Module -2

Quantum Mechanics

Wave particle duality:

- The Photoelectric Effect and Compton Effect conclusively established the particle behavior of light.
- The phenomena of interference, diffraction and polarization give exclusive evidence for the wave behavior of light.
- Therefore light behaves as an advancing wave in some phenomena and it behaves as a flux of particles in some other phenomena.

de-Broglie matter waves:

De-Broglie extended the wave particle dualism of light to the material particles. This is known as de-Broglie hypothesis. According to this hypothesis, material particles in motion possess a wave character. The waves associated with material particles are called matter waves or de-Broglie waves.

According to Planck's theory of radiation,

$$E = h\upsilon \qquad \text{---------} \qquad (1)$$

Where, υ is the frequency associated with the radiation.

According to Einstein's mass-energy relation,

$$E = mc^2 \qquad \text{---------} \qquad (2)$$

where m is the mass of the photon and c is the velocity of light

Combining (1) and (2),

$$\text{i.e., } h\upsilon = mc^2 \quad \Rightarrow \frac{hc}{\lambda} = mc^2 \qquad (\text{since} = \frac{c}{\lambda})$$

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

Therefore momentum associated with the particle is given by p = mc,

$$\text{or, } \lambda = \frac{h}{p} \qquad \text{where } \lambda \text{ is called de-Broglie wavelength.}$$

de-Broglie wavelength associated with the accelerated electron:

A beam of high energy electrons can be obtained by accelerating them in an electric field. Consider an electron starting from rest when accelerated with a potential difference V, the kinetic energy (E) acquired by the electron is given by,

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

$$\text{Thus,} \qquad \frac{1}{2}mv^2 = eV$$

$$\text{or} \qquad \frac{m^2v^2}{2m} = eV$$

$$\text{i.e.,} \qquad \frac{p^2}{2m} = eV = E$$

where ‘v’ is the velocity of the electron, ‘m’ its mass and ‘p’ the momentum.

Now the momentum may be expressed as,

$$p = \sqrt{2mE} = \sqrt{2meV}$$

Hence the de-Broglie wavelength $\boxed{\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}}}$

Case II: If gas molecule moves at some temperature T after receiving thermal energy then the motion is according to degree of freedom n.

n=3 for mono-atomic gas

n=5 for dia-atomic gas

n=6 for tri-atomic gas

The thermal energy or kinetic energy $E = \frac{1}{2}nkT$

For mono-atomic gas n=3

$$E = \frac{3}{2}nkT$$

We know de-broglie wavelength

$$\lambda = \frac{h}{\sqrt{2m_0K}}$$

∴

$$\lambda = \frac{h}{\sqrt{2m_0\frac{3}{2}kT}}$$

$$\lambda = \frac{h}{\sqrt{3m_0kT}}$$

Detection Of Matter Wave

According to de-broglie, the matter waves are generated by every microscopic or macroscopic bodies but the magnitude of de-broglie wavelength of matter wave in case of macroscopic bodies is extremely small such that it can not be detected by any instrument nor is there any hope of their being detected. This clealy explain why the wave nature of matter wave is not observed in our daily observations. Now some example for supporting above statement:

I. De-broglie wavelength of earth:
Mass of earth = 6.0×10^{24} kg, orbital velocity v= 3×10^{4} m/s and h=6.63×10^{-34}
Then De-broglie wavelength=3.68×10^{-63}m

II. De-broglie wavelength of stone:
Mass of stone = 100 g, speed v= 1 m/s and h=6.63×10^{-34}
Then De-broglie wavelength=6.625×10^{-33}m

III. De-broglie wavelength of electron
Mass of electron = 9.1×10^{-31} kg, orbital velocity v= 10^5 m/s and h=6.63×10^{-34}
Then De-broglie wavelength=6.625×10^{-9}m

The wavelength of the wave attached with moving earth and moving stone is very small. It cannot be detected by any instrument. The wavelength of the wave attached with moving electron is of the order of wavelength of X-ray which can be detected.

