

## QUANTUM MECHANICS

Quantum Mechanics is a branch of mechanics that deals with the mathematical description of the motion and interaction of subatomic particles. It incorporates the concepts of quantization of energy, wave-particle duality and the uncertainty principle.

### Matter Waves

In 1924, Louis de Broglie proposed that just like radiation, particles also have wave-particle dual nature. Waves associated with a particle in motion are called de Broglie waves.

In case of photons of frequency  $\nu$ , energy can be expressed as

$$E = h\nu = h \frac{c}{\lambda} \quad (\text{wave nature})$$

$$E = mc^2 \quad (\text{Particle nature})$$

$$mc^2 = h \frac{c}{\lambda} \quad (\text{wave- particle dual nature})$$

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

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

de Broglie suggested that this equation can be applied to any moving particle to find the wavelength of the matter wave. In general, for a particle of mass 'm' and velocity 'v', the associated matter wave is of wavelength

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

For an electron accelerated through a potential 'V', the associated matter wave is of wavelength

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

Substituting the values ,

$$\lambda = \sqrt{\frac{150}{V}} \text{ \AA}$$

### Heisenberg's Uncertainty Principle

The Heisenberg's uncertainty principle states that it is not possible to know the position and the momentum of a particle simultaneously with precision. In other words, the product of uncertainty in position ( $\Delta x$ ) and uncertainty in momentum ( $\Delta p$ ) is greater than or equal to  $h/4\pi$ ,

$$\Delta p \Delta x \geq \hbar/2$$

Similar relations can be written for other pairs of canonical variables like angle & angular momentum and energy & time.

$$\Delta E \Delta t \geq \hbar/2$$

where  $\Delta E$  and  $\Delta t$  are the uncertainties in determining energy and time, respectively and

$$\Delta J \Delta \theta \geq \hbar/2$$

$\Delta J$  and  $\Delta \theta$  are the uncertainties in the measurement of angular momentum and angle, respectively.

## Applications of uncertainty principle

The uncertainty principle can be used to explain many atomic phenomena. Two of them are explained below.

### 1. Absence of Electron inside nucleus

Radii of typical nuclei are of the order of  $10^{-14}\text{m}$ . For an electron confined inside the nucleus, position may not exceed this limit and so the uncertainty in position is  $\Delta x = 10^{-14}\text{m}$ . Corresponding uncertainty in momentum is

$$\Delta p = \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{10^{-14}} = 1.1 \times 10^{-20} \text{kgms}^{-1}$$

If this is the uncertainty in momentum of electron, the momentum itself is of the order of this magnitude.

Momentum of electron is  $p \approx 1.1 \times 10^{-20} \text{kgms}^{-1}$

Neglecting rest mass energy, kinetic energy of the electron is

$$T = pc = 1.1 \times 10^{-20} \text{kgms}^{-1} \times 3 \times 10^8 \text{ms}^{-1}$$

$$T = 3.3 \times 10^{-12} \text{J}$$

$$T = \frac{3.3 \times 10^{-12}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 20 \text{ MeV}$$

So an electron requires 20 MeV energy to stay inside nucleus. But experiments show that electrons associated with even the unstable atoms never have more than a fraction of this energy. Hence, we can conclude that electrons cannot be present inside nuclei.

### 2. Uncertainty in frequency of light emitted by an atom/Natural Line Broadening

Typical lifetime in an excited state of an atom is  $10^{-8}\text{s}$ . So the uncertainty of de-excitation is  $\Delta t = 10^{-8}\text{s}$ . The corresponding uncertainty in energy is

$$\Delta E \approx \frac{\hbar}{\Delta t}$$

$$\Delta E \approx \frac{1.054 \times 10^{-34} \text{ Js}}{10^{-8} \text{ s}} \approx 1.054 \times 10^{-26} \text{ J}$$

We have  $E = h\nu$  where  $\nu$  is the frequency of light

$$\Delta E = h\Delta\nu$$

Hence uncertainty in the frequency of light is

$$\Delta\nu = \frac{1.054 \times 10^{-26} \text{J}}{6.6 \times 10^{-34} \text{Js}}$$

$$= 1.6 \times 10^7 \text{Hz} = 16 \text{MHz}$$

This is the irreducible limit of accuracy with which we can determine the frequency of light emitted by an atom. That means the emitted spectral line is not sharp but has some width. This broadening of spectral line which cannot be reduced further is known as natural line broadening.

