

QUANTUM MECHANICS

1) Introduction:

During the last decade of 19th century it was generally believed that all that to be discovered in nature was discovered, and all the laws of nature were formulated. The Newtonian mechanics, Maxwell's electromagnetic theory and thermodynamics came to be known later as classical physics. The early years of 20th century, number of new phenomena such as black body radiation, radioactivity, photoelectric effect, x-rays, Compton effect etc., were discovered which defied explanation based on classical physics. A search for correct solutions led to abandon the old ideas and to invoke radically new concepts. The new laws applicable for atoms and subatomic particles constitute quantum mechanics.

In the case of classical mechanics, it is unconditionally accepted that position, mass, velocity, etc., of a particle or a body can be measured accurately. The classical mechanics is embodied with a deterministic approach and a body may have any value (for example energy), and variation in the value is continuous. The quantum mechanics is embodied with a probabilistic approach and a body can not have any value, i.e., only in quanta (for example energy), and variation in the value is discrete. It is to be noted that classical mechanics is simply an approximate version of quantum mechanics.

2) Explain de Broglie's theory of Matter Waves.

Radiations including visible light, infra-red, ultraviolet, x-rays etc., behave as waves in experiments based on interference, diffraction etc. Planck's quantum theory was successful in explaining black body radiation, the photoelectric-effect, the Compton effect etc., clearly established that radiant energy in its interaction with matter behaves as particles of light called photons. Hence radiation has wave-particle dualism. Radiation cannot exhibit its particle and wave properties simultaneously in a single experiment.

Following symmetry considerations, de Broglie extended the wave particle dualism of radiant energy to all the fundamental entities of physics such as electrons, protons, neutrons, atoms and molecules etc. According to de Broglie, like radiation, matter also should exhibit wave-like behaviour. A moving particle is associated with a wave which is known as de Broglie wave or matter wave. Considering the Planck's theory of radiation, the energy of a photon is given by

$$E = h\nu = \frac{hc}{\lambda}, \text{ where } c \text{ is velocity of light in vacuum and } \lambda \text{ is its wavelength.}$$

According to Einstein's mass-energy relation, $E = mc^2$.

$$\therefore m c^2 = \frac{h c}{\lambda} \text{ or } m c = \frac{h}{\lambda} \text{ or } \lambda = \frac{h}{m c} \text{ or } \lambda = \frac{h}{p}$$

where p is the momentum of the associated photon. When we apply the above equation to moving particles of matter, we get the de Broglie wavelength,

$$\lambda = \frac{h}{m v} = \frac{h}{p}$$

where p is the relativistic momentum of the particle. The wave-particle duality of radiant energy and matter is an essential part of nature: waves exhibit particle-like properties and particles exhibit wave-like properties.

3) What are deBroglie Matter Waves?

According to de Broglie, like radiation, matter also should exhibit wave-like behaviour. A moving particle is associated with a wave which is known as de Broglie wave or matter wave.

$$\text{de Broglie wavelength} = \lambda = \frac{h}{m v} = \frac{h}{p}$$

4) State the properties of Matter waves.

- 1) Lighter the particle, greater is the wavelength associated with it.
- 2) Smaller the velocity of the particle, greater is the wavelength associated with it.
- 3) Matter waves are generated by the motion of particles. Matter waves are produced whether the moving particles are charged particles or uncharged particles. Matter waves are not electromagnetic waves but a new kind of waves.
- 4) The velocity of matter waves depends on the velocity of matter particle.
- 5) The velocity of matter waves is greater than the velocity of light. We know that

$$E = h \nu = m c^2 \text{ or } \nu = \frac{m c^2}{h}$$

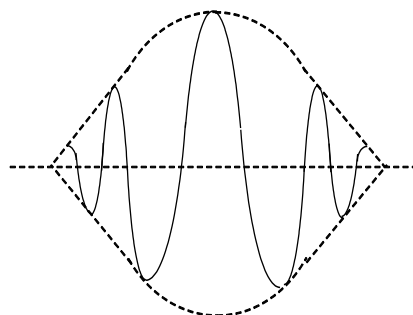
Matter wave velocity =

$$W = \nu \lambda = \frac{m c^2}{h} \frac{h}{m v} = \frac{c^2}{v}.$$

As the particle velocity v cannot exceed the velocity of light c , W is greater than velocity of light. This indicates that matter waves are not physical waves.

