Quantum mechanics

Introduction Discovery of microscopic particles of atomic dimensions of the order of 10^{-10} m and their experimental observations could not be explained by Newtonian mechanics (classical mechanics). The attempts made to explain the experimental results like black body radiation spectrum, specific heat of solids at low temperatures, photoelectric effect, Compton effect, atomic spectra etc…. led to the development of quantum mechanics.

In 1924 de Broglie extended wave particle duality to micro particles, which says that particles in motion possess wave nature along with particle nature. In 1926 Erwin Schrodinger developed an equation for the waves associated with these elementary particles which would describe the behaviour of particles. The Schrodinger equation plays the same role in quantum mechanics as that played by Newton's laws and conservation laws in classical mechanics.

Wave function: Every microscopic particle or system particles are associated with a quantity called wave function whose variation makes up the de Broglie waves or matter waves. It describes the quantum state of the particle.

The wave function $\psi(r,t)$ determines the entire space – time behaviour of a system. The value of wave function associated with a moving particle at a particular point x, y, z in space at the time 't' is related to the probability of finding the particle there at that time.

Properties of wavefunction

1. The wave function contains all measurable information about the particle.
2. The wave function ψ must be single valued everywhere in space. It should be unique and should not possess more than one value at the same location.
3. ψ must be finite everywhere in space. ie. The wave function cannot be infinite at a point as it signifies a large probability of finding the particle. This violates the uncertainty principle and the wave function is unacceptable.
4. ψ and its first derivatives with respect to its variables must be continuous everywhere.
5. For bound states, ψ must vanish at infinity. If ψ is a complex function then $\psi^*\psi$ must vanish at infinity.
6. ψ must be normaizable. This means ψ must go to zero as $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$ and $z \rightarrow \pm\infty$ in order that $\int|\psi|^2 dV$ over all space be a finite quantity.
7. The wave function allows energy calculations by using Schrodinger's equation.

8. The wave function allows the calculation of effective average value of a variable (Expectation value).
9. The wave function for a free particle is a sine function, implying precisely determined momentum and highly uncertain position of a particle (Heisenberg Uncertainty principle).

Physical significance of wave function

1. The wave function signifies the probability of finding the particle at the point (x, y, z) and at time t.
2. The wave function can interfere with itself. (Electron diffraction)
3. The wave function ψ is a complex quantity and has no direct physical significance by itself. The product $\psi\psi^*$ is a real quantity where ψ^* is the complex conjugate of ψ.
4. **Probability density** - It is the probability of finding the particle per unit volume. It is given by $\psi\psi^*$ or $|\psi|^2$. Thus the term $|\psi(r,t)|^2 = \psi^*(r,t)\,\psi(r,t)dV$ is proportional to the probability of finding the particle in the interval V and V + dV at the time t. The total probability of finding the particle anywhere in space is $P = \int_{-\infty}^{+\infty}|\psi(r,t)|^2 dV$.

Max Born's interpretation of wave function

The space time behaviour of an atomic system is determined by the laws of probability. The intensity of light at different points in interference or diffraction experiments is determined by square of the amplitude of electric vector of light wave (E^2) . Similarly in case of an atomic system like electron, the probability of finding the electron at a point in space is determined by the square of amplitude of wave function.

Max Born also proposed four conditions on the wave function which are used in finding many solutions of the Schrödinger equation.

Max Born's conditions to be imposed on the wave function are

1. The wave function must be single valued. This means that for any given values of x and t, $\psi(x,t)$ must have a unique value. This is a way of guaranteeing that there is only a single value for the probability of the system being in a given state.
2. The wave function must be square-integrable. In other words, the integral of $|\psi|^2$ over all space must be finite. This is another way of saying that it must be possible to use $|\psi|^2$ as a probability density, since any probability density must integrate over all space to give a value of 1, which is clearly not possible

if the integral of $|\psi|^2$ is infinite. One consequence of this proposal is that ψ must tend to 0 for infinite distances.

3. The wave function must be continuous everywhere. That is, there are no sudden jumps in the probability density when moving through space.
4. All first-order derivatives of the wave function must be continuous. Following the same reasoning as in condition 3, a discontinuous first derivative would imply an infinite second derivative, and since the energy of the system is found using the second derivative, a discontinuous first derivative would imply an infinite energy, which again is not physically realistic.

Normalization of wave function : As ψ itself is complex quantity and has no physical significance but ψ^2 has the significance. The integral of ψ^2 taken over all space must be equal to one. ie. $\int_{-\infty}^{+\infty}|\psi(r,t)|^2 dV = 1$ such a wave function is called normalized wave function.

The process of integration over all space to give unity is called normalization.

If $\psi(r,t)$ is multiplied by a constant C such that $\psi_N(r,t) = C\psi(r,t)$ where $\psi_N(r,t)$ satisfies the relation $\int_{-\infty}^{+\infty}|\psi_N(r,t)|^2 dV = |C|^2 \int_{-\infty}^{+\infty}|\psi(r,t)|^2 dV = 1$ then $\psi_N(r,t)$ is said to be normalized wave function. The term $|C|^2$ is given by $|C|^2 = \frac{1}{\int_{-\infty}^{+\infty}|\psi(r,t)|^2 dV}$ where C is called the normalization constant. Thus a wave function is normalizable if $\int_{-\infty}^{+\infty}|\psi(r,t)|^2 dV$ remains finite over all space.

Time dependent Schrodinger's equation (Free particle)

Consider a plane wave travelling in the X – direction with a frequency ν, wavelength λ and velocity v so that $\omega = 2\pi\nu$ and $k = \frac{2\pi}{\lambda}$ where ω is the angular frequency and k is the propagation constant of the wave. The equation of a wave can be represented by $\psi = A\, e^{-i(\omega t - kx)}$ …….(1)

According to quantum theory, the energy of the wave is $E = h\nu$ and hence $\nu = \frac{E}{h}$.

As $\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar}$ where $\hbar = \frac{h}{2\pi}$.

Momentum p_x of the wave along the positive x-direction is given by

$p_x = \frac{h}{\lambda}$ or $\frac{1}{\lambda} = \frac{p_x}{h}$.

The propagation constant is given by $k = \frac{2\pi}{\lambda} = \frac{2\pi p_x}{h}$ or $k = \frac{p_x}{\hbar}$

Substituting for $\omega = \frac{E}{\hbar}$ and $k = \frac{p_x}{\hbar}$ in equation (1) we get $\psi = A\, e^{-i\left(\frac{E}{\hbar}\, t - \frac{p_x}{\hbar} x\right)}$

or $\boldsymbol{\psi = A\, e^{\frac{i}{\hbar}(p_x x - Et)}}$ ……(2) where ψ is the one dimensional wave function of a unrestricted particle (free particle) which is a function of x and t.

Differentiating equation (2) with respect to time t

$\frac{\partial\psi}{\partial t} = A\, e^{\frac{i}{\hbar}(p_x x - Et)} \left(-\frac{i\,E}{\hbar}\right)$ or $\frac{\partial\psi}{\partial t} = \left(-\frac{i\,E}{\hbar}\right)\psi$ ….(3) where $\psi = A\, e^{\frac{i}{\hbar}(p_x x - Et)}$

Rearranging equation (3), $E\,\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$ or $E\,\psi = i\hbar\frac{\partial\psi}{\partial t}$ …….(4)

Differentiating equation (2) with respect to x, we get

$\frac{\partial\psi}{\partial x} = A\, e^{\frac{i}{\hbar}(p_x x - Et)} \left(\frac{i\,p_x}{\hbar}\right) = \left(\frac{ip_x}{\hbar}\right)\psi$ ….(5)

Differentiating equation (5) again, we get $\frac{\partial^2\psi}{\partial x^2} = A\, e^{\frac{i}{\hbar}(p_x x - Et)} \left(\frac{i\,p_x}{\hbar}\right)^2$

or $\frac{\partial^2\psi}{\partial x^2} = \left(\frac{i\,p_x}{\hbar}\right)^2\psi$, rearranging this equation, we get $p_x^2\psi = -\hbar^2\,\frac{\partial^2\psi}{\partial x^2}$ …..(6)

For a particle of mass m moving with a velocity v, the total energy of the particle is given by $E = E_K + E_P$ where E_K is the kinetic energy and E_P is the potential energy represented by V.

E_K is given by $E_K = \frac{1}{2}\,mv^2$. Multiplying and dividing this equation by m

we get $E_K = \frac{m^2v^2}{2m}$. As $p_x = mv$, we get $E_K = \frac{p_x^2}{2m}$.

