{2}, x = \dfrac{5a}{6}$

The energy of the particle in the second excited state is $E_3 = 9 E_0$.

QUESTION BANK MODULE-2

Q1).State and explain Heisenberg Uncertainty principle with its physical significance. 4M (MQP-2 2018-19, July 2019, Jan 2019, Jan 2020, Sep 2020).

Q2). Show that the electron emitted during β-decay does not pre-exist inside the nucleus using uncertainty principle. 6M (MQP-2 2018-19, July 2019, Jan 2019, Jan 2020, Sep 2020, Jan /Feb 2021).

Q3). Setup 1-dimensional time independent Schrodinger wave equation also mention the equation for 3-dimensional case 8M (MQP-1 2018-19, Jan 2019, 8M (Jan /Feb 2021).

Q4). What is wave function and Probability density? Give the qualitative explanation of Max Born's interpretation of wave function. 6M (MQP-2 2018-19).

Q5). Assuming the time independent Schrodinger equation discuss the solution for a particle in one dimensional potential well of infinite height. Obtain the normalized wave function & Energy Eigen value. 10M (MQP11 2018-19, July 2019, Jan 2020, Sep 2020)

Q6). Explain about eigen functions and eigen values. 4M.

Q7). Explain about the principle of complementarity and Expectation value. 4M.

Q8). Sketch the Wave functions, probability densities and energy levels for particle in an infinite potential well for first three permitted states. 6M.

***************ALL THE BEST****************