UNIT II – QUANTUM MECHANICS

Introduction:

At the beginning of the 20th century, Newton's laws of motion were able to successfully describe the motion of the particles in classical mechanics (the world of large, heavy and slow bodies) and Maxwell's equations explained phenomena in classical electromagnetism. However the classical theory does not hold in the region of atomic dimensions. It could not explain the stability of atoms, energy distribution in the black body radiation spectrum, origin of discrete spectra of atoms, etc. It also fails to explain the large number of observed phenomena like photoelectric effect, Compton Effect, Raman Effect, Quantum Hall effect, superconductivity etc. **The insufficiency of classical mechanics led to the development of quantum mechanics (QM).**

Quantum mechanics gives the description of motion and interaction of particles in the small scale atomic system where the discrete nature of the physical world becomes important. With the application of quantum mechanics, most of the outstanding problems have been solved. The direct implications of QM though very subtle have dramatic effect in our day to day life. For example, QM successfully introduced the concept of discrete energy which led to the conception and advancements in quantum computing, it also paved way for efficient long distance transfer of large quantities of data electronically. By understanding the electronic spin and related atomic properties, QM has aided in realizing energy efficient materials that can be applied to consumable electronic equipment and in commercial transport vehicles like Hyper loop, Maglev trains among others.

Black Body Radiation

Black-body radiation is the type of electromagnetic **radiation** emitted by a **black body** (an opaque and non-reflective **body**) held at constant, uniform temperature. In nature there are no perfect black bodies.

Black Body Spectrum: It is a graph showing the variation of the energy of the black body radiations as a function of their wavelengths or frequencies. The energy distribution in the black body spectrum is explained by **Wien's distribution law** in the lower wavelength region and **Rayleigh Jeans law** explains the energy distribution in the larger wavelength region.

Wien's law:

$$E_\lambda d\lambda = A\lambda^{-5} e^{\frac{-B}{\lambda T}} d\lambda$$

Rayleigh Jeans law

$$E_\lambda d\lambda = 8\pi k\, T\lambda^{-4} d\lambda$$

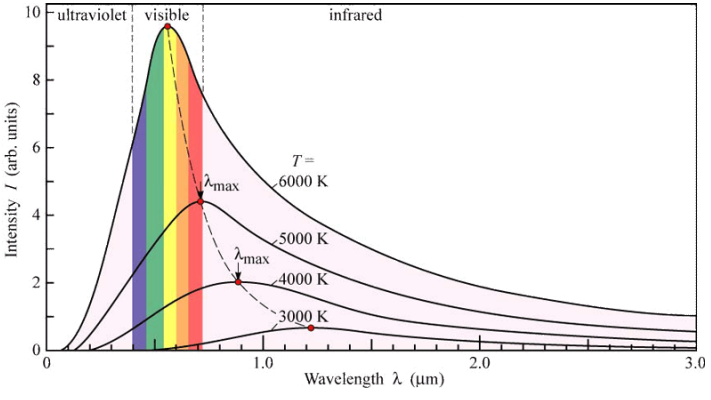


Fig: Blackbody Radiation spectrum

Neither Wien's law nor Rayleigh- jean's law could explain the energy distribution in the entire blackbody spectrum. The energy distribution in the entire blackbody spectrum was successfully explained by Max. Planck by quantum Theory.

Planck's quantum theory

The energy distribution in the black body radiation spectrum was successfully explained by Max Planck in the year 1900. According to Planck's quantum theory thermal energy is not emitted or absorbed continuously, but it is emitted or absorbed in discrete quantities called quanta. Each quanta has an energy 'hν' where h is the Planck's constant. Applying the Planck's quantum theory an expression for the energy distribution in the black body spectrum was obtained and it is called Planck's formula.

The Planck's formula is as follows

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{(hc/\lambda kT)} - 1} d\lambda$$

Where k is the Boltzmann's constant; h- Planck's constant and c is the velocity of light, λ is the wavelength of the black-body radiation and ω is the angular frequency of light.

Photoelectric effect:

When the light of a **suitable wavelength** shines on certain materials, then electrons are **spontaneously** emitted from the surface of material. It can be observed in any material but most

readily in metals and good conductors. This phenomenon is known as **the photoelectric effect**.

The materials that exhibit photoelectric effect are called photosensitive materials and the emitted electrons are called photoelectrons. Heinrich Hertz first observed this phenomenon in 1887.

The electrons are emitted only when the photons reach or exceed a threshold frequency (energy) and below that threshold, no electrons are emitted from the metal regardless of the light intensity or the length of time of exposure to the light. To explain this phenomenon, Albert Einstein proposed that light be seen as a collection of discrete bundles of energy (photons), each with energy $h\upsilon$, where υ is the frequency of the light that is being quantized and h is known as the Planck constant.

Einstein's photoelectric equation:

Einstein, in 1905, proposed that the light energy is localized in small packets similar to the Planck's idea of quanta, and named such packets as photons. According to Einstein, in photoelectric effect one photon is completely absorbed by one electron, which thereby gains the quantum of energy and may be emitted from the metal.

Thus the photon energy is used in the following two parts:

i). A part of its energy is used to free the electron from the atoms of the metal surface. This energy is known as a photoelectric work function of metal (W_o)

ii) The other part is used in giving kinetic energy (½ mv^2) to the electron.

$$\text{Thus } h\nu = W_o + \frac{1}{2}mv^2$$

where 'v' is the velocity of the emitted electron.