Thus the total energy is $E = \frac{p_x^2}{2m} + V$ or $E\,\psi = \frac{p_x^2}{2m}\psi + V\,\psi$ …….(7)

Substituting for E and p_x from (4) and (6) in (7) we get,

$\boldsymbol{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\,\psi}$ ……..(6) This is the schrodinger's time dependent equation in one dimension for a free particle.

Extending it to three dimensions, we have $i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\,\psi$

As $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The above equation can be written as $\boldsymbol{i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\,\psi}$

Time independent schrodinger's equation : (Steady state equation)

The Schrodinger time dependent equation is given by $i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi$ …(1)

In the above equation, potential energy depends both on position and time. The Schrodinger equation in which potential energy of the system is independent of time and varies only with the position is called the steady state equation or time independent Schrodinger equation. This equation can be arrived at using separation of variables as given below. The one dimensional wave function of an unrestricted particle can be written in the form

$$\psi = A\, e^{-\frac{i}{\hbar}(Et - p_x x)} \quad \text{or} \quad \psi = A\, e^{-\left(\frac{i}{\hbar}E\right)t}\, e^{\left(\frac{i}{\hbar}p_x\right)x}$$

or $\psi = \psi_0\, e^{-\left(\frac{i}{\hbar}E\right)t}$ …..(2) where, we assume $\psi_0 = A\, e^{\left(\frac{i}{\hbar}p_x\right)x}$

Equation (2) shows that ψ is the product of position dependent function ψ_0 and a time dependent function $e^{-\left(\frac{i}{\hbar}E\right)t}$.

Differentiating equation (2) with respect to time t, we get

$$\frac{\partial \psi}{\partial t} = \left(-\frac{i\,E}{\hbar}\right)\psi_0\, e^{-\left(\frac{i}{\hbar}E\right)t} \quad \text{….(3)}$$

Differentiation equation (2) with respect to x, $\frac{\partial \psi}{\partial x} = \frac{\partial \psi_0}{\partial x}\, e^{-\left(\frac{i}{\hbar}E\right)t}$

Differentiating the above equation again, $\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial^2 \psi_0}{\partial x^2}\, e^{-\left(\frac{i}{\hbar}E\right)t}$ ….. (4)

By substituting equations (3) and (4) in (1), we get, we get

$$i\hbar\left(-\frac{i\,E}{\hbar}\right)\psi_0\, e^{-\left(\frac{i}{\hbar}E\right)t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2}\, e^{-\left(\frac{i}{\hbar}E\right)t} + V\psi_0\, e^{-\left(\frac{i}{\hbar}E\right)t}$$

Cancelling the exponential terms on either side of the above equation, we get

$E\,\psi_0 = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi_0}{\partial x^2} + V\psi_0$ Rearranging $\frac{\partial^2 \psi_0}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\,\psi_0 = 0$.

The above equation in general can be written as $\boldsymbol{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\,\psi = 0}$

This is the steady state form of Schrodinger's equation or the time independent Schrodinger's equation. In three dimensions, the above equation is written as

$$\boldsymbol{\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\,\psi = 0} \quad \textbf{or} \quad \boldsymbol{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\,\psi = 0}$$

Where $\hbar$ is expressed as $\hbar = \frac{h}{2\pi}$.

Operators in quantum mechanics

An operator is a mathematical rule (or procedure) operating on one function transforms it into another function. For example an operator like differential d/dx operated on a function x^3 results in another function $3x^2$.

In quantum mechanics each dynamic variable is represented by an operator. An operator (α) is said to be an linear operator if $\alpha(\psi_1 + \psi_2) = \alpha\,\psi_1 + \alpha\,\psi_2$ and $\alpha(a\psi) = a\alpha\psi$. An operator α acting on any two wave functions ψ_1 *and* ψ_2 is said to be Hermitian, if $\int \psi_1^* \,(\alpha\psi_2)\, d\tau = \int \psi_2\, (\alpha\psi_1)^* d\tau$.

An operator when applied to a wave function gives the corresponding observable quantity of the system multiplied by the wave function.

1. The wave function is $\psi = A\, e^{\frac{i}{\hbar}(p_x x - Et)}$. Differentiating this equation with respect to x, we get $\frac{\partial\psi}{\partial x} = A\, e^{\frac{i}{\hbar}(p_x x - Et)} \left(\frac{i\,p_x}{\hbar}\right) = \left(\frac{ip_x}{\hbar}\right)\psi$. simplifying, we get $p_x\psi = \left(\frac{\hbar}{i}\right)\frac{\partial\psi}{\partial x}$ or $p_x\psi = -i\hbar\frac{\partial\psi}{\partial x}$. This equation shows that p_x is the momentum operator given by $\boldsymbol{p_x = -i\hbar\frac{\partial}{\partial x}}$ and when operated on ψ gives $p_x(\psi) = -i\hbar\frac{\partial}{\partial x}(\psi)$. The observable quantity here is the linear momentum p_x multiplied by the wave function ψ.
2. The wave function is $\psi = A\, e^{\frac{i}{\hbar}(p_x x - Et)}$. Differentiating with respect to time $\frac{\partial\psi}{\partial t} = \left(-\frac{i\,E}{\hbar}\right)\psi$ or $E\,\psi = i\hbar\frac{\partial\psi}{\partial t}$. Here the operator is $E = i\hbar\frac{\partial}{\partial t}$. The observable quantity is the total energy E multiplied by the wave function ψ.

The table below gives list of operators used in quantum mechanics

Operator (quantity)	**Classical definition**	**Quantum operator**
Position	R	r
Linear momentum	P	$-i\hbar\frac{\partial}{\partial x}$ or $-i\hbar\nabla$
Angular momentum	r ×p	$-i\hbar(r \times \nabla)$
Kinetic energy	$\frac{p^2}{2m}$	$-\frac{\hbar^2}{2m}\nabla^2$
Potential energy	V	V
Total energy (time dependent)	E	$i\hbar\frac{\partial}{\partial t}$
Hamiltonian (time independent)	$H = \frac{p^2}{2m} + V$	$-\frac{\hbar^2}{2m}\nabla^2 + V$

Eigenvalues and Eigenfunctions

If an operator $\tilde{A}$ operating on a function $\psi(x)$ multiplies the latter by a constant λ, then $\psi(x)$ is called the eigen function of $\tilde{A}$ belonging to the eigen value λ.

A set of eigen values λ_n and a set of eigen functions $\psi_n(x)$ belong to an operator $\tilde{A}$, then $\tilde{A}\,\psi_n(x) = \lambda_n\psi_n(x)$. This equation is referred to as an eigen value equation.

Hence eigen functions $\psi_n(x)$ are a set of functions which when operated by an operator $\tilde{A}$ remains unchanged and are multiplied by the corresponding eigen values λ_n. (eigen means proper or characteristic)

Example : If $\tilde{A} = \frac{d^2}{dx^2}$ and $\psi(x) = \alpha\, e^{-2x}$, then $\tilde{A}\,\psi(x) = \frac{d^2}{dx^2}(\alpha\, e^{-2x}) = 4\alpha\, e^{-2x}$ or $\tilde{A}\,\psi(x) = 4\psi(x)$ where 4 is the eigen value and $\psi(x)$ is the eigen function.

The wave function for a given physical system contains the measurable information about the system. To obtain specific values for physical parameters, for example energy, you operate on the wave function with the quantum mechanical operator associated with that parameter. The operator associated with energy is the Hamiltonian, and the operation on the wave function is the Schrodinger equation. Solutions exist for the time independent Schrodinger equation only for certain values of energy, and these values are called "eigenvalues" of energy.
Corresponding to each eigenvalue is an "eigen function". The solution to the Schrodinger equation for a given energy E_i involves also finding the specific function ψ_i which describes that energy state.
The Schrodinger's wave equation is $i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\,\psi$

where $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V = H_{op}$ is the Hamiltonian which is the operator and $i\hbar\frac{\partial}{\partial t} = E$ is the energy eigen value. Thus the above equation can be written as $H_{op}\psi_i = E_i\psi_i$ which is the solution of the time independent Schrodinger equation.

The eigenvalue concept is not limited to energy. When applied to a general operator Q, it can take the form

$$\underbrace{Q_{op}}_{\text{operator}}\psi_i = \underbrace{q_i}_{\text{eigenvalue}}\overbrace{\psi_i}^{\text{eigenfunction}}$$

If the function ψ_i is an eigen function for that operator, the eigenvalues q_i may be discrete, and in such cases we can say that the physical variable is "quantized" and that the index i plays the role of a "quantum number" which characterizes that state.

