UNIT II

QUANTUM MECHANICS

Wave particle dualism:

It is bit difficult to conceive the idea of conception of dual nature of matter. i.e., matter behaves as both particle and wave nature.

The characteristics of a particle are: it has a mass, it occupies a definite point on a space, it can move from one point to another point. So it has momentum. Thus the particles can be specified by

a) mass b) velocity c) momentum d) energy and e) two particles cannot occupy a single space simultaneously. A wave is specified by

a) wavelength b) frequency c) amplitude d) Intensity and e) phase

Thus the characteristics of particles are quite different from those of wave. But from the experimental facts it has been established that the radiations such as light some time behave as wave and some time as a particle.

To explain the phenomenon such as interference, diffraction, etc. a radiation should behave as wave. To explain photoelectric effect, Compton Effect, etc. the radiation should behave as particle (photon).

Thus radiation has dual nature. But it is to be noted that the radiation cannot exhibit both the properties of particle and wave simultaneously.

De Broglie's concept of matter wave:

The origin of quantization of energy lies in the dual behavior observed in nature in particle and wave aspects. Consider x – rays, Compton observed that the scattering of x – rays by electron is the confirmation of law of conservation of energy and it is a case of elastic collision of two particles. So from the physics point of view, x – rays assumes the status of a particle. Also x – rays are diffracted by a crystal. Since diffraction is a wave phenomenon, x – rays behaves as waves. Because of this dual nature of radiation, Louis de Broglie in 1924, given an hypothesis which states that "since nature likes symmetry, if the radiation behaves as particle under certain circumstances, and as waves under certain other circumstances, then one can even expect that entities which ordinarily behave as particles to exhibit properties attributable to only waves under appropriate circumstances and he termed them as matter waves”.

Energy carried by a photon is given by, $E=h\upsilon$
From Einstein’s mass energy relation, $E=mc^2$

Therefore $mc^2=h\upsilon$

$mc=\frac{h\upsilon}{c}$ or

$p=\frac{h\upsilon}{c}$ (as $c=\upsilon\lambda$)

in terms of wavelength λ,

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

Wavelength of a photon is related to its momentum

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

de Broglie argued that, since nature loves symmetry the particles should also behave as waves. As per the above equation wavelength is related to momentum. In similar way, if $p=mv$ is the momentum of the particle, the de Broglie wavelength associated with it is given by

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

These waves which are due to particles are called matter waves or de Broglie waves.

De Broglie wavelength of an accelerated electron:

If the electron accelerated under the potential difference V, then its energy is eV. If m is the mass of the electron and v is its velocity then for non relativistic case,

$$\frac{1}{2}mv^2=eV \qquad \Rightarrow v=\sqrt{\frac{2eV}{m}}$$

Following the de Broglie hypothesis,

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2eV}{m}}}$$

So, $$\lambda = \frac{h}{\sqrt{2meV}}$$

Which can be written as,

$$\lambda = \frac{1}{\sqrt{V}}\left(\frac{h}{\sqrt{2me}}\right)$$

Substituting all the values,

i.e., $$\lambda = \frac{1}{\sqrt{V}}\left(\frac{6.63x10^{-34}}{\sqrt{2x9.11x10^{-31}x1.6x10^{-19}}}\right)$$

$$\lambda = \frac{1.226x10^{-9}}{\sqrt{V}}\ m \qquad \text{OR} \qquad \lambda = \frac{12.26}{\sqrt{V}}\ \text{Å}$$

Relation between kinetic energy and de Broglie wavelength:

Since Kinetic energy of an electron is given by $E = \frac{1}{2}mv^2$

So E = eV

$$\therefore \lambda = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mE}} \qquad \text{OR} \qquad \lambda = \frac{h}{\sqrt{2mE}}$$

Phase velocity:

