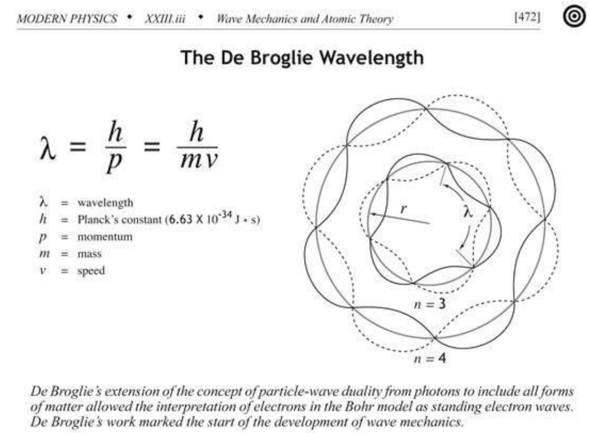
QUANTUM MECHANICS

UNIT II
Quantum Mechanics
Lecture-5

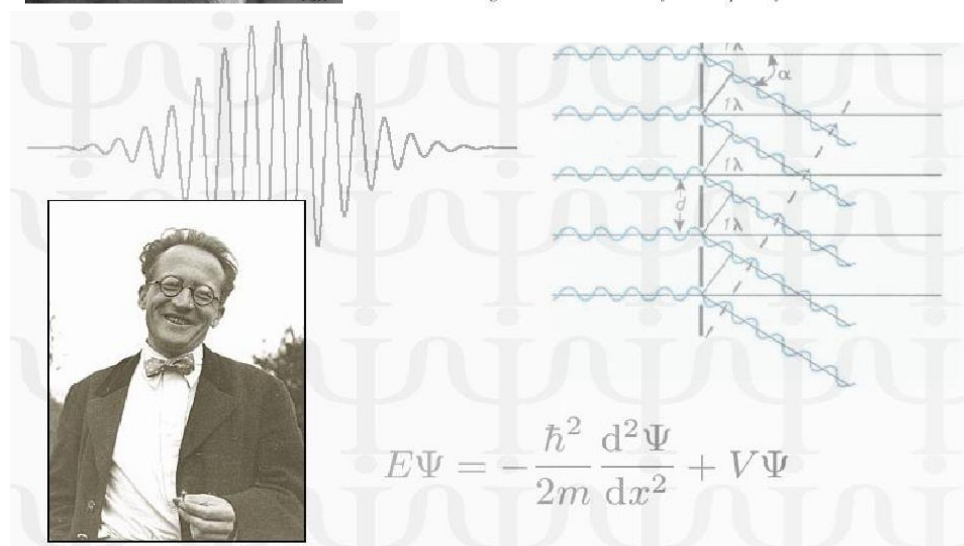

MODERN PHYSICS • XXIII.iii • Wave Mechanics and Atomic Theory [472]

The De Broglie Wavelength

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

λ = wavelength
h = Planck's constant (6.63×10^{-34} J • s)
p = momentum
m = mass
v = speed

De Broglie's extension of the concept of particle-wave duality from photons to include all forms of matter allowed the interpretation of electrons in the Bohr model as standing electron waves. De Broglie's work marked the start of the development of wave mechanics.



WAVE FUNCTION (ψ)

- ✓ **In case of electromagnetic waves, the electric and magnetic fields vary periodically, whereas in sound waves, pressure varies periodically.**
- ✓ **Similarly, in water waves the height of water surface varies periodically.**
- ✓ **Now, one can ask what varies in matter waves.**
- ✓ **In matter waves, a quantity called wave function, denoted by ψ, varies.**
- ✓ **Schrödinger described the amplitude of matter waves in terms of wave function ψ. Wave function ψ (x, y, z) is a complex quantity, which gives the idea of the probability of finding the particle (to which it is concerned) in a particular region of space.**

PHYSICAL SIGNIFICANCE OF WAVE FUNCTION (ψ)

- In the beginning, it was considered that the wave function Ψ is merely an auxiliary mathematical quantity employed to facilitate computations relative to the experimental results.
- Very soon, it was realised that it is not reasonable, because the introduction of an isolated mathematical function without enquiring into its physical significance is not justified.
- The simple effort was made by Schrödinger himself for the physical interpretation of ψ in terms of charge density.
- The quantity ψ^2 is the measure of charge density. Since ψ is a complex quantity, therefore, it is usually written as $\psi^* \psi$ instead of ψ^2, where ψ^* is the complex conjugate of ψ.