Degeneracy : In quantum mechanics, an energy level is said to be degenerate if it corresponds to two or more different measurable states of a quantum system. Conversely, two or more different states of a quantum mechanical system are said to be **degenerate** if they give the same value of energy upon measurement. The number of different states corresponding to a particular energy level is known as the degree of degeneracy of the level. It is represented mathematically by the Hamiltonian for the system having more than one linearly independent eigenstate with the same eigenvalue

Expectation values of dynamical variables

To relate a quantum mechanical calculation to an observation made in the laboratory, the "expectation value" of the measurable parameter is calculated. For the position x, the expectation value is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, x\, \psi(x,t)\, dx$$

This integral can be interpreted as the average value of x that we would expect to obtain from a large number of measurements. Alternatively it could be viewed as the average value of position for a large number of particles which are described by the same wave function. For example, the expectation value of the radius of the electron in the ground state of the hydrogen atom is the average value you expect to obtain from making the measurement for a large number of hydrogen atoms.

While the expectation value of a function of position has the appearance of an average of the function, the expectation value of momentum involves the representation of momentum as a quantum mechanical operator.

The expectation value of momentum is given by $\langle p \rangle = \int_{-\infty}^{+\infty} \psi^* (-i\hbar\nabla)\psi \, dV$

The expectation value of energy is given by $\langle E \rangle = \int_{-\infty}^{+\infty} \psi^* \left(i\hbar \frac{\partial}{\partial t}\right) \psi \, dV$

The expectation value of position variable is $\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* \, x \, \psi \, dV$.

The Postulates of Quantum Mechanics

1. Associated with any particle moving in a conservative field of force is a wave function which determines everything that can be known about the system.
2. With every physical observable q there is associated an operator Q, which when operating upon the wave function associated with a definite value of that observable will yield that value times the wave function.
3. Any operator Q associated with a physically measurable property q will be Hermitian.

4. The set of eigen functions of operator Q will form a complete set of linearly independent functions.
5. For a system described by a given wave function, the expectation value of any property q can be found by performing the expectation value integral with respect to that wave function.
6. The time evolution of the wave function is given by the time dependent Schrodinger equation.

Applications of Schrodinger's wave equation

1. Free particle

A free particle is one which is subject to no forces of any kind. Thus it moves in a region of constant potential. The particle motion is confined to x – direction only. Let the potential be considered as zero i.e. V = 0.

The time independent Schrodinger's equation is $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$

As V = 0, thus $\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}E\right)\psi = 0$ ....(1) or $\frac{d^2\psi}{dx^2} + k^2\psi = 0$ .....(2)

where $k^2 = \frac{2m}{\hbar^2}E$ or $k = \frac{\sqrt{2mE}}{\hbar}$

The solution of the equation (2) is $\psi = Ae^{ikx} + Be^{-ikx}$ .....(3)

Let B = 0, then the above equation becomes $\psi = Ae^{ikx}$ .....(4)

Equation (4) describes a particle moving in the positive x – direction.

A free particle in an ideal condition has infinite length. There are no boundaries.

To normalize the wave function, consider the equation $\int_{-\infty}^{+\infty} \psi^* \psi \, dx = 1$.

Substituting for the wave function $\int_{-\infty}^{+\infty} Ae^{-ikx}Ae^{ikx} \, dx = 1$.

This equation becomes $\int_{-\infty}^{+\infty} A^2 \, dx = 1$ or $A^2 \int_{-\infty}^{+\infty} dx = 1$

$\int_{-\infty}^{+\infty} dx$ is infinite. Thus A must be zero. This difficulty arises since we are considering an ideal case of infinite length. But in practice, the particle is confined to a finite length so that normalization is possible. For a free particle, there is no restriction on the energy. Generally, for bound systems like electron trapped in an atom, the energies are discrete. But the unbound systems like free particle will give continuum energy.

The probability density for the particle is $\psi^*\psi = A^2$, a constant independent of x. Consequently the particle is equally likely to be found any where. So we have an

infinite amount of uncertainty in its position i.e. $\Delta x = \infty$. According to the uncertainty expression $\Delta x\, \Delta p_x \geq \frac{\hbar}{2}$, Δp must be zero.

Let us prove this, $\langle p \rangle = \int_{-\infty}^{+\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi\, dx = \hbar k \int_{-\infty}^{+\infty} \psi^* \psi\, dx = \hbar k$.

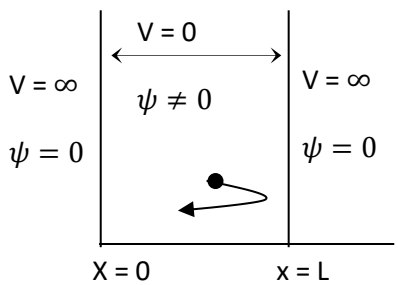
From the above relation it is clear that $\langle p \rangle$ is positive, ie the particle has momentum exactly $\hbar k$ and is moving towards right.

$$\langle p^2 \rangle = \int_{-\infty}^{+\infty} \psi^* (-\hbar^2) \frac{\partial^2}{\partial x^2} \psi\, dx = -\hbar^2(-k^2) \int_{-\infty}^{+\infty} \psi^* \psi\, dx = \hbar^2 k^2$$

$\therefore\ (\Delta p)^2 = \langle p^2 \rangle - \langle p \rangle^2 = 0$. Thus the momentum of the particle is precisely defined.

2. Particle in a one dimensional box (particle in a infinite potential well)

Consider a particle of mass m trapped in a one dimensional box of length L. The walls are of infinite potential energy. The particle is restricted to move inside the box between x = 0 and x = L.



The particle does not lose energy when it collides with the walls of the box, so that its total energy remains constant.

The potential energy V of the particle is $V = 0 \quad for \quad 0 < x < L$.

The wave function ψ is $\psi \neq 0 \quad for \quad 0 < x < L$

$$\psi = 0 \quad for \quad x \leq 0 \ and \quad x \geq L .$$

These are the boundary conditions. The particle cannot exist outside the box as it cannot have infinite amount of energy.

From the steady state Schrodinger wave equation in one dimension (time independent wave equation), we have

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \ldots\ldots\ldots\ldots(1)$$

As V = 0 inside the box, we have $\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}E\right)\psi = 0$

or $\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad \ldots\ldots\ldots(2)$ where $k^2 = \frac{2m}{\hbar^2}E$ or $k = \frac{\sqrt{2mE}}{\hbar}$

The general solution of equation (2) is of the form

$\psi = A\, sinkx + B\, coskx$ or $\psi = A\, sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x + B\, cos\left(\frac{\sqrt{2mE}}{\hbar}\right)x$ …..(3)

where A and B are the constants to be evaluated using boundary conditions.

Expression for Energy eigen value

Applying the first boundary condition $\psi = 0 \quad at \quad x = 0$ to equation (3)

$0 = A\, sin\left(\frac{\sqrt{2mE}}{\hbar}\right) \times 0 + B\, cos\left(\frac{\sqrt{2mE}}{\hbar}\right) \times 0$ or $B = 0$.

Now the equation (3) can be written as $\psi = A\, sin\left(\frac{\sqrt{2mE}}{\hbar}\right)x$ ……(4)

Applying the second boundary condition $\psi = 0 \quad at \quad x = L$ and $B = 0$,

Now the equation (3) becomes $0 = A\, sin\left(\frac{\sqrt{2mE}}{\hbar}\right)L$

As $A \neq 0$, thus $sin\left(\frac{\sqrt{2mE}}{\hbar}\right)L = 0$.

This implies $\frac{\sqrt{2mE_n}}{\hbar}L = n\,\pi$ …..(5) or $\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{L}$

Squaring the above equation $\frac{2mE_n}{\hbar^2} = \frac{n^2\pi^2}{L^2}$ or $E_n = \frac{n^2\pi^2\,\hbar^2}{2mL^2} = \frac{n^2\,h^2}{8mL^2}$ where $\hbar = \frac{h}{2\pi}$

The energy of the particle in a one dimensional box is $\boldsymbol{E_n = \frac{n^2\,h^2}{8mL^2}}$.

The above equation indicates that the energy of the particle can have only certain values which are called eigen values. These eigen values constitute the energy levels of the system. For different levels the eigen values are

$for\ n = 1 \quad E_1 = \frac{h^2}{8mL^2}$, $for\ n = 2 \quad E_2 = \frac{4\,h^2}{8mL^2}$, $for\ n = 3 \quad E_3 = \frac{9h^2}{8mL^2}$ etc….