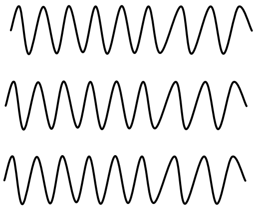
v = $\frac{\omega}{k}$ is the velocity with which the wave disturbance is carried and is referred to as phase velocity. Hence phase velocity is written as

$$v_{phase} = \frac{\omega}{k}$$

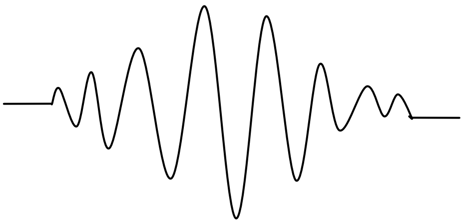
Definition: If a point is imagined to be marked on a traveling wave, then it becomes a representative point for a particular phase of the wave, and the velocity with which it is transported owing to the motion of the wave, is called phase velocity.

Group velocity:

Group velocity is the velocity with which the envelop enclosing a wave group called wave packet formed due to superimposition of two or more traveling waves of slightly different wavelengths is transported or it is the velocity with which the energy transmission occurs in a wave packet.



a) Individual Waves



b) Amplitude variation after Superposition

The velocity with which the variation in amplitude is transmitted in the resultant wave is called group velocity and is given by

$$v_{group} = \frac{d\omega}{dk}$$

Relation between v_{group} and v_{phase} :

We have the equations for group velocity and phase velocity as

$$v_{group} = \frac{d\omega}{dk} \quad \text{---------------------} \quad (1)$$

$$v_{phase} = \frac{\omega}{k} \quad \text{--------------------} \quad (2)$$

Where ω – angular frequency, K – wave vector,

From (2), $\omega = k \, . \, v_{phase}$

$$v_{group} = \frac{d\omega}{dk} = \frac{d\,(k.v_{phase})}{dk}$$

$$v_{group} = v_{phase} + k..\frac{dv_{phase}}{dk}$$

Above equation can be written as

$$v_{group} = v_{phase} + k\left(\frac{dv_{phase}}{d\lambda}\right)\left(\frac{d\lambda}{dk}\right) \text{ ------------------------ (3)}$$

We know that, $k = \frac{2\pi}{\lambda}$, $\because k = \frac{\omega}{v} = \frac{2\pi f}{f\lambda} = \frac{2\pi}{\lambda}$

Differentiate w.r.t. λ, we get

$$\therefore \quad \frac{dk}{d\lambda} = -\frac{2\pi}{\lambda^2} \quad or \quad \frac{d\lambda}{dk} = -\frac{\lambda^2}{2\pi}$$

$$\therefore \quad k\left(\frac{d\lambda}{dk}\right) = \left(\frac{2\pi}{\lambda}\right).\left(\frac{-\lambda^2}{2\pi}\right) = -\lambda \text{ ------------------------- (4)}$$

Use equation (4) in above equation

$$v_{group} = v_{phase} - \lambda\left(\frac{dv_{phase}}{d\lambda}\right)$$

This is the relation between group velocity and phase velocity.

Relation between v_{group} and $v_{particle}$:

We know that, $v_{group} = \frac{d\omega}{dk}$ --------------------- (1)

But $\omega = 2\pi\gamma = 2\pi\frac{E}{h}$ --------------------- (2) (since E = hγ)

$\therefore$ $d\omega = \frac{2\pi}{h}dE$ -------------------- (3)

Also, we have k = $\frac{2\pi}{\lambda} = 2\pi\frac{P}{h}$ (since λ = $\frac{h}{P}$)

∴ dk = $\left(\frac{2\pi}{h}\right)dP$ ------------------ (4)

Equation (3) divided by equation (4)

$$\frac{d\omega}{dk} = \frac{dE}{dP} \qquad \text{----------------- (5)}$$

We know that E = $\frac{P^2}{2m}$

where P → momentum of a particle

∴ dE = $\frac{2P\,dP}{2m} = \frac{P}{m}.dp$ or $\frac{dE}{dp} = \frac{P}{m}$

but P = m v $_{\text{particle}}$

$$\therefore \quad \frac{dE}{dp} = \frac{mv_{particle}}{m} = v_{particle} \quad \text{-------------------- (6)}$$

From equations (1), (5) and (6) we have

$$v_{\text{group}} = v_{\text{particle}}$$

∴ The de Broglie wave group associated with a particle travels with a velocity equal to the velocity of the particle itself.