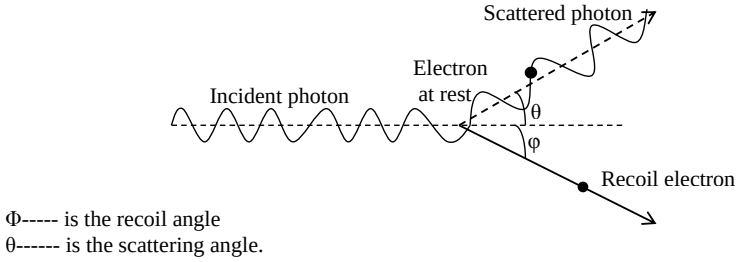
This equation is known as Einstein's photoelectric equation. When the photon's energy is of such a value that it can just liberate the electron from metal, then the kinetic energy of the electron will be zero. Then the above equation reduces to $h\nu_o = W_o$, where ν_o is called the threshold frequency.

Threshold frequency is defined as the minimum frequency which can cause photoelectric emission. Below this frequency no emission of electron takes place.

Compton Effect:

When a monochromatic beam of high frequency radiation (X – rays, γ – rays, etc.) is scattered by a substance, then the scattered radiation contains two components - one having a lower frequency or greater wavelength called as modified radiation and the other having the same frequency or wavelength called as unmodified

radiation. This phenomenon is known as Compton effect and was discovered by Prof. A.H. Compton in 1921. The process of recoiling of electron and scattering of photon is as shown in the following figure:



Schematic diagram of Compton Effect

According to the quantum concept of radiation, the radiation is constituted by energy packets called photons. The energy of photon is hν, where h is Planck's constant and ν is the frequency of radiation. The photons move with velocity of light c, possess momentum hν/c and obey all the laws of conservation of energy and momentum. According to Compton, the phenomenon of scattering is due to an elastic collision between two particles, the photon of incident radiation and the electron of the scatterer. When the photon of energy hν collides with the electron of the scatterer at rest, it transfers some energy to the electron, i.e., it loses the energy. The scattered photon will therefore have a smaller energy

and consequently a lower frequency (ν') or greater wavelength (λ') than that of the incident photon. The observed change in frequency or wavelength of the scattered radiation is known as Compton Effect. In the scattering process, the electron gains kinetic energy and thus recoils with a velocity v. The changed wavelength of the photon scattered through an angle θ is given by

$$\Delta\lambda = (\lambda' - \lambda) = \frac{h}{m_0 c}[1 - \cos\vartheta]$$

Wave and particle duality of radiation

To understand the wave and particle duality, it is necessary to know what a particle is and what a wave is.

A particle is a localized mass and it is specified by its mass, velocity, momentum, energy, etc. In contrast a wave is a spread out disturbance. A wave is characterized by its wavelength, frequency, velocity, amplitude, intensity, etc. It is hard to think mass being associated with a wave. Considering the above facts, it appears difficult to accept the conflicting ideas that radiation has a wave particle duality. However this acceptance is essential because the radiation exhibits phenomena like interference, diffraction, polarization, etc., and shows the wave nature and it also exhibits the particle nature in the black-body radiation effect, photoelectric effect, Compton Effect etc.

Radiation, thus, sometimes behave as a wave and at some other time as a particle, this is the wave particle duality of radiation.

De Broglie's concept of matter waves.

Louis de-Broglie in 1924 extended the wave particle dualism of radiation to fundamental entities of physics, such as electrons, protons, neutrons, atoms, molecules, etc. de-Broglie put a bold suggestion that like radiation, matter also has dual characteristic, at a time when there was absolutely no experimental evidence for wavelike properties of matter waves. **de Broglie Hypothesis** of matter waves is as follows.

- In nature energy manifests itself in two forms, namely matter and radiation.
- Nature loves symmetry.
- As radiation can act like both wave and a particle, material particles (like electrons, protons, etc.) in motion should exhibit the property of waves.

These waves due to moving matter are called matter waves or de-Broglie waves or pilot waves.

Wavelength of matter waves:

The concept of matter waves is well understood by combining Planck's quantum theory and Einstein's theory. Consider a photon of energy E, frequency γ and wavelength λ.

By Planck's theory $E = h\gamma = \frac{hc}{\lambda}$

By Einstein's mass-energy relation $E = mc^2$

By equating and rearranging the above equations, we get

$$mc^2 = \frac{hc}{\lambda}$$

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

Where, p is the momentum of the photon and h is a Planck's constant.

Now consider a particle of mass m moving with a velocity v and momentum p. According to the do-Broglie hypothesis matter also has a dual nature. Hence the wavelength λ of matter waves is given by

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

This is the equation for the de-Broglie wavelength.

De Broglie wavelength of an electron

Consider an electron of mass 'm' accelerated from rest by an electric potential V. The electrical work done (eV) is equal to the kinetic energy E gained by the electron.

$$E = eV$$

$$\therefore E = \frac{1}{2}mv^2$$

$$\therefore m^2v^2 = 2mE$$

$$mv = \sqrt{2mE}$$

Therefore wavelength of electron wave

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

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

But $E = eV$

$$\therefore \lambda = \frac{h}{\sqrt{2meV}} = \frac{h/\sqrt{2me}}{\sqrt{V}}$$

Substituting the values of e, m and h, we get

$$\frac{h}{\sqrt{2me}} = 12.28 A^o$$

$$\therefore \lambda = \frac{12.28}{\sqrt{V}} A^o$$

Note: Instead of a an electron, if a particle of charge ‘q’ is accelerated through a potential difference V, then

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

Properties of matter waves and how they are different from electromagnetic waves

1. Lighter the particle, greater would be the wavelength of matter waves associated with it.
2. Smaller the velocity of the particle, greater would be the wavelength.
3. For $p = 0$, λ is infinity ie., the wave becomes indeterminate. This means that matter waves are associated with moving particles only.
4. Matter waves are produced by charged or uncharged particles in motion. Whereas electromagnetic waves are produced only by a moving charged particle. Hence matter waves are non – electromagnetic waves.
5. In an isotropic medium the wavelength of an electromagnetic wave is a constant, whereas wavelength of a matter wave changes with the velocity of the particle. Hence matter waves are non- electromagnetic waves.
6. A particle is a localized mass and a wave is a spread out disturbance. So, the wave nature of matter introduces a certain uncertainty in the position of the particle.
7. Matter waves are probability waves because waves represent the probability of finding a particle in space.

