CHAPTER 7

Quantum Mechanics

Quantum mechanics is the systematic theory of behaviour of matter and light. It is different in many aspects from Newtonian Mechanics .Newton first thought that light was made up of particles. In 1803,Young discovered that light behaves like a wave.

The particle nature of electromagnetic radiation was described by Planck in 1900.The wave like character of matter was considered by De Broglie in 1924.This character of electrons was established by Davison and Germer(1927) and G.P. Thompson in 1928.

De Broglie Hypothesis*

de Broglie proposed that just like radiation, particles have dual nature – wave nature and particle nature.

De Broglie wavelength

According to Quantum theory $E = h\nu$
According to Einstein $E = mc^2$.

$$h \times \frac{c}{\lambda} = mc^2$$

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

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

or

$$\lambda = \frac{h}{P}, \quad mc = P$$

If we consider a particle of mass m moving with velocity v, then

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

where λ corresponds to wave nature and m and v corresponds to particle nature.

Note :- $$P = \frac{h}{\lambda}$$

$$P = \frac{h \times 2\pi}{2\pi \times \lambda}$$

$$P = \hbar k$$

Electron Wave*

Consider an electron of mass m and charge e is accelerated through a potential of V volt with velocity v , then

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

$$2eV = mv^2$$

$$2meV = m^2v^2$$

$$2meV = P^2$$

$$P = \sqrt{2meV}$$

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

Substitute the value of m, e, h we get,

$$\lambda = \sqrt{\frac{150}{V}}\,\text{Å} = \frac{12.24}{\sqrt{V}}\,\text{Å}$$

Properties of **Matter Waves**

- Matter wave can be considered as a probability amplitude wave.
- Matter waves exhibit diffraction phenomenon (Davisson-Germer experiment).
- Matter waves are neither electromagnetic nor acoustic waves.
- It does not require any material medium for propagation.
- Just like X-rays, matter waves form diffraction pattern by passing through a thin metallic film. (G.P. Thomson's experiment)
- Superposition of matter waves gives a wave packet that obeys Schrödinger's equation.
- On passing through a very thin section of a material, matter waves form images (electron microscope).

Wave Function (ψ)

In a wave there is something that varies periodically. In water waves the quantity that varies periodically is the height of the water surface and in light electric and magnetic field vary periodically. The quantity that varies in matter waves is called wave function (ψ). It is a mathematical function, which describes the state of a particle on a system. It is a function of both position coordinates and time coordinates.

$$\psi = \psi(x, y, z, t)$$

1. Calculate the de Broglie wavelength of an electron with a speed 107 m/s.

$$\lambda = \frac{h}{mv} \qquad v = 107\ m/s$$

$$= \frac{6.62\times10^{-34}}{9.1\times10^{-31}\times107} \qquad \lambda = ?$$

$$= \mathbf{6.8\times10^{-6}\ m}$$

Physical Significance of ψ

Wave function ψ itself has no physical significance. The only quantity having physical significance is square of its magnitude

$|\psi^2| = \psi\psi^*$ where ψ^* is the complex conjugate of ψ. Here $|\psi^2|$ is called probability density. The probability of finding a particle in a small volume ($d\tau$=dxdydz) is given by,

$$\text{Probability} = |\psi^2|\,d\tau$$

Normalization Condition

The probability of finding a particle in a small volume $d\tau$ = dx dy dz is given by $|\psi^2|$dx dy dz .Since the particle is certainly to be present somewhere in space , the total probability of finding the particle in entire space is unity.

$$\text{i.e.,} \quad \int |\psi^2|\,dxdydz = 1$$

Any wave function satisfying the above equation is said to be normalized.

Problems

1. Find the de Broglie wavelength of 10 k eV electron?

$V = 10\times10^3 V.$

$$\lambda = \frac{12.24}{\sqrt{V}}\,\text{Å} = \frac{12.24}{\sqrt{10\times10^3}}\,\text{Å} = \mathbf{0.1224Å}$$

2. Calculate the de Broglie wavelength of α particle accelerated through a p.d of 25000V.

$V = 25000$

$\lambda_\alpha = ?$

$m_\alpha = 4\times1.67\times10^{-27}\text{kg} \qquad \because m_\alpha = 4m_p$

7.4

$$\lambda = \frac{h}{\sqrt{2emV}} = \frac{6.625\times10^{-34}}{\sqrt{2\times2\times1.6\times10^{-9}\times4\times1.67\times10^{-27}\times25000}}$$

$$= \mathbf{6.41\times10^{-14}\ m}$$

3. Calculate the De Broglie wavelength of electron having K.E. a) 1eV b) 10eV

(a) K.E. = 1eV = 1.6×10^{-19}J

$$\lambda = \frac{h}{\sqrt{2mE}} = \frac{6.625\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}}} = \mathbf{1.22\times10^{-9}\ m}$$

