

Introduction to quantum mechanics

Quantum mechanics is a physical science dealing with the behaviour of matter and energy on the scale of atoms and subatomic particles / waves.

It also forms the basis for the contemporary understanding of how very large objects such as stars and galaxies, and cosmological events such as the Big Bang, can be analyzed and explained.

Quantum mechanics is the foundation of several related disciplines including nanotechnology, condensed matter physics, quantum chemistry, structural biology, particle physics, and electronics. The term "quantum mechanics" was first coined by Max Born in 1924.

Inadequacy of Classical Mechanics:

According to the classical mechanics, if we consider the case of an electron moving round the nucleus, its energy should decrease (because the accelerated charged particle loses energy in the form of electromagnetic waves) and therefore its velocity should decrease continuously. The ultimate result is that the electron comes closer and closer to the nucleus until it collapses. This shows the instability of the atom; it is in contradiction to the observed fact of the stability of an atom. Thus the classical mechanics fails to explain the stability of an atom.

The classical mechanics also failed to explain the spectrum of the hydrogen atom. According to the classical theory, the excited atoms of hydrogen emit electromagnetic radiations of all wavelengths continuously, while it is observed that they emit the radiation of certain wavelengths only.

Dual Nature of Radiation (Light) [Wave and Matter (Particles)]

(De-Broglie Hypothesis of Matter Waves)

The universe is made of radiation (light) and matter (particles). The light exhibits the dual nature (i.e.) it can behave both a wave (interference, diffraction, phenomenon) and as a particle (Compton Effect, photo electric effect etc.)

In 1924, Louis de-Broglie suggested that similar to light dual nature "every moving matter has an associated wave". The wave associated with the moving particle is known as matter wave or de-Broglie wave.

De-Broglie wavelength of matter waves

Considering a photon as a particle the total energy of the photon is given by

$$E = mc^2 \dots\dots\dots (1)$$

Where

'm' is the mass of the particle

'c' is the speed of light

Considering the photon as a wave, the total energy is given by

$$E = hv \dots\dots\dots (2)$$

Where 'h' is the Planck's constant and $h = 6.626 \times 10^{-34} \text{Js}$

From equations (1) and (2)

$$mc^2 = h\nu$$

$$\text{since } \nu = \frac{c}{\lambda}$$

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

$$mc = h/\lambda$$

$$\lambda = h/mc$$

Thus

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

If a particle of mass 'm' moving with a velocity v carries a momentum $p = mv$ and it must be associated with the wave of wavelength

$$\lambda = \frac{h}{mv}$$

The above relation is known as de-Broglie equation and the wavelength λ is known as de-Broglie wavelength.

De-Broglie wavelength associated with an accelerated particle

If a charged particle, say an electron is accelerated by a potential difference of V volts, then its kinetic energy is given by

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

$$v = \sqrt{\frac{2eV}{m}}$$

Then the electron wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{m} \sqrt{\frac{m}{2eV}}$$

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

De-Broglie wavelength expressed in term of kinetic energy

If a particle has kinetic energy K.E., then

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

$$p = \sqrt{2mK.E.}$$

From de-Broglie wavelength

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

Substituting the value of p in above equation

$$\lambda = \frac{h}{\sqrt{2m(K.E.)}}$$

De-Broglie wavelength associated with particle in thermal equilibrium

If the particle is in thermal equilibrium at temperature T , then their kinetic energy is given by

$$K.E. = \frac{3}{2}KT$$

Then the de-Broglie of particle

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

Where $K = 1.38 \times 10^{-23} \text{ J/K}$

For an electron

$$m = 9.1 \times 10^{-31} \text{ Kg};$$

$$e = 1.6 \times 10^{-19} \text{ C};$$

$$h = 6.62 \times 10^{-34} \text{ J.s}$$

Therefore

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

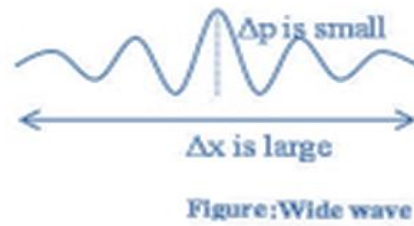
$$\lambda = \frac{12.27}{\sqrt{V}} \text{ \AA}$$

Uncertainty Principle

In 1927 Heisenberg proposed “the uncertainty principle”. This principle is a result of the dual nature of matter.

In quantum mechanics a particle is described by a wave packet, which represents and symbolizes all about particle and moves with group velocity. According to Born’s probability interpretation “**the particle may be found anywhere within the wave packet**”. This implies that the position of the particle is uncertain within the limits of wave packet.

Hence “**it is impossible to determine simultaneously both the position and momentum (or velocity) of a particle with accuracy**”.