Wave Packet

A **wave packet** refers to the case where two (or more) waves exist simultaneously. A wave packet is often referred to as a wave group. This situation is permitted by the principle of superposition. In physics, a **wave packet** (or **wave train**) is a short "burst" or "envelope" of localized wave action that travels as a unit. A wave packet can be analyzed into, or can be synthesized from, an infinite set of component sinusoidal waves of different wavenumbers, with phases and amplitudes such that they interfere constructively only over a small region of space, and destructively elsewhere. Each component wave function, and hence the wave packet, are solutions of a wave equation. Depending on the wave equation, the wave packet's profile may remain constant (no dispersion) or it may change (dispersion) while propagating.

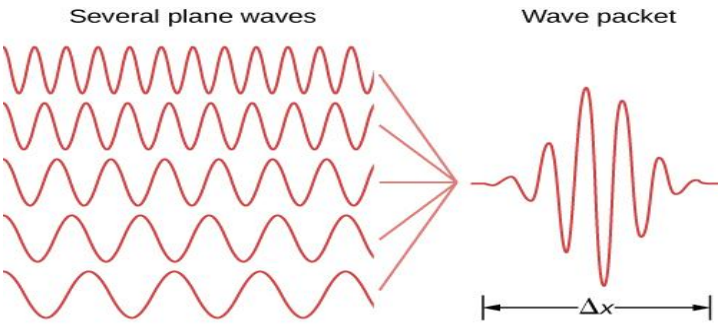
Phase velocity and Group velocity

A monochromatic wave has velocity called the **phase velocity** given by $v_p = \frac{\omega}{k} = \upsilon\lambda$ where ω is the angular frequency, $k = \frac{2\pi}{\lambda}$ is the wave number, υ is the frequency. However, if we have a compound wave(wave packet) that is composed of individual waves with a range of frequencies, each individual wave has its phase velocity, but the amplitudes of the waves add up to produce a wave packet which has a velocity all its own. This

velocity is called the **group velocity** (v_g) and is usually different from the individual phase velocities of the waves that make up the wave packet. Such a wave packet possesses both wave and particle properties. Schrodinger postulated that moving particle (electron, proton..etc) is equivalent to a wavepacket rather than a single wave. The velocity with which the resultant envelope of the group waves travels is called group velocity (v_g) and is equal to the particle velocity (v).

It is given by the expression

$$v_g = \frac{\Delta\omega}{\Delta k} = \frac{d\omega}{dk} = v$$



Schematic diagram of Wave Packet

Quantum mechanics ascribes a special significance to the wave packet; it is interpreted as probability amplitude. The modulus square of the probability amplitude describes the probability density that a particle in a particular state will be measured to have

a given position or momentum. The equation that describes the evolution of this wave packet is the Schrödinger equation. It can be Time independent or Time dependent.

Relation between group velocity and phase velocity

Consider a non-relativistic particle of mass m having v_p and v_g as the phase velocity and group velocity respectively. If λ is the de Broglie Wavelength and ν the frequency of the wave, then

$$\text{Phase velocity } v_p = \frac{\omega}{k}$$

Where ω is the angular frequency of the wave and k is the wave vector

$$\Rightarrow \omega = v_p k$$

$$\text{Group velocity } v_g = \frac{d\omega}{dk} = \frac{d(v_p k)}{dk}$$

$$= v_p + k\frac{dv_p}{dk}$$

$$= v_p + (k)\frac{dv_p}{d\lambda}\frac{d\lambda}{dk}$$

$$\text{Where } k = \frac{2\pi}{\lambda} \quad or \quad \lambda = \frac{2\pi}{k}$$

$$\text{Differentiating, } \frac{d\lambda}{dk} = \frac{d}{dk}\left(\frac{2\pi}{k}\right) = \frac{-2\pi}{k^2}$$

$$v_g = v_p + (k)\frac{dv_p}{d\lambda}\left(\frac{-2\pi}{k^2}\right)$$

$$v_g = v_p - \frac{2\pi}{k}\left(\frac{dv_p}{d\lambda}\right) \qquad \because \lambda = \frac{2\pi}{k}$$

This equation shows that $\boldsymbol{v_g}$ is less than $\boldsymbol{v_p}$, medium is dispersive. For a light wave in vaccum, there is no dispersion. Hence $dv_p / d\lambda = 0$, so that $v_g = v_p = c$. This is true for elastic waves in a homogenous medium.

Heisenberg's uncertainty principle

Heisenberg's uncertainty principle is a direct consequence of the dual nature of matter. In classical mechanics, a moving particle at any instant has a fixed position in space and a definite momentum which can be determined if the initial values are known **(we can know the future if we know the present)**

In wave mechanics a moving particle is described in terms of a wave group or wave packet. According to Max Born's probability interpretation the particle may be present anywhere inside the wave packet. When the wave packet is large, the momentum can be fixed, but there is a large uncertainty in its position. On the other hand, if the wave packet is small the position of the particle may be fixed, but the particle will spread rapidly and hence the momentum (or velocity) becomes indeterminate. In this way certainty in momentum involves uncertainty in position and

the certainty in position involves uncertainty in momentum. Hence it is impossible to know within the wave packet where the particle is and what is its exact momentum. **(We cannot know the future because we cannot know the present)**. Thus we have Heisenberg's uncertainty principle.

