

MODULE - 2

Wave Mechanics**Introduction**

Wave mechanics, also known as quantum mechanics, is a branch of physics that describes the behavior of matter and energy at the atomic and subatomic level. It is based on the concept of wave-particle duality, which states that particles such as electrons and photons can exhibit both wave-like and particle-like behavior. In wave mechanics, the state of a quantum system is described by a wave function, which gives the probability of finding a particle in a particular location or with a particular energy. The behavior of the wave function is governed by the Schrödinger equation, which describes how it evolves over time.

One of the most significant contributions of quantum mechanics to engineering is the development of quantum computing, which has the potential to revolutionize computing by enabling much faster and more efficient algorithms than classical computers. Other applications of quantum mechanics in engineering include the development of high-performance materials, such as superconductors and semiconductors, as well as the design of nanoscale devices such as transistors and sensors. Quantum mechanics also plays a crucial role in modern communication technologies, such as quantum cryptography, which uses the principles of quantum mechanics to enable secure communication. Additionally, quantum mechanics has applications in fields such as optics, where it is used to study the behavior of light and other electromagnetic waves at the quantum level. Overall, quantum mechanics has many important applications in engineering and is an essential tool for understanding and developing cutting-edge technologies.

Heisenberg's Uncertainty Principle

The Uncertainty Principle is named after Werner Heisenberg, a German physicist who first proposed it in 1927. It is based on the wave-particle duality of quantum mechanics, which suggests that particles can behave both like waves and like particles. The Uncertainty Principle has important implications for many areas of physics and engineering, including the design of electronic devices and the behavior of subatomic particles. It is a key concept in our understanding of the nature of matter and energy at the quantum level.

Statement: “The simultaneous determination of the exact position and momentum of a moving particle is impossible”

Explanation: According to this principle if Δx is the error involved in the measurement of position and Δp is the error involved in the measurement of momentum during their simultaneous measurement, then the product of the corresponding uncertainties is given by

$$\Delta x \times \Delta p \geq \frac{h}{4\pi} \quad \text{similarly} \quad \Delta E \times \Delta t \geq \frac{h}{4\pi}$$

The product of the errors is of the order of Planck’s constant. If one quantity is measured with high accuracy then the simultaneous measurement of the other quantity becomes less accurate.

Physical significance: According to Newtonian physics the simultaneous measurement of position and momentum are “exact”. But the existence of matter waves induces serious problems due to the limit to accuracy associated with the simultaneous measurement. Hence the “Exactness” in Newtonian physics is replaced by “Probability” in quantum mechanics.

Suggested reading: Principle of complementarity and Schrodinger’s cat.

Application of Heisenberg’s uncertainty principle

Non-existence of the electron in the nucleus: Beta rays are emitted by the nucleus. When it was first observed it was believed that electrons exist inside the nucleus and are emitted at certain instant. If the electron can exist inside the atomic nucleus then uncertainty in its position must not exceed the diameter of the nucleus. The diameter of the nucleus is of the order of 10^{-14} . Applying Heisenberg’s uncertainty principle for an electron expected to be inside the nucleus we get

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

$$\Rightarrow \Delta p \geq \frac{h}{4\pi \Delta x}$$

Substituting for Δx and h we get

$$\Rightarrow \Delta p \geq \frac{h}{4\pi \Delta x} \geq \frac{6.625 \times 10^{-34}}{4 \times 3.142 \times 10^{-14}} \geq 0.52 \times 10^{-20} \text{ N s}$$

is the uncertainty in the measurement of momentum. Thus, the momentum of the electron must be at least equal to the uncertainty in the momentum. Therefore $p_x = 0.52 \times 10^{-20} \text{ N s}$

The energy of the electron is given by relativistic equation $E = p_x c$

Where $c = 3 \times 10^8$ m/s is the velocity of light. Substituting the values, the energy of the electron expected to be inside the nucleus is given by

$$E = 1.5 \times 10^{-12} \text{ J} \sim 9.7 \text{ MeV}$$

According to experiments, the energy associated with the **Beta ray emission is around 3 MeV** which is much lesser than the energy of the electron expected to be inside the nucleus. Hence electrons do not exist inside the nucleus.