6) The wave and particle aspects of moving bodies can never appear together in the same experiment.

7) The wave nature of matter introduces an uncertainty in the location of the position of the particle because a wave has a spread in space. A pure sine wave is characterized by a precise wavelength and momentum. It is of infinite extent and completely non-localized. Hence a mono-frequency wave can not represent a particle which is an entity confined to a very small volume. It implies that de Broglie matter waves are not harmonic waves but could be a combination of several waves. It is known that a superposition of several waves having slightly different frequencies gives rise to a wave packet. Such a wave packet possesses both wave and particle properties. The regular separation between maxima in a wave packet is characteristic of a wave and at the same time it has a particle-like localization in space.



Davisson-Germer experiment & G. P. Thomson experiment confirmed the de Broglie hypothesis.

5) State and prove Heisenberg's Uncertainty principle.

The Heisenberg's Uncertainty principle helps to resolve the paradox that particles sometimes behave like waves and waves like particles. The principle states that it is impossible to determine precisely and simultaneously the values of both the members of a particular pair of physical variables that describe the behaviour of an atomic system. The pairs of such physical variables are called canonically conjugate pairs. Position-linear momentum, energy-time and angular momentum-angular displacement are conjugate pairs of variables. The Heisenberg's uncertainty principle is of no practical importance for heavy bodies where the deBroglie wavelength is negligibly small.

Position x and momentum p of a particle constitute a pair of such physical variables. Suppose that we try to measure both the position and momentum of an electron moving in the x -direction. Let Δx be the uncertainty in the measurement of its position and Δp_x , the uncertainty in the measurement of its momentum. Heisenberg's principle states that $\Delta x \Delta p_x \cong h$, where h is the Planck's constant. The product of the two uncertainties must remain fixed and is of the order of the Planck's constant. If Δx is small, Δp_x will be large and vice versa. It means that if one quantity is measured accurately, the other quantity becomes less accurate. Thus any instrument can not measure the quantities more accurately than

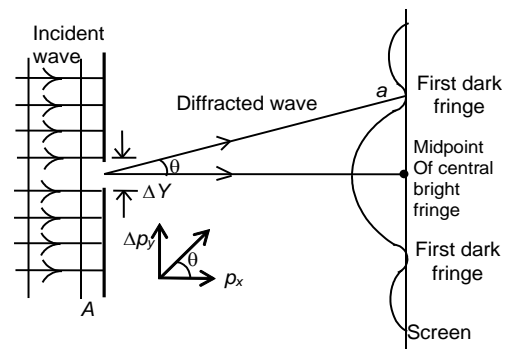
predicted by Heisenberg's principle of uncertainty. This is a fundamental limitation imposed by nature and has nothing to do with the limitations of measuring instruments. Because momentum and position are vectors, a relation like the above equation holds for y and z coordinates as well, i.e.,.

$$\Delta y \Delta p_y \cong h \text{ and } \Delta z \Delta p_z \cong h.$$

An electron passing through a slit

Consider the case of electron diffraction at a single slit to understand how the principle of uncertainty is at work.

Let an electron, represented by an incident matter wave, fall on a slit of width Δy in screen A (Figure). Let us try to pin down the vertical position and momentum components of the electron at the instant it passes through the slit. If the electron gets through the slit, we can pin down the vertical position of the electron as closely as we like by controlling the slit width.



However, matter waves, like all waves, brings out the wave character by diffraction when they pass through the slit. Moreover, the narrower the slit, the wider is diffraction pattern. From the particle point of view, this means that electron acquires a vertical component of momentum as it passes through the slit. Some electrons acquire only a little vertical momentum, others a lot, so that there is an uncertainty.

There is one particular value of the vertical momentum component that will carry the electron to the first minimum of the diffraction pattern, point 'a' on the screen of Figure. We can take this value as a measure of the uncertainty Δp_y in the measurement of the vertical momentum component of the electron.

From the theory of single-slit diffraction in optics, we know that the first minimum of the diffraction pattern occurs at an angle θ given by

$$\sin \theta = \frac{\lambda}{\Delta y}$$

If θ is small enough, we can replace $\sin \theta$ by θ . Also the de Broglie wavelength $\lambda = \frac{h}{p}$. The

equation then becomes $\theta \cong \frac{h}{p_x \Delta y}$, in which p_x is the horizontal momentum component. To

reach the first minimum, θ must be such that $\theta = \frac{\Delta p_y}{p_x}$. Equating the expressions for θ , we

get $\frac{h}{p_x \Delta y} = \frac{\Delta p_y}{p_x}$ or we find that $\Delta y \Delta p_y \cong h$, which is the uncertainty principle.