Statement of uncertainty principle: “The product of uncertainties in determining the position and momentum of the particle at the same time instant is at best of the order of ‘ \hbar ’.

$$\Delta x \cdot \Delta p \geq \hbar \text{ or } \Delta x \cdot \Delta p \geq \hbar/2$$

Where $\hbar = h/2\pi$, Δx is uncertainty in determining position of the particle and Δp is that in determining the momentum.

Then
$$\Delta x \cdot \Delta p \geq h/4\pi$$

Wave Function:

In quantum mechanics the motion of an atomic particle is described by the wave function ψ . Thus we say that the wave function determines the entire space-time behavior of a quantum particle.

However $\psi(\vec{r}, t)$ has no physical significance as it is not an observable quantity.

Probability:

The square of absolute magnitude is proportional to the probability of finding the particle there at that time.

$$P = |\psi(\vec{r}, t)|^2 = \psi(\vec{r}, t) \psi^*(\vec{r}, t)$$

Where $\psi^*(\vec{r}, t)$ is complex conjugate of $\psi(\vec{r}, t)$

To find the particle somewhere in given space

$$P = \int_{-\infty}^{\infty} |\psi(\vec{r}, t)|^2 dV \text{ (must be finite)}$$

Where $dV = dx dy dz$

Normalization condition

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

The wave function satisfying above equation is said to be normalized and this condition is called Normalization Condition.

Orthogonal condition

Let ψ_i and ψ_j are two different wave functions satisfying the wave function for the wave equation for a given system.

$$\text{If } \int \psi_i \psi_j^* dV = 0 ; i \neq j$$

Then these wave function (ψ_i and ψ_j) are said to be mutually orthogonal*. This is the condition of orthogonally of two wave functions.

Properties of wave function

1. The wave function must be finite.
2. The wave function is single valued
3. The wave function and its all derivatives are continuous

Physical significance of wave function (ψ):

1. The variable quantity that characterizes d-Broglie wave is called wave function.
2. The wave function represents the variations in the matter waves and it connects the particle nature and its associated wave nature statistically.
3. 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 instant and at that point.
4. The probability 0 corresponds to the certainty of not finding the particle and probability 1 corresponds to the certainty of finding the particle.

$$\iiint \psi^* \psi d\tau = 1 \text{ if particle is present}$$

$$\iiint \psi^* \psi d\tau = 0 \text{ if particle is not present}$$

5. If the wave function is a complex quantity that cannot be measured.
6. The probability of finding a particle at particular region must be real and positive, but the wave function ψ is in general a complex quantity. The probability density is given by

$$P(r, t) = |\psi(r, t)|^2 = \psi\psi^*$$

Schrodinger Wave Equation

Schrodinger wave equation, is the fundamental equation of quantum mechanics, same as the second law of motion is the fundamental equation of classical mechanics. This equation has been derived by Schrodinger in 1925 using the concept of wave function on the basis of de-Broglie wave and plank's quantum theory.

Time independent Schrödinger wave equation:

Consider a system of stationary waves to be associated with the particle. Let $\Psi(\vec{r}, t)$ be the wave displacement for the de-Broglie waves at any location $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$ at time t . Then according to Maxwell's wave equation, the differential equation of the wave motion in three dimensions can be written as

$$\nabla^2 \psi = \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} \dots \dots \dots (1)$$

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

and c is the velocity of the wave

The solution of equation (1) gives ψ as a periodic displacement in terms of time

$$\psi(\vec{r}, t) = \psi_0(\vec{r})e^{-i\omega t} \dots \dots \dots (2)$$

Where $\psi_{o,}$ is the amplitude of the wave. It is function of \mathbf{r} not of time t .

Differentiating equation (2) twice with respect to t , we get

$$\frac{\partial \psi}{\partial t} = \psi_0(-i\omega)e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = \psi_0(-\omega^2)e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi$$

Substituting this in equation (1), we get

$$\nabla^2 \psi = -\frac{1}{c^2} \omega^2 \psi$$

$$\nabla^2 \psi + \frac{1}{c^2} \omega^2 \psi = 0 \dots \dots \dots (3)$$

Since $\omega = 2\pi\nu$ and

$$\omega = 2\pi \frac{c}{\lambda}$$

$$\frac{\omega}{c} = \frac{2\pi}{\lambda}$$

$$\frac{\omega^2}{c^2} = \frac{4\pi^2}{\lambda^2}$$

Substituting the value of ω^2/c^2 in eq. no (3), we get

$$\nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \dots \dots \dots (4)$$

Introducing the concept of quantum mechanics, we must put from de-Broglie's equation $\lambda = \frac{h}{mv}$ in equation (4), we get

$$\nabla^2 \psi + \frac{4\pi^2 m^2 v^2}{h^2} \psi = 0 \dots \dots \dots (5)$$

If E and V are the total and potential energies of the particle respectively then its kinetic energy,

$$\frac{1}{2}mv^2 = E - V$$

This gives

$$m^2 v^2 = 2m(E - V)$$

Substituting this in equation (5), we get

$$\nabla^2 \psi + \frac{4\pi^2 2m(E - V)}{h^2} \psi = 0 \dots \dots (6)$$

$$\nabla^2 \psi + \frac{2m(E - V)}{\hbar^2} \psi = 0 \dots \dots \dots (7)$$

$$\text{Where } \hbar = \frac{h}{2\pi}$$

The above equation is called Schrödinger time independent wave equation. The quantity ψ is wave function