Wave Function

According to De Broglie's hypothesis the relation between momentum and wavelength is found to be experimentally valid for both photons and particles. The quanta of matter or radiation can be represented in agreement with uncertainty principle by wave packets. Thus, it suggests that concentrated bunches of waves might be used to describe localized particles and quanta of radiation. Hence, we shall consider a wave function that depends on space (x, y and z) and time (t) and is denoted by ψ (psi). The wave function for a wave packet moving along +ve X axis is given by

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

Time-Independent Schrödinger Wave Equation

The wave equation which has variations only with respect to position and describes the steady state is called **Time-Independent Schrodinger wave equation**.

Consider a particle of mass ' m ' moving with velocity ' v ' along +ve X-axis. The deBroglie wavelength ' λ ' is given by

$$\lambda = \frac{h}{mv} \quad \dots\dots\dots (1)$$

The wave equation for one dimensional propagation of waves is given by

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2} \quad \dots\dots\dots (2) \quad \text{along +ve X - axis}$$

Where ' v ' is Wave Velocity

$$\text{Here } \psi = \psi_0 e^{-i(\omega t - kx)} \quad \dots\dots\dots (3)$$

Where ψ_0 is the amplitude at the point of consideration ω is angular frequency and k is Wave Number.

Differentiating ψ twice with respect to time (t), we get

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2 \psi_0 e^{-i(\omega t - kx)} \dots\dots\dots(4)$$

Substituting equation (4) in equation (2)

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} (-\omega^2 \psi) = \frac{1}{(f\lambda)^2} (-2\pi f)^2 \psi \quad \text{Here } f \text{ is the frequency of the wave and } \lambda \text{ is the wavelength}$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} = -\left(\frac{4\pi^2}{\lambda^2}\right) \psi$$

$$\Rightarrow \frac{\partial^2 \psi}{\partial x^2} + \left(\frac{4\pi^2}{\lambda^2}\right) \psi = 0$$

Substituting for λ from equation (1) we get

$$\frac{\partial^2 \psi}{\partial x^2} + \left(\frac{4\pi^2}{\left(\frac{h}{mv}\right)^2}\right) \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \left(\frac{4\pi^2}{h^2}\right) \frac{2m^2 v^2}{2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \left(\frac{8\pi^2 m}{h^2}\right) \frac{1}{2} mv^2 \psi = 0 \quad \dots\dots\dots(5)$$

The kinetic energy of the particle $\frac{1}{2} mv^2$ is given by

$$\frac{1}{2} mv^2 = E - V \quad \text{here } E \text{ is the Total Energy of the particle and } V \text{ is the Potential Energy}$$

Therefore equation (5) becomes

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

Generalizing the equation for three dimensions we get

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

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

$$\Delta^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Here

Hence the Time-Independent Schrodinger Wave equation for three dimensions.

Physical significance of wave function (Physical Interpretation)

The wave function ψ just as itself has no direct physical meaning. It is more difficult to give a physical interpretation to the amplitude of the wave. The amplitude of the wave function ψ is certainly not like displacement in water wave or the pressure wave nor the waves in stretched string. It is a very different kind of wave. But the quantity, the squared Absolute amplitude gives the probability for finding the particle at given location in space and is referred to as probability density. It is given by

$$P(x) = |\psi|^2$$

Thus, in one dimension the probability of finding a particle in the width 'dx' of length 'x'

$$P(x) dx = |\psi|^2 dx$$

Similarly, for three dimension, the probability of finding a particle in a given small volume dV of volume V is given by

$$P dV = |\psi|^2 dV \quad \text{here } dV = dx dy dz.$$

Here 'P' Probability of finding the particle at given location per unit volume and is called Probability Density.