6) State and explain Heisenberg's Uncertainty principle.

The Heisenberg's Uncertainty principle helps to resolve the paradox that particles sometimes behave like waves and waves like particles. The principle states that it is impossible to determine precisely and simultaneously the values of both the members of a particular pair of physical variables that describe the behaviour of an atomic system. The pairs of such physical variables are called canonically conjugate pairs. Position-linear momentum, energy-time and angular momentum-angular displacement are conjugate pairs of variables. The Heisenberg's uncertainty principle is of no practical importance for heavy bodies where the deBroglie wavelength is negligibly small.

7) Write a short note on Wave function. Explain the physical significance of Wave function.

We know that all kinds of waves are associated with a variable physical quantity. For waves on strings, for example, the wave disturbance may be identified by a transverse displacement y , or for sound waves it may be measured by a pressure variation p , or for electromagnetic waves the electric field vector \mathbf{E} may be taken as a measure of the wave disturbance.

The quantity that is waving in a matter wave is called the wave function ψ . It is a measure of the wave disturbance of matter waves. The variation of ψ with position and time represents the wave aspect of a moving particle.

The wave function corresponding to a matter wave packet provides all possible information about the associated matter particle. It can not be an observable quantity and it has no direct physical meaning. Max Born first suggested the physical meaning of ψ . He stated that the wave function associated with a moving particle at a particular instant of time and at a particular point in space is related to the probability of finding the particle at that time at that point. The square of the absolute value of the wave function $|\psi|^2$ is called the probability density. In other words, $|\psi|^2$ at any particular instant of time and at any particular point in a de Broglie wave packet is a measure of the probability that the particle will be near that point at that time. More exactly, if a volume element dV is constructed at that point, the probability that the particle will be found in the volume element at a given instant is $|\psi|^2 dV$. This

interpretation of ψ provides a statistical connection between the wave and the associated particle; it tells us where the particle is likely to be, not where it is.

The wave function can be either real or complex. When it is complex, it can be expressed in the form $\psi = A + iB$. Then the probability density is

$P = \psi\psi^* = (A + iB)(A - iB) = A^2 + B^2$. Hence the wave function may be complex but the probability density P is always real and positive. The amplitude of any wave may be negative as well as positive and a negative probability is meaningless. Hence ψ has no direct physical meaning. The only quantity having a physical meaning is the probability density $P = |\psi|^2 = \psi\psi^*$. The probability of finding a particle in a volume $dx dy dz$ is $|\psi|^2 dx dy dz$. Further, since the particle is certainly to be found somewhere in space, $|\psi|^2 dx dy dz = 1$. A wave function ψ satisfying this relation is called a normalized wave function.

To arrive at results consistent with physical observations, several additional requirements are imposed on the wave function ψ :

1. ψ must be single-valued, continuous everywhere, and finite for all values of x, y, z .
2. The wave function $\psi(x)$ must approach zero as $x \rightarrow \pm\infty$.
3. Partial derivatives of the wave function along the three coordinate axes must be finite, continuous, and single-valued.

8) Derive the time dependent Schrodinger Equation?

A differential equation of the form $\frac{\partial^2 y}{\partial t^2} = v^2 \frac{\partial^2 y}{\partial x^2}$ represents all kinds of waves, where v is the wave propagation velocity and y is the displacement. Of the numerous possible solutions of the above equation, the solution corresponding to unrestricted, undamped, monochromatic harmonic waves in the positive x -direction is

$$y = Ae^{-i\omega(t - \frac{x}{v})} \text{ or } y = A \cos\omega(t - \frac{x}{v}) - iA \sin\omega(t - \frac{x}{v})$$

Only the real part of the equation has significance in the case of unbounded harmonic waves like waves on a long stretched string or sound waves propagating in a long gas-filled tube.

