1 Quantum Physics

LIMITATIONS OF CLASSICAL MECHANICS

- The mechanics based on the Newton's laws of motion is referred to as classical mechanics or Newtonian mechanics.

- The classical mechanics successfully explains the motion of macroscopic bodies including terrestrial bodies. However, it fails to explain the motion of atomic particles. For example, if classical mechanics is applied to an atom, the electrons moving around the nucleus experience centripetal acceleration and hence must radiate energy in the form of electromagnetic waves. Therefore, the energy of the electron should decrease continuously and ultimately they should collapse in the nucleus, contrary to the reality.

- The classical mechanics also failed to explain photoelectric effect, Compton effect, Raman effect, black body radiations, discrete nature of atomic spectra, etc.

Photon

A packet or bundle of energy is called a photon.

Energy of a photon is $E = h\nu = \dfrac{hc}{\lambda}$

Properties of photons:

(i) A photon travels at a speed of light c in vacuum. (i.e. 3×10^{-8} m/s)

(ii) It has zero rest mass. i.e. the photon can not exist at rest.

(iii) The kinetic mass of a photon is,

(iv) The momentum of a photon is, $p = \dfrac{E}{c} = \dfrac{h}{\lambda}$

(v) Photons travel in a straight line.

(vi) Energy of a photon depends upon frequency of the photon; so the energy of the photon does not change when photon travels from one medium to another.

(vii) Wavelength of the photon changes in different media; so, velocity of a photon is different in different media.

(viii) Photons are electrically neutral.

(ix) Photons may show diffraction under given conditions.

(x) Photons are not deviated by magnetic and electric fields.

COMPTON EFFECT

According to Compton, when a monochromatic beam of high frequency radiation like X-rays, and γ-rays is scattered by a substance, the scattered radiation contains the radiation of greater wavelength along with the radiation of the incident wavelength. The radiation of unchanged wavelength in the scattered light are called unmodified radiations while the radiations of greater wavelength are called modified radiations. The phenomenon is called Compton effect.

Compton's Experimental Arrangement

The schematic experimental arrangement is shown in figure. According to Compton the scattering process act as a particle like collision between a single photon of energy hv and an electron. During collision, the incident photon transfers some of its energy to the electron. Hence, the scattered photon must have a lower energy hv' (v' < v) i.e. a higher wavelength λ'.

Using law of conservation of momentum we get:-

Along x-axis:- $\dfrac{h\nu}{c} = \dfrac{h\nu'}{c}\cos\theta + p_e\cos\phi$ (1)

Along y-axis:- $0 = \dfrac{h\nu'}{c}\sin\theta - p_e\sin\phi$ (2)

where pe is the momentum of the electron after scattering.

Using principle of conservation of energy we get:

$h\nu = h\nu' + k_e$ or $k_e = h(\nu - \nu')$ (3)

where k_e is the kinetic energy of scattered electron. Equations (1) and (2) can be written as:-

$p_e c \cos\phi = h\nu - h\nu'\cos\theta$ (4)

$p_e c \sin\phi = h\nu'\sin\theta$ (5)

Squaring and adding eq. (4) & (5) we get:-

$p_e^2 c^2 = h^2\nu^2 + h^2\nu'^2 - 2h^2\nu\nu'\cos\theta$ (6)

Let m_0 be the rest mass of electron. From equation (3):-

Total Energy of electron $= k_e + m_0 c^2 = h(\nu - \nu') + m_0 c^2$ (7)

From theory of relativity, the energy of the recoiling electron is:-

$E_e = \left(c^2 p_e^2 + m_0^2 c^4\right)^{\frac{1}{2}}$ (8)

From equation (7) and using equation (8) we get:-

$\left(c^2 p_e^2 + m_0^2 c^4\right)^{\frac{1}{2}} = h(\nu - \nu') + m_0 c^2$ (9)

using eq. (6) in (9) and squaring eq. (9) and we get:-

$h^2\nu^2 + h^2\nu'^2 - 2h^2\nu\nu'\cos\theta = h^2(\nu - \nu')^2 + 2h(\nu - \nu')m_0 c^2$

or $h^2\nu\nu'\cos\theta - h^2\nu\nu' + h(\nu - \nu')m_0 c^2 = 0$ (10)

Since $\nu = \dfrac{c}{\lambda}$ and $\nu' = \dfrac{c}{\lambda'}$ equation (10) reduces to