(b) K.E. = 10 eV = $1.6\times10^{-19}\times10$

$= 1.6\times10^{-18}$J

$$\lambda = \frac{6.625\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-18}}} = \mathbf{3.87\times10^{-10}\ m}$$

4. What is the velocity and K.E. of an electron having de Broglie wavelength 1Å.

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

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

$$v = \frac{h}{m\lambda} = \frac{6.625\times10^{-34}}{9.1\times10^{-31}\times10^{-10}}$$

$$= \mathbf{7.28\times10^{6}\ m/s}$$

$$K.E. = \frac{1}{2}mv^2 = \frac{1}{2}\times9.1\times10^{-31}\times(7.28\times10^{6})^2$$

$$= \mathbf{2.4\times10^{-17}J}$$

5. What velocity must an electron travel with for its momentum to be equal to that of a photon of wavelength 5000Å.

$\lambda_p = 5000$ Å

$= 5000\times10^{-10}$ m

$V_e = ?$

$$\lambda_P = \frac{h}{P}$$

$$P = \frac{h}{\lambda} = \frac{6.625 \times 10^{-34}}{5000 \times 10^{-10}}$$

$$P_P = P_e = mv_e$$

$$V_e = \frac{P_P}{m} = \frac{6.625 \times 10^{-34}}{5000 \times 10^{-10} \times 9.1 \times 10^{-31}} = \mathbf{1.45 \times 10^3\ m/s}$$

6. The equivalent wavelength of moving electron is 0.24 A°. What voltage is applied to stop it ?

$$\lambda = 0.24 \times 10^{-10} m$$
$$V = ?$$

$$\lambda = \frac{12.24}{\sqrt{V}} \text{Å}$$

$$\sqrt{V} = \frac{12.24}{\lambda} \text{Å}$$

$$\sqrt{V} = \frac{12.24 \text{ Å}}{0.24 \text{ Å}}$$

$$V = \frac{(12.24)^2}{(0.24)^2} = \mathbf{2601V}$$

> Conditions Necessary for an Ideal Wavefunction

* The wave function should be Finite
* The wave function should vanish at Infinity.
* Wave function must be single-valued.
* Wave function and its derivatives Should be Continuous.
* Wave function must be square integrable.

> explain the conditions for normalization of a wavefunction.

Normalization condition :-

The probability of finding a particle in a small volume is given by,

$|\psi^2| \, dx\,dy\,dz$.

A wavefunction that satisfies the condition,

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

is called Normalized wavefunction and is called Normalization condition. This condition means that the probability to find the particle in entire space is unity.

Schrodinger Equation

Schrodinger equation is the most fundamental equation in quantum mechanics. Schrodinger equation is a second order differential equation in position and time. On solving schrodinger equation we get a mathematical function or wave function which completely represent the state of a quantum system. Different dynamic variables can be extracted from wave function.

Schrodinger equation is of two types.

1. Time dependent schrodinger equation
2. Time Independent schrodinger equation.

1. Time dependent schrodinger equation :-

If a quantum systems is changes with time, the wave function will be a function of position and time. In such systems time dependent schrodinger.

equation is used

2. Time independent schrodinger equation

If a quantum system do not change with time, the wave function representing the system depends only on position.

For such systems, time independent schrodinger equation is used.

→ Derive Time dependent schrodinger equation from the solution of a plane wave.

Ans. The differential equation for a wave associated with a particle and propagating along x direction is,

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi}{\partial t^2}$$

A solution of this equation is,

$$\psi = A e^{i(kx - \omega t)} \qquad (1)$$

Where k is the wave vector given by $k = \frac{2\pi}{\lambda}$
and ω is the angular Frequency, $\omega = 2\pi\nu$

According to Einstein's Formula For photon energy is,

$$E = h\nu = \frac{h\omega}{2\pi} \quad \left(\nu = \frac{\omega}{2\pi}\right)$$

ie, $\boxed{E = \hbar\omega}$ $(\hbar = h/2\pi)$ ——— (a)

$\omega = E/\hbar \rightarrow$ (a)

De broglie's expression For wavelength of matter waves is given by,

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

We know that $k = \frac{2\pi}{\lambda}$

$$k = \frac{2\pi}{h/p} = \frac{2\pi p}{h}$$

$$k = \frac{p}{h/2\pi} = p/\hbar$$

ie, $p = \hbar k$

$\boxed{k = p/\hbar}$ ——— (b)

Substitute the values of ω and k in equation (1), we get

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

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

$$\Rightarrow \quad \psi = A e^{i\left(P/\hbar\, x - \frac{E}{\hbar} t\right)}$$

$$\boxed{\psi = A e^{i/\hbar\,[px - Et]}} \quad \text{——— (2)}$$

Differentiate equation (2) with respect to t partially.