According to the Heisenberg's uncertainty principle *"It is impossible to specify precisely and simultaneously certain pairs of physical quantities like position and momentum that describe the behavior of an atomic system".* Qualitatively, this principle states that in any simultaneous measurement the product of the magnitudes of the uncertainties of the pairs of physical quantities is equal to or greater than $h/4\pi$ (or of the order of h)

Considering the pair of physical quantities such as position and momentum, we have

$$\Delta p \Delta x \geq h/4\pi \qquad \ldots\ldots 1$$

Where Δp and Δx are the uncertainties in determining the momentum and the position of the particle. Similarly, we have other canonical forms as

$$\Delta E \Delta t \geq h/4\pi \qquad \ldots\ldots 2$$

$$\Delta J \Delta \theta \geq h/4\pi \qquad \ldots\ldots 3$$

Where ΔE and Δt are uncertainties in determining energy and time while ΔJ and $\Delta \theta$ are uncertainties in determining angular momentum and angular position.

Illustration of Heisenberg's uncertainty principle

Broadening of spectral lines

When an atom absorbs a photon, it rises to the excited state and it will stay in the excited state for certain time called the lifetime. Lifetime of atoms in the excited levels is of the order of 10^{-8}s. When the atom comes to the ground state it emits a photon of energy exactly equal to the energy difference between the two levels as shown in the figure.

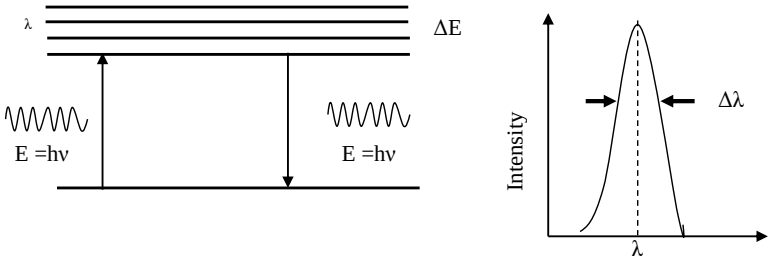


Fig. Line width for emitted photons

The energy of the emitted photon is given by

$$E = h\nu = \frac{hc}{\lambda} \quad \text{.....(1)}$$

Where h is a Planck's constant, ν is the frequency, c is the velocity of light and λ is the wavelength.

Differentiating equation (1) with respect to wavelength (λ), we get

$$\Delta E = -\frac{hc\Delta\lambda}{\lambda^2}$$

$$|\Delta E| = \frac{hc\Delta\lambda}{\lambda^2} \text{.....(2)}$$

According to Heisenberg's uncertainty principle, the finite lifetime Δt of the excited state means there will be an uncertainty in the energy of the emitted photon is given by

$$\Delta E \geq \frac{h}{4\pi\Delta t}$$

Substituting for ΔE from (2) and applying the condition of minimum uncertainty, we get

$$\frac{hc\Delta\lambda}{\lambda^2} = \frac{h}{4\pi\Delta t}$$

or $$\Delta\lambda \geq \frac{\lambda^2}{4\pi c\Delta t}$$

This shows that for a finite lifetime of the excited state, the measured value of the emitted photon wavelength will have a spread of wavelengths around the mean value λ. This uncertainty in the measured value of wavelength demands for very narrow spread, the lifetime of the excited state must be very high (of the order of 10^{-3}s). Such excited levels are called **Metastable states. This concept is adopted in the production of laser light.**

SCHRÖDINGER'S WAVE EQUATION

In1926 Schrödinger starting with de-Broglie equation ($\lambda = h/mv$) developed it into an important mathematical theory called wave mechanics which found a remarkable success in explaining the behavior of the atomic system and their interaction with electromagnetic radiation and other particles. In water waves, the quantity that varies periodically is the height of water surface. In sound waves it is pressure. In light waves, electric and magnetic fields vary. *The quantity whose variation gives matter waves is called* ***wave function (ψ).*** The value of wave function associated with a moving body at a particular point x in space at a time t is related to the likelihood of finding the body there at a time. A wave function ψ(x,t) that describes a particle with certain uncertainty in position, moving in a positive x-direction with precisely known momentum and kinetic energy may assume any one of the following forms:

Sin(ωt - kx) , cos(ωt - kx), $e^{i(\omega t - kx)}$, $e^{-i(\omega t - kx)}$ or some linear combinations of them.

Schrödinger wave equation is the wave equation of which the wave functions are the solutions. **It cannot be derived from any basic principles,** but can be arrived at, by using the de-Broglie hypothesis in conjunction with the classical wave equation.

Time Independent one dimensional Schrödinger wave equation (TISE)

In many situations the potential energy of the particle does not depend on time explicitly; the force that acts on it, and hence the potential energy vary with the position of the particle only. The Schrödinger wave equation for such a particle is time independent wave equation. Let $\psi(x,t)$ be the wave function of the matter wave associate with a particle of mass m moving with a velocity v. The differential equation of the wave motion is as follows.

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 \psi}{\partial t^2} \text{.....(1)}$$

The solution of the Eq.(1) as a periodic displacement of time t is

$$\psi(x,t) = \psi_0(x)\, e^{-i\omega t} \text{ .....(2)}$$

Where $\psi_0(x)$ is the amplitude of the matter wave.