$\dfrac{h^2 c^2}{\lambda\lambda'}\cos\theta - \dfrac{h^2 c^2}{\lambda\lambda'} + h\left(\dfrac{c}{\lambda} - \dfrac{c}{\lambda'}\right)m_0 c^2 = 0$

Multiplying both sides by $\lambda\lambda'$ and rearranging, we get:-
$$h(1-\cos\theta) = c(\lambda'-\lambda)m_0$$

$$(\lambda'-\lambda) = \frac{h}{m_0 c}(1-\cos\theta) \tag{11}$$

$$\Delta\lambda = \frac{h}{m_0 c}(1-\cos\theta) \tag{12}$$

This is the expression for the Compton shift.

Direction of Recoil Electron

Dividing equation (5) by equation (4), we get

$$\tan\phi = \frac{h\nu'\sin\theta}{h\nu - h\nu'\cos\theta} = \frac{c/\lambda'\sin\theta}{c/\lambda - c/\lambda'\cos\theta}$$

$$\tan\phi = \frac{\lambda\sin\theta}{(\lambda'-\lambda\cos\theta)} \tag{11}$$

Kinetic Energy of the Recoil Electron

The kinetic energy of the recoil electron is given by

$$k_e = (m - m_0)c^2 \tag{12}$$

Also,
$$k_e = h\nu - h\nu' \tag{13}$$

or
$$k_e = \frac{hc}{\lambda} - \frac{hc}{\lambda'} = hc\left(\frac{\lambda'-\lambda}{\lambda\lambda'}\right) \tag{14}$$

From equation (11), we have

$$\lambda' = \lambda + \frac{h}{m_0 c}(1-\cos\theta)$$

or
$$\frac{c}{\nu'} = \frac{c}{\nu} + \frac{h}{m_0 c}(1-\cos\theta)$$

$$\frac{1}{\nu'} = \frac{1}{\nu}\left[1 + \frac{h\nu}{m_0 c^2}(1-\cos\theta)\right]$$

$$\nu' = \frac{\nu}{1 + \frac{h\nu}{m_0 c^2}(1-\cos\theta)} = \frac{\nu}{1 + x(1-\cos\theta)} \tag{15}$$

where, $x = \frac{h\nu}{m_0 c^2}$

Substituting value of ν' from equation (15) in equation (13), the kinetic energy of the recoil electron is

$$k_e = h\nu - h\left[\frac{\nu}{1 + x(1-\cos\theta)}\right]$$

$$= h\nu\left[1 - \frac{1}{1 + x(1-\cos\theta)}\right]$$

$$k_e = h\nu\left[\frac{x(1-\cos\theta)}{1 + x(1-\cos\theta)}\right] \tag{16}$$

where, $x = \frac{h\nu}{m_0 c^2}$

Variation in Compton shift as θ varies from 0° to 180°

The change in wavelength $\Delta\lambda(=\lambda'-\lambda)$ changes from zero to twice the Compton wavelength as changes from 0° to 180°. We have

$$\lambda'-\lambda = \frac{h}{m_0 c}(1-\cos\theta)$$

For $\theta = 0^o, \lambda'-\lambda = \Delta\lambda = \frac{h}{m_0 c}(0) = 0$

For $\theta = 90^o, \lambda'-\lambda = \Delta\lambda = \frac{h}{m_0 c}(1-0) = \frac{h}{m_0 c}$

for $\theta = 180^o, \lambda'-\lambda = \Delta\lambda = \frac{h}{m_0 c}(1-(-1)) = \frac{2h}{m_0 c}$

PAIR PRODUCTION AND ANNIHILATION

When γ - ray photon passes close to an atomic nucleus and it possess energy greater than 1.02 MeV, it gets converted into electron-positron pair. This process is termed as pair production. In this process, electromagnetic energy gets converted into matter.

Annihilation is the inverse of pair production which occurs when a positron and an electron come together under the influence of their opposite electric charges. Both the particles vanish and their mass is converted into energy. The process can be represented as follows: $e^+ + e^- \rightarrow \gamma + \gamma$

DEBROGLIE WAVES – MATTER WAVES

According to de Broglie matter have dual nature i.e., matter exhibit particle as well as wave-like behaviour.

According to de-Broglie, a wave is associated with every moving material particle. These waves, associated with moving material particles, are called de-Brogile waves or matter waves.