### **Wave function ( $\Psi$ )**

In a wave there is something that varies periodically. In case of electromagnetic waves, the electric and magnetic fields vary periodically, whereas in sound waves, pressure varies periodically. In water waves the height of water surface varies periodically. Similarly in matter waves, a quantity that varies is called wave function, denoted by  $\Psi$ . It is a mathematical function in terms of position and time that represent state of a particle.

Wave function  $\Psi$  is a complex quantity, which gives 'the idea of the probability of finding the particle' in a particular region of space.

### **Properties / Physical Significance of Wave Function ( $\Psi$ )**

1. The wave function  $\Psi$  is complex quantity, so one cannot measure it.
2. The wave function relates the particle nature and wave nature statistically.
3. Square of the wave function  $|\psi|^2$  is a real quantity and gives the probability of finding a particle in region of space.

$$\text{Position probability density, } P = \int |\Psi^2| d\tau$$

Value of P is between 0 and 1. For ex; if P=0.4, it means there is a 40% chance for the presence of particle.

4. It does not predict the exact location of the particle, but it says where the particle is likely to be.

### **Normalization of Wave function**

A wave function, which satisfies equation  $\int |\Psi^2| d\tau = 1$  is said to be normalized to unity or simply normalized. This means particle which exist in a particular region must be found somewhere in that region, i.e., the probability of finding the particle in that region will be 100%, i.e., unity.

### **Wave function of a particle with energy E and momentum p**

Consider a particle moving in x-direction with momentum 'p'. The wave function of the particle can be written in the form

$$\Psi = ae^{-i[\omega t - kx]} \text{-----(1)}$$

where 'a' is the amplitude,  $\omega = \frac{2\pi}{T}$  and  $k = \frac{2\pi}{\lambda}$

$$\omega = \frac{2\pi}{T} = 2\pi\nu$$

$$\omega = \frac{2\pi h\nu}{h} = \frac{2\pi}{h} E$$

$$\omega = \frac{E}{\hbar} \text{-----(2)}$$

where E-energy of particle and  $\hbar = \frac{h}{2\pi}$

We have

$$k = \frac{2\pi}{\lambda}$$

Using de Broglie wave equation,

$$k = \frac{2\pi p}{h} = \frac{p}{\hbar} \text{-----(3)}$$

Using eqn (2) and (3) in (1)

$$\Psi = ae^{-i\frac{[Et-px]}{\hbar}}$$

This is the wave function of a particle with energy E and momentum 'p'.

### TIME-DEPENDENT SCHRÖDINGER EQUATION

Consider a particle moving in x-direction with momentum 'p'. Wave function of the particle is

$$\Psi = ae^{-i\frac{[Et-px]}{\hbar}} \text{-----(1)}$$

Differentiating (1) w.r.t. 't'

$$\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} Eae^{-i\frac{[Et-px]}{\hbar}}$$

$$\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} E\Psi$$

$$E\Psi = i\hbar \frac{\partial \Psi}{\partial t} \text{-----(2)}$$

Differentiating (1) w.r.t. 'x' twice

$$\frac{\partial \Psi}{\partial x} = \frac{i}{\hbar} p ae^{-i\frac{[Et-px]}{\hbar}}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{i}{\hbar} p \frac{i}{\hbar} p ae^{-i\frac{[Et-px]}{\hbar}}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{-p^2}{\hbar^2} \Psi$$

$$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} \text{-----(3)}$$

Total energy of the particle is the sum of KE and PE

$$E = \frac{p^2}{2m} + V$$

Multiplying by  $\Psi$

$$E\Psi = \frac{p^2}{2m} \Psi + V\Psi \text{-----(4)}$$

Using eqns (2) and (3) in eqn(4)

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi$$

This is the time dependent Schrodinger equation in one dimension. In 3dimension,

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \nabla^2 \Psi + V\Psi$$

where  $\nabla^2$  is the Laplacian operator

### TIME INDEPENDENT SCHRÖDINGER EQUATION

In many cases the potential (V) is independent of time and depends only on position. In such steady state /stationary cases, the Schrodinger equation can be simplified by separating the time dependent and independent parts.