$$\frac{\partial \psi}{\partial t} = A \frac{-i}{\hbar} E\, e^{i/\hbar\,(px - Et)}$$

$$\frac{\partial \psi}{\partial t} = \frac{-i}{\hbar} E\, A e^{i/\hbar\,(px - Et)}$$

$$\frac{\partial \psi}{\partial x} = \frac{-iE}{\hbar}\psi$$

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

$$E\psi = -\frac{\hbar}{i}\frac{\partial \psi}{\partial t} \times \frac{i}{i} \quad (i^2 = -1)$$

io, $$\boxed{E\psi = i\hbar\frac{\partial \psi}{\partial t}} \quad \text{———} \quad (3)$$

Differentiate equation (2) with respect to position (x) twice, partially,

$$\frac{\partial \psi}{\partial x} = A\frac{iP}{\hbar}e^{i/\hbar\,(px - Et)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = A\frac{iP}{\hbar}\cdot\frac{iP}{\hbar}e^{i/\hbar\,(px - Et)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-p^2}{\hbar^2}Ae^{i/\hbar\,(px - Et)}$$

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

$$\boxed{p^2\psi = -\hbar^2\frac{\partial^2 \psi}{\partial x^2}} \quad \text{———} \quad (4)$$

For a moving particle total energy of a particle is the sum of kinetic energy and potential energy.

TE = KE + PE

$$\text{Total energy} = \frac{p^2}{2m} + V$$

Multiply above equation with ψ we get,

$$E\psi = \frac{p^2\psi}{2m} + V\psi \quad \text{———} \quad (5)$$

Substitute for $p^2\psi$ from equation (4) and $E\psi$ from equation (3) in equation (5)

∴ equation (5) becomes.

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

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

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

This is the one dimentional time dependent schroedinger equation.

In three dimension,

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

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

This is the one dimensional time dependent schroedinger equation.

In three dimension,

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

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

Where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

where

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

→ Deduce time independent schrodinger equation from time dependent form.

Time dependent schrodinger equation is given by,

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi \quad \text{——— (1)}$$

on solving the ~~The~~ above equation we get a wave function and which is a function of both position and time. We can derive time independent Schredinger equation from the above equation.

Since the position and time are independent variables, wavefunction ψ can be written as a product of two functions $\psi(x)$ (function of position only) and $\phi(t)$ (function of time only).

Thus $\Psi(x,t) = \psi(x)\phi(t)$ —— ②

Substitute equation (2) in equation (1)

we get,

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

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

Divide the above equation with $\psi(x)\phi(t)$

∴ we get

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

$$\boxed{i\hbar \frac{1}{\phi(t)} \frac{\partial \phi(t)}{\partial t} = \frac{-\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + V} \quad \text{—③}$$

In the above equation, LHS depends only on time and RHS depends only on position. In such cases LHS and RHS can be seperately equated to a common constant. The common constant in this case is total energy E.

equating RHS,

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}+V=E$$

~~On rearranging w~~

On rearranging, we get,

$$\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2}+(E-V)=0.$$

multiply using $\psi(x)$, we get.

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

Dividing with $\hbar^2/2m$, we get.

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{(E-V)}{\hbar^2}\times 2m\,\psi(x)=0.$$

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

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

This is schrodinger time independent equation in one dimension.

In three dimension,

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

For free particle $V = 0$.

schrodinger equation for free particle is given by,

$$\boxed{\nabla^2 \psi + \frac{2mE}{\hbar^2}\psi = 0}.$$

The wave function obtained, as a solution to Schrödinger's equation must be well behaved

i.e. ψ should be,

1. finite and should be tends to zero when $(x \to \pm\infty)$

2. $\psi_{(x)}, \dfrac{\partial\psi}{\partial x}, \dfrac{\partial^2\psi}{\partial x^2}$ should be continuous.

3. $\psi_{(x)}$ should be single valued at a point.

time dependent equation.

Wave Function and its Physical Significance

- Suitable solutions of Schrödinger's equation are called wave functions. A wave function is denoted by $\Psi(\mathbf{r},t)$. A wave function is generally a complex-valued function which contains $i = \sqrt{-1}$. Complex conjugate of the wave function $\Psi(\mathbf{r},t)$ is denoted by $\Psi^*(\mathbf{r},t)$.
- Max Born introduced the probability interpretation of the wave function. According to this, the quantity $\Psi\Psi^* dxdydz$ is proportional to the probability of finding the particle in the small volume $dxdydz$ about the point (x,y,z). If the wavefunction is normalised,

i.e., $$\int_{-\infty}^{\infty} \Psi\Psi^* dxdydz = 1 \qquad (12)$$

then $\Psi\Psi^*$ dxdydz itself gives the probability of the particle to be seen in the small volume dxdydz about the point at time 't'.

- $\Psi\Psi^* = |\Psi|^2$ is a probability density function for locating the particle if Ψ is normalised. For a wave motion $\Psi\Psi^*$ is a measure of intensity of the wave. Following this, the wavefunction Ψ may be called the probability amplitude function (intensity $\propto$ amplitude^2).