The energy corresponding to n = 1 is called the ground state energy. The other energies are called the excited state energies.

Expression for Eigen function

The wave function for particle in a box is given by substituting B = 0 in equation (3)

$\psi_n = A\, sin\left(\frac{\sqrt{2mE_n}}{\hbar}\right)x$ ……(6)

Also from equation (5) $\frac{\sqrt{2mE_n}}{\hbar}L = n\,\pi$ or $\frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{L}$ …….(7)

Thus from (6) and (7) , we get $\boldsymbol{\psi_n = A\, sin\left(\frac{n\pi}{L}\right)x}$ …….(8)

Equation (7) gives the Eigen function corresponding to energy eigen value E_n.

Normalization of wave function – To find constant A

From the normalization condition $\int_{-\infty}^{+\infty} |\psi|^2 dx = 1$ ……(9)

As the particle is confined to a one dimensional box, the limits are x = 0 to x = L .

Thus substituting for ψ from (8) in (9), we get $\int_0^L \left| A\, sin\left(\frac{n\pi}{L}\right) x \right|^2 dx = 1$

or $\int_0^L A^2\, sin^2\left(\frac{n\pi}{L}\right) x dx = 1$. This equation can be written as $\frac{A^2}{2}\int_0^L 2\, sin^2\left(\frac{n\pi}{L}\right) x dx = 1$

or $\frac{A^2}{2}\int_0^L \left[1 - cos\left(\frac{2n\pi}{L}\right) x\right] dx = 1$ ($\because 2sin^2\theta = 1 - cos2\theta$)

Integrating the above equation, $\frac{A^2}{2}\left[x - \frac{\sin\left(\frac{2\pi n}{L}\right)x}{\left(\frac{2\pi n}{L}\right)}\right]_0^L = 1$

$\frac{A^2}{2}[(L-0) - 0] = 1$ or $\frac{A^2 L}{2} = 1$ or $A = \sqrt{\frac{2}{L}}$

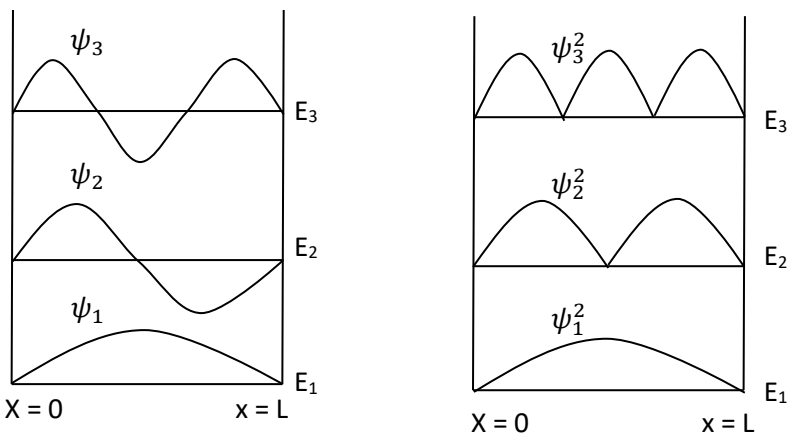
Thus the normalizes wavefunction of a particle in a one dimensional box is given by

$$\boldsymbol{\psi_n = \sqrt{\frac{2}{L}}\, sin\left(\frac{n\pi}{L}\right) x}$$

The Eigen functions corresponding to the states n = 1, 2, 3, ….. are

$\psi_1 = \sqrt{\frac{2}{L}}\, sin\left(\frac{\pi}{L}\right) x$, $\psi_2 = \sqrt{\frac{2}{L}}\, sin\left(\frac{2\pi}{L}\right) x$, $\psi_3 = \sqrt{\frac{2}{L}}\, sin\left(\frac{3\pi}{L}\right) x$ etc……..

These functions are identical with the allowed amplitude functions for the stationary waves in a vibrating string fixed at both the ends.



The energy levels, corresponding wave functions and the probability densities for the first three states are as shown in the graph.

Schrodinger's equation for a particle in a three dimensional box

Consider a particle of mass m which is restricted to move in a box with sides a, b and c. The potential function V(x,y,z) is equal to zero inside the box.

i.e. $V = 0\ for\ 0 < x < a$ and $V = 0\ for\ 0 < x < b$ and $V = 0\ for\ 0 < x < c$

The potential outside the box is infinite. The Schrodinger's time independent wave equation for particle inside the box is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2} E\,\psi = 0 \quad .....(1)$$

This equation can be solved by the method of separation of variables. Assuming that function ψ can be written as product of three functions X, Y and Z,

$$\psi(x, y, z) = X(x)\,Y(y)\,Z(z) \quad .....(2)$$

Each function depends on only one of the co-ordinates

$$\frac{\partial^2\psi}{\partial x^2} = X''Y\,Z\,, \qquad \frac{\partial^2\psi}{\partial y^2} = X\,Y''Z \qquad \text{and } \frac{\partial^2\psi}{\partial z^2} = X\,Y\,Z''$$

Substituting the above in equation (1) and dividing by XYZ , we get

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} + \frac{2mE}{\hbar^2} = 0 \qquad .....(3)$$

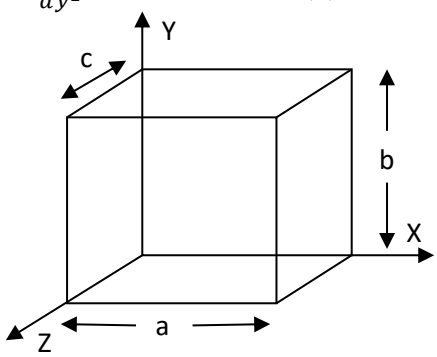
Each variable is independent. For this equation to be valid, each term in equation (3) must be equal to a constant. Thus

$$\frac{X''}{X} = -\alpha^2\ , \quad \frac{Y''}{Y} = -\beta^2 \quad \text{and} \quad \frac{Z''}{Z} = -\gamma^2 \qquad .....(3a)$$

Now equation (3) becomes $\alpha^2 + \beta^2 + \gamma^2 = \frac{2mE}{\hbar^2}$

The equations (3a) can be written as $\frac{d^2\psi}{dx^2} + \alpha^2\,X = 0\,,$ .....(4) $\frac{d^2\psi}{dy^2} + \beta^2\,Y = 0$ ....(5)

and $\frac{d^2\psi}{dz^2} + \gamma^2\,Z = 0$ .....(6)



The general solutions of equations (4), (5) and (6) are

$$X = A_1\,sin\alpha x + B_1 cos\alpha x$$

$$Y = A_2\,sin\beta y + B_2 cos\beta y \qquad .....(7a)$$

$$Z = A_3\,sin\gamma z + B_3 cos\gamma z$$

Applying the boundary conditions, i.e. $\psi = 0$ at the boundary walls at which V = ∞

$$\psi(0, y, z) = \psi\,(x, 0, z) = \psi\,(x, y, 0) = 0 \quad ....(7b)$$

and $\psi(a, y, z) = \psi\,(x, b, z) = \psi\,(x, y, c) = 0$ .....(7c)

Applying the boundary condition (7b) to (7a) we get $B_1 = B_2 = B_3 = 0$

Applying condition (7c) in (7a) we get $sin\alpha a = 0 \quad or \quad \alpha a = n_x\pi \;\; or\; \alpha = \frac{n_x\pi}{a}$

Similarly $\beta = \frac{n_y\pi}{b}$ and $\gamma = \frac{n_z\pi}{c}$ where n_x , n_y and n_z are the integers.