PHYSICAL SIGNIFICANCE OF WAVE FUNCTION (ψ)

- It has been observed that in some cases, ψ is appreciably different from zero in some finite region known as wave packet.

- Now, the natural question arises "Where is the particle in relation to the wave packet?" .

- In view of the answer of this question it has been suggested that $\psi \psi^* = |\psi|^2$ gives the probability of finding the particle in the state ψ i.e., ψ^2 is a measure of probability density.

CONDITION FOR NORMALIZATION OF WAVE FUNCTION

- If ψ is not a normalized wave function and it is the solution of a wave equation, then (N ψ) will also be the solution of the same wave equation, where N is a constant quantity.
- Now, the next problem arises to select the proper value of N, such that the new wave function is a normalized function.
- For the normalization of this new wave function, it must satisfy the following requirement:

$$\int (N\psi)^* (N\psi) dx\, dy\, dz = 1$$

where $$d\tau = dx\, dy\, dz$$

or $$|N|^2 \int \psi\psi^* dx\, dy\, dz = 1$$

$$|N|^2 = \frac{1}{\int \psi\psi^* dx\, dy\, dz}$$

Where |N| is termed as the normalization constant and N ψ is known as the normalized wave function.

SCHRÖDINGER WAVE EQUATION

- Schrödinger worked extensively on wave mechanics, used to deal with the matter waves.
- He suggested two important equations for the motion of matter waves.

➢ **TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION**

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TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION

Let ψ (x, y, z) be the wave displacement for the matter wave at any time t. ψ is the wave function, which is a finite, single-valued, and periodic function. The classical differential equation of a wave motion is

$$\nabla^2\psi = \frac{1}{\upsilon^2}\frac{\partial^2\psi}{\partial t^2}$$

or
$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{1}{\upsilon^2}\frac{\partial^2\psi}{\partial t^2}$$

where υ is the wave velocity.

The solution of Eq. (23.46) is given by

$$\psi(r, t) = \psi_0 e^{-2\pi i\left(\nu t - \frac{x}{\lambda}\right)}$$

$$= \psi_0 e^{-i\left(2\pi\nu t + \frac{2\pi}{\lambda}x\right)}$$

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

TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION Contd..

- Where ψ_0 is the amplitude of the wave at the considered point and is the function of position only [i.e., (x, y, z)].

- Differentiating above equation twice with respect to t, substituting this value in parent equation and using the de-Broglie hypothesis we get we get

$$\nabla^2\psi + \frac{4\pi^2 m^2 \upsilon^2}{h^2}\psi = 0$$

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

TIME-INDEPENDENT SCHRÖDINGER WAVE EQUATION Contd..

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

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

Substituting this value of m ^{2} v ^{2} in above Eq. , we get

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

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

This Equation is the Schrödinger time-independent wave equation.

TIME-DEPENDENT SCHRÖDINGER WAVE EQUATION

Time-dependent Schrödinger equation may be obtained by eliminating E from time independent wave equation

From the definition of ψ we know that

$$\psi(r, t) = \psi_0 e^{-2\pi i(\nu t - x/\lambda)}$$

Differentiating the above equation with respect to t, we get

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

TIME-DEPENDENT SCHRÖDINGER WAVE EQUATION

Substituting the value of E ψ in time independent wave equation we get

$$\nabla^2\psi + \frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right] = 0$$

$$\nabla^2\psi = -\frac{2m}{\hbar^2}\left[i\hbar\frac{\partial\psi}{\partial t} - V\psi\right]$$

or

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

or

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

Equation we get is known as time independent wave equation. Sometime it is also expressed as

$$H\psi = E\,\psi$$

EIGENVALUES AND EIGENFUNCTIONS

- In an atom eigenvalues correspond to the energy values associated with different orbits in the atom.