Wave function of a particle moving in x-direction with momentum 'p' is

$$\Psi = ae^{\frac{-i}{\hbar}[Et-px]}$$

$$\Psi = ae^{\frac{-i}{\hbar}Et} e^{\frac{i}{\hbar}px}$$

$$\Psi = \Psi_0 e^{\frac{-i}{\hbar}Et} \text{-----(1)}$$

where  $\Psi_0$  is a function that depend on position only

Differentiating eqn (1) w.r.t. 't'

$$\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} E\Psi_0 e^{\frac{-i}{\hbar}Et} \text{-----(2)}$$

Differentiating eqn (1) w.r.t. 'x' twice

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{\partial^2 \Psi_0}{\partial x^2} e^{\frac{-i}{\hbar}Et} \text{-----(3)}$$

The time dependent Schrodinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \text{-----(4)}$$

Using (1), (2) and (3) in (4)

$$i\hbar \frac{-i}{\hbar} E\Psi_0 e^{\frac{-i}{\hbar}Et} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi_0}{\partial x^2} e^{\frac{-i}{\hbar}Et} + V\Psi_0 e^{\frac{-i}{\hbar}Et}$$

$$E\Psi_0 e^{\frac{-i}{\hbar}Et} = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi_0}{\partial x^2} e^{\frac{-i}{\hbar}Et} + V\Psi_0 e^{\frac{-i}{\hbar}Et}$$

$$E\Psi_0 = \frac{-\hbar^2}{2m} \frac{\partial^2 \Psi_0}{\partial x^2} + V\Psi_0$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_0}{\partial x^2} + (E - V)\Psi_0 = 0$$

This is the time independent Schrodinger equation in one dimension. In three dimensions it takes the form

$$\frac{\hbar^2}{2m} \nabla^2 \Psi_0 + (E - V)\Psi_0 = 0$$

For studying the nature of a moving particles

- Find the potential energy 'V' and substitute in Schrodinger equation
- Solve the equation to find  $\Psi$ .

The wave functions  $\Psi(x)$  obtained as solutions must satisfy the conditions:

- $\Psi(x)$  is finite and should tend to zero when  $x$  tends to  $\pm\infty$
- $\Psi(x)$  should be single valued at a point.
- $\Psi(x)$ ,  $\frac{\partial \Psi}{\partial x}$ ,  $\frac{\partial^2 \Psi}{\partial x^2}$  etc should be continuous.

### ONE DIMENSIONAL INFINITE SQUARE WELL POTENTIAL (PARTICLE IN A ONE-DIMENSIONAL BOX)

Consider a particle of mass 'm' confined in an infinite square well potential (one dimensional potential box) of width L defined by

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

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

The time independent Schrodinger equation of the particle in the region II (where  $V=0$ ) is

$$\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + (E - 0)\Psi = 0$$

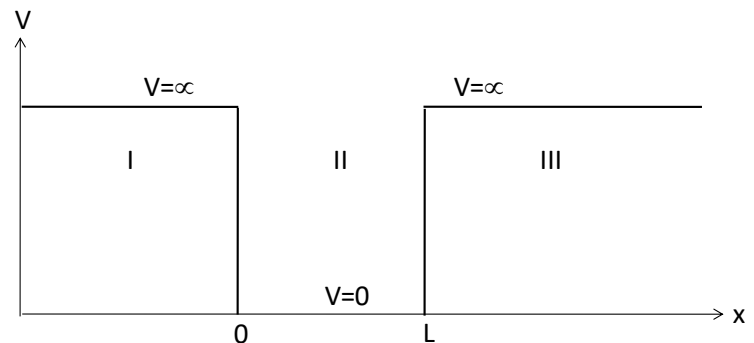
$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} E\Psi = 0$$

$$\frac{\partial^2 \Psi}{\partial x^2} + k^2\Psi = 0 \quad \text{-----(1)}$$

$$\text{where } k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{-----(2)}$$

General solution of eqn (1) is

$$\Psi(x) = A \cos(kx) + B\sin(kx) \quad \text{-----(3)}$$



The probability of finding the particle outside the well is zero. So  $\Psi^*\Psi$  must be zero at walls; i.e. at  $x=0$  and  $x=L$ . This means  $\Psi$  must be zero at walls; at  $x=0$  and  $x=L$