For free particle i.e. $V=0$

Then equations (6) and (7) becomes

$$\nabla^2 \psi + \frac{4\pi^2 2mE}{h^2} \psi = 0 \dots \dots (8)$$

$$\nabla^2 \psi + \frac{2mE}{\hbar^2} \psi = 0 \dots \dots \dots (9)$$

Time dependent Schrödinger wave equation:

Schrodinger time dependent wave equation is derived from Schrodinger time independent wave equation by eliminating Energy operator $E\psi$.

The solution of classical differential equation of the wave motion is given by

$$\psi(x, y, z, t) = \psi_0(x, y, z) e^{-i\omega t} \dots \dots \dots (1)$$

Differentiating equation (1) with respect to time t we get

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= -i\omega \psi_0 e^{-i\omega t} \\ \frac{\partial \psi}{\partial t} &= -i(2\pi\nu) \psi_0 e^{-i\omega t} \quad (\because \omega = 2\pi\nu) \\ \frac{\partial \psi}{\partial t} &= -i(2\pi\nu) \psi_0 e^{-i\omega t} \quad (\because \omega = 2\pi\nu) \\ \frac{\partial \psi}{\partial t} &= -2\pi i \frac{E}{h} \psi \quad \left(\because E = h\nu \Rightarrow \nu = \frac{E}{h} \right) \\ \frac{\partial \psi}{\partial t} &= -i \frac{E}{\hbar} \psi \quad \left(\because \hbar = \frac{h}{2\pi} \right) \dots \dots \dots (4) \end{aligned}$$

$$\begin{aligned} i \frac{\partial \psi}{\partial t} &= -i \times i \frac{E}{\hbar} \psi = -i^2 \left(\frac{E}{\hbar} \right) \psi \\ i \frac{\partial \psi}{\partial t} &= \left(\frac{E}{\hbar} \right) \psi \quad (\because i \times i = i^2 = -1) \end{aligned}$$

$$\text{or} \quad E\psi = i\hbar \frac{\partial \psi}{\partial t} \dots \dots \dots (5)$$

We have that Schrodinger time independent wave equation is given by

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \dots \dots \dots (6)$$

Substituting the value of $E\psi$ from equation (5) in equation (6), we get

$$\begin{aligned} \nabla^2 \psi + \frac{2m}{\hbar^2} \left(i\hbar \frac{\partial \psi}{\partial t} - V\psi \right) &= 0 \\ \nabla^2 \psi &= -\frac{2m}{\hbar^2} \left(i\hbar \frac{\partial \psi}{\partial t} - V\psi \right) \\ -\frac{\hbar^2}{2m} \nabla^2 \psi &= i\hbar \frac{\partial \psi}{\partial t} - V\psi \\ -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi &= i\hbar \frac{\partial \psi}{\partial t} \end{aligned}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = i\hbar\frac{\partial\psi}{\partial t} \dots\dots\dots (7)$$

$$\text{or} \quad H\psi = E\psi \dots\dots\dots (8)$$

The equation (8) is known as Schrodinger's time dependent equation.

Where

$$\textbf{Hamiltonian Operator } H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$$

and

$$\textbf{Energy Operator } E = i\hbar\frac{\partial}{\partial t}$$

Quantum Operators

An operator is a rule by means of which a given function is changed into another function. The measurable quantities like energy, momentum, position, etc. are called observables. Each observable has a definite operator associated with it.

i) Energy operator:

The Schrödinger wave equation $H\psi = E\psi$ shows that the operator associated with energy E is Hamiltonian H .

$$\text{i.e.} \quad E_{op} \text{ or } E = H$$

The time independent form of E_{op} is

$$E_{op} = H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

The time dependent Schrödinger equation is

$$H\psi = i\hbar\frac{\partial\psi}{\partial t}$$

Therefore the time dependent value of Hamiltonian is

$$H = i\hbar\frac{\partial}{\partial t}$$

Thus we have

$$E_{op} = H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$E_{op} = i\hbar\frac{\partial}{\partial t}$$

ii) Momentum operator:

$$\text{As Hamiltonian } H = K.E. + P.E. = \frac{p^2}{2m} + V$$

Also

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$\frac{P^2}{2m} + V = -\frac{\hbar^2}{2m}\nabla^2 + V$$

$$P^2 = -\hbar^2\nabla^2$$

$$P^2 = \frac{\hbar^2}{i^2}\nabla^2$$

$$\text{i.e. } P_{op} = \frac{\hbar}{i}\nabla$$

Eigenvalues and Eigen Functions

The wave function for a given physical system contains the measurable information about the system. To obtain specific values for physical parameters, for example energy, you operate on the wave function with the quantum mechanical operator associated with that parameter. The operator associated with energy is the Hamiltonian, and the operation on the wave function is the Schrodinger equation. Solutions exist for the time independent Schrodinger equation only for certain values of energy, and these values are called "eigenvalues*" of energy.