Thus practically electrons have wave character while other is not or these bodies are said to have no wavelength. Hence, any material body in motion can have wavelength but it is measureable or significant only for microscopic bodies such as electron, proton, atom, and molecule. Thus, **dual nature of matter is significant for microscopic bodies only**.

Difference between Matter Waves and Electromagnetic Waves

Matter Waves

1. The matter waves are generated by moving charged particle as well as by moving neutral particle
2. Matter waves are neither emitted by the particles nor radiated into space. These are simply associated with the particles.
3. The velocity of matter waves depand upon the velocity of the material particles.
4. The wavelength of the matter waves or de-broglie waves is given by $\lambda = \frac{h}{mv}$
   Where m= mass of particle
   v= velocity of particle and h = plank's constant
5. The velocity of matter waves is generally greater than the velocity of light $v_p = \frac{c^2}{v}$
   Where c= velocity of light
   v= velocity of particle
   but v<<c $\therefore$ $v_p = c^2$

Electromagnetic waves

1. Electromagnetic waves are produced only by accelerated charged particles.
2. Electromagnetic waves can be radiated into space.
3. The velocity of EM waves is equal to the velocity of light.
4. The wavelength of EM waves is given by $\lambda = \frac{c}{\nu}$
   Where c=Velocity of light (EM wave)
   υ=frequency
5. The velocity of EM waves is equal to the velocity of light.

Properties of Matter Waves: $\lambda = \frac{h}{p}$

1. The de-broglie's wave length of wave associated with moving light particle is greater than the wave length associated with heavier particle.
2. The de-broglie's wave length of wave associated with slow moving particle is greater than the wave length associated with fast moving particle.
3. For particle at rest (v=0) $\lambda=\infty$ i.e wave become indeterminate and if $v=\infty$ then $\lambda=0$
   This indicates that the matter waves are generated only when the material particles are in motion.

Wave function:

The quantity whose variations make up de-Broglie waves is called the wavefunction $\psi(x,y,z,t)$. According to Max Born, the wave function $\psi(x,y,z,t)$ itself has no physical significance but the square of its magnitude $|\psi|^2$ gives the probability of finding the particle there at that time.

Physical significance:

- Generally the wave function Ψ is a complex function, but the probability must be real.
- The square of the absolute value of the wavefunction ($|\psi|^2$) or $\psi^*\psi$ is related to the moving particle and is known as the **Probability density**.
- The quantity $|\psi|^2dV$ or $\psi^*\psi dxdydz$ is proportional to the probability of finding the particle in the volume element dxdydz about the point (x,y,z).
- Since the particle exist somewhere at all times,

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

The wavefunction ψ satisfying the above condition is called normalized wavefunction.

Properties of Wavefunction:

- The wavefunction ψ must be continuous, finite and single valued everywhere.
- $\partial\psi/\partial x$, $\partial\psi/\partial y$ and $\partial\psi/\partial z$ must also be continuous, finite and single valued everywhere.
- If $\int_{-\infty}^{\infty} \psi^*\psi dxdydz = 0$, the particle does not exist.
- If $\int_{-\infty}^{\infty} \psi^*\psi dxdydz = \infty$, the particle is everywhere simultaneously.

Schrödinger wave equation:

It is a differential type equation of motion for wavy particle. It can be divided into following two parts:

(a) Schrödinger time independent equation:

Let x,y,z be the co-ordinates of the particle and ψ, the wave displacement for de-Broglie waves at any time t. The classical differential equation of a wave motion is given by

$$\left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2}\right) = \frac{1}{v^2}\frac{d^2\psi}{dt^2}$$

$$\nabla^2\psi = \frac{1}{v^2}\frac{d^2\psi}{dt^2} \qquad (1)$$

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

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

Differentiating above eq. twice w.r.t 't'