Applying boundary condition; at  $x=0$ ,  $\Psi(x) = 0$

$$\Psi(0) = A\cos(k0) + B\sin(k0) = 0$$

$$A\cos(k0) = 0$$

This is valid only if  $A=0$

$$\therefore \Psi = B\sin(kx)$$

Applying boundary condition; at  $x=L$ ,  $\Psi(x) = 0$

$$\Psi(L) = B\sin(kL) = 0$$

This is valid only when  $kL = n\pi$

$$k = \frac{n\pi}{L} \quad \text{-----(4)}$$

$$\therefore \Psi_n(x) = B\sin\left(\frac{n\pi}{L}x\right)$$

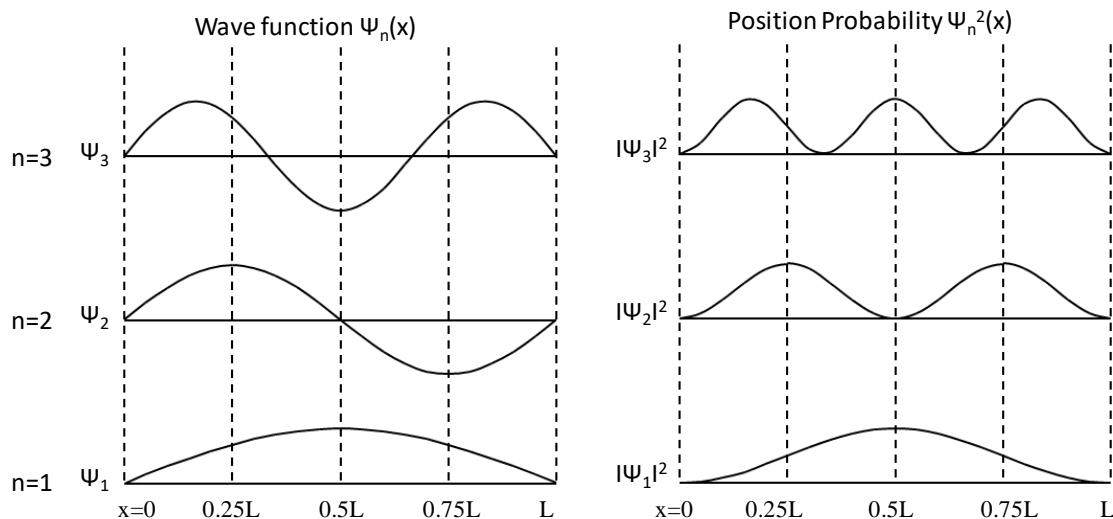
By using the normalization condition and applying limits it can be shown that  $B = \sqrt{\frac{2}{L}}$

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

where  $n=1,2,3 \dots$

$n=0$  is not admissible because when  $n=0$ ,  $\Psi(x) = 0$  inside the box which means particle is not present inside the box. So the possible values of  $n$  are  $1,2,3 \dots$

Wave function and probability of finding the particle are represented below figure.



(Note: when  $x$  varies from  $0$  to  $L$ ,  $\frac{x}{L}$  varies from  $0$  to  $1$  and  $\frac{n\pi}{L}x$  varies from  $0$  to  $n\pi$ )

In ground state ( $n=1$ ) maximum probability of finding the particle is at the midpoint. But for  $n=2$ , the maximum probabilities are at  $\frac{1}{4}$ th and  $\frac{3}{4}$ th distance from one end of the box.

## Allowed Energy Levels

From (2) and (4)

$$\frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Using  $\hbar = h/2\pi$

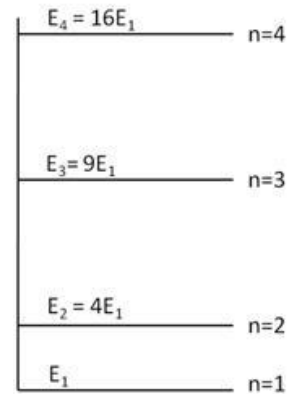
$$E_n = \frac{n^2h^2}{8mL^2}$$

when  $n=1$ ,  $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$

when  $n=2$ ,  $E_2 = \frac{4\pi^2\hbar^2}{2mL^2}$

when  $n=3$ ,  $E_3 = \frac{9\pi^2\hbar^2}{2mL^2}$

when  $n=4$ ,  $E_4 = \frac{16\pi^2\hbar^2}{2mL^2}$



This means that particle cannot have any arbitrary energy value but can have only certain discrete values. Also the particle cannot have zero energy.  $E_1$  for  $n=1$  is the minimum energy a particle can have and is called zero-point energy. The number 'n' is the quantum number.

