Modern Physics & Quantum Mechanics

Wave – particle dualism:

It is well known that light exhibits the phenomenon of interference, diffraction, and polarization. This phenomenon can be explained using wave theory of light. This phenomenon shows light behave as a wave, light has wave nature, but photoelectric effect, Compton Effect and black body radiation can be explained on the basis of quantum theory. According to which light propagates in small packets of energy $h\gamma$. These packets are called photons or quanta, which behaves like a particle. Thus light possesses waves as well as particles. It is referred to as wave-particle dualism or dual nature of light and matter. The wave associated with moving particles is called as matter wave. According to de-Broglie, a moving particle behaves sometimes as wave and sometimes as a particle.

De-Broglie hypothesis:

According to de-Broglie, a moving particle behaves sometimes as wave and sometimes as a particle. The waves associated with moving material particle are called matter waves or de-Broglie waves.

"Since nature loves symmetry, if the radiation behaves like a particle under certain circumstances and as waves under certain other circumstances. Then one can even expect that entities, which ordinarily behave as a particle to exhibit properties attributable to, only wave under appropriate circumstances".

Therefore
$$\mathbf{p} = \frac{h}{\lambda}$$
 or $\lambda = \frac{h}{p}$

De-Broglie suggested that this equation applies as well to particle of mass 'm', moving with a velocity 'v'. Thus for a particle, P=mv. λ is the wavelength of the waves associated with a particle of mass 'm' moving with a velocity 'v', de-Broglie called these waves as matter waves.

Thus wavelength of matter waves, $\lambda = \frac{h}{mv}$, [p=m v]this result is known as *de-Broglie* equation.

Matter waves:

> Matter waves are the waves that are associated with a moving particle. The wavelength λ' and frequency 'v' of the waves are given by $\lambda=h/P$ and v=E/h h-planks constant

p-momentum of the particle E-energy of the particle.

The amplitude of the matter waves at a particular region and time depends on the probability of finding the particle at the same region and time.

De-Broglie wavelength of an accelerated electron:

Consider an electron of mass 'm' accelerated through a potential difference of 'V'. The energy

acquired by the electron is eV. The velocity acquired by the electron is v. Then,

$$eV = \frac{1}{2}mv^2$$
.

p=mv

Squaring on both sides, we get,

 $p^2 = m^2 v^2$ $mv^2 = p^2/m$

Substituting in Kinetic energy equation we get, $eV = p^2/2m$

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

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.602 \times 10^{-19} \times V}} = \frac{1.226 \times 10^{-9}}{\sqrt{V}} m$$

$$\lambda = \frac{1.226 \times 10^{-9}}{\sqrt{V}} m$$

Relation between Kinetic energy and de-Broglie wavelength of electron:

The kinetic energy of an electron is, $E = \frac{1}{2} mv^2$.

The momentum of an electron is, p=mv

Squaring on both sides, we get,

 $p^{2}=m^{2}v^{2}$ $mv^{2}=p^{2}/m$

Substituting in Kinetic energy equation we get, $eV = p^2/2m$

$$p = \sqrt{2mE}$$
$$\lambda = \frac{h}{\sqrt{2mE}}$$

HEISENBERGS UNCERTAINTY PRINCIPLE

According to classical mechanics, a particle can occupy a definite position and momentum at any instant of time. That is the trajectory of particle can be continuously traced. But, in atomic scale such notion does not work. According to quantum mechanics [wave mechanics] it is impossible to determine both position and momentum of particle simultaneously and accurately. If Δx is uncertainty (error) in the measurement of position and ΔP_x is the uncertainty in the measurement of momentum, then $\Delta x \Delta P_x \ge \frac{h}{4\pi}$ this is called Heisenberg uncertainty principle.

It shows that if position is measured with higher accuracy then measurement in momentum P will have lower accuracy and vice versa.

Statement of Heisenberg's uncertainty principle (HUP):

"In any simultaneous determination of position and momentum of the particle, the product of the

corresponding uncertainty inherently present in the measurement is equal to or greater than $\frac{h}{4\pi}$.

 $\Delta x. \Delta P_x \ge \frac{h}{4\pi}$

The H U P would also be expressed as in terms of uncertainties involved in the measurement of physical variable pairs such as Energy and time, Angular displacement (θ) and angular momentum (L).