Expression for wavelength of de Broglie wave:-

According to quantum theory of radiation, the energy (E) of a photon of radiation of frequency ν is given by :
$$E = h\nu \tag{1}$$
where, h is Planck's constant.

The relativistic energy of a particle of rest mass mo is given by
$$E = \sqrt{m_0^2 c^4 + p^2 c^2}$$

For a photon, mass $m_0 = 0$
$$E = pc \tag{2}$$

From equations (1) and (2), we have
$$pc = h\nu$$

or
$$p = \frac{h\nu}{c}$$

or,
$$p = \frac{h\nu}{\nu\lambda}$$

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

Therefore, de-Broglie wavelength, $\lambda = \frac{h}{p} \tag{3}$

$$\therefore \quad \lambda = \frac{h}{mv}$$

This is known as de-Broglie equation.   (4)

Note:

1. If the velocity of the particle (v) is comparable to the velocity of light (c), then mass of the particle is given by

$$m = \frac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}$$

Therefore, de-Broglie relation is given by :

$$\lambda = \frac{h}{\dfrac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}\, v}$$

or,

$$\lambda = \frac{h\sqrt{1 - \dfrac{v^2}{c^2}}}{m_0 v}$$

2. Let an electron of mass m, charge e and velocity v is accelerated through a potential difference of V.

Kinetic energy gained by the electron $= \dfrac{1}{2}mv^2$

Work done on the electron = eV

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

or,

$$v = \sqrt{\frac{2eV}{m}}$$

Using de-Broglie equation: $\lambda = \dfrac{h}{mv}$ We get:

$$\lambda = \frac{h}{m\sqrt{\dfrac{2eV}{m}}} = \frac{h}{\sqrt{2meV}}$$

Putting h = 6.62 x 10⁻³⁴ Js, m = 9.1 x 10⁻³¹ kg, e = 1.6 x 10⁻¹⁹ C, we get

$$\lambda = \frac{12.27}{\sqrt{V}}\, \mathring{A}$$

WAVE FUNCTION

1. The wave function Ψ has no direct physical significance.
2. The square of the absolute value of the function, which is known as probability density $|\psi|^2$
3. The probability of experimentally finding the body at a particular time is described by $|\psi|^2$
4. The linear momentum, angular momentum and energy of the body are other quantities that can be obtained from Ψ.
5. Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity.
6. The porbability density $|\psi|^2$ for a complex Ψ is taken as the product $\Psi^* \Psi$ (Ψ and its complex conjugate Ψ^*).
7. Wave function $\Psi = A + iB$, where A and B are real function.
8. The complex conjugate Ψ^* of Ψ is = A – iB and so $\Psi^* \Psi = A^2 -$

$i^2 B = A^2 + B^2$ Thus, $\Psi^* \Psi$ is always a positive and real quantity.

9. Since is proportional to the probability density P of finding the body described by Ψ, the integral of $|\psi|^2$ over all space must be finite because the body is present somewhere.

10. If $\displaystyle\int_{-\infty}^{\infty} |\psi||^2 \, dv = 0,$

11. Also $|\psi|^2$ cannot be negative or complex.

12. If $|\psi|^2$ is equal to P, then $\displaystyle\int_{-\infty}^{\infty} |\psi|^2 z\, dv = 1$ (Normalization)

13. Since if the particle exists somewhere at all times

$$\int_{-\infty}^{\infty} P\, dv = 1$$

15. Besides being normalizable, Ψ must be single valued, since P can have only one value at a particular place and time, and continuous.

16. Momentum considerations require that the partial derivatives $\dfrac{\partial \psi}{\partial x}, \dfrac{\partial \psi}{\partial y}, \dfrac{\partial \psi}{\partial z}$, be finite, continuous, and single-valued.

A wave function must satisfy the following conditions:-
1. Ψ must be continuous and single-valued everywhere. $\dfrac{\partial \psi}{\partial x}, \dfrac{\partial \psi}{\partial y}, \dfrac{\partial \psi}{\partial z}$, must be continuous and single-valued everywhere.