But since ψ is complex the probability density $|\psi|^2$ is given by

$$|\psi|^2 = \psi \psi^*$$

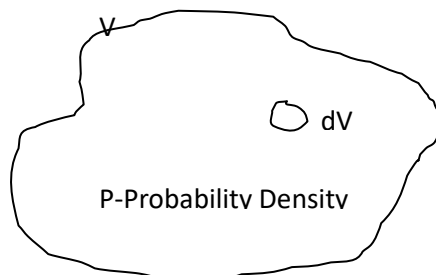
Where ψ^* is the complex conjugate of ψ and the above product results in real number.

Normalization and Normalized wave function

Since the particle exists somewhere in volume V then the probability of finding the particle in the given volume V is equal to 1.

$$\int_0^V |\psi|^2 dV = 1 = \int_0^V P dV$$

Thus



If we are unable to locate the particle in volume V then the notion can be extended to the whole space with

$$\int_{-\infty}^{\infty} |\psi|^2 dx dy dz = 1$$

But, normally, the value of the above integral will not be unity but contains an indefinite constant which can be determined along with sign using above considerations. The process is called normalization and the wave function which satisfies the above condition is called normalized wave function.

Eigen functions and Eigen values

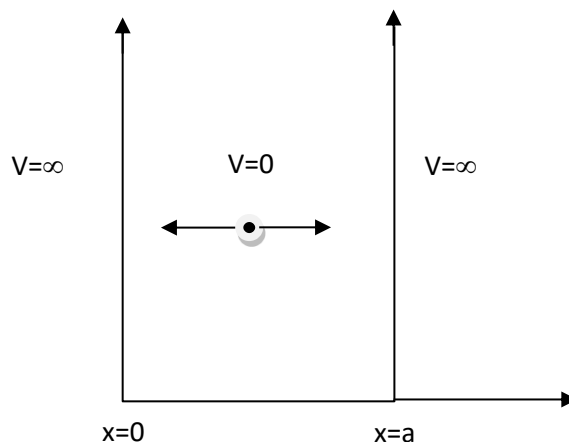
The Schrodinger wave equation is a second order differential equation. Thus solving the Schrodinger wave equation to a particular system, we get many expressions for wave function (ψ). However, all wave functions are not acceptable. Only those wave functions which satisfy certain conditions are acceptable. Such wave functions are called Eigen functions for the system. The energy values corresponding to the Eigen functions are called Eigen values. The wave functions are acceptable if they satisfy the following conditions

- 1) ψ must be finite everywhere (not zero everywhere)
- 2) ψ must be single valued which implies that solution is unique for a given position in space.
- 3) ψ and its first derivatives with respect to its variables must be continuous everywhere.

Applications of Schrödinger wave equation 10 marks

Particle in a one-dimensional box or one-dimensional potential well of infinite height

Consider a particle of mass 'm' bouncing back and forth between the walls of one-dimensional potential well. The particle is said to be under bound state. Let the motion of the particle be confined along the X-axis in between two infinitely hard walls at $x=0$ and $x=a$. Since the walls are infinitely hard, no energy is lost by the particle during the collision with walls and the total energy remains constant.



In between walls i.e., $0 < x < a$, the potential energy $V=0$.

Beyond the walls i.e., $x \leq 0$ and $x \geq a$, the potential energy $V=\infty$.

Beyond the walls

Since the particle is unable to penetrate the hard walls, it exists only inside the potential well. Hence $\psi=0$ and the probability of finding the particle outside the potential well is also zero.