Equations (7a) becomes $X = A_1\, sin\frac{n_x\pi x}{a}$, $Y = A_2\, sin\frac{n_y\pi y}{b}$ and $Z = A_3\, sin\frac{n_z\pi z}{c}$

Substituting these values in equation (2) we get

$$\psi(x,y,z) = A_1A_2\, A_3 sin\frac{n_x\pi x}{a}\; sin\frac{n_y\pi y}{b}\; sin\frac{n_z\pi z}{c} = A\, sin\frac{n_x\pi x}{a}\; sin\frac{n_y\pi y}{b}\; sin\frac{n_z\pi z}{c}$$

where a is the normalization constant. A can be found using normalization condition

$$\int_0^a\int_0^b\int_0^c \psi\,\psi^*\, dx\, dy\, dz = 1$$

or $$\int_0^a\int_0^b\int_0^c sin^2\left(\frac{n_x\pi x}{a}\right) sin^2\left(\frac{n_y\pi y}{b}\right) sin^2\left(\frac{n_z\pi z}{c}\right)\, dx\, dy\, dz = 1$$

This results in $A^2\frac{a}{2}\frac{b}{2}\frac{c}{2} = 1$ or $A = \frac{2\sqrt{2}}{\sqrt{abc}}$

The normalizes wave function is $\psi(x,y,z) = \sqrt{\frac{8}{abc}}\, sin\frac{n_x\pi x}{a}\; sin\frac{n_y\pi y}{b}\; sin\frac{n_z\pi z}{c}$ ....(8)

As $\alpha^2 + \beta^2 + \gamma^2 = \frac{2mE}{\hbar^2}$

Substituting for $\alpha, \beta\; and\; \gamma$ in the above equation, we get $\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{b^2} + \frac{n_z^2\pi^2}{c^2} = \frac{2mE}{\hbar^2}$

Simplifying, $E_{n_xn_yn_z} = \frac{\hbar^2\pi^2}{2m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]$ …….(8)

For a cubical system $= b = c$, thus $E_{cube} = \frac{\hbar^2\pi^2}{2ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]$

For the ground state, energy values are found by putting $n_x = n_y = n_z = 1$.

Thus $E_{111} = \frac{3\hbar^2\pi^2}{2ma^2}$. There is only one set of quantum numbers that gives this energy state and this level is said to be non-degenerate.

For the first excited state, there are three possibilities $n_x = 2,\; n_y = n_z = 1$ and

$n_y = 2,\; n_x = n_z = 1$ and $n_z = 2,\; n_x = n_y = 1$

This results in the equation $E_{211} = E_{121} = E_{112} = \frac{3\hbar^2\pi^2}{ma^2}$.

In this case there are three sets *(211), (121) and (112)* of the quantum numbers n_x, n_y *and* n_z that will give the same energy level. i.e. several distinct quantum states

possess the same energy level. This property is called **degeneracy**. In this case the level is triply degenerate.

Equation (8) indicates that the energy value of a particle in a box (infinitely deep potential well) are not continuous but discrete. The particle has different bound states inside the potential well.

3. One dimensional linear harmonic oscillator (LHO)

If a system vibrates about an equilibrium position such that (a) the magnitude of the force acting on it is directly proportional to displacement from the equilibrium position and (b) the direction of the force is opposite to that of displacement, then it is called linear harmonic oscillator.

Let x be the displacement of a particle of mass m, at any instant of time t, during its vibration, then the restoring force is directly proportional to the displacement.

i.e. $F \propto x$ or $F = -kx$ .....(1) where k is a constant. From Newton's second law, $= ma = m\frac{d^2x}{dt^2}$. Thus $m\frac{d^2x}{dt^2} = -kx$

or $\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$ or $\frac{d^2x}{dt^2} + \omega^2 x = 0$ .....(2) where $\omega^2 = \frac{k}{m}$, ω is called the angular frequency given by $\omega = 2\pi\nu$.

The restoring force is given by $F = -\frac{dV(x)}{dx}$ where $V(x)$ is the potential energy of the particle. Substituting for F in equation (1), we get $-\frac{dV(x)}{dx} = -kx$ ....(3)

Integration equation (3) $\int_0^x -\frac{dV(x)}{dx} = -\int_0^x -kx\, dx$ Thus $V(x) = \frac{1}{2}kx^2$ ....(4)

As $k = m\omega^2$, equation (4) can be written as $V(x) = \frac{1}{2}m\omega^2x^2$ ....(5)

From the Schrodinger time independent equation, we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x) = E\,\psi \quad \text{or} \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi = 0 \quad .....(6)$$

Substituting for $V(x)$ from (5) in (6), we get $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2x^2\right)\psi = 0$

Simplifying the above equation, $\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi - \left(\frac{m^2\omega^2}{\hbar^2}\right)x^2\,\psi = 0$ ....(7)

Let $\frac{2mE}{\hbar^2} = \alpha$ and $\frac{m^2\omega^2}{\hbar^2} = \beta^2$ or $\frac{m\omega}{\hbar} = \beta$

Thus the Schrodinger's equation is $\frac{d^2\psi}{dx^2} + (\alpha - \beta^2x^2)\,\psi = 0$ ....(8)

Let an independent variable be introduced as y given by $y = \sqrt{\beta}\, x$ or $x^2 = \frac{y^2}{\beta}$

Also $\frac{d\psi}{dx} = \frac{d\psi}{dy} \times \frac{dy}{dx} = \frac{d\psi}{dy} \times \sqrt{\beta}$. (since $y = \sqrt{\beta}\, x$ and $\frac{dy}{dx} = \sqrt{\beta}$)

$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{dx}\right) = \frac{d}{dx}\left(\frac{d\psi}{dy}\frac{dy}{dx}\right) = \frac{d}{dy}\left(\frac{d\psi}{dx}\right)\frac{dy}{dx} = \frac{d}{dy}\left(\frac{d\psi}{dy}\sqrt{\beta}\right)\frac{dy}{dx} = \frac{d^2\psi}{dy^2}\beta$. (since $\frac{dq}{dx} = \sqrt{\beta}$)

The above equation is $\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{dy^2}\beta$

Substituting the above term in equation (8), we get

$\beta\frac{d^2\psi}{dy^2} + \left(\alpha - \beta^2\frac{y^2}{\beta}\right)\psi = 0$ or $\beta\frac{d^2\psi}{dy^2} + (\alpha - \beta y^2)\psi = 0$

or $\frac{d^2\psi}{dy^2} + \left(\frac{\alpha}{\beta} - y^2\right)\psi = 0$

or $\frac{d^2\psi}{dy^2} + (\lambda - y^2)\,\psi = 0$ ....(9) where $\lambda = \frac{\alpha}{\beta} = \frac{2E}{\hbar\omega}$.

Eigen value of LHO

For the acceptable solution of the above equation, $\lambda = (2n+1)$ where $\lambda = \frac{2E_n}{\hbar\omega}$

Thus from the above equations $2n + 1 = \frac{2E_n}{\hbar\omega}$

or $E_n = (2n+1)\frac{\hbar\omega}{2}$ or $\boldsymbol{E_n = \left(n + \frac{1}{2}\right)\hbar\omega}$ where n = 0, 1, 2, 3, ...

or $\boldsymbol{E_n = \left(n + \frac{1}{2}\right)h\nu}$ where $\hbar\omega = \frac{h}{2\pi} \times 2\pi\nu = h\nu$

The above equation indicates that energy eigen values are discrete that are equally spaced. For n = 0, $E_0 = \frac{1}{2}h\nu$ for n = 1 $E_1 = \frac{3}{2}h\nu$ for n = 2 $E_2 = \frac{5}{2}h\nu$ .....

For n =0, $E_0 = \frac{1}{2}h\nu$ Here E_0 is called zero point energy of the oscillator.

Significance of the zero point energy

According to old quantum theory, the energy of the oscillator is given by $E_n = nh\nu$. For n = 0, the value of E is zero, i.e., the ground state energy of the oscillator is zero. But from the new quantum mechanical theory of the oscillator the ground state energy is not zero but is given by $E_0 = \frac{1}{2}h\nu$. Thus a clear contradiction between the two theories exist.

The existence of the zero point energy is consistent with the Heisenberg uncertainty principle. The old quantum theory is not consistent with the uncertainty principle as explained below.

If both the kinetic and the potential energy of the oscillator are zero, then the ground state total energy of the oscillator is zero. As $x = 0$, $\Delta x = 0$. Also as kinetic energy is zero, the momentum is also zero i.e. $\Delta p_x = 0$. Therefore, $\Delta x\, \Delta p_x = 0$ which is a contradiction to uncertainty relation $\Delta x\, \Delta p_x \geq \hbar$.

But the zero point energy of LHO according to the new quantum theory is consistent with the uncertainty principle.