2. Ψ must be normalizable, i.e. Ψ must go to 0 as x → ± ∞ , y → ± ∞ , z → ± ∞ in order that

$$\int |\psi|^2 \, dv$$

3. For a particle restricted to motion in the x-direction, the probability of finding it between x_1 and x_2 is given by

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\psi|^2 \, dx$$

BRA-KET NOTATION IN QUANTUM MECHANICS

Paul Dirac developed bra-ket notation, to describe quantum states. Dirac notation uses a ket vector |i > to describe a quantum state instead of a wave function Ψ_i, which is the basis of Schrodinger's notation.

The complex conjugate of the wave function ψ_i^* is represented by a bra vector < i|.

The inner product of two complex functions can be described by the bra – ket notation as:-

$$\int \psi_i^* \psi_j \, dv = <\psi_i | \psi_j> = <i|j> \qquad (1)$$

If a wave function is normalized, the following must hold

$$\int \psi \psi^* \, dv = \int |\psi|^2 \, dv = <\psi|\psi> = 1 \qquad (2)$$

EXPECTATION VALUES

In Schrodinger eq., the resulting wave function $\Psi(x, y, z, t)$ contains all information about the particle which is in the form of probabilities. Let us calculate the expectation value $< x >$ of the position of a particle confined to the x-axis that is described by the wave function $\Psi(x, t)$.

The average position of a number of identical particles distributed along the x axis in such a way that there are N_1 particles of x_1, N_2 particles at x_2, and so on is same as the centre of mass of the distribution i.e.

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \dots}{N_1 + N_2 + N_3} = \frac{\sum x_i N_i}{\sum N_i}$$

For a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i. This probability is

$$P_i = |\Psi_i|^2 \ dx \qquad (1)$$

where Ψ_i is the particle wave function evaluated at $x = x_i$. The expectation value of the position of the single particle is

$$< x > = \frac{\int_{-\infty}^{\infty} x |\psi|^2 \ dx}{\int_{-\infty}^{\infty} |\psi|^2 \ dx} \qquad (2)$$

If Ψ is a normalized wave function, the denominator of equation (2) equals the probability that the particle exists somewhere between $x = -\infty$ and $x = \infty$ and therefore has the value 1. In this case

Expectation value for position $< x > = \int_{-\infty}^{\infty} x |\psi|^2 dx$ (3)

This formula states that $< x >$ is located at the centre of mass of $|\Psi|^2$. If $|\Psi|^2$ is plotted versus x on a graph, the balance point will be at $< x >$.

Similarly, we can obtain the expectation value $< G(x) >$ of any quantity e.g., potential energy $U(x)$ – which is a function of the position x of a particle described by a wave function Ψ. i.e.

Expectation value $< G(x) > = \int_{-\infty}^{\infty} G(x) |\psi|^2 dx$ (4)

OPERATORS IN QUANTUM MECHANICS

In quantum mechanics, physical quantities or measurements are represented by linear operators. An operator may be defined as a rule by which, given any function, we can find one function by using the other.

Thus, we can define an operator P as : multiply the function by an independent variable, i.e., $Pf(x) = xf(x)$. Similarly, we can define an operator Q as the differentiation w.r.t. the independent variable, i.e., $Qf(x) = f'(x)$. The result obtained by the action of P followed by Q is different from that obtained by the action of Q followed by P as shown below.

$PQ\ f(x) = P[Qf(x)] = x\ f'(x)$

$QP\ f(x) = Q[Pf(x)] = x\ f'(x) + f(x)$

For the two operators α and β, if $\alpha\beta = \beta\alpha$, α and β are said to commute or be commutable. In this sense, the operators P and Q are not commutable.

Operators representing some important physical quantities :

Physical quantities	Symbol	Operator
Position	q (or r)	q (or x, y, z; r)
Energy	E	$i\hbar\dfrac{\partial}{\partial t}$
Kinetic energy	T	$-h^2\dfrac{\nabla^2}{2m}$
Momentum	p	$-i\hbar\nabla$ $\left(-i\hbar\dfrac{\partial}{\partial x}, -i\hbar\dfrac{\partial}{\partial y}, -i\hbar\dfrac{\partial}{\partial z} \text{ for x, y and z – components respectively}\right)$
Velocity	v	$-i\hbar\nabla$ $\left(\dfrac{-i\hbar}{m}\dfrac{\partial}{\partial x}, \dfrac{-i\hbar}{m}\dfrac{\partial}{\partial y}, \dfrac{-i\hbar}{m}\dfrac{\partial}{\partial z}\right)$
Hamiltonian	H	$i\hbar\dfrac{\partial}{\partial t}$

For example:-
1. Schrodinger equation
$H\ \Psi = E\ \Psi$
can be expressed as $H\psi = i\hbar\dfrac{\partial\psi}{\partial t}$ or $(H)\psi = \left(i\hbar\dfrac{\partial}{\partial t}\right)\psi$

where $\hbar = \dfrac{h}{2\pi}$ and h is Planck's constant.

