KUNTHAVAI NAACHIYAAR GOVT ARTS COLLEGE FOR WOMEN

DEPARTMENT OF PHYSICS

I M.SC PHYSICS

QUANTUM MECHANICS

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UNIT – I

SCHRODINGER'S EQUATION AND GENERAL FORMULATION

Posulates of Quantum Mechanics

1. The state of a system is completely described by a wave function Ψ (**r**,t). $\Psi = \Psi(x, y, z, t)$ [*Here system means any free particle*].

2. Each dynamical variable is represented by a linear operator (called Hermitian operator). The operator gives the only possible result of observable. [Here dynamical variable means measurable quantities].

Quantity	Classical definition /dynamical variable	Operators
Position	r	**r**
Momentum	p	$-i\,\hbar\,\Delta$ $-i\,\dfrac{h}{2\pi}\,\Delta$
Angular momentum	r x p	$-i\hbar\,r$ x Δ $-i\,\dfrac{h}{2\pi}\,r$ x Δ
Kinetic energy	½ mv² = p²/2m (p=mv)	$T = -\left(\dfrac{\hbar^2}{2m}\right)\Delta^2$ OR $-\left(\dfrac{h^2}{8\pi^2 m}\right)\Delta^2$
Potential energy	V	V=V(x, y, z)
Total energy	p²/2m + V(r)	$\hat{H} = -\left(\dfrac{h^2}{8\pi^2 m}\right)\Delta^2 + V(r)$ (time independent) $i\hbar\,\dfrac{\partial}{\partial t}$ (time dependent)

3. If a large number of measurements of a dynamical variable **A** is made on a particle for which the wave function is Ψ, we get different values of **A** during different trials. The probable value of A (known as expectation value) is given by

$$\langle A \rangle = \int \Psi^* \hat{A}\ \Psi\ dV$$

$\hat{A}$ − operator

Ψ^* − complex conjugate of Ψ

<u>Examples-</u>

1. <u>Expectation value of momentum</u> is

$$\langle \vec{p} \rangle = \int\limits_{-\infty}^{\infty} \Psi^*(-i\frac{h}{2\pi}\Delta)\ \Psi\ dV$$

$$\langle \vec{p} \rangle = \int\limits_{-\infty}^{\infty} \Psi^*(-i\frac{h}{2\pi}\Delta)\ \Psi\ dxdydz$$

2. <u>Expectation value of energy</u> is

$$\langle E \rangle = \int\limits_{-\infty}^{\infty} \Psi^*(i\hbar\frac{\partial}{\partial t})\ \Psi\ dxdydz$$

4. The only possible values observed for the measurement of the observables are the eigen values which satisfies the equation

$$\hat{A}\ \Psi = \alpha\ \Psi$$

α represents the eigen values and Ψ represents the eigen function.

5. The equation of motion of the system is given by

$$\hat{H}\ \Psi = i\hbar\frac{\partial}{\partial t}\ \Psi \qquad \text{OR}\ \ H\Psi = E\Psi$$

$\hat{H}$ is the Hamiltonian of the system.

The time evolution of the wavefunction is given by the time dependent schrodinger wave equation.

Derivation of Schrodinger's Wave Equation

It is the mathematical equation to describe the dual nature of matter waves.

Schrodinger's Time Independent wave equation:

Schrodinger described the wave nature of a particle in a mathematical form by connecting de-Broglie wavelength with classical wave equation of a moving particle.

The classical wave equation is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} ------ (1)$$

Ψ is wave displacement or wave function

Laplacian operator $\quad \nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

From eqn. (1) $\quad \left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right)\Psi = \dfrac{1}{v^2}\dfrac{\partial^2 \Psi}{\partial t^2}$

$$\nabla^2 \Psi = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} ----------- (2)$$

Solution for the above equation is $\quad \Psi = \Psi_0 e^{-i\omega t} --- (3)$

Ψ_0 is the amplitude of the wave at the point (x,y,z). It is a function of position. That is
$\Psi(x, y, z, t) = \Psi_0(x, y, z)e^{-i\omega t}$

Differentiate eqn. (3) twice w.r.t. 't'

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi_0 e^{-i\omega t} \quad ; \quad \frac{\partial^2 \Psi}{\partial t^2} = i^2 \omega^2 \Psi_0 e^{-i\omega t}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -\omega^2 \Psi ------(4)$$