Thus confinement of particle in a potential well leads to;

1. *Certain preferred positions of maximum probability of finding the particle.*
2. *Particle is allowed to have certain discrete energy levels only.*
3. *There is a minimum limit to the energy that particle can have.*

## Quantum Mechanical Tunneling

According to classical mechanics, when a particle of lower kinetic energy approaches a larger potential barrier ( $E < V_0$ ), it bounces off. But in quantum mechanics the wave function representing the particle does not vanish on the other side of the barrier. This means there is a finite probability of particle penetrating the barrier exists. Phenomenon of penetration of particle through barriers higher than their own energy is known as quantum mechanical tunnelling.

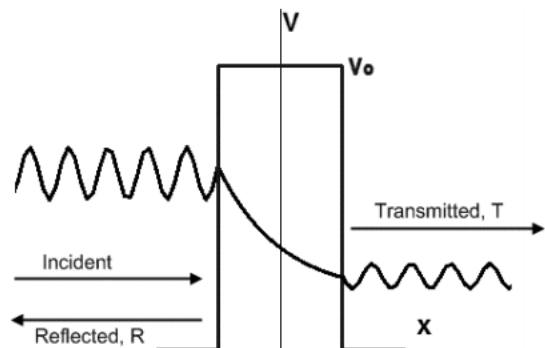
Wave function of the incident particle is

$$\Psi_1 = Ae^{ikx} + Be^{-ikx}$$

Where A represent the amplitude of incident wave and B represent the amplitude of reflected wave.

Wave function of the transmitted particle is

$$\Psi_3 = Fe^{ikx} + Ge^{-ikx}$$





Where F represent the amplitude of transmitted wave and B represent the amplitude of reflected wave. But there is no reflection in region 3 and therefore

$$\Psi_3 = Fe^{ikx}$$

Since the probability of finding the particle is proportional to the square of the amplitude, quantum mechanical tunneling probability is

$$T = \frac{|F|^2}{|A|^2}$$

### Applications

1. Explanation of Zener break down
2. Explanation of Josephson effect

### Quantum Mechanical Operators

In mathematics, an operator transforms one function into another. Ex:  $\frac{d}{dx}$  is the differential operator. Similarly in quantum mechanics each dynamic variable is represented by an operator

### Properties of Operators in Quantum Mechanics

Operators in quantum mechanics are linear. An operator is linear if it satisfies below conditions;

$$\hat{A}(\psi_1 + \psi_2) = \hat{A}\psi_1 + \hat{A}\psi_2$$

$$\hat{A}(c\psi_1) = c \hat{A}\psi_1 ; \text{where } c \text{ is a constant}$$

### Energy & Momentum Operators

Wave function of a particle is  $\Psi = ae^{\frac{-i}{\hbar}[Et - px]}$

$$\frac{\partial \Psi}{\partial t} = \frac{-i}{\hbar} E \Psi$$

$$E \Psi = i \hbar \frac{\partial \Psi}{\partial t}$$

The dynamic variable E can be represented as energy operator

$$\hat{E} = i \hbar \frac{\partial}{\partial t}$$

Similarly the momentum operator is

$$\hat{p} = -i\hbar \frac{\partial}{\partial x}$$

### Eigen Value and Eigen Function of Operator

If the effect of an operator  $\hat{A}$  operating on function  $\Psi$  is merely to multiply  $\Psi$  with a constant factor  $K$ , i.e.  $\hat{A} \Psi = K\Psi$

then  $\Psi$  is an Eigen function and  $K$  is the Eigen value of operator  $\hat{A}$ .

Example:

The time independent Schrodinger eqn is

$$\frac{-\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V \Psi = E\Psi$$

$$\left\{ \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V \right\} \Psi = E\Psi$$

$$\hat{H}\Psi = E\Psi$$

Where  $\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$  is Hamiltonian operator.