6. PRINCIPLES OF QUANTUM MECHANICS

Introduction: Quantum mechanics is a new branch of study in physics which is indispensable in understanding the mechanics of particles in the atomic and sub-atomic scale.

The motion of macro particles can be observed either directly or through microscope. Classical mechanics can be applied to explain their motion. But classical mechanics failed to explain the motion of micro particles like electrons, protons etc...

Max Plank proposed the Quantum theory to explain Blackbody radiation. Einstein applied it to explain the Photo Electric Effect. In the mean time, Einstein's mass – energy relationship ($E = mc^2$) had been verified in which the radiation and mass were mutually convertible. Louis deBroglie extended the idea of dual nature of radiation to matter, when he proposed that matter possesses wave as well as particle characteristics.

The classical mechanics and the quantum mechanics have fundamentally different approaches to solve problems. In the case of classical mechanics it is unconditionally accepted that position, mass, velocity, acceleration etc of a particle can be measured accurately, which, of course, true in day to day observations. In contrast, the structure of quantum mechanics is built upon the foundation of principles which are purely probabilistic in nature. As per the fundamental assumption of quantum mechanics, it is impossible to measure simultaneously the position and momentum of a particle, whereas in the case of classical mechanics, there is nothing which contradicts the measurements of both of them accurately.

Plank's Quantum Theory:

Max Plank, a German physicist derived an equation which successfully accounted for the spectrum of the blackbody radiation. He incorporated a new idea in his deduction of Plank eqn. that the probability of emission of radiation decreases as its frequency increases so that, the curve slopes down in the high frequency region. The oscillators in the blackbody can have only a discrete set of energy values. Such an assumption was radically different from the basic principles of physics.

The assumption in the derivation of Plank's law is that the wall of the experimental blackbody consists of a very large number of electrical oscillators, with each oscillator vibrating with a frequency of its own. Plank brought two special conditions in his theory.They are

(1) Only an integral multiple of energies $h\nu$ where 'h' is Plank's constant and 'ν ' is frequency of vibration i e, the allowed energy values are $E = n h \nu$ where $n = 0 , 1 , 2 , \ldots\ldots$

(2) An oscillator may lose or gain energy by emitting or absorbing radiation of frequency $\nu = (\Delta E / h)$, where ΔE is the difference in the values of energies of the oscillator before and the emission or absorption had taken place.

Based on the above ideas, he derived the law governing the entire spectrum of the Blackbody radiation, given by

$$U_\lambda \, d\lambda = (8\Pi hc / \lambda^{5)} [1 / (e^{h\nu/kT} - 1)] \, d\lambda \quad (\text{since } \nu = c / \lambda)$$

This is called Plank's radiation law.

Waves and Particles: deBroglie suggested that the radiation has dual nature i e both particle as well as wave nature. The concept of particle is easy to grasp. It has mass, velocity, momentum and energy. The concept of wave is a bit more difficult than that of a particle. A wave is spread out over a relatively large region of space, it cannot be said to be located just here and there, and it is hard to think of mass being associated with a wave. A wave is specified by its frequency, wavelength, phase, amplitude, intensity.

Considering the above facts, it appears difficult to accept the conflicting ideas that radiation has dual nature. However this acceptance is essential because radiation sometimes behaves as a wave and at other times as a particle.

(1) Radiations behaves as waves in experiments based on interference, diffraction, polarization etc. this is due to the fact that these phenomena require the presence of two waves at the same position and at the same time. Thus we conclude that radiation behaves like wave.

(2) Plank's quantum theory was successful in explaining blackbody radiation, photoelectric effect, Compton Effect and had established that the radiant energy, in its interaction with the matter, behaves as though it consists of corpuscles. Here radiation interacts with matter in the form of photons or quanta. Thus radiation behaves like particle.