Relation between velocity of light, v_{group} and v_{phase}:

We know, $v_{\text{phase}} = \frac{\omega}{k}$

Substitute ω = 2πγ = 2π$\frac{E}{h}$ and k = $\frac{2\pi}{\lambda} = 2\pi\frac{P}{h}$

$$\therefore \quad v_{\text{phase}} = \frac{2\pi\, E/h}{2\pi\, P/h} = \frac{E}{P} = \frac{mc^2}{m\,v_{particle}} \qquad \because v_{\text{group}} = v_{\text{particle}}$$

$$v_{phase} = \frac{c^2}{v_{group}}$$

$$\therefore\ v_{phase} \cdot v_{group} = c^2$$

Particle velocity is always less than 'c', $\Rightarrow$ the phase velocity is always greater than 'c'

Matter waves:

All matter can exhibit wave-like behavior. For ex. A beam of electrons can be diffracted just like a beam of light. Matter waves are a central part of the theory of quantum mechanics, an example of wave-particle duality. Matter waves are often referred to as de Broglie waves.

Wave-like behavior of matter was first experimentally demonstrated in the Davisson-Germer experiment using electrons, and it has also been confirmed for other elementary particles, neutral atoms and even molecules. The wave-like behavior of matter is crucial to the modern theory of atomic structure and particle physics.

Characteristics of matter waves:

The characteristics of matter waves are

i) Matter waves are the waves that are associated with a moving particle. The wavelength and frequency of the waves are

ii) $\lambda = \frac{h}{p}$ *and* $\gamma = \frac{E}{h}$ where 'h' is planck's constant.

iii) The velocity of matter waves is not constant and it depends only on the material particle.

iv) The relation, $\lambda = \frac{h}{p} = \frac{h}{mv}$, shows that the wavelength of matter waves is larger for a lighter particle and the wavelength increases with the decrease in velocity of the particle.

v) The particle and the wave properties of a moving particle never appear simultaneously. One can say that the particle has wave-like property and the wave has particle-like property. These two properties are liked in such a way that they are inseparable.

vi) 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.

vii) The wave velocity or the phase velocity of the matter wave are given by

$$v_{phase} = \frac{c^2}{v_{group}}$$

where, v_{group} is the particle velocity which is always less than ‘c’. Thus the velocity of the matter waves is always greater than ‘c’, i.e., they are not physical waves.

viii) Unlike any electromagnetic waves, which always travel with a constant velocity c, the wave velocity of different matter waves may differ depending on the mass and velocity of the particle.

Heisenberg’s Uncertainty Principle:

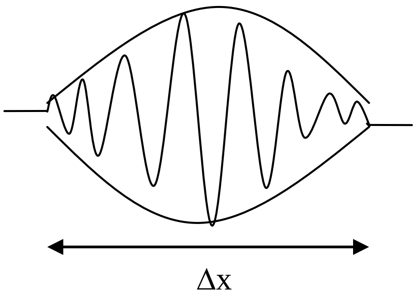
According to de Broglie, a particle can be considered as a group or packet of waves. As this wave packet is spread in space, we cannot accurately find the position of a particle. It can only said that, the particle is somewhere within the region over which the wave packet is spread.

Let the motion of the particle be along x – axis. Let Δx is the distance at which the amplitude is zero and corresponding points are called nodes. There will be a minimum error ‘Δx’ in the measurement of the position of the particle. This is inevitable due to the wave nature of matter.