Differentiating Eq.2 partially twice w.r.t. to t, we get

$$\frac{\partial \psi}{\partial t} = -i\omega\ \psi_0(x)\, e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = i^2\omega^2\ \psi_0(x)\, e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\omega^2\ \psi_0(x)\, e^{-i\omega t}$$

$$\frac{\partial^2 \psi}{\partial t^2} = -\ \omega^2\ \psi \text{ ……...(3)}$$

Substituting Eq.3 in Eq.1 $\frac{\partial^2 \psi}{\partial x^2} = -\frac{\omega^2}{v^2}\psi$ …(4)

We have $$\frac{\omega^2}{v^2} = k^2 = \left(\frac{2\pi}{\lambda}\right)^2 = \frac{4\pi^2}{\lambda^2}$$

Substituting this in Eq4, we get

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2}\psi \text{.....(5)}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \text{.....(6)}$$

Substituting the wavelength of the matter waves λ=h/mv in Eq.6 we get

$$\frac{\partial^2\psi}{\partial x^2} + 4\pi^2\frac{m^2v^2}{h^2}\psi = 0 \text{.....(7)}$$

If E and V are the total and potential energies of the particle respectively, then the kinetic energy of the particle

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

$$\therefore m^2v^2 = 2m(E-V)$$

Substituting this in Eq.7, we get

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

Hence ψ is a function of *x* alone and is independent of time. This equation is called the Schrödinger time- independent one dimensional wave equation.

Physical significance of the wave function

The wave function ψ(x, t) is the solution of Schrödinger wave equation. It gives a quantum-mechanically complete description of the behavior of a moving particle. The wave function ψ cannot be measured directly by any physical experiment. However, for a given ψ, knowledge of usual dynamic variables, such as position, momentum, angular momentum, etc., of the particle is obtained by performing suitable mathematical operations on it.

The most important property of ψ is that it gives a measure of the probability of finding a particle at a particular position. ψ is also called the **probability amplitude**. In general ψ is a complex quantity, whereas the probability must be real and positive. Therefore a term called probability density is defined. The **probability density P (x,t)** is a product of the wave function ψ and its complex conjugate ψ^*.

$$\therefore P(x,t) = \psi\psi^* = |\psi(x,t)|^2$$

Normalization of wave function

If ψ is a wave function associated with a particle, then $\psi^2 d\tau$ is the probability of finding the particle in a small volume dτ. If it is certain that the particle is present in a volume τ then the total probability in the volume τ is unity i.e., $\int_\tau \psi^2 d\tau = 1$. This is the normalization condition**.**

In one dimension the normalization condition is $\int_x \psi^2 dx = 1$

Note: When the particle is bound to a limited region the probability of finding the particle at infinity is zero i.e., $\psi\psi^*$ at $x = \infty$ is zero.

Properties of wave function:

The wave function ψ should satisfy the following properties to describe the characteristics of matter waves.

1.ψ must be a solution of Schrödinger wave equation.

2.The wave function ψ should be continuous and single valued everywhere. Because it is related to the probability of finding a particle at a given position at a given time, which will have only one value.

3.The first derivative of ψ with respect to x should be continuous and single valued everywhere, since it is related to the momentum of the particle which should be finite.

4.Ψ must be normalized so that ψ must go to 0 as $x \to \pm\infty$, so that $\int \psi^2 d\tau$ over all the space be a finite constant.

Eigen functions and Eigen values

The Schrödinger wave equation is a second order partial differential equation; it will have many mathematically possible solutions (ψ). All mathematically possible solutions are not physically acceptable solutions. The physically acceptable solutions are called **Eigen functions (ψ).**

The physically acceptable wave functions ψ has to satisfy the following conditions:

1. ψ is single valued.
2. ψ and its first derivative with respect to its variable are continuous everywhere.
3. ψ is finite everywhere.

Once the Eigen functions are known, they can be used in Schrödinger wave equation to evaluate the physically measurable quantities like energy, momentum, etc., these values are called Eigen values.

In an operator equation $\hat{O}\psi = \lambda\psi$ where $\hat{O}$ is an operator for the physical quantity and ψ is an Eigen function and λ is the Eigen value. For example :

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

Where H is the total energy (Hamiltonian) operator, ψ is the Eigen function and E is the total energy in the system. We can have similar equations for the momentum

$$\hat{P}\psi = p\psi$$

Where P is the momentum operator and p denotes the momentum eigen values. Another example would be :

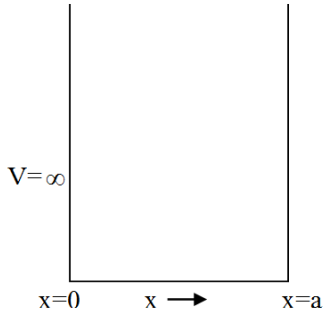
$$\hat{L}_z\psi = m\hbar\psi$$

Where L_z is the z-component of angular momentum operator and m is the azimuthal quantum number.

Applications of Schrodinger's wave equation

1. For a Particle in an one-dimensional potential well of infinite depth (Particle in a box)

Consider a particle of mass 'm' moving freely in x- direction in the region from x=0 to x=a. Outside this region potential energy 'V' is infinity and within this region V=0. Outside the box Schrodinger's wave equation is



$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-\infty)\Psi=0.....(1)$$

This equation holds good only if ψ =0 for all points outside the box i.e., $|\Psi|^2=0$, which means that the particle cannot be found at all outside the box. Inside the box V = 0, hence the Schrodinger's equation is given by,

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}E\Psi=0$$

$$\frac{\partial^2\Psi}{\partial x^2}+k^2\Psi=0.....(2)$$

where, $k^2=\frac{8m\pi^2 E}{h^2}$.....(3)

Discussion of the solution

The solution of the above equation 2 is given by

$$\Psi = A\cos kx + B\sin kx \text{.....(4)}$$

Where A & B are constants which depending on the boundary conditions of the well.