2. If P and Q are the momentum and position operators respectively, the PQ Ψ can be represented as

$$PQ\psi = -i\hbar\frac{\partial}{\partial q}(q\psi) = -i\hbar\psi - i\hbar q\frac{\partial\psi}{\partial q}$$

$$QP\psi = q\left(-i\hbar\frac{\partial\psi}{\partial q}\right) = -i\hbar q\frac{\partial\omega}{\partial q}$$

Thus, we see that

$$(PQ - QP)\psi = -i\hbar\psi \neq 0$$

SCHRODINGER EQUATION : TIME DEPENDENT FORM

Ψ is same as y of wave motion, but Ψ is not a measurable quantity and is complex. Let Ψ for a particle moving freely in the + x direction is given by:-

$$\psi = Ae^{-i\omega\left(t - x/v\right)} \qquad (1)$$

using $\omega = 2\pi v$ and $v = v\lambda$ we get:-

$$\psi = Ae^{-2\pi i\left(vt - \frac{x}{\lambda}\right)} \qquad (2)$$

As we know:- $E = hv = 2\pi\hbar v$ and $\lambda = \dfrac{h}{p} = \dfrac{2\pi\hbar}{p}$

$\therefore$ For free particle $\Rightarrow \psi = Ae^{-(i/\hbar)(Et - px)}$ (3)

Eq. (3) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the + x direction. Let us discuss the significance of the result:-

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{p^2}{\hbar^2}\psi \Rightarrow p^2\psi = -\hbar^2\frac{\partial^2\psi}{\partial x^2} \qquad (4)$$

Differentiating eq. (3) w.r.t. t gives

$$\frac{\partial\psi}{\partial t} = -\frac{iE}{\hbar}\psi \Rightarrow E\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t} \qquad (5)$$

At very small speeds the total energy E of a particle is the sum of

its kinetic energy $\frac{p^2}{2m}$ and its potential energy U. where U is a function of position x and time t, i.e.,

$$E = \frac{p^2}{2m} + U(x,t) \qquad (6)$$

Multiplying both sides of equation (6) by Ψ, we get

$$E\psi = \frac{p^2\psi}{2m} + U\psi \qquad (7)$$

Substituting for E Ψ and p² Ψ from eq. (5) and (4), we get time dependent form of Schrodinger equation in one dimension:-

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi \qquad (8)$$

In 3-D, the time-dependent form of Schrodinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi \qquad (9)$$

Note:-
1. Any restrictions on the particle's motion will affect the potential energy U.
2. Schrodinger equation is a basic principle itself and cannot be derived from other basic principles of physics.
3. Schrodinger equation is accurate in predicting the results of experiments for atomic and subatomic particles.

SCHRODINGER'S EQUATION : (TIME INDEPENDENT)

In various cases, the potential energy of a particle does not depend on time. Hence, Schrodinger equation may be simplified by eliminating t.
One-dimensional wave function Ψ may be expressed as:-

$$\psi(t) = Ae^{-(i/\hbar)(Et-px)} = A(e^{-i(E/\hbar)t} e^{+(ip/\hbar)x}) \qquad (1)$$

$$= \psi(0)e^{-(iE/\hbar)t}$$

$$\begin{bmatrix} \because \psi(0) = Ae^{-(i/\hbar)(E(0)-px)} \\ \Rightarrow \psi(0) = Ae^{-(i/\hbar)(px)} \end{bmatrix}$$

Substituting Ψ of eq. (1) in the time – dependent form of Schrodinger equation

$$\left(i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi\right), \text{ we get}$$

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m}e^{-(iE/\hbar)t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0 \qquad (2)$$

Eq.(3) is the steady state form (time independent form) of Schrodinger's equation. In 3 – D the corresponding Schrodinger equation is:-

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0 \qquad (4)$$

As $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \Rightarrow \nabla^2\psi + \frac{2m}{\hbar^2}(E-U)\psi = 0 \qquad (5)$