The amplitude of the wave packet is given by $2A\cos\left[(\frac{\Delta\omega}{2})t - (\frac{\Delta k}{2})x\right]$

At nodes, the amplitude is zero.

i.e., $$2A\cos\left[(\frac{\Delta\omega}{2})\, t - (\frac{\Delta k}{2})x\right] = 0$$



since 2A $\neq$0, $\Rightarrow \cos\left[(\frac{\Delta\omega}{2})t-(\frac{\Delta k}{2})x\right]=0$

or $(\frac{\Delta\omega}{2})t-(\frac{\Delta k}{2})x=\frac{\pi}{2},\frac{3\pi}{2},.............(2n+1)\frac{\pi}{2}$

If x_1 and x_2 are the positions at which the nodes are formed, then for the first node.

$$(\frac{\Delta\omega}{2})t-(\frac{\Delta k}{2})x_1=(2n+1)\frac{\pi}{2} \text{ ------------------------- (1)}$$

Since, there is a change of phase π, between the successive nodes, the eaquation for the second node is,

$$(\frac{\Delta\omega}{2})t-(\frac{\Delta k}{2})x_2=(2n+1)\frac{\pi}{2}+\pi \text{ --------------------- (2)}$$

Subtracting equation (1) from equation (2), we get

$$\frac{\Delta k}{2}(x_1-x_2)=\pi \qquad \sin ce\ \ x_1-x_2=\Delta x$$

$$\frac{\Delta k}{2}(\Delta x)=\pi \quad or \quad \Delta x=\frac{2\pi}{\Delta k} \text{ ----------------------- (3)}$$

we know that, k = $\frac{2\pi}{\lambda}=\frac{2\pi P_x}{h}$ $or\ \ \Delta k=\frac{2\pi(\Delta P_x)}{h}$ ----------------- (4)

where ΔP_x represents the fundamental error in the measurement of momentum of the particle.

Substitute equation (4) in equation (3), we get

$$\Delta x=\frac{h}{\Delta P_x}$$

This is the case of superposition of two waves. In general if there are more than two waves.

$$\Delta x=\frac{1/2}{\Delta k} \text{ ---------------- (5)}$$

Substitute equation (4) in equation (5)

$$\Delta x=\frac{h}{4\pi(\Delta P_x)}$$

or $$\Delta x.\Delta P_x=\frac{h}{4\pi} \text{----------------(6)}$$

The fundamental error in ‘x’ and ‘P_x’ could be equal to, or greater them Δx and ΔP_x respectively, then equation (6) can be written as

$$\Delta x \,.\, \Delta P_x \geq \frac{h}{4\pi} \text{----------------(7)}$$

Statement:

"In any simultaneous determination of the position and momentum of the particle, the product of the corresponding uncertainties inherently present in the measurement is equal to, or greater than $(\frac{h}{4\pi})$ " OR

"It is impossible to measure both the position and momentum of a particle simultaneously and accurately"

The Heisenberg's uncertainty principle could also be expressed in terms of the uncertainties involved in the measurement of physical variables-pair, angular displacement (θ) and angular momentum (L) etc.

Thus, we have the uncertainty relations,

$$\Delta x \, \Delta Px \geq (\frac{h}{4\pi})$$

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

$$\Delta L \, \Delta \theta \geq (\frac{h}{4\pi})$$

Where, the notation Δ in association with the respective variables indicates the minimum uncertainty involved in the measurement of the corresponding variable.

Physical significance of Heisenberg Uncertainty principle:

By knowing the particle position and momentum at any given instant of time, it is possible to evaluate it position and momentum at any later point of time, and the trajectory of the particle could be continuously traced. But in wave mechanics it is impossible to determine simultaneously both the position and momentum of a particle accurately. Suppose if we made the measurement of position of the particle such as electron very accurately, then there is a large uncertainty in the measurement of momentum, and vice versa. So one should not think the exact position or an accurate value for momentum of a particle. Instead one should think of the **probability** of finding the particle at a certain position or of the **probable** value for the momentum of the particle.