Now apply boundary conditions for this,

Condition: I at x =0, $\psi = 0$.

Substituting the condition I in the equation 4, we get A =0 and $B \neq 0$. (If B is also zero for all values of x, ψ is zero. This means that the particle is not present in the well.)

Now the equation 4 can be written as $\Psi = B\sin kx$.....(5)

Condition: II at x =a, $\psi = 0$

Substituting the condition II in equation 5 we get

$0 = B \sin(ka)$

Since $B \neq 0$,

$\sin ka = 0$

$\therefore ka = n\pi$ where,n= 1,2,3…….

$$k = \frac{n\pi}{a}$$

$$k^2 = \frac{n^2\pi^2}{a^2}$$

Substitute the value of k^2 in equation (3).

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

$$E = \frac{n^2 h^2}{8ma^2} \text{.....(6)}$$

The equation (6) gives energy values or Eigen value of the particle in the well. When n=0, $\psi_n = 0$. This means to say that the electron is not present inside the box, which is not true. Hence the lowest value of 'n' is 1.

$\therefore$ The lowest energy corresponds to 'n'=1 is called the zero-point energy or Ground state energy.

$$E_{zero-point} = \frac{h^2}{8ma^2}$$

All the states of n > 1 are called excited states.

To evaluate B in equation (3), one has to perform normalization of wave function.

Normalization of wave function:

Consider the equation, $\psi = B\sin kx = \text{B}\sin\frac{\text{n}\pi}{\text{a}}x$

The integral of the wave function over the entire space in the box must be equal to unity because there is only one particle within the box, the probability of finding the particle is 1.

$$\int_0^a |\Psi|^2 dx = 1$$

$$B^2 \int_0^a \sin^2 \frac{n\pi}{a} x dx = 1$$

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

$$\frac{B^2}{2} \int_0^a \left(1 - \cos \frac{2n\pi x}{a}\right) dx = 1`$$

$$\frac{B^2}{2} \left[\int_0^a dx - \int_0^a \cos \frac{2n\pi x}{a} dx\right] = 1$$

$$\frac{B^2}{2} \left[x - \frac{a}{2n\pi} \sin\left(\frac{2n\pi x}{a}\right)\right]_0^a = 1$$

$$\frac{B^2}{2} \left[a - \frac{a}{2n\pi} \sin 2n\pi - 0\right] = 1$$

$$\therefore \frac{B^2 a}{2} = 1$$

$$\therefore B = \sqrt{2/a}$$

Thus the normalized wave function of a particle in a one-dimensional box is given by,

$$\Psi_n = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}\right) x \quad \text{where, n=1,2,3……}$$

This equation gives the Eigen functions of the particle in the box.

The Eigen functions for n=1,2,3.. are as follows.

$$\Psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right)x$$

$$\Psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}\right)x$$

$$\Psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}\right)x$$

Since the particle in a box is a quantum mechanical problem we need to evaluate the most probable location of the particle in a box and its energies at different permitted state.

Let us consider the three lowest energy solutions:

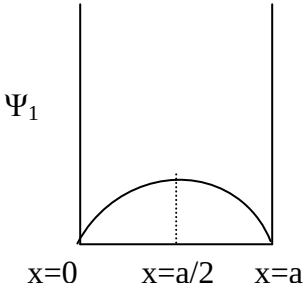
Case (1): n=1

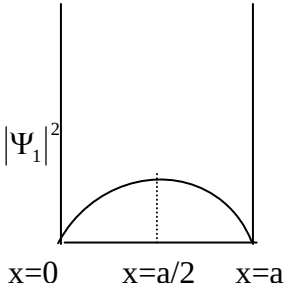
This is the ground state and the particle is normally found in this state. For n=1, the Eigen function is

$$\Psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right)x$$

In the above equation $\Psi = 0$ for both x=0 & x=a. But Ψ_1 has a maximum value for x=a/2.

$$\Psi_1 = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}\right)\frac{a}{2} = \sqrt{\frac{2}{a}} \quad \text{and} \quad \psi_1^2 = \frac{2}{a}$$





A plot of $|\Psi_1|^2$ the probability density versus 'x' is as shown. From the figure, it indicates the probability of finding the particle at different locations inside the box.

$\therefore$ $|\Psi_1|^2 = 0$ at x = 0 and x = a, also $|\Psi_1|^2$ is maximum at x = (a/2).

This means that in the ground state the particle cannot be found at the walls of the box and the probability of finding the particle is maximum at the central region. The Energy in the ground state is given by $E_1 = \frac{h^2}{8ma^2}$.

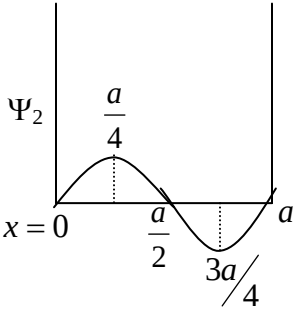
Case (2): n=2

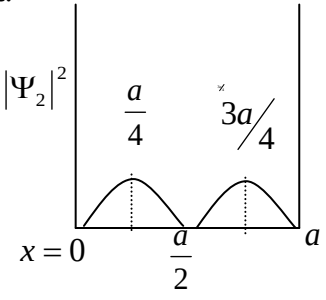
This is the first excited state. The Eigen function for this state is given by $\Psi_2 = \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi}{a}\right)x$

Now, $\Psi_2 = 0$ for the values $x = 0, a/2$ and a

and Ψ_2 reaches maximum for the values $x = a/4, 3a/4$

These facts are seen in the following plot.