<u>Wave functions for LHO</u>

The possible solution of equation (9) is $\psi(y) = e^{-y^2/2} f(y)$ .....(10)

Differentiating equation (10) and putting in (9), we get

$$\frac{d^2 f}{dy^2} - 2y\frac{df}{dy} + (\lambda - 1) f = 0 \quad ....(11)$$

Writing $\lambda - 1 = 2n$ above equation becomes $\frac{d^2 f}{dy^2} - 2y\frac{df}{dy} + 2n\, f = 0$ ….(12)

The above equation is called Hermite's equation. The solutions of equation (12) are called Hermite polynomials, given by $H_n(y) = f(y) = (-1)^n \exp y^2 \frac{d^n}{dy^n}\left(exp(-y^2)\right)$

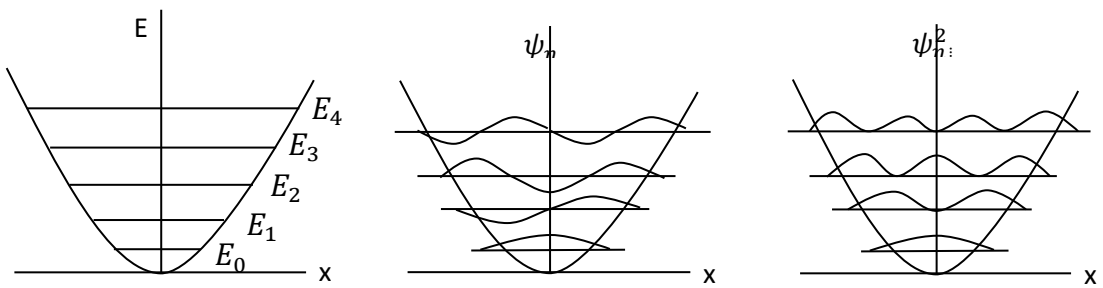
Therefore the eigen function of harmonic oscillator is $\psi_n(y) = NH_n(y)exp(-y^2/2)$

where N is the normalization constant.

The normalized general formula for the nth wave function is

$$\psi_n = \left(\frac{2mv}{\hbar}\right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2}$$

The energy level diagram and the corresponding wave functions are plotted as shown.



Characteristics of LHO

1. The energies are quantized.
2. The possibility of finding the particle outside the allowed classical range is not zero. (Continuous curve in the above graph is the classical range)
3. For all odd states, the probability of finding the particle at the centre is zero.
4. Foa a large n, the classical and quantum position distributions are almost same.
5. The least energy of the classical oscillator is zero but the quantum oscillator has a zero point energy $E_0 = \frac{1}{2}h\nu$ according to uncertainty principle.

4. Hydrogen atom

A hydrogen atom has a single electron moving around a nucleus having a proton under the action of a central force arising out of the Coulombian electrostatic attractive force.

The potential energy of such a system is $V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

The Schrodinger's time independent equation of the this system is

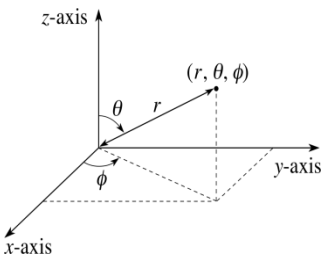
$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\left(E - V(r)\right)\psi = 0$$

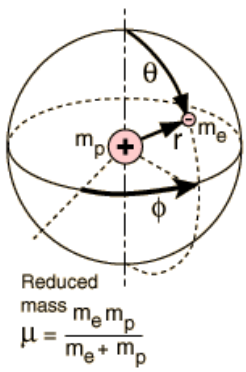
In spherical polar co-ordinates, the position of the electron is given by co-ordinates r (radius vector), θ (the polar angle) and ϕ (the azimuth angle) as shown.

The rectangular co-ordinates are related to polar co-ordinates as

$$r = \sqrt{x^2 + y^2 + z^2}, \quad \theta = \cos^{-1}\left(\frac{z}{r}\right)$$

and $\phi = \tan^{-1}\left(\frac{y}{x}\right)$.





Also $x = r\,sin\theta\,cos\phi$, $y = r\,sin\theta\,sin\phi$ and $z = r\,cos\theta$

Schrodinger's equation in polar co-ordinates is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 m}{h^2}\left(E - V(r)\right)\psi = 0 \quad \ldots\ldots(1)$$

This equation can be separated by variables r , θ and ϕ by substituting

$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$ where R is the radial function and Y is the angular function. Thus equation (1) can be written as

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)Y + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)R + \frac{1}{r^2 sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}R + \frac{8\pi^2 m}{h^2}\left(E - V(r)\right)RY = 0$$

Multiplying entire equation by r^2/RY and rearranging, we get

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2 m r^2}{h^2}\left(E - V(r)\right) = -\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

The LHS of the above equation depends on R and RHS depends on θ *and* ϕ.

For the above equation to be correct, both sides of the equation should be equal to a constant, say $l(l+1)$. Thus the above equation can written as

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2 m r^2}{h^2}\left(E - V(r)\right) = l(l+1) \quad .....(2)$$

$$-\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = l(l+1) \quad .....(3)$$

Equation (3) can be further separated by substituting $Y(\theta,\phi) = \boldsymbol{\theta}(\theta)\,\boldsymbol{\Phi}(\phi)$. This gives

$-\frac{1}{\boldsymbol{\theta}\boldsymbol{\Phi}}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right)\boldsymbol{\Phi} + \frac{1}{sin^2\theta}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}\boldsymbol{\theta}\right] = l(l+1)$. Multiplying this equation by $sin^2\theta$ and rearranging we get $\frac{1}{\boldsymbol{\theta}}\,sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\boldsymbol{\theta}}{\partial\theta}\right) + l(l+1)sin^2\theta = -\frac{1}{\boldsymbol{\Phi}}\frac{\partial^2\boldsymbol{\Phi}}{\partial\phi^2}$

Again for this equation to be correct, both sides of the above equation should be equal to a constant say, m_l^2. Thus the above equation can be written as

$$\frac{1}{\boldsymbol{\theta}}sin\theta\,\frac{d}{d\theta}\left(sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right) + l(l+1)sin^2\theta = m_l^2 \quad .....(4) \quad \text{and} \quad -\frac{1}{\boldsymbol{\Phi}}\frac{d^2\boldsymbol{\Phi}}{d\phi^2} = m_l^2 \quad .....(5)$$

Equation (5) can be written as $\frac{d^2\boldsymbol{\Phi}}{d\phi^2} + m_l^2\boldsymbol{\Phi} = 0 \quad .....(6)$

The solution of equation (6) is $\boldsymbol{\Phi}_{m_l}(\phi) = Ae^{im_l\phi}$ where $m_l = 0, \pm1, \pm2, \ldots\ldots$ and m_l is called magnetic quantum number.

The azimuth wave function is $\boldsymbol{\Phi}(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_l\phi} \quad .....(7)$

Equation (4) can be written as $\frac{1}{sin\theta}\frac{d}{d\theta}\left(sin\theta\frac{d\boldsymbol{\theta}}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{sin^2\theta}\right]\boldsymbol{\theta} = 0 \quad ....(8)$

The solution equation (8) is $\boldsymbol{\theta}_{lm_l}(\theta) = N_{lm_l}P_l^{|m|}(cos\theta)$ where $P_l^{|m|}(cos\theta)$ is the associated Legendre polynomial where $l = |m_l|, |m_l+1|, |m_l+2| \ldots\ldots$

or $m_l = 0, \pm1, \pm2, \ldots\ldots\ldots \pm l$. l is called the orbital quantum number.

The solution of equation (2) is $R_{nl}(r) = N_{nl}e^{-Ze/na_0}\left(\frac{2Ze}{na_0}\right)^2 L_{n+1}^{2l+1}\left(\frac{2Ze}{na_0}\right)$

Here $L_{n+1}^{2l+1}\left(\frac{2Ze}{na_0}\right)$ is the associated Laguerre polynomial.

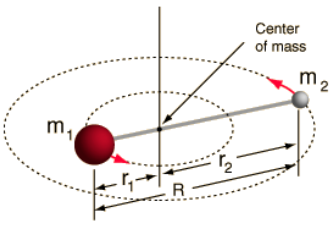
In the above equation a_0 is the first Bohr radius given by $a_0 = \frac{h^2\varepsilon_0}{\pi me^2}$ and the corresponding energy of the nth state is $E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$ where n is called the principal quantum number given by $n = l+1, l+2, \ldots\ldots$ or $l = 0, 1, 2, 3, \ldots (n-1)$.

The total eigen function of the hydrogen atom is

$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)\ \boldsymbol{\theta}_{lm_l}(\theta)\ \boldsymbol{\Phi}_{m_l}(\phi)$. The ground state eigen function is

$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Ze/a_0}$ where Z = 1 with n = 1 and the ground state energy is $E_1 = -\frac{me^4}{8\varepsilon_0^2 h^2}$. The value of E_1= - 13.6 eV and for n = 2, E_2 = - 3.4 eV…… The degeneracy of the nth state is $N(n) = \sum_{l=0}^{n-1}(2l+1) = n^2$, where degeneracy is the number of eigen states for a given eigen value.