Corresponding to each eigenvalue is an "Eigen function*". The solution to the Schrodinger equation for a given energy E involves also finding the specific function ψ which describes that energy state. The solution of the time dependent Schrodinger equation takes the form

$$H_i\psi_i = E_i\psi_i$$

The eigenvalue concept is not limited to energy. When applied to a general operator Q , it can take the form

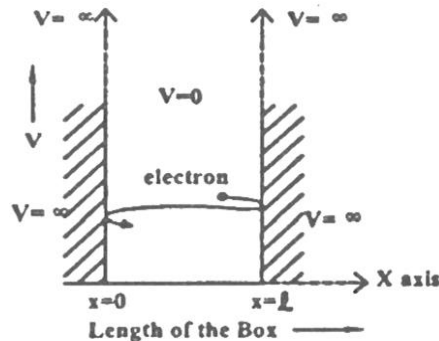
$$\underset{\text{operator}}{Q_{op}}\psi_i = q_i \underset{\text{eigenvalue}}{\overset{\text{eigenfunction}}{\psi_i}}$$

If the function ψ_i is an Eigen function for that operator. The eigenvalues q_i may be discrete, and in such cases we can say that the physical variable is "quantized" and that the index i plays the role of a "quantum number" which characterizes that state.

Application of Schrodinger Wave Equations:

Particle in a One Dimensional Deep Potential Well (box)

Let us consider a particle of mass 'm' in a deep well restricted to move in a one dimension (say x). Let us assume that the particle is free inside the well except during collision with walls from which it rebounds elastically.



The potential function is expressed as

$$V = 0 \quad \text{For } 0 < x < L \dots\dots\dots(1)$$

$$V = \infty \quad \text{For } x \leq 0, x \geq L \dots\dots\dots(2)$$

The probability of finding the particle outside the well is zero (i.e. $\psi=0$). Inside the well, the Schrödinger's time independent wave equation is written as

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

For free particle, i.e. $V=0$

$$\nabla^2\psi + \frac{8\pi^2mE}{h^2}\psi = 0 \dots\dots\dots(3)$$

Let $\frac{8\pi^2mE}{h^2} = k^2 \dots\dots\dots(4)$

Then equation (3) becomes

$$\nabla^2\psi + k^2\psi = 0$$

and writing the Schrodinger's wave equation for 1-D

$$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0 \dots\dots\dots(5)$$

The general equation of above equation may be expressed as

$$\psi = A\sin kx + B\cos kx \dots\dots\dots(6)$$

Where A and B are constants to be determined by boundary conditions

Condition I:

At $x = 0$, potential energy $V=\infty$. Therefore, there is no chance for finding the particle at wall of the box i.e. $\psi = 0$

Therefore from equation (6)

$$0 = A\sin 0 + B\cos 0$$

$$\therefore B = 0$$

∴ equation (6) can be written as

$$\psi = A \sin kx \dots \dots \dots (7)$$

Condition II:

At $x = L$, potential energy $V = \infty$. Therefore, there is no chance for finding the particle at wall of the box
i.e $\psi = 0$

Therefore from equation (7) becomes

$$0 = A \sin kL$$

Here either $A=0$ or $\sin kL=0$; but $A \neq 0$ because if $A=0$, the entire function will be zero as $B=0$

Therefore $A \neq 0$ then $\sin kL = 0$ or $kL = n\pi$

$$k = \frac{n\pi}{L} \dots \dots \dots (8) \text{ where } n = 1, 2, 3, 4$$

Now from equation (7) wave function becomes

$$\psi = A \sin \frac{n\pi}{L} x \dots \dots \dots (9)$$

Substituting the value of k from (8) in (4), we get

$$\left(\frac{n\pi}{L}\right)^2 = \frac{8\pi^2 mE}{h^2}$$

This gives $E \rightarrow E_n$ (say)

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

or

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \dots \dots \dots (10)$$

Where $n = 1, 2, 3, 4, \dots$

From equation (10) E_n is the energy value (**Eigen Value**) of the particle in a well. It is clear that the energy values of the particle in box (well) are discrete not continuous i.e. the energy of the particle is quantized.