$$\frac{d^2\psi}{dt^2} = i^2\omega^2 Ae^{i(kx-\omega t)}$$

$$\frac{d^2\psi}{dt^2} = -\omega 2Aei(kx - \omega t)$$

$$\frac{d^2\psi}{dt^2} = -\omega 2\psi \qquad (2)$$

Substituting the value of $\frac{d^2\psi}{dt^2}$ from equation (2),

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

$$\nabla^2\psi = \frac{-(2\pi\nu)^2}{(\nu\lambda)^2}\psi =$$

$$\nabla^2\psi = \frac{-(4\pi)^2}{(\lambda)^2}\psi \qquad (3)$$

Thus Total energy of the particle

E = Kinetic energy + Potential energy

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

$$\text{Or, } E - V = \frac{p^2}{2m}$$

$$E - V = \frac{(\frac{h}{\lambda})^2}{2m}$$

$$\therefore \frac{1}{\lambda^2} = \frac{2m(E-V)}{h^2}$$

Substituting this in equation (3), we have

$$\nabla^2\psi = [\frac{-4\pi^2 2m(E-V)}{h^2}]\psi$$

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

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

This is known as Schrödinger's time independent wave equation.

(b) Schrödinger's time dependent wave equation:

The Schrödinger's time dependent wave equation may be obtained from Schrödinger's time independent wave equation by eliminating E.

Again, $$\psi = Ae^{i(kx-\omega t)}$$

Differentiating above eq. w.r.t 't'

$$\therefore \frac{d\psi}{dt} = -i\omega Ae^{i(kx-\omega t)}$$

or $$\frac{d\psi}{dt} = -i\omega\psi$$

$$\frac{d\psi}{dt} = -i(2\pi\nu)\psi$$

$$\frac{d\psi}{dt} = -i2\pi\frac{E}{h}\psi$$

$$\frac{d\psi}{dt} = -i\frac{E}{\hbar}\psi$$

or $$E\psi = i\hbar\frac{d\psi}{dt}$$

Substituting the value of $E\psi$ in Schrödinger's time independent wave equation, we get

$$\nabla^2\psi + [\frac{8\pi^2 m}{h^2}(i\hbar\frac{d\psi}{dt} - V)]\psi = 0$$

or $$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{d\psi}{dt}}$$

This equation is known as Schrödinger's time dependent wave equation. Above equation can also be written as

$$\boxed{H\psi = E\psi}$$

Where $H = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]$ is known as Hamiltonian operator

and$E = i\hbar\frac{d}{dt}$ is known as energy operator.

Particle in one dimensional potential box:

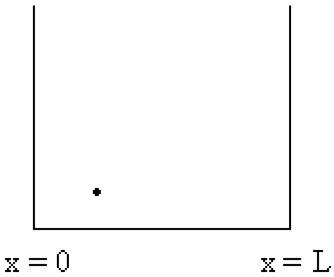


Fig. 2.6

Consider the motion of a particle confined to move inside a potential well of infinite height at x = 0 and x =L. The width of the well is L. Assuming there is no interaction between the walls of the well and particle, the potential energy V of the particle is taken to be zero. Schrödinger time independent wave equation in this case is

$$\text{i.e },\frac{d^2\psi}{dx^2} + [\frac{8\pi^2 mE}{h^2}]\psi = 0$$

Let $$K^2 = \frac{8\pi^2 mE}{h^2} \qquad \text{----------------(1)}$$

Then $$\frac{d^2\psi}{dx^2} + K^2\psi = 0$$

The solution of this equation is

$$\psi = A\sin Kx + B\cos Kx \qquad \text{------(2)}$$

Since the particle is inside the well,

$$\psi = 0 \text{ at } x < 0 \text{ and also at } x > L.$$

This is possible only if $\psi = 0$ at x = 0 and x = L as demanded by the continuity condition.

These are the boundary conditions of this problem.

At $x = 0$, $\psi = 0$

Therefore equation (2) becomes,

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

or $B = 0$

Therefore $\psi = A\sin Kx$ ------(3)

At $x = L$, $\psi = 0$

Now equation (2) becomes,

$$0 = A\sin KL \qquad \text{(Since B=0)}$$

But $A \neq 0$ (because if A=0 then eq(2) becomes zero which is not possible)

Hence $\sin KL = 0$

Therefore $KL = n\pi$

or $K = \frac{n\pi}{L}$ -----(4)

Therefore $\psi = A\sin(\frac{n\pi x}{L})$ ------ (5)