Hence radiation cannot exhibit both particle and wave nature simultaneously.

deBroglie hypothesis : The dual nature of light possessing both wave and particle properties was explained by combining Plank's expression for the energy of a photon $E = h\nu$ with Einstein's mass energy relation $E = m c^2$ (where c is velocity of light , h is Plank's constant , m is mass of particle)

$$\Rightarrow \quad h\nu = m c^2$$

Introducing $\nu = c / \lambda$, we get $h c / \lambda = m c^2$

$$\Longrightarrow \quad \lambda = h / mc = h / p \text{ where p is momentum of particle}$$

λ is deBroglie wavelength associated with a photon.

deBroglie proposed the concept of matter waves , according to which a material particle of mass 'm' moving with velocity 'v' should be associated with deBroglie wavelength 'λ' given by

$$\lambda = h / m\nu = h / p$$

The above eqn. represents deBroglie wave eqn.

Characteristics of Matter waves:

Since $\lambda = h / m v$

1. Lighter the particle, greater is the wavelength associated with it.
2. Lesser the velocity of the particle, longer the wavelength associated with it.
3. For $v = 0$, $\lambda = \infty$. This means that only with moving particle, matter waves is associated.
4. Whether the particle is changed or not, matter waves is associated with it.
5. It can be proved that matter waves travel faster than light.

   We know that $E = h \nu$ and $E = m c^2$

   $\Rightarrow$ $h \nu = m c^2$ or $\nu = m c^2 / h$

   Wave velocity (ω) is given by

   $$\omega = \nu \lambda = m c^2 \lambda / h = (m c^2 / h) (h / m v)$$

   $\Rightarrow$ $\omega = c^2 / v$

   As the particle velocity 'v' cannot exceed velocity of light, ω is greater than the velocity of light.
6. No single phenomena exhibit both particle nature and wave nature simultaneously.
7. The wave nature of matter introduces an uncertainty in the location of the particle & the momentum of the particle exists when both are determined simultaneously.

Davisson and Germer's experiment:

C. J. Davisson and L. H. Germer were studying scattering of electrons by a metal target and measuring the intensity of electrons scattered in different directions.

Experimental Arrangement:

An electron gun, which comprises of a tungsten filament is heated by a low tension battery B1, produces electrons. These electrons are accelerated to desired velocity by applying suitable potential from a high tension source B2. The accelerated electrons are collimated into a fine beam by allowing them to pass through a system of pin holes provided in the cylinder. The whole instrument is kept in an evacuated chamber.

The past moving beam of electrons is made to strike the Nickel target capable of rotating about an axis perpendicular to the plane. The electrons are now scattered in all directions by the atomic planes of crystals. The intensity of the electron beam scattered in a direction can be measured by the electron collector which can be rotated about the same axis

as the target. The collector is connected to a galvanometer whose deflection is proportional to the intensity of the electron beam entering the collector.

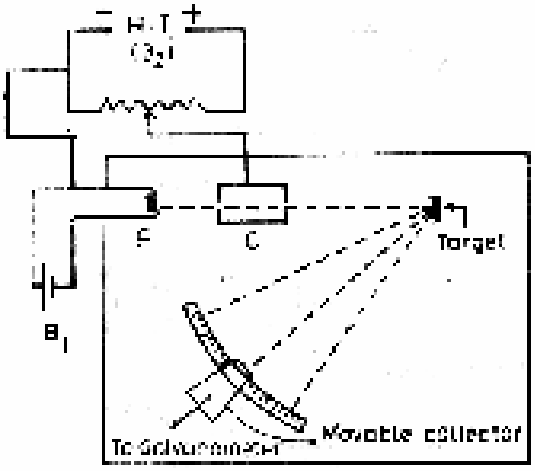


Fig. Davisson and Germer's Apparatus

The electron beam is accelerated by 54 V is made to strike the Nickel crystal and a sharp maximum is occurred at angle of 50^{o} with the incident beam. The incident beam and the diffracted beam in this experiment make an angle of 65^{o} with the family of Bragg's planes.

d = 0.091nm (for Ni crystals)

According to Bragg's law for maxima in diffracted pattern,

$2d \sin\theta = n\lambda$

For n =1, $\lambda = 2d \sin\theta$

$= 2 \times 0.91 \times 10^{-10} \times \sin 65^{o}$

= 0.165 nm

For a 54 V electron, the deBrogllie wavelength associated with the electron is given by

$= 12.25 / \sqrt{V} = (12.25 / \sqrt{54})\ ^{o}A$

= 0.166 nm.

This value is in agreement with the experimental value. This experiment provides a direct verification of deBroglie hypothesis of wave nature of moving particles.