From the figure it can be seen that

$|\Psi_2|^2 = 0$ at x = 0, $a/2, a$ and $|\Psi_2|^2 = 2/a$ at $x = a/4, 3a/4$

This means that in the first excited state the particle cannot be observed either at the walls or at the center. The energy is $E_2 = 4E_1$.

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

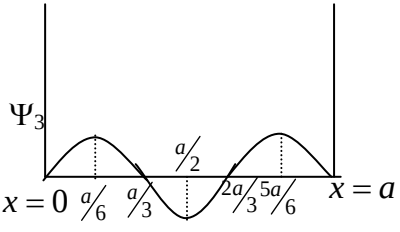
Case 3: n =3.

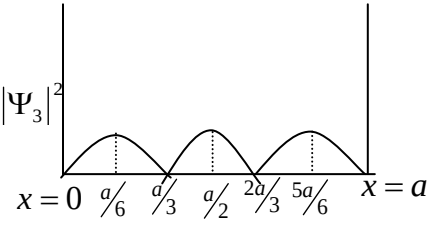
This is the second excited state and the Eigen function for this state is given by

$$\Psi_3 = \sqrt{\frac{2}{a}} \sin\left(\frac{3\pi}{a}\right)x$$

Now, Ψ_3 =0 for the values $x = 0, a/3, 2a/3, a$

and Ψ_2 reaches maximum $\sqrt{\frac{2}{a}}$ at $x = a/6, a/2, 5a/6$





$|\Psi_3|^2$ =0 for the values $x = 0, a/3, 2a/3, a$ and

$|\Psi_3|^2$ reaches maximum 2/a at $x = a/6, a/2, 5a/6$

at which the particle is most likely to be found.

The energy corresponds to second excited state is given by $E_3 = 9E_1$.

2. Free Particle:

Free particle means, it is not under the influence of any kind of field or force. Thus, it has zero potential, i.e., V=0 over the entire space. Hence Schrodinger's equation becomes,

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\Psi = 0$$

$$-\frac{h}{8\pi^2 m}\left(\frac{\partial^2\Psi}{\partial x^2}\right) = E\psi$$

The above equation holds good for a particle for which the potential V=0 over the entire space (no boundaries at all).

Since, for a free particle, V=0 holds good everywhere, we can extend the case of particle in an infinite potential well to the free particle case, by treating the width of the well to be infinity, i.e., by allowing a = ∞.

We have the equation for energy Eigen values for a particle in an infinite potential well as, $E = \frac{n^2h^2}{8ma^2}$. Where n = 1, 2, 3…

Rearranging, we have, $$n = \frac{2a}{h}\sqrt{2Em}$$

Here, we see that, for a particle with constant energy E but confined in the well 'n' depends solely on 'a'. In the limiting case when a $=\infty$, it also follows that n $=\infty$, which essentially means that free particle can have any energy Eigen values or possible values of energy are infinite in number. Hence as, a $\rightarrow\infty$, n $\rightarrow\infty$. Keeping in mind the energy level representation, we say that the permitted energy values are continuous not discrete.

UNIT II – QUANTUM MECHANICS

Q.No	Sample Questions	CO
1.	State De Broglie hypothesis.	**1**
2.	What is wave function? Give its physical significance and properties.	**1**
3.	State Heisenberg's uncertainty principle. By applying Heisenberg's uncertainty principle, illustrate the broadening of spectral lines.	**1&2**
4.	What are Eigen functions and Eigen values ?	**1**
5.	Setup time independent one-dimensional Schrodinger's wave equation for a matter wave.	**1**
6.	Apply the time independent Schrodinger's wave equation to find the solutions for a particle in an infinite potential well of width 'a'. Hence obtain normalized wave function.	**1&2**
7	Solve the Schrodinger's wave equation for a free particle.	**1&2**
8	Set up the differential equation for a particle in a 1D well of finite depth and arrive at an Eigen Value expression.	**2**

PNo.	Problems	CO
1.	Calculate the de Broglie wavelength associated with a proton moving with a velocity equal to $(1/20)^{th}$ of the velocity of light. **To be found**: de Broglie wavelength, λ **Solution:** $\lambda = \frac{h}{mv} = \frac{6.625\times10^{-34}}{1.67\times10^{-27}\times(1/20)\times3\times10^{8}} = 2.64\times10^{-14}\,m$	3
2.	An electron and a proton are accelerated through the same potential difference. Find the ratio of their de Broglie wavelengths. **To be found:** Ratio of de Broglie wavelength, λ **Solution:** **De Broglie Wavelength, λ** $\lambda = \frac{h}{\sqrt{2mE}}$, $\therefore \lambda \alpha \frac{1}{\sqrt{m}}$ **For electron,** $\lambda_e \alpha \frac{1}{\sqrt{m_e}}$ **For proton,** $\lambda_p \alpha \frac{1}{\sqrt{m_p}}$ **Ratio of De Broglie Wavelengths,** $\therefore \frac{\lambda_e}{\lambda_p} = \frac{\sqrt{m_p}}{\sqrt{m_e}}$	3