EIGENVALUES AND EIGENFUNCTIONS

The values of energy En for which Schrodinger's (time independent) steady state equation can be solved are called Eigenvalues and the corresponding wave function Ψ_n are called Eigenfunctions. The discrete energy levels of the hydrogen atom

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

are an example of a set of eigenvalues.
An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum L. In the case of the hydrogen atom, the eigenvalues of the magnitude of the total angular momentum are specified by

$$L = \sqrt{l(l+1)}\hbar \qquad l = 0, 1, 2, ... (n-1) \qquad (2)$$

DEGENERATE AND NON-DEGENERATE EIGENFUNCTIONS

When $H\Psi_n = E_n\Psi_n$ is solved, corresponding to each eigenvalue there is only one eigenfunction. In such a situation, the eigenfunction is known as degenerate.

Eigenfunction : However, there are situations when corresponding to a single eigenvalue, there are a number of eigenfunctions, then these eigenfunctions are known as non degenerate eigenfunctions.

In quantum mechanics, there are situations when the eigenvalue depends on principal quantum number n (E_n), however, eigenfunction also depends upon orbital quantum number l and magnetic quantum number m (Ψn/m).

As for each n, l can vary from 0 to n – 1 and for each of these l values, m can vary from – l to + l (2l + 1 values). This leads to degeneracy. The total degeneracy is

$$\sum_{l=0}^{n-1}(2l+1) = \frac{2(n)(n-1)}{2} + n = n^2$$

For n = 2, l = 0, m = 0; l = 1, m = 0; l = 1, m = ± 1, giving four wave functions, i.e., system becomes fourfold degenerate. Similarly we can work out for n = 3, system becomes nine fold degenerate and for n = 4, the system becomes sixteen fold degenerate, and so on.

PARTICLE IN A BOX

The simplest quantum-mechanical problem is that of a particle in a box with infinitely hard walls. We may specify the particle's motion by saying that it is restricted to travel along the x-axis between x = 0 and x = L by infinitely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant.

The potential energy U of the particle is infinite on both sides of the box, while U is a constant (say zero for convenience) inside the box. Because the particle cannot have an infinite amount of energy, it cannot exist outside the box and so its wave function Ψ is 0 for x ≤ 0 and x ≥ L. Let us find the value of Ψ within the box.
As we know Schrodinger equation within a box is:-

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

Since U = 0 inside the box. (The total derivative $\frac{d^2\psi}{dx^2}$ is the same as the partial derivative $\frac{d^2\psi}{dx^2}$ because Ψ is a function of x only. Eq. (1) has the general solution:-

$$\psi = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x \qquad (2)$$

This solution is subject to the boundary conditions that Ψ = 0 for x = 0 and L. Since cos 0 = 1, the second term cannot describe the particle because it does not vanish at x = 0. Hence, we conclude

that B = 0. Since sin 0 = 0, the sine term always yields Ψ = 0 at x = 0, as required, but Ψ will be zero at x = L only when

$$\frac{\sqrt{2mE}}{\hbar}L = n\pi, \qquad n = 1, 2, 3, \ldots\ldots \qquad (3)$$

This is because the sine of the angles π, 2π, 3π, … are all 0. From eq. (3) it is clear that the energy of the particle can have certain values which are the eigenvalues. These eigenvalues, constituting the energy levels of the system and are found by solving eq. (3) for En, which gives:-

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad n = 1, 2, 3, \ldots.. \qquad (4)$$

Wave Functions of A Particle in a Box

The wave functions of a particle in a box whose energies are E_n, from eq. (2) with B = 0, are

$$\psi_n = A\sin\frac{\sqrt{2mE_n}}{\hbar}x \qquad (5)$$

Substituting eq.(4) for En gives

$$\psi_n = A\sin\frac{\sqrt{2m\frac{n^2\pi^2\hbar^2}{2mL^2}}}{\hbar}x = A\sin\frac{n\pi x}{L} \qquad (6)$$

These eigenfunctions meet all the requirements. For each quantum number n, Ψ_n is a finite and single-valued function.
Also, he integral of $|\Psi_n|^2$ is finite. With the help of trigonometry:-