G.P. Thomson's Experiment:

G.P. Thomson investigated high speed electrons produced by applying the high voltage ranges from10 to 50kV. The principle is similar too that of that of powdered crystal method of X- ray diffraction.

In this experiment, an extremely thin (10^{-8}m) metallic film F of gold, aluminium etc., is used as a transmission grating to a narrow beam of high speed electrons emitted by a cathode

C and accelerated by anode A. A fluorescent screen S or a suitable photographic plate P is used to observe the scattered electron beam. The whole arrangement is enclosed in a vacuum chamber.

The electron beam transmitted through the metal foil gets scattered producing diffraction pattern consisting of concentric circulars rings around a central spot. The experimental results and its analysis are similar to those of powdered crystal experiment of X- ray diffraction.

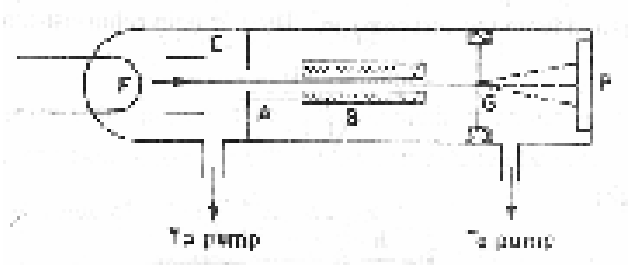
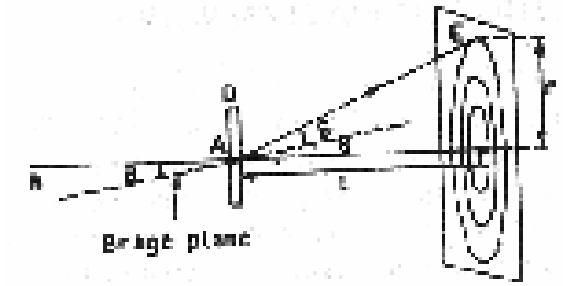


Fig. Thomson Apparatus



L: distance between the foil and screen
R(r): radius of the diffraction ring
θ: glancing angle

The method of interpretation of the experimental results is same as that of the Davisson and Germer experiment. Here also we use Bragg's law and deBroglie wavelength.

We have $2d \sin\theta = n\lambda$

$\theta = n\lambda / 2d$ --→ I since θ is small $\sin\theta = \theta$

From fig.

$R/L = \tan 2\theta \approx 2\theta$

$R = L\, 2\theta$ -→ II

From eqn I, II

$R = L\, 2\, n\lambda / 2d = L\, n\lambda / d$

Since L and d are fixed in the experiment

$R \alpha n\lambda$ or $D \alpha n\lambda$ D is diameter of the ring

Combing with the deBroglie expression

$$\lambda = \sqrt{(150 / V(1+r))}$$

Where (1+r) is the relativistic correction we notice that $D\sqrt{(V(1+r))}$ must be constant for a given order the experiment repeated with different voltages. The data shows that $D\sqrt{(V(1+r))}$ is constant, thus supporting the deBroglie concept of matter waves.

Heisenberg Uncertainty Principle:

According to classical mechanics, a moving particle at any instant has a fixed position in space and a definite momentum which can be determined simultaneously with any desired accuracy. The classical point of view represents an approximation which is adequate for the objects of appreciable size, but not for the particles of atomic dimensions.

Since a moving particle has to be regarded as a deBroglie group, there is a limit to the accuracy with which we can measure the particle properties. The particle may be found anywhere within the wave group, moving with the group velocity. If the group is narrow, it is easy to locate its position but the uncertainty in calculating its velocity or momentum increases. On the other hand, if the group is wide, its momentum can be estimated satisfactorily, but the uncertainty in finding the location of the particle is great. Heisenberg stated that the simultaneous determination of exact position and momentum of a moving particle is impossible.

If Δx is Error in the measurement of position of the particle along X-axis

Δp is Error in the measurement of momentum

Then $\Delta x . \Delta p = h$ ---------- (1) where h is Plank's constant

The above relation represents the uncertainty involved in measurement of both the position and momentum of the particle.