- Thus, we can conclude that Bohr's postulate, according to which the various energy levels exist in an atom, is the direct consequence of the wave mechanical concept.

- The solution of the wave equation for these definite values of E gives the corresponding values of the wave function ψ, known as eigenfunctions.

EIGENVALUES AND EIGENFUNCTIONS

- Only those eigenfunctions have physical significance, which satisfy certain conditions listed as follows:

(i) They must be single-valued functions.

(ii) They should be finite.

(iii) They should be continuous throughout the entire space under consideration.

(iv) In other words, we can say that they should be continuous for all possible values of coordinates (x, y, z), including infinity.

Example-1 The wave function of a free particle in normalized state is represented by

$$\psi(x) = Ne^{-(x^2/2a^2) + jkx}$$

Calculate the normalization factor N and the maximum probability of finding the particle.

Solution

From the normalization condition, we know that

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$

Putting the value of ψ and ψ^* in the above equation, we get

$$\int_{-\infty}^{\infty} Ne^{-(x^2/2a^2)-jkx} Ne^{-(x^2/2a^2)+jkx} dx = 1$$

or $$N^2 \int_{-\infty}^{\infty} e^{-x^2/a^2} dx = 1$$

Since $$\int_{-\infty}^{\infty} e^{-x^2/a^2} dx = a\sqrt{\pi}$$

$\Rightarrow$ $$N^2 a\sqrt{\pi} = 1$$

or $$N = \frac{1}{a^{1/2}\pi^{1/4}}$$

The maximum probability $P(x)$ can be given as

$$P(x) = |\,\psi^*(x)\,\psi(x)\,|$$

$$= N^2 e^{-x^2/a^2}$$

$$= \frac{1}{a\sqrt{\pi}} e^{-x^2/a^2}$$

Example-2

Normalize the eigenfunction $\phi(x) = e^{icx}$ within the region $-a \leq x \leq a$.

Solution

Given that $\phi(x) = e^{icx}$

In order to normalize the wave function $\phi(x)$, let us multiply it by k. Thus,

$$\phi(x) = ke^{icx}$$

To find out the value of c, we apply normalization condition as

$$\int_{-a}^{a} \phi(x)\phi^*(x)dx = 1$$

$$\phi(x) = ke^{icx} \text{ and } \phi^*(x) = ke^{-icx}$$

Now, using these values in the above equation, we get

$$k^2 \int_{-a}^{a} e^{icx} e^{-icx} dx = 1$$

$$k^2 \int_{-a}^{a} dx = 1$$

$$k^2 [x]_{-a}^{a} = 1$$

or $$k^2 \cdot 2a = 1$$

or $$k = \frac{1}{\sqrt{2a}}$$

Hence, the normalized wave function can be given as

$$\phi(x) = \frac{1}{\sqrt{2a}} \cdot e^{icx}$$

Example-3 Write the Hamiltonian operator of a free particle moving in one direction under the influence of zero potential energy.

Solution

According to classical mechanics, the Hamiltonian is given by the sum of kinetic energy and potential energy, i.e.,

$$H = \frac{1}{2}\, m\upsilon^2 + \text{PE}$$

For zero potential energy,

$$H = \frac{1}{2}\, m\upsilon^2 = \frac{1}{2m}\, p_x^{\,2}$$

where p_x is the linear momentum along the X-axis.

But for linear operator, the operator is $\frac{\hbar}{i}\frac{\partial}{\partial x}$. Therefore,

$$\widehat{H} = \frac{1}{2m}\left[\frac{\hbar}{i}\,\frac{\partial}{\partial x}\right]^2$$

$$= \frac{1}{2m}\left[\frac{\hbar}{i}\,\frac{\partial}{\partial x}\right]\left[\frac{\hbar}{i}\,\frac{\partial}{\partial x}\right]$$

$$= -\,\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2}$$

Assignment Based on this Lecture

- Describe the wave function Ψ.
- Give the physical interpretation of wave function Ψ .
- Obtain the expression of Time independent Schrodinger wave equation.
- Obtain the expression of Time dependent Schrodinger wave equation.