5. Rigid rotator



A rigid rotator is a system of two spherical masses m_1 and m_2 situated at fixed distance r_1 and r_2 from the centre of mass of the system. It is capable of rotating about an axis passing through the centre of mass and normal to the plane containing the two particles.

If the particles can rotate in a plane then the axis of rotation is fixed and it is called rigid rotator with fixed axis. If the axis is free to take any orientation in space, then it is called rigid rotator with free axis.

According to classical theory, the kinetic energy of the rigid rotator is

$E = \frac{1}{2}I\omega^2$ … (1) where I is the moment of inertia of the system and ω is the angular frequency of rotation.

If L is the angular momentum of the system, then $L = I\omega$. Putting this in (1) we get

$E = \frac{L^2}{2I}$. The moment of ineria is $= m_1r_1^2 + m_2r_2^2$. Putting the definition of centre of mass $m_1r_1 = m_1r_1$ and $R = r_1 + r_2$ in the above equation, we get $I = \frac{m_1m_2}{m_1+m_2}R^2$

Or $I = \mu R^2$ where μ is the reduced mass of the system.

Wave function for the rigid rotator

The time independent Schrodinger equation is given by

$\nabla^2\psi + \frac{2m}{\hbar^2}(E-V)\psi = 0$. In polar co-ordinates, the equation can be written as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0$$

The wave function $\psi(r,\theta,\phi)$ is a function of , θ *and* ϕ . For a rigid rotator there is no potential energy (V = 0). Thus ψ is independent of *r* . The above equation becomes

$$\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}E\,\psi = 0$$

Rigid rotator can be visualised as equivalent to a system of one particle of mass *I* situated at a distance r = 1 from the origin. In other words, rigid rotator is just like a single particle of mass *I* moving on the surface of a sphere of radius unity.

By putting *r* = 1 and *m* = *I*, in the above equation,

$$\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} = -\frac{2I}{\hbar^2}E\,\psi = 0 \quad .....(1)$$

Putting $\psi = Y(\theta,\phi)$ and rearranging, we get

$$-\hbar^2\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y(\theta,\phi) = 2IE\,Y(\theta,\phi)$$

or $L^2Y(\theta,\phi) = 2IE\,Y(\theta,\phi)$ .....(2) where L^2 is the angular momentum operator.

The eigen function $Y_l^m(\theta,\phi)$ for the rigid rotator are the solutions of the equation (1) and are given by $Y_l^m(\theta,\phi) = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2}(-1)^m e^{im\phi}P_l^m(cos\theta)$ with $0 \le m \le l$.

Also $L^2Y(\theta,\phi) = l(l+1)\hbar^2\ Y(\theta,\phi)$ ....(3)

Comparing (2) and (3) , $2IE = l(l+1)\hbar^2$ or $E_l = \frac{l(l+1)\hbar^2}{2I}$ where $l = 0,1,2,3$ ....

Thus the energy eigen values of the rigid rotator depends on *l* alone. For each *l (l > 0),* there are *2l + 1* values of *m,* i.e. $m = 0, \pm1, \pm2, ...\pm l$. The above equation represents the allowed energy values of the rigid rotator with free axis.

Rigid rotator with fixed axis - When the rotator is confined to rotate in the x-y plane only, the polar angle $\theta = \pi/2$ and ψ does not depend on r. Now the Schrodinger's equation can be written as

$$\frac{d^2\mathbf{\Phi}}{d\phi^2} + \frac{2I}{\hbar^2}E\,\mathbf{\Phi} = 0 \quad \text{or} \quad \frac{1}{\mathbf{\Phi}}\frac{d^2\mathbf{\Phi}}{d\phi^2} = -\frac{2I}{\hbar^2}E \quad \text{or} \quad \frac{1}{\mathbf{\Phi}}\frac{d^2\mathbf{\Phi}}{d\phi^2} = -\frac{2I}{\hbar^2}E = -m^2 \text{ (a constant)}$$

The above equation can be written as $\frac{d^2\mathbf{\Phi}}{d\phi^2} + m^2\mathbf{\Phi} = 0$ ....(4) where $m^2 = \frac{2I}{\hbar^2}E$

The possible solution of equation (4) is $\mathbf{\Phi}_m = A\,e^{im\phi}$ where A is a constant.

A can be found by normalizing the wavefunction as follows.

$\int_0^{2\pi} \mathbf{\Phi}_m^* \mathbf{\Phi}_m d\mathbf{\Phi} = 1$ or $A^2 \int_0^{2\pi} e^{-im\phi}\, e^{im\phi} d\mathbf{\Phi} = 1$ or $A^2 \int_0^{2\pi} d\mathbf{\Phi} = 1$

Simplifying $A^2 2\pi = 1$ Thus $A = \frac{1}{\sqrt{2\pi}}$. The normalized wavefunction is given by $\mathbf{\Phi}_m = \frac{1}{\sqrt{2\pi}}\, e^{im\phi}$.

The energy eigen value of the rigid rotator with a fixed axis is given by $E_m = \frac{m^2\hbar^2}{2I}$.

Descriptive questions, numerical problems and conceptual questions

PART-A

1. a) What is wave function? What are the basic properties of wave function?
   b) Outline Max Born's interpretation of wave function.
2. Arrive at Schrodinger's time independent equation for free particle in one dimension. Write the equation for three diemnsions.
3. (a) Explain the terms eigen value, eigen function and degeneracy.
   (b) What are expectation values? Explain. Explain the concept of normalization.
4. Arrive at Schrodinger's time dependent equation for a free particle in one dimension and write the equation for three diemnsions.
5. Obtain the Schrodinger's equation for a particle in a one dimensional box and solve it to obtain the energy eigen values and eigen functions. Also represent the first three energy eigen functions in a graph.
6. a) Derive an expression for energy eigen values of a particle trapped in one-dimensional box of infinite depth.
   b) Derive an expression for normalised wave function.
7. (a) Define expectation value of an observable in quantum mechanics. What are the expectation values of position and momentum of a particle for a wave function?
   (b) What is probability density? Give Born interpretation of wave function and explain normalization.
8. (a) What are operators? Give two examples.
   (b) Develop the Schrodinger's equation for a free particle. Mention the eigen value and eigen function of the free particle.
9. (a) Develop the Schrodinger's equation for a one dimensional linear harmonic oscillator. Mention the eigen value and eigen function of the oscillator.
10. Show that the energy of a harmonic oscillator is quantised in steps of hν. Explain the existence of zero point energy.

11. Develop the Schrodinger's equation for a rigid rotator. Mention the energy eigen values of the rotator and draw the energy level diagram.
12. Develop the Schrodinger's equation for a hydrogen atom. Mention the energy eigen value and eigen function for the ground state.

PART B

$$h = 6.625 \times 10^{-34} Js, \hbar = \frac{h}{2\pi},$$

$$mass\ of\ the\ electron\ m = 9.1 \times 10^{-31} kg, 1eV = 1.6 \times 10^{-19} J$$

1. An electron is constrained in a one dimensional box of side 1 nm. Obtain the first three eigen values in eV.

   $\left[Hint: Given: L = 1 \times 10^{-9} m,\ E_n = \frac{n^2 h^2}{8mL^2} J, = \frac{n^2 h^2}{8mL^2} \times \frac{1}{1.6 \times 10^{-19}} eV.\ For\ n = 1, 2, 3\ Find\ E_1, E_2, E_3\right]$

2. An electron is confined in a one dimensional box of side 2A^0. How much energy is required to excite the electron from the ground state to the third excited state?

   $\left[Hint: Given\ L = 2 \times 10^{-10} m, n = 1\ for\ ground\ state, n = 4\ for\ third\ excited\ state,\ E_n = \frac{n^2 h^2}{8mL^2},\ Find\ E_1\ for\ n = 1,\ E_4\ for\ n = 4\ and\ calculate\ E_4 - E_1\right]$

4. The eigen value of an electron confined to a one dimensional box of side 0.2 nm is 84.78 eV. What is the order of the state?