To optimize the above error, lower limit is applied to the eqn. (1)

Then $(\Delta x).(\Delta p) \geq \hbar / 2$ where $\hbar = h / 2\Pi$

A particle can be exactly located ($\Delta x \rightarrow 0$) only at the expense of an infinite momentum ($\Delta p \rightarrow \infty$).

There are uncertainty relatio0ns between position and momentum, energy and time, and angular momentum and angle.

If the time during which a system occupies a certain state is not greater than Δt, then the energy of the state cannot be known within ΔE,

i e $(\Delta E)(\Delta t) \geq \hbar / 2$.

Schrödinger's Time Independent Wave Equation:

Schrödinger, in 1926, developed wave equation for the moving particles. One of its forms can be derived by simply incorporating the deBroglie wavelength expression into the classical wave eqn.

If a particle of mass 'm' moving with velocity 'v' is associated with a group of waves.

Let ψ be the wave function of the particle. Also let us consider a simple form of progressing wave like the one represented by the following equation,

$$\Psi = \Psi 0 \sin (\omega t - k x) \text{ --------- (1)}$$

Where $\Psi = \Psi (x, t)$ and $\Psi 0$ is the amplitude.

Differentiating Ψ partially w.r.to x,

$$\partial \Psi / \partial x = \Psi_0 \cos (\omega t - k x) (- k)$$

$$= -k \Psi_0 \cos (\omega t - k x)$$

Once again differentiate w.r.to x

$$\partial^2 \psi / \partial x^2 = (- k) \Psi_0 (- \sin (\omega t - k x)) (- k)$$

$$= - k^2 \Psi 0 \sin (\omega t - k x)$$

$$\partial^2 \psi / \partial x^2 = - k^2 \psi \text{ (from eqn (1))}$$

$$\partial^2 \psi / \partial x^2 + k^2 \psi = 0 \text{ ---------- (2)}$$

$$\partial^2 \psi / \partial x^2 + (4 \Pi^2 / \lambda^2) \psi = 0 \text{ --------- (3)} \quad (\text{since } k = 2 \Pi / \lambda)$$

From eqn. (2) or eqn. (3) is the differential form of the classical wave eqn. now we incorporate deBroglie wavelength expression $\lambda = h / m v$.

Thus we obtain

$$\partial^2 \psi / \partial x^2 + (4 \Pi^2 / (h / m v) 2) \psi = 0$$

$$\partial^2 \psi / \partial x^2 + 4 \Pi^2 m^2 v^2 \psi / h2 = 0 \text{ ---------- (4)}$$

The total energy E of the particle is the sum of its kinetic energy K and potential energy V

$$\text{i e } E = K + V \text{ ---------- (5)}$$

And $K = mv^{2/} 2$ ---------- (6)

Therefore $m^2 v^2 = 2 m (E – V)$ ---------- (7)

From (4) and (7)

$$\Rightarrow \quad \partial^2 \psi / \partial x^2 + [8\Pi 2 m (E-V) / h^2] \psi = 0 \quad \text{---------- (8)}$$

In quantum mechanics, the value h / 2 Π occurs more frequently. Hence we denote,

$$\hbar = h / 2 \Pi$$

Using this notation, we have

$$\partial^2 \psi / \partial x^2 + [2 m (E – V) / \hbar^{2]} \psi = 0 \text{ ---------- (9)}$$

For simplicity, we considered only one – dimensional wave. Extending eqn. (9) for a three – dimensional, we have

$$\partial^2 \psi / \partial x^2 + \partial^2 \psi / \partial y^2 + \partial^2 \psi / \partial z^2 + [2 m (E – V) / \hbar^{2]} \psi = 0 \text{ ---------- (10)}$$

Where $\Psi = \Psi (x, y, z)$.

Here, we have considered only stationary states of ψ after separating the time dependence of Ψ.

Using the Laplacian operator,

$$\nabla^2 = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2 \text{ ---------- (11)}$$

Eqn. (10) can be written as

$$\nabla^2 \Psi + [2 m (E – V) / \hbar^2] \psi = 0 \text{ ---------- (12)}$$

This is the Schrödinger Time Independent Wave Equation.