The discrete energy values are given by

$$\text{when } n = 1 \text{ we get } E_1 = \frac{h^2}{8mL^2}$$

Similarly we can get the other energy values

$$\text{when } n = 2 \text{ we get } E_2 = \frac{4h^2}{8mL^2} = 4E_1$$

$$\text{when } n = 3 \text{ we get } E_3 = \frac{9h^2}{8mL^2} = 9E_1$$

$$\text{when } n = 4 \text{ we get } E_4 = \frac{16h^2}{8mL^2} = 16E_1$$

∴ In general we can write the energy Eigen value as

$$E_n = n^2 E_1 \dots \dots \dots (11)$$

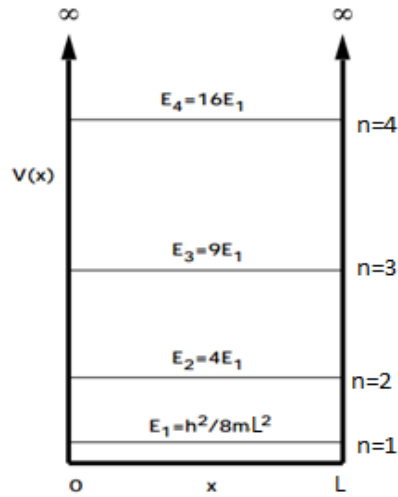


Fig: Energy for Particle

It is found that from the energy levels E_1, E_2, E_3 etc the energy levels of an electron are discrete.

This is the great success which is achieved in Quantum Mechanics than classical mechanics, in which the energy levels are found to be continuous.

Eigen Function (Normalized Wave Function):

It is the process by which the probability (P) of finding the particle (electron) inside the box can be done.

We know that condition of normalization of wave function, the total probability (P) is equal to 1 means then there is a particle inside the box.

For a one dimensional potential box of length 'L' the probability

Equation of wave function is

$$\psi = \psi_n = A \sin \frac{n\pi}{L} x \dots \dots \dots (12)$$

The probability density

$$|\psi|^2 = \psi\psi^* = A^2 \sin^2 \frac{n\pi}{L} x \dots \dots \dots (13)$$

The probability density is zero at $x = 0$ and $x = L$. since the particle is always within the well

$$\begin{aligned} \int_0^L |\psi|^2 dx &= 1 \\ \int_0^L A^2 \sin^2 \frac{n\pi}{L} x dx &= 1 \\ A^2 \int_0^L \sin^2 \frac{n\pi}{L} x dx &= 1 \\ A^2 \int_0^L \left(\frac{1 - \cos \frac{2n\pi}{L} x}{2} \right) dx &= 1 \\ \frac{A^2}{2} \int_0^L \left(1 dx - \cos \frac{2n\pi}{L} x dx \right) &= 1 \\ A^2 \int_0^L 1 dx - \int_0^L \cos \frac{2n\pi}{L} x dx &= 2 \end{aligned}$$

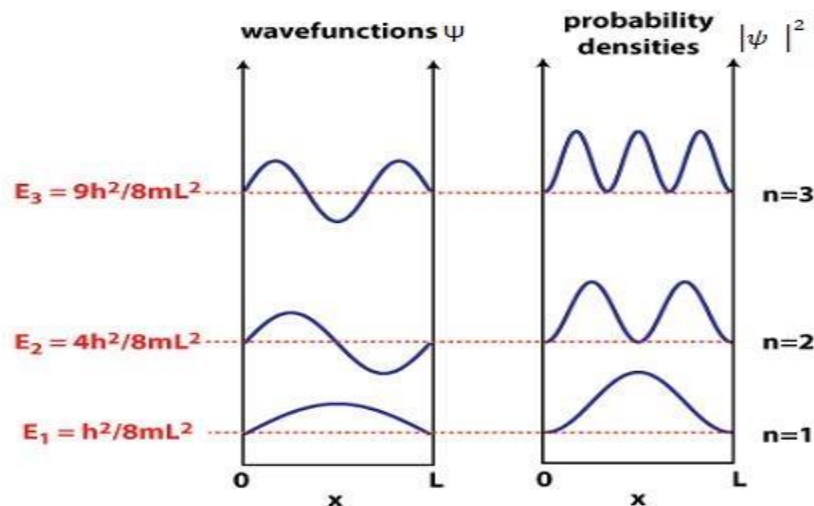
$$A^2 L = 2 \text{ or } A = \sqrt{\frac{2}{L}}$$

Substituting A in equation (12), we get

$$\psi = \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \dots \dots \dots (14)$$

The above equation (14) is normalized wave function (**Eigen function**) belonging to energy value E_n and gives the wave function of the particle enclosed in infinitely deep potential well.