The quantity that characterizes the de Broglie matter waves is called the wave function ψ . Hence the wave function ψ for a particle moving freely in the positive x -direction is

$$\psi = Ae^{-i\omega(t - \frac{x}{v})} \dots\dots\dots (1)$$

where ψ is a function of x and t . If ν is the frequency, then $\omega = 2\pi \nu$ and $\nu = v/\lambda$.

$$\therefore \psi_{(x,t)} = Ae^{-2\pi i \nu (t - \frac{x}{v})} \text{ or } \psi_{(x,t)} = Ae^{-2\pi i (\nu t - \frac{vx}{\lambda})} = Ae^{-2\pi i (\nu t - \frac{x}{\lambda})} \dots\dots\dots(2)$$

Let E be the total energy and p the momentum of the freely moving particle in the positive x -direction. Then $E = h\nu$ and $\lambda = \frac{h}{p}$. Making these substitutions in eq. (2), we get

$$\psi = Ae^{-2\pi i (\frac{Et}{h} - \frac{px}{h})} = Ae^{-\frac{2\pi i}{h} (Et - px)} \dots\dots\dots(3)$$

Differentiating eq. (3) twice with respect to x , we get $\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2 p^2}{h^2} \psi \dots\dots\dots(4)$

Differentiating eq. (3) once with respect to t , we get $\frac{\partial \psi}{\partial t} = -\frac{2\pi i E}{h} \psi \dots\dots\dots(5)$

Neglecting relativistic correction, the total energy E of the particle is the sum of its kinetic energy $\frac{p^2}{2m}$ and its potential energy V . V is, in general, a function of x and t .

$$\therefore E = \frac{p^2}{2m} + V \dots\dots\dots(6). \text{ Multiplying eq. (6) by } \psi, \text{ we get } E\psi = \frac{p^2}{2m} \psi + V\psi \dots\dots\dots(7)$$

From eqs. (5) and (4), we see that

$$E\psi = -\frac{h}{2\pi i} \frac{\partial \psi}{\partial t} \dots\dots\dots(8), \text{ and } p^2 \psi = -\frac{h^2}{4\pi^2} \frac{\partial^2 \psi}{\partial x^2} \dots\dots\dots(9)$$

Substituting these expressions for $E\psi$ and $p^2 \psi$ into eq. (7), we obtain

$$-\frac{h}{2\pi i} \frac{\partial \psi}{\partial t} = -\frac{h^2}{8\pi^2 m} \left[\frac{\partial^2 \psi}{\partial x^2} \right] + V\psi \text{ or } \frac{ih}{2\pi} \frac{\partial \psi}{\partial t} = -\frac{h^2}{8\pi^2 m} \left[\frac{\partial^2 \psi}{\partial x^2} \right] + V\psi \dots\dots\dots(10)$$

This is the time-dependent form of Schrodinger's equation. In the three dimensions, the time-dependent form is

$$\frac{ih}{2\pi} \frac{\partial \psi}{\partial t} = -\frac{h^2}{8\pi^2 m} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] + V\psi$$

9) Deduce Schrodinger time independent wave equation?

In many situations, the potential energy V of a particle does not depend on time explicitly. The forces that act on it, and hence V , vary with the position of the particle only. When this is the case, Schrodinger's equation may be simplified by removing all reference to t .

The one dimensional wave function ψ of an unbounded particle may be written in the form

$$\psi = Ae^{-\left(\frac{2\pi i}{h}\right)(Et - px)} = Ae^{-\left(\frac{2\pi i E}{h}\right)t} e^{\left(\frac{2\pi i p}{h}\right)x}$$

$$\psi = \psi_0 e^{-\left(\frac{2\pi i E}{h}\right)t} \dots\dots\dots(1) \text{ . Here, } \psi_0 = A e^{\left(\frac{2\pi i p}{h}\right)x}.$$

That is, ψ is the product of a position-dependent function ψ_0 and a time-dependent function $e^{-\left(\frac{2\pi i E}{h}\right)t}$. Differentiating eq. (1) with respect to t ,

$$\text{we get } \frac{\partial \psi}{\partial t} = \frac{-2\pi i E}{h} \psi_0 e^{-\left(\frac{2\pi i E}{h}\right)t} \dots\dots\dots(2). \text{ Differentiating eq. (1) twice with respect to } x,$$

$$\text{we get } \frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi_0}{\partial x^2} e^{-\left(\frac{2\pi i E}{h}\right)t} \dots\dots\dots(3). \text{ Substituting these values in the time-dependent form of Schrodinger's equation, we get}$$

$$E \psi_0 e^{-\left(\frac{2\pi i E}{h}\right)t} = -\left(\frac{h^2}{8\pi^2 m}\right) \frac{\partial^2 \psi_0}{\partial x^2} e^{-\left(\frac{2\pi i E}{h}\right)t} + V \psi_0 e^{-\left(\frac{2\pi i E}{h}\right)t}.$$