 $\Delta E \Delta t \ge \frac{h}{4\pi}$ $\Delta L \Delta \theta \ge \frac{h}{4\pi}$

' Δ ' is the minimum uncertainty involved in the measurement of the corresponding variable.

Physical significance of H U P:

The physical significance is that one should not think of exact position, or an accurate value for momentum of a particle. Instead, one should think of probability of finding particle at certain position or probable value for momentum of particle. The estimates of such probability are made by means of certain mathematical function named as probability density function in quantum mechanics.

Application of Heisenberg's uncertainty principle:

Non-existence of an electron inside the nucleus:

The diameter of the nucleus is found to be of the order of $1X10^{-14}$ m. If the electron exists within the nucleus of an atom it can be anywhere within the diameter of the nucleus. The maximum

uncertainty in the position of electron is equal to or less than the diameter of the nuclei. $\Delta x=0.5 \times 10^{-14}$ m.

From H U P, $\Delta x.\Delta P x \ge \frac{h}{4\pi}$

Uncertainty in the momentum of the electron is

$$\Delta P_{x} \ge \frac{h}{4\pi\Delta x} \ge \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-14}}$$

 $\Delta P_x \ge 0.54 \times 10^{-20} \text{Ns},$

which is the uncertainty of the momentum of the electron. Then the momentum of the electron must at least be equal to the uncertainty in momentum.

:
$$P_x = 0.5 \times 10^{-20} \text{Ns}$$

We know by theory of relativity

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

E= energy, m= rest mass of electron, p= momentum of electron.

$$E = \frac{(0.5 \times 10^{20})^2}{2 \times 9.1 \times 10^{31}}$$

$$E \ge 1.372 \times 10^{-11} J \Longrightarrow E \ge \frac{1.372 \times 10^{-11}}{1.6 \times 10^{-19}} eV$$

 $E \ge 85 MeV$

This means that electron to exist inside the nucleus its energy must be greater than or equal to 85MeV

But experimental investigations on β decay reveal that, the kinetic energy of β particles (which are same as electron) is the order of 3 to 4 M eV. This clearly indicates that; electron cannot exist within the nucleus.

Wave function:

The variable quantity characterizing the matter wave is called wave function. It is also called the state function. It is denoted by ψ . The value of the wave function associated with a moving body at particular point x, y, z in space at the time "t" is related to the wave function in quantum mechanics which accounts for the wave like properties of a particle. It is given by ψ (x, y, z, t). Wave function is a complex quantity.

A system is defined by its energy, momentum, position etc. once the wave function ψ corresponding to a system is known, the state of the system can be determined. A wave function corresponding to a system will change when system changes its states. In quantum mechanics it is postulated that the state of the system is completely characterized by a wave function.

Probability density:

If we consider a single particle and ψ is the wave function associated with the particle then $|\psi|^2$ is the probability per unit volume that the particle will be found at the given

point. It can also be stated in the following manner. Let V be a volume inside which a particle is known to be present, but where exactly the particle is situated inside V is not known. Then the probability of finding the particle in a certain element of volume dv of V is equal to $|\psi|^2$ dv. For this reason $|\psi|^2$ is called probability density.



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

 $\psi^*\psi$ is always positive and real quantity. ψ^* is complex conjugate of ψ . Probability of occurrence of on event is a real and positive quantity.

Normalization:

If Ψ is a wave function associated with a particle, then $|\psi|^2 dv$ is the probability of finding the particle in a volumedv.

According to statistical rule

 $\int_{0}^{V} |\psi|^2 dv = 1.$ (1) that means definite presence of particle in the particular region

or space of volume V

If $\int_{0}^{\infty} |\psi|^2 dv = 0$. That means that particle does not exist.

 $\int_{0}^{\infty} |\psi|^2 dv = 1$. That means the particle is there at somewhere in space.

A wave function that obeys equation (1) is said to be normalized.

Properties of wave function:

Property (1) \Rightarrow " Ψ " is single valued everywhere.

In this example f (x) has three values f_1 , f_2 and f_3 for the same value of P at x=P. Since, $f_1 \neq f_2 \neq f_3$.

If f(x) is a wave function then the probability of finding the particle has 3 different values at the same location, which is absurd. Hence the wave function is not acceptable.