The normalized wave function ψ_1 , ψ_2 and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$ and $|\psi_3|^2$



Physical interpretation of wave function:

Let us consider the first three cases:

Case I: For $n=1$ (Ground State): This is known as ground state and the particle is normally found in this state

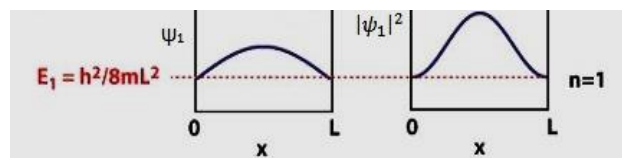
$$E_1 = \frac{h^2}{8mL^2}$$

The Eigen function in this case is given by

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

At $x=0$ and $x=L$, the value of $\psi_1=0$.

ψ_1 has maximum for $x = L/2$



The probability is zero at $x = 0$ and $x = L$ and maximum at $x = L/2$. Therefore in ground state, the particle can not found at the walls of the box and the probability of finding is maximum at central region.

Case II: For $n = 2$ (First Excited state)

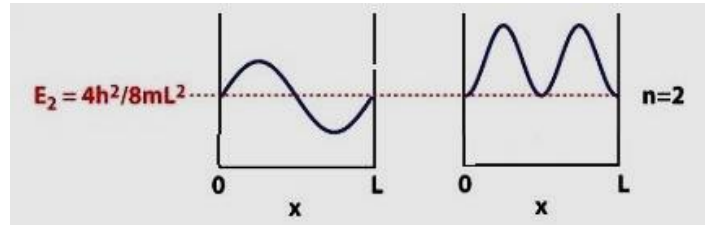
In this case

$$E_2 = \frac{4h^2}{8mL^2} = 4E_1$$

The Eigen function of this case is given by

$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$$

For values of $x = (0, L/2, \text{ and } L)$, $\psi_2 = 0$. Further ψ_2 has maximum value for $x = L/4$ and $x = 3L/4$



From above observation, the particle can not be observed either at walls nor at the center. The maximum probability of finding the particle is either at $x = L/4$ or $3L/4$.

Case III: (Second Excited State):

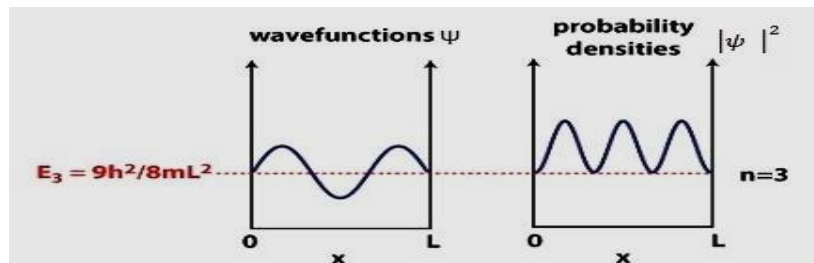
The energy in this state is given by

$$E_3 = \frac{9h^2}{8mL^2} = 9E_1$$

The Eigen wave function is given by

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

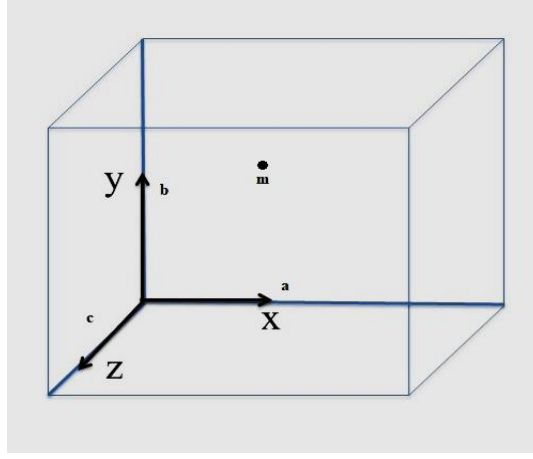
Here $\psi_3 = 0$ for $x = 0, L/3, 2L/3$ and L



It is observed that the particle is most likely found at location $x = L/6, L/3$ and $5L/6$

Particle in three dimensional Potential box:

Let us consider that a particle is trapped in a 3-D rectangular box of sides a , b , and c parallel to x , y and z axis respectively.



The particle can move freely within the region $0 < x < a$, $0 < y < b$, $0 < z < c$. Because the potential inside the box is zero, so there is no force on the particle inside the box. Thus the potential energy can be defined as

$$V(x, y, z) = 0; \text{ for } \begin{cases} 0 < x < a \\ 0 < y < b \\ 0 < z < c \end{cases} \dots \dots \dots (1)$$

$$V(x, y, z) = \infty; \text{ for } \begin{cases} x \leq 0 \text{ and } x \geq a \\ y \leq 0 \text{ and } y \geq b \\ z \leq 0 \text{ and } z \geq c \end{cases} \dots \dots \dots (2)$$

Since the particle cannot penetrate the walls of box due to infinite potential, it cannot exist outside the box. i.e.