Eliminating the common exponential factor, we get

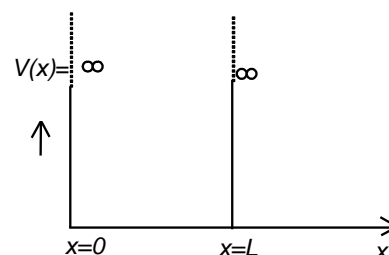
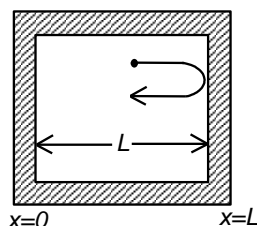
$$\frac{\partial^2 \psi_0}{\partial x^2} + \left(\frac{8\pi^2 m}{h^2}\right) (E - V) \psi_0 = 0 \dots\dots\dots(4)$$

Eq. (4) is the steady state form of Schrodinger equation. In three dimensions, it is

$$\nabla^2 \psi_0 + \left(\frac{8\pi^2 m}{h^2}\right) (E - V) \psi_0 = 0. \text{ Usually it is written in the form } \nabla^2 \psi + \left(\frac{8\pi^2 m}{h^2}\right) (E - V) \psi = 0.$$

10) Apply Schrodinger's equation and find the eigen values & eigen functions for a particle confined to a one-dimensional rigid box?

When the motion of a particle is confined to a limited region such that the particle moves back and forth in the region, the particle is said to be in a bound state. Consider a particle of mass m bouncing back and forth between the walls of a one-dimensional box (Figure). The box has insurmountable potential barriers at $x = 0$ and $x = L$, i.e., the box is supposed to have walls of infinite height at $x = 0$ and $x = L$. The particle position at any instant is given by $0 < x < L$. The potential energy V of the particle is infinite at $x = 0$ and $x = L$. V can be assumed to be zero between $x = 0$ and $x = L$. In terms of the boundary conditions imposed by the problem, the potential function is



$$V = 0 \text{ for } 0 < x < L$$

$$V = \infty \text{ for } x \leq 0$$

$$V = \infty \text{ for } x \geq L$$

The particle can not exist outside the box and so its wave function ψ is 0 for $x \leq 0$ and $x \geq L$. The problem is then to find out what ψ is within the box, i.e., between $x = 0$ and $x = L$. Within the box, the Schrodinger's equation becomes

$\frac{d^2\psi}{dx^2} + \left(\frac{8\pi^2m}{h^2}\right) E\psi = 0$. Putting $\frac{8\pi^2mE}{h^2} = K^2$, the equation becomes $\frac{d^2\psi}{dx^2} + K^2\psi = 0$. The general solution of this equation is

$\psi = A \sin Kx + B \cos Kx$ -----(1). Constants A and B can be evaluated using the boundary conditions of the problem.

$\psi = 0$ at $x = 0$ and hence $B = 0$.

$\psi = 0$ at $x = L$ and hence $A \sin KL = 0$. Since $A \neq 0$, $KL = n\pi$, where n is an integer or $K = \frac{n\pi}{L}$.

Thus $\psi_n(x) = A \sin \frac{n\pi x}{L}$ -----(2).

The particle in a box: wave functions :

It is certain that the particle is somewhere inside the box. Hence for a normalized wave function

$$\int_0^L \psi \psi^* dx = 1 \text{ or } A^2 \int_0^L \sin^2 \frac{n\pi x}{L} dx = 1 \text{ or } A^2 \int_0^L \frac{1}{2} \left[1 - \cos \frac{2\pi nx}{L} \right] dx = 1$$

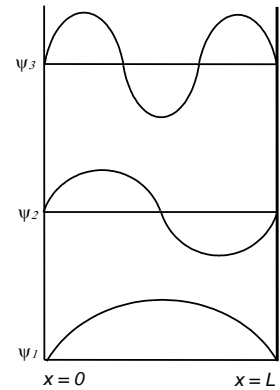
$$\frac{A^2}{2} \left[x - \frac{L}{2\pi n} \sin \frac{2\pi nx}{L} \right]_0^L = 1 \text{ or } \frac{A^2 L}{2} = 1 \text{ or } A = \sqrt{\frac{2}{L}}$$