Inside the potential well

Since the potential inside the well is $V=0$, the Schrodinger wave equation is given by

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

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m E}{h^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \dots\dots\dots(1) \quad \text{Here } k^2 = \frac{8\pi^2 m E}{h^2} \quad \dots\dots\dots(2)$$

For the given value of E, k is constant. The general solution for the equation (1) is given by

$\psi(x) = A \sin kx + B \cos kx \quad \dots\dots\dots(3)$ Where A and B are arbitrary constants. The values of these constants can be obtained by applying the boundary conditions

I) At $x=0$, $\psi(x)=0$. Substituting the values in equation (3) we get

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

$$\therefore B = 0$$

Hence equation(3) becomes $\psi(x) = A \sin kx \quad \dots\dots\dots(4)$

II) At $x=a$, $\psi(x)=0$. Substituting the values in equation (4) we get

$$0 = A \sin ka$$

Since $A \neq 0$ (Otherwise no Solution), $ka = n\pi$ Where $n = 1, 2, 3, \dots$

$$\Rightarrow k = \frac{n\pi}{a} \dots\dots\dots(5)$$

Thus the wave function becomes $\psi(x) = A \sin \frac{n\pi x}{a} \dots\dots\dots(6)$

Also substituting the value of 'k' from eq (5) into eq (2) we get

$$\left(\frac{n\pi}{a}\right)^2 = \frac{8\pi^2 m E}{h^2} \Rightarrow E = \frac{n^2 h^2}{8ma^2} \dots\dots\dots(7) \text{ hence the energy **Eigen values**.}$$

Thus substituting $n=1$ in the equation (7) we get

$$E_1 = \frac{h^2}{8ma^2} \text{ is the ground state energy of the particle and is also called zero point energy.}$$

Hence $E_n = n^2 E_1$ E_2 and E_3 are energies of the first and second excited states respectively and so on. Hence for a particle in the bound state, the energy values are discrete.

Normalization of wave function

The wave function for a particle in a box is given by equation (6)

$$\psi(x) = A \sin \frac{n\pi x}{a}$$

The value of the arbitrary constant 'A' can be determined by the process of normalization. Since the particle has to exist somewhere inside the box we have

$$\int_0^a P(x) dx = \int_0^a |\psi(x)|^2 dx = 1 \text{ Substituting the wave function from equation (6)}$$

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

$$\text{Since } \sin^2 \theta = \frac{1}{2} [1 - \cos 2\theta] \text{ we have}$$

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

Integrating the equation we get

$$\frac{A^2}{2} \left[x - \frac{a}{2n\pi} \sin \left(\frac{2\pi n x}{a} \right) \right]_0^a = 1 \text{ The second term takes the value zero for both the limits}$$

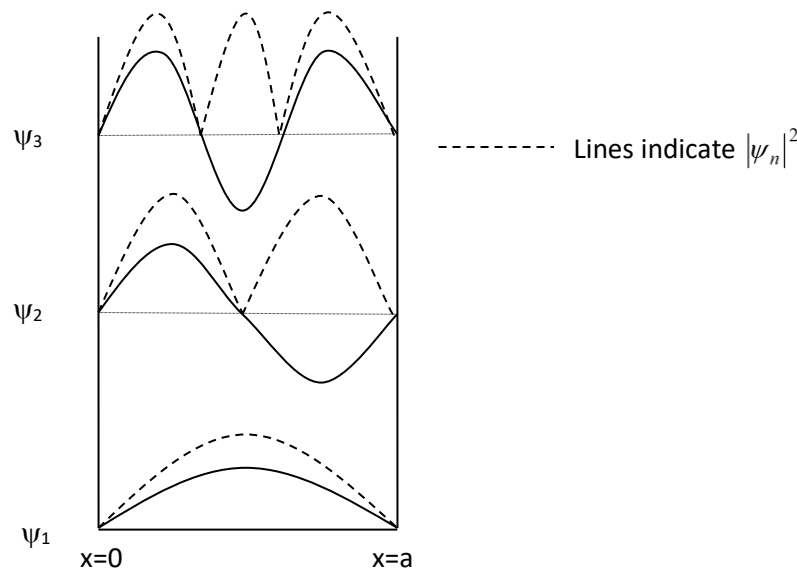
$$\therefore \frac{A^2}{2} [a-0] = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