   $\left[Hint: Given: L = 0.2 \times 10^{-9} m,\ E_n = 84.78\ eV = 84.78 \times 1.6 \times 10^{-19} J,\ As\ E_n = \frac{n^2 h^2}{8mL^2} J,\ n = \sqrt{\frac{8mL^2 E_n}{h^2}} = \frac{L}{h}\sqrt{8mE_n}.\ Find\ n\right]$

5. Find the momentum and energy values for an electron in a box of length 1 A^0 for n = 2 and n = 3. $\left[Hint:\ Given\ L = 1 \times 10^{-10} m,\ p = \hbar k = \frac{h}{2\pi} \times \frac{n\pi}{L} = \frac{nh}{2L}\ and\ E_n = \frac{n^2 h^2}{8mL^2} J\right]$

6. An electron is confined to move between two rigid walls separated by 10 A^0. Find the de Broglie wavelength representing the first three allowed energy states of the electron and the corresponding energies. $\left[Hint: Given\ L = 10 \times 10^{-10} m,\ Distance\ between\ the\ rigid\ walls\ must\ be\ equal\ to\ integral\ multiples\ of\ \frac{\lambda}{2}\right]$

   $\left[Thus\ L = \frac{n\lambda}{2}\ or\ \lambda = \frac{2L}{n}. Calculate\ \lambda\ for\ n = 1, 2, 3.\right]$

7. The third eigen value of an electron confined to a one dimensional box is 77.4 eV. Find the size of the box.

   $\left[Hint: Given: E = 77.4\ eV = 77.4 \times 1.6 \times 10^{-19} J,\ n = 3,\ E_n = \frac{n^2 h^2}{8mL^2}\ or\ L = \frac{nh}{\sqrt{8mE_n}}\right]$

8. The frequency of a linear harmonic oscillator is 6 × 10^{12} Hz. Find the energy of the oscillator in the fourth excited state.

   $\left[Hint: Given\ \nu = 6 \times 10^{12} Hz, For\ fourth\ excited\ state, n = 4, and\ E_n = \left(n + \frac{1}{2}\right) h\nu\ in\ joule\ Convert\ to\ eV\right]$

9 A particle in a 1 dimensional deep potential well of width L has a function $\psi = A\ sin\left(\frac{n\pi}{L}\right)x$ where A is a constant. Normalize the wave function and find the

value of A. What is the normalized wave function? $\left[Hint: See\ the\ normalization\ of\ wave\ function\ in\ case\ of\ 1\ dimensional\ box, A = \sqrt{\frac{2}{L}}\ and\ \psi = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi}{L}\right)x\right]$

10 The wave function of a particle confined to a box of length L is $\psi = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi}{L}\right)x$ in the region $0 < x < L$. Calculate the probability of finding the particle in the region $0 < x < L/2$. $\left[Hint: Probability\ P = \int_0^{L/2} \psi^* \psi\, dx = \frac{2}{L}\int_0^{L/2} sin^2 \frac{\pi x}{L}\ Integrating,\ P = \frac{1}{2}.\right]$

11. The period of linear harmonic oscillator is 1 millisecond. Find its zero point energy. $\left[Hint: Given\ T = 1 \times 10^{-3} s,\ Frequency\ \nu = \frac{1}{T}\ and\ E_0 = \frac{1}{2}h\nu\right]$

12. The energy of a linear harmonic oscillator is 0.2 eV in the third excited state. Calculate its frequency of oscillation.
$\left[Hint: Given\ E_3 = 0.2\ eV\ (convert\ to\ eV)\ n = 3\ \ Use\ E_n = \left(n + \frac{1}{2}\right)h\nu\right]$

13. An eigen value of an electron confined to a one dimensional box of length 0.2 nm is 151 eV. What is the order of excited state?
$\left[Hint : Given: L = 0.2 \times 10^{-9} m,\ E_n = 151\ eV = 151 \times 1.6 \times 10^{-19} J,\ As\ E_n = \frac{n^2 h^2}{8mL^2} J,\ \ n = \sqrt{\frac{8mL^2 E_n}{h^2}} = \frac{L}{h}\sqrt{8mE_n}.\ Find\ n\right]$

14 A proton is confined to a nucleus of radius $r = 10^{-14} m$. Calculate the lowest and the next two energy eigen values of proton, given mass of the proton $m_p = 1.67 \times 10^{-27} kg$. $\left[Hint : Given: r = L = 10^{-14} m,\ E_n = \frac{n^2 h^2}{8m_p L^2} J, = \frac{n^2 h^2}{8m_p L^2} \times \frac{1}{1.6 \times 10^{-19}} eV.\ For\ n = 1, 2, 3\ \ Find\ E_1, E_2, E_3\right]$

15 Calculate the zero point energy in eV and the spacing of energy levels in eV in a one dimensional oscillator of frequency 2.5 kHz.
$\left[Hint: Given, Frequency\ \nu = 2.5 \times 10^3 Hz\ and\ E_0 = \frac{1}{2}h\nu, Calculate\ E_1\ by\ putting\ n = 1\ in\ E_n = \left(n + \frac{1}{2}\right)h\nu. Find\ E_1 - E_0\right]$

16 A particle of mass 1 mg is attached to a spring of spring constant $10^{-3} Nm^{-1}$. Calculate its zero point energy and classical value of amplitude of zero point vibration. $\left[Hint: m = 1 \times 10^{-6} kg, spring\ constant\ k = 10^{-3} Nm^{-1}, Frequency\ \nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}\ \ and\ \ E_0 = \frac{1}{2}h\nu.\ Clssical\ total\ energy\ E = \frac{1}{2}ma^2\omega^2\ \ where\ \omega^2 = \frac{k}{m}. Thus\ E = \frac{1}{2}ka^2. As\ E = E_0,\ amplitude\ a = \sqrt{\frac{2E_0}{k}}\right]$

PART C

1. What is the difference between a free particle and a particle in a box?
*[**Ans:** A free particle moves in space without any restriction in zero potential having continuous energy.*

A particle in a box has a boundary with in a potential well with either finite or zero potential having discrete energies.]

2. A bound particle has quantised energy values whereas it is not so for a free particle. Explain.

   *[**Ans:** A bound particle has a boundary with boundary conditions in a potential well with either finite or zero potential. It takes quantized energies. Thus it has discrete energies A free particle moves in space without any restriction in zero potential. Thus has continuous energy..]*

3. Give the physical significance of zero point energy.

   [Ans: According to old quantum theory, the energy of the oscillator is given by $E_n = nh\nu$. For n = 0, the value of E is zero, i.e., the ground state energy of the oscillator is zero. But according to new quantum mechanical theory of the oscillator $E_n = \left(n + \frac{1}{2}\right) h\nu$. Thus the ground state energy is not zero but is given by $E_0 = \frac{1}{2} h\nu$].

4. Explain the Bohr's stationary orbits on the basis of quantum mechanical model.

   [Ans: From quantum mechanics the allowed wave functions have discrete energies. The probability density and the corresponding energies are time indeoendent and hence non radiating.]

5. What is the significance of probability density?

   [Ans : The wave function ψ is a complex quantity and has no direct physical significance by itself. The product $\psi\psi^*$ is a real quantity where ψ^* is the complex conjugate of ψ. The probability density $\int_{-\infty}^{+\infty} \psi\psi^* dV$ is the probability of find the particle at a position in a given time.]

6. Is zero point energy of a harmonic oscillator zero? Explain.

   [Ans: A*ccording to quantum mechanical theory of the oscillator $E_n = \left(n + \frac{1}{2}\right) h\nu$. Thus the ground state energy is not zero but is given by $E_0 = \frac{1}{2} h\nu$ as $n = 0$*].

7. Why should the wave function representing a moving particle be complex?

   [Ans: The probability density or the probability of finding a particle at a point in space at a given time is found by $\int_{-\infty}^{+\infty} \psi\psi^* dV$ which is real. This is possible if the wave function is complex.]

8. Why do we normalize a wave function?

   *[Ans: $\int_{-\infty}^{+\infty} \psi\psi^* dV$ is the probability density for finding the particle at point x, at time t. It follows that the integral of $\int_{-\infty}^{+\infty} \psi\psi^* dV = 1$ (the particle's got to be somewhere. The time-dependent Schrödinger equation which is a linear and homogeneous, reveals that if Ψ(x,t) is a solution, so too is AΨ(x,t), where A is any (complex) constant. What we must do, then, is pick this undetermined multiplicative factor A so as to ensure $\int_{-\infty}^{+\infty} |\psi^2| dV = 1$ is satisfied. This process is called **normalizing** the wave function].*

9. The concept of trajectory has no significance in quantum mechanics. Explain.

   [Ans: The Heisenberg's uncertainty principle says it is not possible to measure position and momentum of a particle simultaneously. Also quantum mechanics deals with probabilities and not certainty of a particle. Thus trajectories has no significance in quantum mechanics].

10. Can one eigen value have many eigen functions? If so, what are they called?

    *[Ans: **: Yes.** In quantum mechanics, an energy eigen value can have two or more eigen states. It is referred to as degeneracy. Conversely, two or more different states of a quantum mechanical system are said to be **degenerate** if they give the same value of energy upon measurement].*