$$\begin{cases} \psi(x) = 0, \text{ for } x \leq 0 \text{ and } x \geq a \\ \psi(y) = 0, \text{ for } y \leq 0 \text{ and } y \geq b \\ \psi(z) = 0, \text{ for } z \leq 0 \text{ and } z \geq c \end{cases} \dots \dots \dots (3)$$

For this free particle, Schrodinger's time independent equation (3- D time independent) is

$$\begin{aligned} \nabla^2 \psi(\vec{r}) + \frac{8\pi^2 m}{h^2} E \psi(\vec{r}) &= 0 \\ \frac{\partial^2 \psi(\vec{r})}{\partial x^2} + \frac{\partial^2 \psi(\vec{r})}{\partial y^2} + \frac{\partial^2 \psi(\vec{r})}{\partial z^2} + \frac{8m\pi^2}{h^2} E \psi(\vec{r}) &= 0 \dots \dots \dots (4) \end{aligned}$$

To solve this equation we use method of separation of variables. Let us consider

$$\psi(\vec{r}) = X(x)Y(y)Z(z)$$

Where $X(x)$, $Y(y)$ and $Z(z)$ are functions of only x , y , and z respectively. Putting the value of $\psi(\vec{r})$ in equation (4)

$$\frac{\partial^2}{\partial x^2} [X(x)Y(y)Z(z)] + \frac{\partial^2}{\partial y^2} [X(x)Y(y)Z(z)] + \frac{\partial^2}{\partial z^2} [X(x)Y(y)Z(z)] = -\frac{8\pi^2 m}{h^2} E [X(x)Y(y)Z(z)]$$

Or

$$Y(y)Z(z) \frac{\partial^2 X(x)}{\partial x^2} + X(x)Z(z) \frac{\partial^2 Y(y)}{\partial y^2} + X(x)Y(y) \frac{\partial^2 Z(z)}{\partial z^2} = -\frac{8\pi^2 m}{h^2} E [X(x)Y(y)Z(z)]$$

Dividing above equation by $X(x)Y(y)Z(z)$

$$\frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -\frac{8\pi^2 m}{h^2} E \dots \dots (5)$$

Since all three term on LHS are independent to each other so we can take them equal to some constant individually.

For this, let us consider

$$\left\{ \begin{array}{l} \frac{1}{X(x)} \frac{\partial^2 X(x)}{\partial x^2} = -k_x^2 \Rightarrow \frac{\partial^2 X(x)}{\partial x^2} + k_x^2 X(x) = 0 \\ \frac{1}{Y(y)} \frac{\partial^2 Y(y)}{\partial y^2} = -k_y^2 \Rightarrow \frac{\partial^2 Y(y)}{\partial y^2} + k_y^2 Y(y) = 0 \\ \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = -k_z^2 \Rightarrow \frac{\partial^2 Z(z)}{\partial z^2} + k_z^2 Z(z) = 0 \end{array} \right\} \dots \dots \dots (6)$$

And then from equation (5), we get

$$k_x^2 + k_y^2 + k_z^2 = \frac{8\pi^2 m}{h^2} E \dots \dots (7)$$

The general Solution of equation $\frac{\partial^2 X(x)}{\partial x^2} + k_x^2 X(x) = 0$

$$X(x) = A \sin k_x x + B \cos k_x x \dots \dots \dots (8)$$

Condition 1: Applying boundary condition at $x = 0$ potential energy $V = \infty$. Therefore, there is no chance for finding the particle at wall of the box.

$$\text{i.e. } X_{(x)} = 0$$

Then from equation (8), we get

$$0 = A \sin 0 + B \cos 0 \\ \therefore B = 0$$

Putting the value of B in equation (8), we get

$$X(x) = A \sin k_x x \dots \dots \dots (9)$$

Condition 2: At $x = a$, potential energy $V = \infty$. Therefore, there is no chance for finding the particle at wall of the box i.e. $X_{(x)} = 0$

From equation (9), we get

$$0 = A \sin k_x a$$

Here either $A=0$ or $\sin k_x a=0$; but $A \neq 0$ because if $A=0$, the entire function will be zero as $B=0$

Therefore $A \neq 0$ then $\sin k_x a = 0$

$$k_x a = 0, \pi, 2\pi \dots \dots \dots n\pi$$

or

$$k_x a = n\pi$$

$$k_x = \frac{n\pi}{a}$$

Similarly Along Y and Z axis

$$k_y = \frac{n_y \pi}{b}$$

$$k_z = \frac{n_z \pi}{c}$$

Putting the value of k_x , in equation (9), we have

$$X(x) = A \sin \frac{n_x \pi}{a} x \dots \dots \dots (10a)$$

Similarly along Y and Z axis

$$Y(y) = A \sin \frac{n_y \pi}{b} y \dots \dots \dots (10b)$$

$$Z(z) = A \sin \frac{n_z \pi}{c} z \dots \dots \dots (10c)$$

Putting the value of k_x , k_y and k_z in equation (7), we get

$$\frac{n_x^2 \pi^2}{a^2} + \frac{n_y^2 \pi^2}{b^2} + \frac{n_z^2 \pi^2}{c^2} = \frac{8\pi^2 m}{h^2} E$$

Eigen value of particle

$$E_n = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right] \dots \dots \dots (11)$$

Where $n_x, n_y, n_z = 1, 2, 3, \dots$

Eigen Function:

It is the process by which the probability (P) of finding the particle (electron) inside the box can be done.