Thus the **Eigen function** is given by

$$\psi_n(x) = \left[\sqrt{\frac{2}{a}} \right] \sin \frac{n\pi x}{a}$$

The wave functions and the probability densities for the first three values of 'n' are as shown in fig

Thus for ground state (n=1) The probability of finding the particle at the walls is zero and at the centre (a/2) is maximum. The first excited state has three nodes and the second excited state has four nodes.



Stationary states and Eigen values:

The quantum states for which probability density is independent of time are called **stationary states**. Energy corresponding to a particular quantum state is called **Eigen values**.

Let us consider the time dependent Schrodinger wave equation and its general solution.

$$\frac{i\hbar}{2\pi} \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V\psi(x,t)$$

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} + V\psi(x,t)$$

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

The general solution for the above wave equation is,

$$\psi(x, t) = \psi(x)e^{-\frac{iEt}{\hbar}} \dots \dots (1)$$

Now the probability density of above wavefunction is given by,

$$\begin{aligned} P(x, t) &= |\psi(x, t)|^2 \\ P(x, t) &= \psi(x, t) \psi^*(x, t) \\ P(x, t) &= \psi(x)e^{-\frac{iEt}{\hbar}} \psi^*(x)e^{\frac{iEt}{\hbar}} \\ P(x) &= \psi(x) \psi^*(x) \end{aligned} \quad \begin{aligned} \psi(x, t) &= \psi(x)e^{-\frac{iEt}{\hbar}} \\ \psi^*(x, t) &= \psi^*(x)e^{\frac{iEt}{\hbar}} \end{aligned}$$

Thus, probability density of time dependent wavefunction is time independent and corresponding energy states are called stationary states.

General solution of the time dependent Schrödinger equation in terms of linear combination of stationary states:

We have, the solution of time dependent Schrodinger wave equation,

$$\psi(x, t) = \psi(x)e^{-\frac{iEt}{\hbar}}$$

Now the solution for n^{th} stationary states will be,

$$\psi_n(x, t) = \psi_n(x)e^{-\frac{iE_n t}{\hbar}}$$

Where, E_n is Eigen value corresponding to n^{th} stationary state.

Then the different possible solutions of time dependent wavefunction are

$$\psi_1(x, t), \psi_2(x, t), \psi_3(x, t), \dots \dots \dots \psi_n(x, t).$$

Then the linear combination of the solution of stationary states will be given by

$$\psi(x, t) = C_1 \psi_1(x, t) + C_2 \psi_2(x, t) + C_3 \psi_3(x, t), \dots \dots \dots + C_n \psi_n(x, t)$$

$$\psi(x, t) = \sum_n C_n \psi_n(x, t)$$

Where C_n is an expansion coefficient.

Hence, the linear combination of the solution of stationary states of time dependent Schrödinger equation is also a solution.

Gaussian wave packet:

A wave packet for which the product of uncertainties in position and momentum involved in their simultaneous measurement is minimum is called Gaussian wave packet.

$$\text{ie., } \Delta x \cdot \Delta p = \frac{h}{4\pi}$$

The wavefunction for Gaussian wave packet is given by,

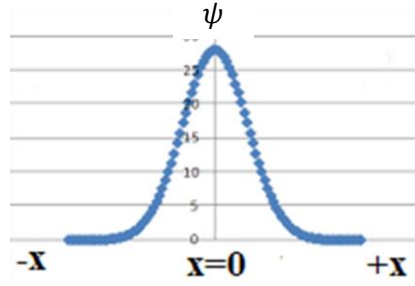
$$\psi = N e^{-\alpha^2 x^2} \dots \dots (1)$$