Put (4) in (2)

$$\nabla^2 \Psi = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} = \frac{1}{v^2}(-\omega^2 \Psi)$$

$$\nabla^2 \Psi = -\frac{\omega^2}{v^2}\Psi ------- (5)$$

Angular frequency $\omega = 2\pi \upsilon = \dfrac{2\pi v}{\lambda} ---(6)$

Put (6) in (5)

$$\nabla^2 \Psi = -\frac{4\pi^2}{\lambda^2}\Psi$$

$$\nabla^2 \Psi + \frac{4\pi^2}{\lambda^2}\Psi = 0 ----- (7)$$

de-Broglie wavelength $\lambda = \dfrac{h}{mv}$

Eqn. (7) becomes $\nabla^2 \Psi + \dfrac{4\pi^2 m^2 v^2}{h^2}\Psi = 0 ----(8)$

Let E be the total energy of the particle and V is the potential energy and kinetic energy $= \frac{1}{2}mv^2$

$$E = V + \frac{1}{2}mv^2 ; \qquad 2(E - V) = mv^2$$

multiply through out by m

$$2m(E - V) = m^2 v^2 ----(9)$$

Put (9) in (8)

$$\nabla^2 \Psi + \frac{4\pi^2 2m(E-V)}{h^2}\Psi = 0 \qquad \boxed{\hbar = \frac{h}{2\pi} ; \ \hbar^2 = \frac{h^2}{4\pi^2}}$$

$$\nabla^2 \Psi + \frac{8\pi^2 m(E - V)}{h^2}\Psi = 0 \quad ;$$

$$\boxed{\nabla^2 \Psi + \frac{2m(E - V)}{\hbar^2}\Psi = 0 ----(10)}$$

Eqn.(10) is known as *Schrodinger Time Independent equation.*

For 1-D the above eqn becomes,

$$\frac{d^2 \Psi}{\partial x^2} + \frac{2m(E - V)}{\hbar^2}\Psi = 0$$

For a free particle V=0, $\quad \dfrac{d^2 \Psi}{\partial x^2} + \dfrac{2mE}{\hbar^2}\Psi = 0$

Schrodinger's Time Dependent wave equation:

The classical wave equation is

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2}$$

$$\nabla^2 \Psi = \frac{1}{v^2}\frac{\partial^2 \Psi}{\partial t^2} \ ----------- (1)$$

Solution for the above equation is $\quad \Psi = \Psi_0 e^{-i\omega t} \ --- (2)$

Differentiate eqn. (2) w.r.t. 't'

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi_0 e^{-i\omega t}$$

$$\frac{\partial \Psi}{\partial t} = -i\omega \Psi$$

Angular frequency $\quad \omega = 2\pi \upsilon$

$$\frac{\partial \Psi}{\partial t} = -i2\pi \upsilon \Psi$$

$E = h\upsilon \ ;$

$\upsilon = \frac{E}{h} \ ;$

$\hbar = \frac{h}{2\pi}$

$$\therefore \frac{\partial \Psi}{\partial t} = -i2\pi \frac{E}{h}\Psi = -i2\pi \frac{E}{2\pi\hbar}\Psi = -i\frac{E}{\hbar}\Psi$$

$$E\,\Psi = -\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = i\hbar\frac{\partial\Psi}{\partial t} ---- (3)$$

Now time independent wave eqn is $\quad \nabla^2\Psi + \frac{2m(E-V)}{\hbar^2}\Psi = 0$

Substitute for $E\,\Psi$

$$\nabla^2\Psi + \frac{2m}{\hbar^2}\left(i\hbar\frac{\partial\Psi}{\partial t} - V\Psi\right) = 0$$

$$\frac{2m}{\hbar^2}\left(i\hbar\frac{\partial\Psi}{\partial t}\right) = -\nabla^2\Psi + \frac{2m}{\hbar^2}V\Psi$$

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = \left[V - \frac{\hbar^2}{2m}\nabla^2\right]\Psi ----- (4)}$$

$$E\,\Psi = H\,\Psi ------- (5)$$

$$\textbf{Where } E = i\hbar\frac{\partial}{\partial t}$$

$$H = V - \frac{\hbar^2}{2m}\nabla^2$$

The eqn (4) & (5) is known as *Schrodinger's Time Dependent wave equation.*

Physical meaning and conditions on the wave function (Ψ)

→ Wave function is a variable quantity that is associated with a moving particle at any position (x,y,z) and at any time (t)

→ Wavefunction is the probability of finding the particle at any position and at any time.