Application of Heisenberg Uncertainty principle

Non - existence of electron in the nucleus:

We know that from Heisenberg's uncertainty

$$\Delta x \,.\, \Delta Px \geq \frac{h}{4\pi} \qquad \text{-------------------------- (1)}$$

We know that the diameter of the nucleus is of the order of 10^{-14} m. if suppose the electron exists inside the nucleus, then uncertainty in its position Δx must not be more than the size of the nucleus.

i.e., $\Delta x \leq 10^{-14}$ m

Then, the uncertainty in its momentum is

$$\Delta Px \geq \frac{h}{4\pi.\Delta x} = \frac{6.625\ x10^{-34}}{4\pi\ x10^{-14}}$$

$$\Delta Px \geq 0.5\ x10^{-20}\ Ns \qquad \text{---------------------- (2)}$$

We know the energy momentum relation as

$$E^2 = P^2c^2 + m_o^2c^4 \qquad \text{---------------------- (3)}$$

From theory of relativity, the energy, E of a body is

[Ref: $E = mc^2$ So $E^2 = m^2c^4$

$P = mv$ So $P^2 = m^2v^2$ But $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$

We get $E^2 - P^2c^2 = m_o^2c^4$]

Rest mass of electron $m_o = 9.11 \text{ x } 10^{-31}$ kg

Substitute all the values of equation (3)

$$E^2 \geq (0.5 \text{ x } 10^{-20})^2\ (3 \text{ x } 10^8)^2 + (9.11 \text{ x } 10^{-31})^2 \text{ x } (3 \text{ x } 10^8)^4$$

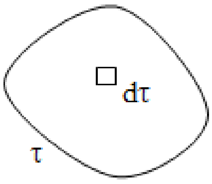
$$E^2 \geq 1.5 \text{ x } 10^{-12} \text{ J}$$

or $E \geq 9.4$ MeV

If electron exist inside the nucleus, its energy must be greater than 9.4 MeV. But the experimental investigation on beta – decay says, the K E of the electron is of the order of 3 to 4 MeV. This clearly indicates that, electrons cannot exist within the nucleus.

Physical interpretation of the wave function (ψ):

In classical mechanics, I α A^2, where I is the intensity of radiation and 'A' is the amplitude of radiation. Similar interpretation is applied to de Broglie waves, associated with electron or any particle. Hence if we consider a system of electrons and ψ is the wave function associated with electron or any particle, then $|\psi^2|$ may be regarded as a measure of density of electrons.



Consider a volume τ, inside which an electron is known to present, but where exactly the electron is situated inside τ is not known. If ψ is the wave function associated with the electron, then the probability of finding the electron in a certain element of volume dτ of τ is equal to $|\psi|^2 d\tau$. For this reason $|\psi|^2$ is called the probability function. This is the interpretation given by Max Born in 1926.

Probability of occurrence of an event is a real and positive quantity. But wave functions may be complex. Hence, in order to get a value that is positive and real while evaluating $|\psi|^2$, the wave function ψ is multiplied with its complex conjugate ψ *. The product $\psi * \psi$ is always a positive real quantity.

$\therefore$ Probability density is given by, $|\psi|^2 = \psi * \psi$.

Normalization of wave function (ψ):

Since the electron must be somewhere inside the volume τ, then the integration of $|\psi|^2$ over the whole volume τ must be unity, so that

$$\int |\psi|^2 . d\tau = 1$$

Above condition is called Normalization of wave function.

Every solution of Schrodinger's wave equation should be normalizable.

Properties of wave function (ψ):

The wave function ψ should obey few conditions to be a solution of Schrodinger's wave equation. The conditions are:

1. ψ should be continuous.
2. ψ should be single valued, and
3. derivatives of ψ, i.e. $\frac{d\psi}{dx}$ should also be continuous.
4. For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi^*\psi$ must vanish at infinity.

The ψ which satisfy the above conditions are acceptable solutions of Schrodinger's wave equation.

Schrödinger equation

The wave function in quantum mechanics accounts for the wave-like properties of a particle. It is obtained by solving a fundamental equation called Schrödinger equation. The response of the wave properties of a particle to an external force follows a basic of quantum mechanics that, in its mathematical form, is known as the Schrödinger equation.