3.	Compare the energy of a photon with that of a neutron when both are associated with wavelength of $1A^o$. Given that the mass of neutron is 1.67×10^{-27}kg. **To be found**: Comparison of energy of photon with that of neutron **Solution:** **Energy of neutron**, $E_n = \frac{P^2}{2m} = \frac{h^2}{2\lambda^2 m} = \frac{(6.625\times10^{-34})^2}{2\times(1\times10^{-10})^2\times1.67\times10^{-27}} = 13.1\times10^{-21} J$ $=0.082$eV **Energy of photon**, $E_p = \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3\times10^8}{1\times10^{-10}} = 19.89\times10^{-16} J$ $=12421.9$eV **Ratio of energies**, $\frac{E_p}{E_n} = 1.5148\times10^5$	3
4.	An electron has a speed of 4.8 x 10^5 m/s accurate to 0.012 %. With what accuracy with which its position can be located. **To be found**: Uncertainty in position, Δx **Solution:** **Uncertainty principle** is given by, $\Delta x \Delta p \geq \frac{h}{4\pi}$	3

	Uncertainty in speed, $\Delta v = 4.8 \times 10^5 \times \frac{0.012}{100} = 57.6 m/s$ **Uncertainty in position**, $\Delta x = \frac{h}{4\pi m \Delta v} = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 57.6} = 1 \times 10^{-6} m$	
5.	The inherent uncertainty in the measurement of time spent by Iridium-191 nuclei in the excited state is found to be 1.4×10^{-10} s. Estimate the uncertainty that results in its energy in the excited state. **To be found**: Uncertainty in energy, ΔE **Solution: Uncertainty principle** is given by, $\Delta E \Delta t \geq \frac{h}{4\pi}$ $\therefore \Delta E \geq \frac{h}{4\pi \Delta t} \geq \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 1.4 \times 10^{-10}} \geq 3.77 \times 10^{-25} J$	3
6.	The position and momentum of 1 keV electron are simultaneously determined and if its position is located within 1Å. What is the percentage of uncertainty in its momentum? **To be found**: Percentage of uncertainty in momentum of electron, Δp	3

	Solution: Uncertainty principle is given by, $\Delta x \Delta p \geq \frac{h}{4\pi}$ **Uncertainty in momentum**, $\Delta p = \frac{h}{4\pi \Delta x} = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 1 \times 10^{-10}} = 0.53 \times 10^{-24} kg.m/s$ **Momentum**, $p = \sqrt{2mE} = \sqrt{2 \times 9.1 \times 10^{-31} \times 1 \times 10^{-16}} = 1.707 \times 10^{-23} kgm/s$ **Percentage of uncertainty in momentum of electron**, $\frac{\Delta p}{p} \times 100 = 3.1$	
7.	Show that the energy Eigen value of a particle in second excited state is equal to 9 times the zero point energy. **To be found: E**nergy Eigen value for second excited state is equal to 9 times the zero point energy. **Solution: Energy Eigen value equation is given by,** $E = \frac{n^2 h^2}{8ma^2}$ **n=1, zero-point energy state,** $E_1 = \frac{h^2}{8ma^2}$ **n=3, second excited state,** $E_3 = \frac{9h^2}{8ma^2} = 9E_1$	3

8.	An electron is bound in a one-dimensional potential well of width 1Å, but of infinite height. Find the energy value for the electron in the ground state. **To be found:** Energy Eigen value **Solution:** Energy Eigen value equation is given by**,** $E = \frac{n^2 h^2}{8ma^2}$ **For n=1, ground state energy**, $E_1 = \frac{\left(6.625\times10^{-34}\right)^2}{8\times9.1\times10^{-31}\times\left(10^{-10}\right)^2} = 37.65eV$	3
9.	An electron is bound in one dimensional potential well of infinite potential of width 0.12 nm. Find the energy values in the ground state and also the first two exited state. **To be found:** Energy Eigen value **Solution:** Energy Eigen value equation is given by**,** $E = \frac{n^2 h^2}{8ma^2}$ **For n=1, ground state energy**,	3

	$E_1 = \frac{\left(6.625\times10^{-34}\right)^2}{8\times9.1\times10^{-31}\times\left(0.12\times10^{-9}\right)^2} = 26.16eV$ **For n=2 and 3,first and second excited state,** $E_2 = 4E_1 = 104.61eV \quad E_3 = 9E_1 = 235.44eV$	
10.	An electron is trapped in a potential well of a width 0.5nm. If a transition takes place from the first excited state to the ground state find the wavelength of the photon emitted. **To be found**: Wavelength of the photon emitted, λ **Solution:** For n=1, ground state energy, $E_1 = \frac{\left(6.625\times10^{-34}\right)^2}{8\times9.1\times10^{-31}\times\left(0.5\times10^{-9}\right)^2} = 2.41\times10^{-19}J = 1.507eV$ For n=2,first excited state, $E_2 = 4E_1 = 9.64\times10^{-19}J = 6.025eV$ Energy difference, $\Delta E = E_2 - E_1 = 7.23\times10^{-19}J = 4.518eV$ W**avelength of the photon emitted** , $\lambda = \frac{hc}{\Delta E} = \frac{6.625\times10^{-34}\times3\times10^8}{7.23\times10^{-19}J} = 274.8nm$	3

Things to think about! (CO3)

1. Taking Planck's law as the starting point derive Rayleigh – Jeans law in the limit of high λ.
2. How can we naturally reconcile the dual Wave and Particle nature of matter ?
3. Is there any connection between the position – momentum and energy-time uncertainty relationship? Discuss.
4. Is the derivation for particle in a box done above valid for highly energetic relativistic particles ? Discuss.
5. With respect to the particle in a box problem, find out what is tunneling. What is its utility in different engineering domains?