Property $2 \Rightarrow "\Psi"$ is finite everywhere.

In this example f(x) is not finite at x=R. At x=R, f(x)=infinity

If f(x) is a wave function then it signifies that large probability of finding the particle at a single location (x=R). At x=R $f(x) =\infty$. Thus f(x) is not finite everywhere. To be an acceptable wave function the function must have finite value. But here f(x) is not acceptable function.



FUNCTION NOT FINITE AT A POINT

Property $3 \Rightarrow \Psi$ and its first derivative with respect to its variable are continuous everywhere

At x=Q, f(x) is discontinuous f(x) is truncated at A & restarts at B, between A and B it is not defined.

If f(x) is a wave function then the state of the system at x=Q is not continuous. The function f(x) is not defined between A and B. Thus f(x) is not an acceptable wave function. To be an acceptable wave function the function must have continuous. To be an acceptable wave function the function the function

must have finite value. But here f(x) is not acceptable function. Hence wave function is not acceptable. Also when the ψ is not continuous its first derivatives and second derivatives will not be finite.



Property 4 \Rightarrow For bound states Ψ must vanish at infinity. If Ψ is a complex function, then $\Psi^*\Psi$ must vanish at infinity.

One – dimensional time independent Schrodinger's wave equation:

According to the de-Broglie theory for a particle of mass m, moving with a velocity of V, the wave length $\lambda = \frac{h}{p}$ ------ (1)

P=m v = momentum of the particle

The wave equation for a de-Broglie wave considered traveling in positive x direction can be written in complex notation as

 $\psi = A e^{i(kx - w t)}$ -----(2)

A=constant, w=angular frequency of the wave, k=propagation constant

By differentiating equation (2) twice with respect to "t" we will get Department of Physics, NCET

$$\frac{d\psi}{dt} = A e^{i(kx-wt)}(-i\omega)$$

$$\frac{d^2\psi}{dt^2} = A e^{i(kx-wt)}(-i\omega)(-i\omega)$$

$$\frac{d^2\psi}{dt^2} = -\omega^2 A e^{i(kx-wt)} = -\omega^2 \psi \qquad -----(3)$$

The travelling wave equation is given by,

 $\frac{d^2 y}{dx^2} = \frac{1}{v^2} \frac{d^2 y}{dt^2}$

By analogy, we can write the wave equation for de-Broglie wave for the motion of free particle as,

The above equation represents wave traveling with a velocity v, and ψ is the displacement at the instant t.

From equation (3) and (4), $\frac{d^2\psi}{dx^2} = (\frac{-\omega^2}{v^2})\psi.$

 λ and γ are the wavelength and the frequency of the wave, then $\omega = 2\pi\gamma$ and $v = \gamma\lambda$, substituting for ω and v

$$\frac{d^2\psi}{dx^2} = \frac{-4\pi^2\psi}{\lambda^2}$$

Or, $\frac{1}{\lambda^2} = -\frac{1}{4\pi^2\psi} \frac{d^2\psi}{dx^2}$ (5)

For a particle of mass m moving with a velocity v,

Kinetic energy =
$$\frac{1}{2}$$
 m v² = $\frac{m^2 v^2}{2m} = \frac{p^2}{2m}$ ------ (6), But we know p= $\frac{h}{\lambda}$
 \therefore Kinetic energy = $\frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{h^2}{\lambda^2 2m} = \frac{h^2}{2m} (\frac{1}{\lambda^2}) = \frac{h^2}{2m} (-\frac{1}{4\pi^2 \psi} \frac{d^2 \psi}{dx^2})$
 \therefore Kinetic energy = $-\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2}$ ------ (8)
The total energy E is the sum of K.E + potential energy

E = K E + PE

Potential energy =V

Therefore $E = -\frac{h^2}{8\pi^2 m\psi} \frac{d^2\psi}{dx^2} + V$ (9)

Or
$$-\frac{h^2}{8\pi^2 m \psi} \frac{d^2 \psi}{dx^2} = (E-V)$$
------(10)
 $\frac{d^2 \psi}{dx^2} = -\frac{8\pi^2 m}{h^2} (E-V) \psi$

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

This is the time independent Schrodinger's equation in one dimension

Eigen values and Eigen function:

We have Schrodinger wave equation given by,

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

In order to determine the wave function Ψ , the Schrodinger equation has to be solved. SWE is a second order differential equation; there are many solutions.