By applying normalized wave condition, for one dimensional case,

$$\int_0^L \psi\psi^* \, dx = 1.$$

Substituting the value of ψ from equation (5),

$$\int_0^L A\sin(\frac{n\pi x}{L})\, A\sin(\frac{n\pi x}{L})\, dx = 1$$

$$\text{i.e.,} \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

or, $\frac{A^2}{2}\int_0^L \{1 - \cos(\frac{2n\pi x}{L})\}dx = 1$ $\{\text{since } \sin^2\theta = \frac{(1-\cos 2\theta)}{2}\}$

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

or $\frac{A^2}{2}[x]_0^L = 1$

or, $\frac{A^2 L}{2} = 1$

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

Substituting this value in equation (5),we have

$$\boxed{\psi_n = \sqrt{\frac{2}{L}}\sin(\frac{n\pi x}{L})} \qquad \text{-------------(6)}$$

Equation (6) represents the Eigen functions of the particle inside the potential well.

Substituting the value of K from equation (4) in equation (1),

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

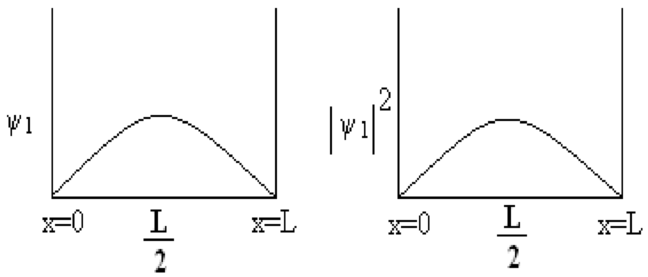
i.e., $$\boxed{E_n = \frac{n^2h^2}{8mL^2}}$$

The energy values E_n are called eigenvalues.

Case 1: When n = 1 (Ground state):

The Eigen function is $\psi_1 = \sqrt{\frac{2}{L}}\sin(\frac{\pi x}{L})$.

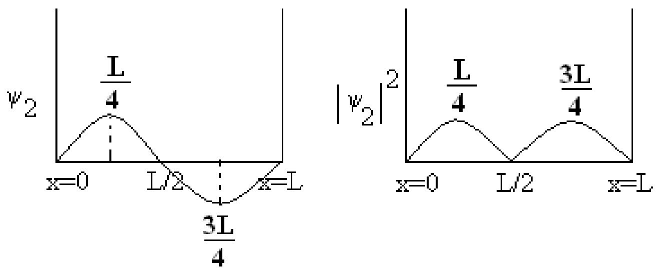
Plot of ψ_1 versus x and $|\psi_1|^2$ versus x are as shown in the figure



Case 2: When n = 2 (First excited state):

The Eigen function is $\psi_2 = \sqrt{\frac{2}{L}}\sin(\frac{2\pi x}{L})$

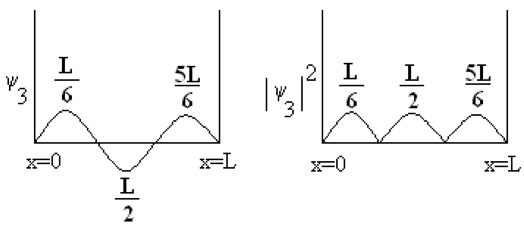
Plot of ψ_2 versus x and $|\psi_2|^2$ versus x are as shown in the figure



Case 3: When n = 3 (Second excited state):

The Eigen function is $\psi_3 = \sqrt{\frac{2}{L}}\sin(\frac{3\pi x}{L})$

Plot of ψ_3 versus x and $|\psi_3|^2$ versus x are as shown in the figure



<u>**Eigen values and Eigen functions**</u>**:**

By solving the Schrödinger equation, we obtain the possible set of ψ functions. In case of bound particles, the acceptable solutions for the differential equations are possible only for certain specified values of energy. These descrete values of energy $E_1, E_2, \ldots\ldots\ldots, E_n$ are called **energy eigen values** of the particle. The solutions $\psi_1, \psi_2, \ldots\ldots\ldots\ldots, \psi_n$ corresponding to the eigen values are called **eigenfunctions**.