To solve the Schrödinger equation it requires the knowledge of,

(1) Potential energy of the particle

(2) Initial conditions and

(3) Boundary conditions

The Schrödinger equation can be set up in two different contexts. One, which in general takes care of both the position and time variations of the wave function, is called time dependent Schrödinger equation. It involves the imaginary quantity, 'i'. The other one is applicable only to steady state conditions in which case, the wave function can have variation only with position but not with time. It is called time-dependent Schrödinger equation and is simpler than the other one. It does not involve, 'i'.

The time dependent Schrödinger equation is given by,

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}+V\psi=-\frac{ih}{2\pi}\frac{d\psi}{dt}$$

The time independent Schrödinger equation is given by,

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

Time independent Schrödinger wave equation:

Schrödinger in 1925 developed an equation for the wave associated with the material particles like electron, proton, neutron, etc. which would describe the behavior of the particles. He used de Broglie ideas of matter waves.

A wave eqn. for a de Broglie wave is given by

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

Differentiating twice eqn.(1) with respect to t we get

$$\frac{\partial^2\psi}{\partial t^2} = -\,\omega^2\left[A\, e^{i(kx-\omega t)}\right]$$

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

Displacement 'y' of a wave is given by *y = A sin[ωt-kx]-------(A)*

Differentiating twice w.r.t 't' we get $\frac{\partial^2 y}{\partial t^2} = -\,\omega^2 y$*----------(B)*

Similarly differentiating twice w.r.t 'x' we get

$$\frac{\partial^2 y}{\partial x^2} = -\,k^2 y = -\left(\frac{\omega}{v}\right)^2 y = -\left(\frac{1}{v}\right)^2 \omega^2 y \text{ ----}(C)$$

Comparing eqns (B) & (C) we get $\frac{\partial^2 y}{\partial x^2} = \left(\frac{1}{v^2}\right)\frac{\partial^2 y}{\partial t^2}$ ------ (3)

By analogy eqn. for a traveling de Broglie wave is given by

$$\frac{\partial^2\psi}{\partial x^2} = \left(\frac{1}{v^2}\right)\frac{\partial^2\psi}{\partial t^2} \text{ ------ } (4)$$

Comparing eqns. (2) & (4) $\frac{\partial^2\psi}{\partial x^2} = -\left(\frac{\omega}{v}\right)^2\psi$; where ω = 2πν and v = νλ

$$\frac{\partial^2\psi}{\partial x^2} = -\left[\frac{4\pi^2}{\lambda^2}\right]\psi \quad \text{or} \quad \frac{1}{\lambda^2} = -\left[\frac{1}{4\pi^2\psi}\right]\frac{\partial^2\psi}{\partial x^2} \text{ --------}(5)$$

For a particle of mas 'm' moving with a velocity 'v'

Kinetic energy = ½ $mv^2 = m^2v^2/2m = p^2/2m$

But $p = h/\lambda$

Therefore, $KE = [1/\lambda^2]\,[h^2/2m]$

Substituting for $1/\lambda^2$ from eqn (5) we get

$$KE = -\left[\frac{1}{4\pi^2\psi}\right]\left[\frac{h^2}{2m}\right]\frac{\partial^2\psi}{\partial x^2} = -\left[\frac{h^2}{8\pi^2 m}\right]\left[\frac{1}{\psi}\right]\frac{\partial^2\psi}{\partial x^2}$$

Total energy is given by

$$E = PE + KE = V - \left[\frac{h^2}{8\pi^2 m}\right]\left[\frac{1}{\psi}\right]\frac{\partial^2\psi}{\partial x^2}$$

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

$$\boldsymbol{\frac{\partial^2\psi}{\partial x^2} + \left[\frac{8\pi^2 m}{h^2}\right](E - V)\psi = 0}$$

It may be noted that, the time dependent Schrödinger equation is the most useful equation employed in majority of the cases in quantum mechanical problems as compared to time-dependent Schrödinger equation.