All of them may not be acceptable to our conditions. Hence, that wave function which would be corresponding meaningfully to a physical system must be selected. To be an acceptable a wave function

(1) Wave function must be a singled valued.

(2) Wave function must be finite everywhere.

(3) Wave function and its first derivative must be continuous everywhere.

(4) Wave function must vanish at infinite for bound state.

Such acceptable wave functions are named in quantum mechanics as Eigen functions.

Definition: "Eigen functions are those wave functions of quantum mechanics which possess the properties that are single valued, finite everywhere and also their first derivatives with respect to their variable are continuous everywhere".

Eigen values:

When Eigen functions are known, quantum mechanical operators are used to evaluate physical quantities. There is only a restricted set of Eigen function; there is also restricted set of energy values. These values are called **Eigen values**. The wave function must be such that the operator operating on it must reproduce the wave function multiplied by a constant. This constant value is the Eigen value.

Application of Schrodinger wave equation:

Particle in one-dimensional potential well of infinite height(Particle in a box): Consider a particle of mass "m" which is free to move in the x-direction only in the region from x=0 to x=a. Outside this region, the potential V is taken to be infinite and within this region it is zero (which mean that the particle is bound within the limits x=0 to x=a) such a type of potential in space is called infinite potential well.



PARTICLE IN AN INFINITE POTENTIAL WELL

The Schrodinger equation is,

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

Outside the well the Schrodinger equation is,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E-\infty) \psi = 0 - \dots - (1) \text{ (since V=\infty)}$$

This equation holds good if $\psi=0$ for all points outside the well,

 $|\psi|^2=0$, which means that the particle cannot be found at all outside the well.

Inside the well the Schrodinger, s equation is given by,

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

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

In the equation (2) we have to put $\frac{8\pi^2 m}{h^2} E = k^2$,

We have,
$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$
------(3)

Discussion of the solutions;

The solution of the above equation (3) is given by

 $\psi = C \cos(kx) + D \sin(kx)$ -----(4)

But $\psi = 0$ at x=0, \therefore equation (4) becomes, $0 = C\cos(k0) + D\sin(k0)$.

Therefore, C=0----- (5)

Also $\psi = 0$ at x=a, \therefore equation (4) becomes $0 = C\cos(ka) + D\sin(ka)$.

But C=0 from equation (5), hence $D \sin(ka)=0$, here $D\neq 0$

 \therefore sin (ka)=0 or ka= n π , where n= 1,2,3... n is called quantum number which is either zero or positive integer.

Substituting for "C" and "k" from equation (5) and (6) in the equation (4).

$$\psi = 0\cos(\frac{n\pi}{a}x) + D\sin(\frac{n\pi}{a}x)$$
$$\psi_n = D\sin(\frac{n\pi}{a})x - \dots (7)$$
Energy Eigen value:

Consider,

$$\frac{8\pi^2 m}{h^2} E = k^2, \text{ since } k = \frac{n\pi}{a}$$

$$\frac{n^{2}\pi^{2}}{a^{2}} = \frac{8\pi^{2}m}{h^{2}}E$$

$$E = \frac{n^{2}\pi^{2}}{a^{2}} / \frac{8\pi^{2}m}{h^{2}} = \frac{n^{2}\pi^{2}h^{2}}{8\pi^{2}ma^{2}} = \frac{n^{2}h^{2}}{8ma^{2}}$$

$$E_{n} = \frac{n^{2}h^{2}}{8ma^{2}}$$
This is Energy Eigen value equation.
When n=0,E=0, value zero for n is not acceptable.
Because when n=0, $\psi_{n}=0$
For n=1, $E_{1} = \frac{h^{2}}{8ma^{2}} = \text{ground state energy}=\text{zero point energy}$
For n=2, $E_{2} = \frac{4h^{2}}{8ma^{2}} = 4E_{1}$

Thus the energy in the **first excited state** is 4 times the zero point energy.

For n=3, E3 =
$$\frac{9h^2}{8ma^2} = 9E_1$$

Thus the energy in the **second excited state** is 9 times the zero point energy.