∴ The normalised wave functions of the particle = $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$

The normalized wave functions ψ_1 , ψ_2 and ψ_3 are plotted in Figure.

$$\therefore \text{ The energy of the particle } = E_n = \frac{\hbar^2 k^2}{8\pi^2 m} = \frac{\hbar^2 n^2 \pi^2}{L^2 8\pi^2 m} = \frac{n^2 \hbar^2}{8m L^2} \dots \dots \dots (3)$$

For each value of n , there is an energy level and the corresponding wave function is given by eq. (2). Each value of E_n is called an 'eigen value' and the corresponding ψ_n is called 'eigen function'. Thus, bounding the particle in a box has led to quantization. The particle in a box can only have discrete energy values specified by eq. (3).



SOLVED EXAMPLES

Example 1: Calculate the de Broglie wavelength of an electron accelerated to a kinetic energy of 54 eV. Given the mass of electron is 9.1×10^{-31} Kg.

Relativistic correction of mass is not needed.

The velocity of the electrons is found from, Kinetic energy = $K = \frac{1}{2}mv^2$ or $v = \sqrt{\frac{2K}{m}}$

$$v = \sqrt{\frac{2 \times 54 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}}{9.1 \times 10^{-31} \text{ Kg}}}$$

$$\text{Momentum} = p = mv = 9.1 \times 10^{-31} \text{ Kg} \times \sqrt{\frac{2 \times 54 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}}{9.1 \times 10^{-31} \text{ Kg}}}$$

De Broglie wavelength $\lambda =$

$$\frac{h}{p} = \frac{6.6 \times 10^{-34} \text{ J sec}}{9.1 \times 10^{-31} \text{ Kg} \times \sqrt{\frac{2 \times 54 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}}{9.1 \times 10^{-31} \text{ Kg}}}} = 1.64 \text{ \AA}$$

Example 2: An electron has a speed of 600 m/s with an accuracy of 0.005%. Calculate the certainty with which the position of the electron can be located.

Relativistic correction of mass is not needed. Hence the accuracy in the measurement of momentum is also 0.005%.

$$\Delta p = \frac{0.005}{100} = 5 \times 10^{-5}$$

$$\text{Accuracy in the measurement of position} = \Delta x = \frac{h}{\Delta p} = \frac{6.63 \times 10^{-34}}{5 \times 10^{-5}} = 1.326 \times 10^{-29}$$

Example 3: Calculate the permitted energy levels of an electron in a box of 1 \AA wide ?

Here, m = mass of the electron = $9.1 \times 10^{-31} \text{ Kg}$; $L = 1 \text{ Å} = 10^{-10} \text{ m}$.

The permitted electron energies =

$$E_n = \frac{n^2 h^2}{8mL^2} = \frac{n^2 (6.626 \times 10^{-34})^2}{8(9.1 \times 10^{-31})(10^{-10})^2} = 6 \times 10^{-18} n^2 \text{ Joule} = 38 n^2 \text{ eV}$$

The minimum energy the electron can have is, $E_1 = 38 \text{ eV}$ corresponding to $n = 1$. The other values of energy are $E_2 = 4 E_1 = 152 \text{ eV}$, $E_3 = 9 E_1 = 342 \text{ eV}$ and so on.

Example 4: A particle is moving in a one-dimensional box (of infinite height) of width 10 Å . Calculate the probability of finding the particle within an interval of 1 Å at the centre of the box, when it is in its state of least energy.

The wave function of the particle in its state of least energy, i.e., in the ground state ($n = 1$) is

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}.$$

The probability of finding the particle in unit interval at the centre of the box ($x = \frac{L}{2}$) is

$$P = \psi_1^2 = \frac{2}{L} \sin^2 \frac{\pi}{2} = \frac{2}{L}$$

∴ The probability of finding the particle within an interval of Δx at the centre of the box =

$$W = |\psi_1|^2 \Delta x = \frac{2}{L} \Delta x$$

Here, $L = 10 \times 10^{-10} \text{ m}$ and $\Delta x = 10^{-10} \text{ m}$ ∴ $W = \frac{2}{10 \times 10^{-10}} \times 10^{-10} = 0.2$