Physical Significance of Wave Function:

Max Born in 1926 gave a satisfactory interpretation of the wave function ψ associated with a moving particle. He postulated that the square of the magnitude of the wave function $|\psi|^2$ (or $\psi\ \psi^*$ it ψ is complex), evaluated at a particular point represents the probability of finding the particle at the point. $|\psi|^{2\ is}$ called the probability density and ψ is the probability amplitude. Thus the probability of the particle within an element volume dt is $|\psi|^2\ d\tau$. Since the particle is certainly somewhere, the integral at $|\psi|^2 d\tau$ over all space must be unity i.e.

$$\int_{-\infty}^{\infty} |\psi|^2 \, .d\tau = 1 \text{ _____ (28)}$$

A wave function that obeys the above equations is said to be normalized. Energy acceptable wave function must be normalizable besides being normalizable; an acceptable wave function should fulfill the following requirements (limitations)

.

1. It must be finite everywhere.
2. It must be single valued.
3. It must be continuous and have a continuous first derivative everywhere.

Normalization Of a wave function:

Since $|\psi(x, y, z)^2| .d\nu$ is the probability that the particle will be found in a volume element dν. Surrounding the point at positron (x, y, z), the total probability that the particle will be somewhere in space must be equal to 1. Thus, we have

$$\int_{-\infty}^{\infty} |\psi(x, y, z)^2| .d\nu = 1$$

Where ψ is a function of the space coordinates (x, y, z) from this 'normalization condition' we can find the value of the complaint and its sign. A wave function which satisfies the above condition is said to be normalized (to unity).

The normalizing condition for the wave function for the motion of a particle in one dimension is

$$\int_{-\infty}^{\infty} |\psi(x)|^2 .dx = 1$$

From these equations, we see that for one – dimensional case, the dimension of $\psi(x)$ in $L^{-1/2}$ and for the three – dimensional case the dimension of $\psi(x, y, z)$ in $L^{-3/2}$.

Particle in One Dimensional Potential Box:

Consider a particle of mass 'm' placed inside a one-dimensional box of infinite height and width L.



Fig. Particle in a potential well of infinite height.

Assume that the particle is freely moving inside the box. The motion of the particle is restricted by the walls of the box. The particle is bouncing back and forth between the walls of the box at x = 0 and x = a. For a freely moving particle at the bottom of the potential well, the potential energy is very low. Since the potential energy is very low, moving particle energy is assumed to be zero between x =0 and x = a.

The potential energy of the particle outside the walls is infinite due to the infinite P.E outside the potential well.

The particle cannot escape from the box

i.e. $V = 0$ for $0 < x < a$

$V = \infty$ for $0 \geq x \geq a$

Since the particle cannot be present outside the box, its wave function is zero

i e $|\psi|^2 = 0$ for $0 > x > a$

$|\psi|^2 = 0$ for $x = a \;\&\; x = 0$

The Schrödinger one – dimensional time independent eqn. is

$$\nabla^2 \Psi + [2m(E - V)/\hbar^2]\psi = 0 \text{ ----------(1)}$$

For freely moving particle $V = 0$

$$\nabla^2 \Psi + [2mE/\hbar^2]\psi = 0 \text{ ----------(2)}$$

Taking $2mE/\hbar^2 = K^2$ ---------- (3)

Eqn.(1) becomes $\partial^2 \psi / \partial x^2 + k^2 \Psi = 0$ ----------(4)
Eqn. (1) is similar to eq. of harmonic motion and the solution of above eqn. is written as

$\Psi = A \sin kx + B \cos kx$ ----------(5) where A, B and k are unknown quantities and to calculate them it is necessary to construct boundary conditions.

Hence boundary conditions are

When $x = 0$, $\Psi = 0$ => from (5) $0 = 0 + B$ => $B = 0$ -------- (6)

When $x = a$, $\Psi = 0$ => from (5) $0 = A \sin ka + B \cos ka$ ---------- (7)

But from (6) B = 0 therefore eqn. (7) may turn as

$$A \sin ka = 0$$

Since the electron is present in the box $a \neq 0$

$$\text{Sin } ka = 0$$

$$Ka = n \Pi$$

$$k = n \Pi / a \quad \text{---------- (8)}$$

Substituting the value of k in eqn. (3)

$$2 m E / \hbar^2 = (n \Pi / a)^2$$

$$E = (n \Pi / a)^2 (\hbar^2 / 2 m) = (n \Pi / a)^2 (h^2 / 8 m \Pi^2)$$

$$E = n^2 h^2 / 8 m a^2$$

In general $E_n = n^2 h^2 / 8 m a^2$ ----------(9)