Thus n=1, E_1 - Ground state energy or zero point energy.

n=2, E₂- First excited state energy

n=3, E₃- Second excited state energy.

Normalization:

The integral of the wave function over the entire space in the well must be unity because, there is only one particle is present inside the well somewhere else.

$$\int_{0}^{a} |\psi_{n}|^{2} dx = 1$$
(8)

Substituting for ψ_n from equation (7), we will get,

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

But we know that $\sin^2 \theta = \frac{1}{2} (1 - \cos 2\theta).$

$$\int_{0}^{a} D^{2} \frac{1}{2} \left\{ 1 - \cos 2 \left(\frac{n\pi x}{a} \right) \right\} dx = 1$$

$$D^{2} \int_{0}^{a} dx - \frac{1}{2} \int_{0}^{a} \cos\left(\frac{2n\pi x}{a}\right) dx = 1$$

Or $\frac{D^{2}}{2} [x]_{0}^{a} - \frac{D^{2}}{2} \left[\frac{\sin\left(\frac{2n\pi x}{a}\right)}{\frac{2n\pi}{a}}\right]_{0}^{a} = 1$
 $\frac{D^{2}}{2} (a - 0) - \frac{D^{2}}{2} \frac{a}{2n\pi} \left[\sin\left(\frac{2n\pi a}{a}\right) - \sin\left(\frac{2n\pi 0}{a}\right)\right] = 1$
 $\frac{D^{2}a}{2} = 1$, [since, sin (2n\pi)=0, sin (0)=0]

$$D = \sqrt{\frac{2}{a}}$$

Thus the normalized wave function of a particle in one-dimensional potential well is

$$\psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$
 ------ (9) This is the **Eigen function**

Wave functions, probability densities and Energy levels for particle in an infinite potential well:

The most probable location of the particle in the well and its energies are to be evaluated for the different permitted sates.

We can write the eigen functions ψ_1 , ψ_2 , $\psi_{3..}$ For a particle in the well by considering n=1, 2, 3 respectively in the equation.

Let us consider the first 3 cases.

Case (i) : n=1

This is the ground state and the particle is normally found in this state.

For n=1, the eigen function is,

$$\psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right), \text{ from equation (9)}$$

 $\psi_1=0$, for both x=0 and x =a.

But Ψ_1 has maximum value for $x = \left(\frac{a}{2}\right)$.

Thus a plot of ψ_1 versus "x" will be shown in figure

And a plot of $|\psi_1|^2$, the probability density verses "x" is also shown below.



It indicates the probability of the finding the particle at different location inside the well.

 $|\psi_1|^2$ is 0 both at x=0, and at x=a.

 ψ is maximum at $x = \left(\frac{a}{2}\right)$ it says that the particle is cannot be found at all at the walls of the well, and the probability of finding the particle is maximum at the central region. If n=1

This isground state energy or zero point energy.

Case (ii):n=2

This is the first excited state i.e. the next immediate higher state permitted for the particle after the ground state.

Department of Physics, NCET

Quantum Mechanics

The eigenfunction for this state is

$$\psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi x}{a}\right),$$

Now $\psi_2=0$ for the values x=0, $\frac{a}{2}$, and a, also ψ_2 is maximum for x=($\frac{a}{4}$) and ($\frac{3a}{4}$).

The plot of $|\psi_2|^2$ verses x in this figure $|\psi_2|^2=0$ at x=0, $\frac{a}{2}$ and a.

It means that in the first excited state the particle cannot be observed either at the walls, or at the center. If n=2, energy equation $E_2 = 4E_1$, First excited state.



Thus the energy in the first excited state is 4 times the zero point energy. **Case (iii)**, n=3:

The Eigen function for the second excited state as,

$$\psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi x}{a}\right), \quad \Psi 3 = 0, \text{ for } x = 0, \frac{a}{3}, \frac{2a}{3} \text{ and } a.$$

 ψ_3 will be a maximum value for $x = \frac{a}{6}$, $\frac{a}{2}$ and $\frac{5a}{6}$.

The plot of ψ_3 verses x and $|\psi|^2$ verses x is as shown bellow.



For n=3, E3 = $\frac{9h^2}{8ma^2} = 9E_1$

Thus the energy in the second excited state is 9 times the zero point energy.