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

we get:-

$$\int_{-\infty}^{\infty}|\psi_n|^2 dx = \int_o^l|\psi_n|^2 dx = A^2\int_0^l \sin^2\left(\frac{n\pi x}{L}\right)dx = \frac{A^2}{2}\left[\int_o^l dx - \int_o^l \cos\left(\frac{2\pi nx}{l}\right)dx\right]$$

$$= \frac{A^2}{2}\left[x - \left(\frac{L}{2n\pi}\right)\sin\frac{2n\pi x}{L}\right]_o^l = A^2\left(\frac{L}{2}\right) \qquad (2)$$

To normalize Ψ we must assign a value to A such that $|\psi_n|^2 dx$ is equal to the probability Pdx of finding the particle between x and x + dx.
If $|\psi_n|^2 dx$ is equal Pdx, then:-

$$\int|\psi|^2 dx = 1 \qquad (8)$$

Comparing eq. (7) and (8), we get the normalized wave function of a particle in a box:- $A = \sqrt{\frac{2}{L}} \qquad (9)$

The normalized wave functions of the particle are:-

$$\psi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad n = 1, 2, 3, \ldots\ldots\ldots \qquad (10)$$

Ψ_n may be negative as well as positive but $|\Psi_n|^2$ is always + ve and since Ψ_n is normalized, its value at a given x is equal to the probability density of finding a particle there.
In every case $|\Psi_n|^2 = 2$ at x = 0 and x = L.
At a particular place in the box the probability of finding a particle may be different for different quantum numbers.
For example $|\Psi_1|^2$, has its maximum value of in the middle of the Box.

SIMPLE HARMONIC OSCILLATOR

There are many quantum systems in a simple harmonic oscillator. For example, the variation of diatomic molecules and motions of atoms in a crystal lattice can be considered as the motion of particles in harmonic fields. Potential energy U (x) of a harmonic oscillator of mass m is *given by:-*

$$U(x) = \frac{1}{2}kx^2 \qquad (1)$$

where k(= m ω²) is the spring constant. The Schrodinger equation for this system can be written as:-

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{k}{2}x^2\right)\psi = 0 \qquad (2)$$

The solution of the Schrodinger equation gives:-

$$\psi_n = A_n H_n(z)e^{-z^2/2}$$

$$= A_n H_n\left[\left(\frac{mk}{\hbar}\right)^{1/4}x\right]\exp\left[-\frac{1}{2}\left(\frac{mk}{\hbar^2}\right)^{1/2}x^2\right] \qquad (3)$$

and eigenvalues

$$E_n = \hbar\sqrt{\frac{k}{m}}\left(n + \frac{1}{2}\right)$$

$$= \left(n + \frac{1}{2}\right)\hbar\omega, \qquad n = 0, 1, 2, \ldots. \qquad (4)$$

where An and Hn (z) (Hermite polynomials) are given by:-

$$A_n = \left[\frac{\left(\frac{mk}{\hbar}\right)^{\frac{1}{2}}}{2^n n!\pi^{\frac{1}{2}}}\right]^{\frac{1}{2}}$$

$$H_n(z) = (-1)^n \exp(z^2)\frac{d^n}{dz^n}\exp(-z^2) \qquad (5)$$

$\Psi_n(x)$ and $|\psi_n(x)|^2$ have a finite values. The probability density oscillates between the turning points and decreases exponentially beyond the turning points. The energy levels (eq. (4)) are equally spaced. For the ground state (n = 0), from eq. (4), *we get:-*

$$E_o = \frac{1}{2}\hbar\omega \qquad (6)$$

Thus, the oscillator will have this energy even at absolute zero. This energy is referred to as zero point energy. This is in contradiction with Planck oscillator for which

$$E_n = nh\omega \text{ and so for n = 0, } E_0 = 0.$$

The existence of zero point energy is in accordance with the uncertainty principle. The laws of quantum mechanics do not permit the harmonic oscillator to have zero energy and the smallest allowed energy is the zero point energy. If the oscillator has zero energy, it will also have zero momentum and therefore can be located exactly at the position of minimum potential energy, which will not be in accordance with the uncertainly principle.

A comparison of energy values $\left(E_n = \left(n + \frac{1}{2}\right)h\omega \text{ vs } E_n = nh\omega\right)$

makes it evident that the quantum mechanical values are higher by $\frac{1}{2}h\omega$

Also, since $H_0(z) = 1$, the ground state wave function can be shown to be

$$\psi_o = \left(\frac{m\omega}{h\pi}\right)^{1/4}\exp\left(-\frac{m\omega x^2}{2h}\right) \qquad (7)$$