The wave eqn. can be written as

$$\Psi = A \sin (n \Pi x / a) \text{ ---------- (10)}$$

Let us find the value of A, if an electron is definitely present inside the box, then

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

$$=> \int_0^a A^2 \sin^2 (n \Pi x / a) \, dx = 1$$

$$=> \int_0^a \sin^2 (n \Pi x / a) \, dx = 1 / A^2$$

$$=> \int_0^a [1 - \cos (2 \Pi n (x / a)) / 2] \, dx = 1 / A^2$$

$$A = \sqrt{2} / a \quad \text{---------- (11)}$$

From eqn's. (10) & (11)

$$\Psi_n = \sqrt{2} / a \sin (n \Pi x / a) \text{ ----------(12)}$$

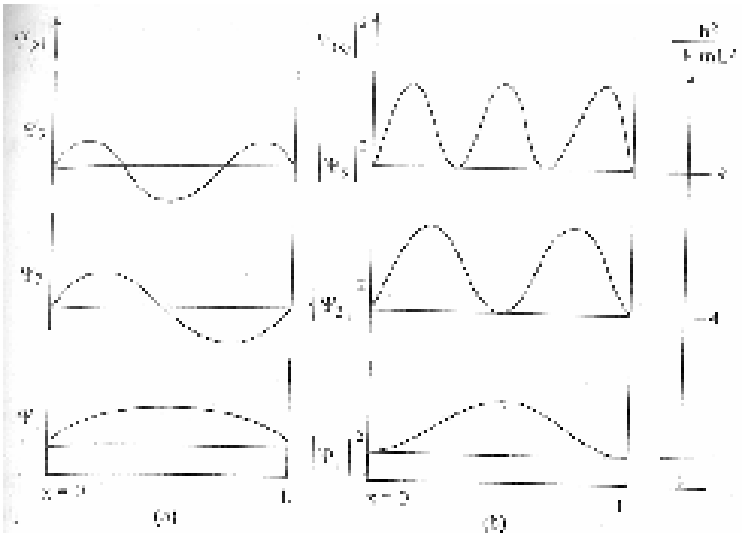
Eqn. (9) represents an energy level for each value of n. the wave function this energy level is given in eqn. (12). Therefore the particle in the box can have discrete values of energies. These values are quantized. Not that the particle cannot have zero energy .The normalized wave functions $\Psi 1$, $\Psi_{2, \Psi 3}$ given by eqn (12) is plotted. the values corresponding to each E_n value is known as Eigen value and the corresponding wave function is known as Eigen function.

The wave function $\Psi 1$, has two nodes at x = 0 & x = a

The wave function $\Psi 2$, has three nodes at x = 0, x = a / 2 & x = a

The wave function $\Psi 3$, has three nodes at x = 0, x = a / 3, x = 2 a / 3 & at x = a

The wave function $\Psi_{n,}$ has (n + 1) nodes



Substituting the value of E in (3), we get

$$(2\ m / \hbar^{2}\ )\ (\ p^{2} / 2\ m) = k^{2}$$

$$\Rightarrow p^{2} / \hbar^{2} = k^{2}$$

$$k = p / \hbar = p / (h / 2\ \Pi) = 2\ \Pi\ p / h$$

$k = 2\ \Pi / \lambda$ where k is known as wave vector.

Questions:

1. What are the matter waves? Explain their properties.
2. Explain de Broglie hypothesis.
3. Explain the duality of matter waves
4. Describe Davisson and Germer's experiment an explain how it enabled the verification of the de Broglie equation.
5. Explain G.P. Thompson's experiment in support of de Broglie hypothesis
6. Explain Heisenberg's uncertainty principle. Give its physical significance.
7. Derive time independent one dimensional Schrödinger's equation.
8. Explain the physical significance of wave function.
9. Write down Schrödinger's wave equation for a particle in one dimensional potential box.