Where, N is normalized constant and is given by, $N = \left(\frac{2\alpha^2}{\pi}\right)^{1/4}$

Or
$$\psi = \left(\frac{2\alpha^2}{\pi}\right)^{1/4} e^{-\alpha^2 x^2} \dots \dots \dots (2)$$

$$\text{Where } \alpha = \frac{1}{2\Delta x}$$

Or
$$\psi = \left(\frac{1}{2\pi(\Delta x)^2}\right)^{1/4} e^{-\frac{x^2}{4(\Delta x)^2}} \dots \dots \dots (3)$$



Properties of Gaussian wave packet:

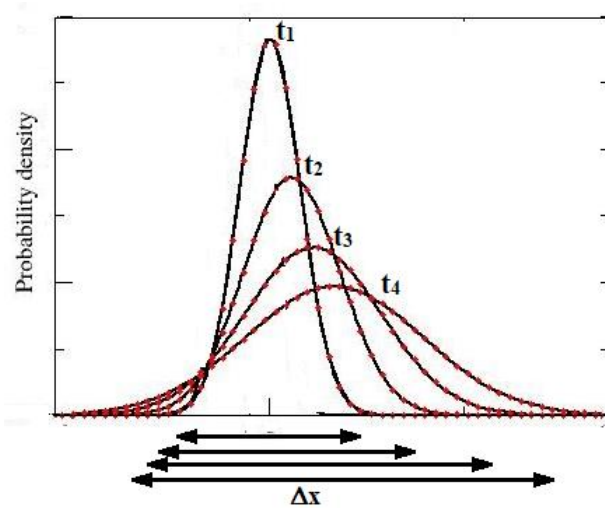
- 1) Wavefunction takes maximum value at $x = 0$
- 2) Greater the value of α the less is the uncertainty in position.
- 3) As $\alpha \rightarrow 0$, $\Delta x \rightarrow \infty$, the Gaussian wave packet becomes flat

Application to spread of Gaussian wave packet for a free particle in one dimension.

As the Gaussian wave packet moves ahead, its width Δx increases and amplitude of the wave packet decreases and consequently localization of the particle decreases with time. This phenomenon is known as the spread of Gaussian wave packet.

The wavefunction of Gaussian wave packet is given by,

$$\psi(x, t) = \left(\frac{1}{2\pi(\Delta x)^2}\right)^{1/4} e^{-\frac{x^2}{4(\Delta x)^2}}$$



Now the equation for final width of the wave packet after time $t = t$ will be given by, (derivation is not included here as it is beyond the scope of the syllabus)

$$(\Delta x)_{(t=t)}^2 = (\Delta x)_{(t=0)}^2 + \frac{\hbar^2 t^2}{4m^2 (\Delta x)_{(t=0)}^2}$$

$$(\Delta x)_{(t=t)}^2 = (\Delta x)_{(t=0)}^2 \left[1 + \frac{\hbar^2 t^2}{4m^2 (\Delta x)_{(t=0)}^4} \right]$$

$$(\Delta x)_{(t=t)}^2 = (\Delta x)_{(t=0)}^2 \left[1 + \frac{t^2}{T^2} \right]$$

$$(\Delta x)_{(t=t)} = (\Delta x)_{(t=0)} \sqrt{\left[1 + \frac{t^2}{T^2} \right]}$$

$(\Delta x)_{(t=t)} \rightarrow$ final width of wave packet

$(\Delta x)_{(t=0)} \rightarrow$ initial width of wave packet

$$T = \frac{2m(\Delta x)^2}{\hbar}$$

The above equation gives the final width of the Gaussian wave packet wave packet after time $t = t$ seconds.

- The spreading of Gaussian wave packet is significant in the dispersive medium.
- If $t \ll T$ – Spreading of the wave packet is not significant.
- If $t \gg T$ – Spreading of the wave packet is significant.

If the initial width of the wave packet $(\Delta x)_{(t=0)}$ is smaller