We know that condition of normalization of wave function, the total probability (P) is equal to 1 means then there is a particle inside the box.

Normalized condition

$$\int_0^a |X_x|^2 dx = 1$$

$$\int_0^a A^2 \sin^2 \frac{n_x \pi}{a} x dx = 1$$

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

Putting the value of 'A' in equation (10a)

$$X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi}{a} x$$

Similarly along y and z directions

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi}{b} y$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi}{c} z$$

With $n_x, n_y, n_z = 1, 2, 3, \dots$

So, the normalized wave function corresponding to wave associate with the particle moving in 3-D box is

$$\psi(\vec{r}) = X(x)Y(y)Z(z)$$

$$\psi(\vec{r}) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x\pi}{a}\right)x \sin\left(\frac{n_y\pi}{b}\right)y \sin\left(\frac{n_z\pi}{c}\right)z \dots \dots \dots (12)$$

And from equation (10), Eigen values of energy for the particle is

$$E_n = \frac{\hbar^2}{2m} \left[\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{b^2} + \frac{n_z^2\pi^2}{c^2} \right]$$

$$E_n = \frac{\hbar^2\pi^2}{2m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

Where $n_x, n_y, n_z = 1, 2, 3, \dots$

\Rightarrow for a cubical box $a = b = c$, then

Eigen value of particle

$$E_n = \frac{\hbar^2\pi^2}{2ma^2} [n_x^2 + n_y^2 + n_z^2]$$

OR

$$E_n = \frac{h^2}{8ma^2} [n_x^2 + n_y^2 + n_z^2] \dots \dots \dots (13)$$

And Eigen function

$$\psi(\vec{r}) = \frac{2\sqrt{2}}{a\sqrt{a}} \sin\left(\frac{n_x\pi}{a}\right)x \sin\left(\frac{n_y\pi}{a}\right)y \sin\left(\frac{n_z\pi}{a}\right)z \dots \dots \dots (14)$$

Concept of degeneracy:

Degenerate state:

When there is only one wave function corresponding to one particular energy Eigen value, the level is known as non-degenerate state. But when there is a number of wave function corresponding to a single energy Eigen value, then the level is known as degenerate. If there are g such levels which correspond to the same energy then state is known a g -fold degenerate state.

For $n_x = n_y = n_z = 1$, $E_{1,1,1} = \frac{\hbar^2\pi^2}{2ma^2} [1^2 + 1^2 + 1^2]$ the energy $E_{1,1,1} = \frac{3\pi^2\hbar^2}{2ma^2}$ corresponds to single Eigen function, the same is true for $n_x = n_y = n_z = 2$ and $n_x = n_y = n_z = 3$ etc. such Eigen states are non-degenerate states.

For $n_x = 1, n_y = 1, n_z = 2$; $n_x = 1, n_y = 2, n_z = 1$; $n_x = 2, n_y = 1, n_z = 1$ the energy Eigen values is $E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = \frac{\hbar^2\pi^2}{2ma^2} [1^2 + 1^2 + 2^2]$

$E = \frac{6\pi^2\hbar^2}{2ma^2}$ corresponds to three Eigen function Ψ_{112} , Ψ_{121} and Ψ_{211} . Such states are known as degenerate state. This state is 3-fold degenerate state or the order of degeneracy is 3.

Energy Levels and order of degeneracy

Energy	Possible combination of	Order of degeneracy
$\frac{3\pi^2\hbar^2}{2ma^2} = 3E_1$	(1,1,1)	1 (non- degenerate state)
$\frac{6\pi^2\hbar^2}{2ma^2} = 6E_1$	(1,1,2),(1,2,1),(2,1,1)	Order of degeneracy = 3
$\frac{9\pi^2\hbar^2}{2ma^2} = 9E_1$	(1,2,2), (2,1,2),(2,2,1)	Order of degeneracy = 3
$\frac{12\pi^2\hbar^2}{2ma^2} = 12E_1$	(2,2,2)	1 (non- degenerate state)
$\frac{11\pi^2\hbar^2}{2ma^2} = 11E_1$	(1,1,3), (1,3,1),(3,1,1)	Order of degeneracy = 3
$\frac{14\pi^2\hbar^2}{2ma^2} = 14E_1$	(1,2,3),(2,3,1),(3,1,2) (3,2,1),(1,3,2),(2,1,3)	Order of degeneracy = 6