Eigen functions and Eigen values:

If the wave function ψ for a system is known, then the state of the system can be determined. A system is defined by its energy, momentum, position etc. In order to find ψ we have to solve Schrödinger's equation. Since Schrödinger's equation is a second order differential equation, there are several solutions. Among all the solutions we have to search the wave function which is best acceptable. For an acceptable solution, the wave function should satisfy the following criteria.

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

In Quantum mechanics, the acceptable wave functions which meaningfully represent a physical system are known as Eigen functions.

Once Eigen functions are known, by using this in Schrödinger's equation we can evaluate the energy. Since there is only restricted set of Eigen functions; there is also restricted set of energy values. These values are called Eigen values (proper or characteristic values).

Mathematically

$(A – \lambda)\ \psi = 0$ → characteristic equation or eigen equation

λ is Eigen values. "A' is operator.

$$A\psi = \lambda\psi$$

Ex: $\frac{d}{dx}e^{ax} = a.e^{ax}$

For a hydrogen atom,

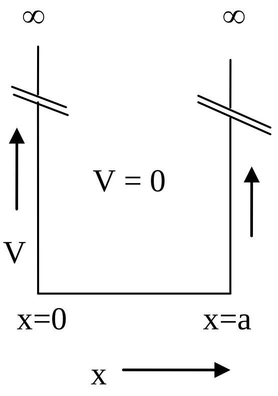
$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0{}^2\hbar^2}\left(\frac{1}{n^2}\right) \text{ where n=1,2,3,………}$$

are eigen values.

Applications of Schrödinger wave equation:

Particle in one dimensional potential well of infinite height.

Consider a particle of mass ‘m’ moving freely in the x – direction only in the region from x = 0 to x = a. Outside this region the potential energy “V’ is taken to be infinite and within this region it is zero. This problem physically represents the motion of electron in periodic lattice.



Outside the well, the Schrödinger equation is

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

This equation holds good only if ψ =0 for all points outside the box. i.e., $|\psi|^2 = 0$ which means that particle does not exist outside the well. ……….(I)

Inside the box, the Schrödinger equation is

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

or

$$\frac{-h^2}{8\pi^2 m}.\left(\frac{d^2\psi}{dx^2}\right) = E\psi \qquad \text{--------------(3)}$$

This is of the form Hψ = Eψ → Eigen equation

Let $\frac{8\pi^2 m}{h^2}E = k^2$ in equation (2), we get

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \text{ ----------------------- (4)}$$

Solutions: The solution for the above equation is given by

$$\psi = C\cos kx + D\sin kx \text{ ---------------------- (5)}$$

Let us find the values of C and D using boundary conditons.

But ψ = 0 at x = 0, as per (I)

∴ Equation (5) → 0 = C cos0 + D sin 0

i.e., C = 0 ----------------- (6)

Also ψ =0 at x = a, as per (I)

Equation (5) → 0 = C cos ka + D sin ka

or D sin ka= 0 (∵ C = 0)

For this to happen, D need not be zero.

∴ sin Ka = 0 (∵ D $\neq$ 0)

or ka = nπ

where n = 0,1,2……………n is called quantum number.

∴ $k = \frac{n\pi}{a}$ -----------------(7)

substitute the value of 'C' and 'k' in equation (5), we get

$$\psi_n = D\sin\frac{n\pi}{a}x \text{ -----------------(8)}$$

which represents the permitted solutions.

We know that $\frac{8\pi^2 m}{h^2}E = k^2$

∴ The corresponding energies are

$$E = \frac{k^2h^2}{8\pi^2 m} = \frac{n^2h^2}{8ma^2} \text{ ---------------- (9)}$$

In equation (9), the value n = 0 is not acceptable because when n = 0, $\psi_n = 0$ by equation (8), which means to say that the particle is not present inside the box, which is not true. Hence the lowest value of n is 1, and the energy corresponding to n =1 is called zero – point energy, which is given by

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

The lowest permitted state of energy is referred to as the ground state energy. Thus zero point energy is taken as the ground state energy. The states corresponding to n > 1 are called excited states. We still need to evaluate D. It can be obtained by normalization of ψ n.

Normalization

As we know the particle must be present at any time, somewhere inside the box only. Therefore the integral value of the probability function over the entire space in the box must be unity.

i.e.,
$$\int |\psi|^2 .dx = 1$$

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

Using the formula, $\text{Sin}^2\theta = \frac{1-\cos 2\theta}{2}$

We can write the above integral as,

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

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

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

or $$\frac{D^2 a}{2} = 1$$

∴ $$D = \sqrt{\frac{2}{a}}$$

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

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

<u>Eigen functions, probability densities and energy Eigen values (energy levels) for particle in a box</u>.

For a particle in an infinite potential well, we have the Eigen function given by,

$\psi_n = D\sin\left(\frac{n\pi}{a}\right)x$ and Eigen values are given by $E_n = \frac{n^2h^2}{8ma^2}$, where n=1, 2, 3,….

<u>Case (i)</u> n = 1: This is the **ground state** and the particle is normally found in this state.

For n = 1, Eigen function is

$$\psi_1 = D\sin\left(\frac{\pi}{a}\right)x$$

Here $\psi_1 = 0$ for both x = 0 and x = a

But ψ_1 has a maximum value for x = $\frac{a}{2}$. Thus a plot of ψ_1 Vs 'x' is shown below.

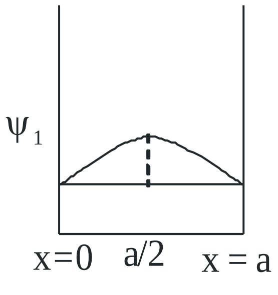


Fig.1a

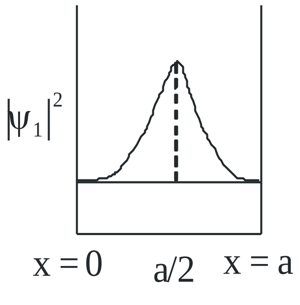


Fig.1b

Here $|\psi_1|^2$ is the probability density. Fig 1 b indicates the probability of finding the particle at different locations inside the box. Also $|\psi_1|^2$ = 0 for both x = 0 and x = a, it is maximum for x = $\frac{a}{2}$. It means that in 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 of this state is the ground state energy which is nothing but zero point energy.

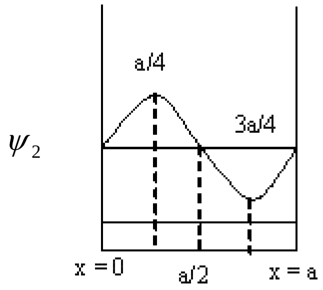
$$E_1 = \frac{h^2}{8ma^2} = E_0 \text{ -------------- (11)}$$

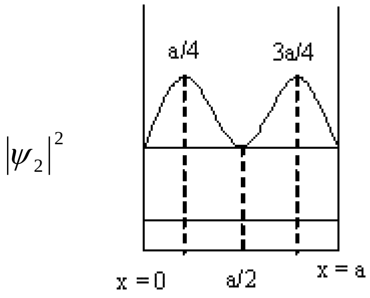
Case (ii) n = 2: This is the **first excited state**. The Eigen function for this state is

$$\psi_2 = D \sin \frac{2\pi}{a} x$$

Now $\psi_2 = 0,$ when x = 0, $\frac{a}{2}$ and a. And ψ_2 is maximum for x = $\frac{a}{4}$ *and* $\frac{3a}{4.}$

Similarly $|\psi_2|^2 = 0$ for x = 0, $\frac{a}{2}$ and a. And $|\psi_2|^2$ is maximum for x = $\frac{a}{4}$ *and* $\frac{3a}{4.}$





It means that in the first excited state the particle cannot be observed either at the walls or at the centre.

Energy equation for this state is

$$E_2 = 4.\frac{h^2}{8ma^2} = 4.E_0$$

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

---------------- *Best Wishes* --------------