→ It relates the particle and wave statistically

That is, $\quad \Psi = \Psi_0 e^{-i\omega t}$

→ It gives information about particle behaviour.

→ It is a complex quantity and cannot be measured.

→ $|\Psi|^2 = \Psi^*\Psi$ is real and positive

→ $|\Psi|^2$ represents the probability density. i.e., probability of finding the particle per unit volume.

→ For a given volume $d\tau$, the probability of finding the particle is,

$$P = \iiint |\Psi|^2 \, d\tau \, ; \qquad d\tau = dxdydz$$

If P=0, there is no chance of finding the particle within the given limits.

If P=1, there is 100% chance of finding the particle

If P=0.5, there is 50% chance of finding the particle.

Expectation Values

The absolute square of the wavefunction is a measure of the probability of finding a particle at a particular point in space. When a large number of measurements are made on some dynamical quantity, we get different values during each observation. The average value or expected value of any dynamical variale A is given as,

$$\langle A \rangle = \int \Psi^* \hat{A} \ \Psi \ dV$$

$\hat{A}$ is operator and Ψ^* is complex conjugate of Ψ.

The above formula holds only if the wavefunction is normalised. If the wavefunction is not normalised, then the following formula is used.

$$\langle A \rangle = \frac{\int \Psi^* A_{op} \ \Psi \ dV}{\int \Psi^* \ \Psi \ dV}$$

Thus the expectation value is the mathematical expectation for the result of a single measurement or it is the average of the large number of measurements on independent systems.

The expectation value of position is

$$\langle r \rangle = \int \Psi^*(r,t) \ r \ \Psi(r,t) \ dV$$

This is equivalent to th following three expressions.

$$\langle x \rangle = \int \Psi^* x \ \Psi \ dV$$

$$\langle y \rangle = \int \Psi^* y \ \Psi \ dV$$

$$\langle z \rangle = \int \Psi^* z \ \Psi \ dV$$

$\langle x \rangle$, $\langle y \rangle$, $\langle z \rangle$ are the expectation values of the coordinates x,y and z of the particle respectively.

The expectation value of potential energy V is

$$\langle V \rangle = \int \Psi^*(r,t) \; V\,(r,t) \; \Psi(r,t) \; d\tau$$

$d\tau$ is the volume instead of dV to avoid confusion with P.E.

The expectation value of energy is

$$\langle E \rangle = \int \Psi^* \left(i\hbar \frac{\partial}{\partial t} \right) \Psi \; d\tau$$

$$\langle E \rangle = i\hbar \int \Psi^* \frac{\partial \Psi}{\partial t} \; d\tau$$

The expectation value of momentum is

$$\langle p \rangle = \int \Psi^*(-i\hbar \nabla) \; \Psi \; d\tau = -i\hbar \int \Psi^* \nabla \Psi \; d\tau$$

The three components of momentum is

$$\langle p_x \rangle = -i\hbar \int \Psi^* x \; \Psi \; d\tau$$

$$\langle p_y \rangle = -i\hbar \int \Psi^* y \; \Psi \; d\tau$$

$$\langle p_z \rangle = -i\hbar \int \Psi^* z \; \Psi \; d\tau$$

$\langle p_x \rangle, \langle p_y \rangle, \langle p_z \rangle$ are the expectation values of the components of the momentum along x, y and z axes.

Ehrenfest's Theorem

The theorem states that "the quntum mechanical expectation value of dynamical quantities gives the same result as classial mechanics".

The theorem can be proved for one dimensional motion of a particle by showing that,

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p_x\rangle}{m}$$

Proof

Let x be the position coordinate of a particle of mass m, at time t.

The expectation value of x is given by

$$\langle x\rangle = \int_{-\infty}^{\infty} \Psi^* \, x \, \Psi \, dx ----- 1$$

Differentiation with respect to 't'

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} x \frac{\partial}{\partial t}(\Psi^* \, \Psi) \, dx$$

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} x \left(\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}\right) dx ----2$$

Schrodinger's time dependent (1-D) wave equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}$$

$$\frac{\partial \Psi}{\partial t} = \frac{1}{i\hbar}\left(V\Psi - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2}\right) ------3$$

Complex conjugate is,

$$\frac{\partial \Psi^*}{\partial t} = -\frac{1}{i\hbar}\left(V\Psi^* - \frac{\hbar^2}{2m} \frac{\partial^2 \Psi^*}{\partial x^2}\right) ------4$$

Substitute equation 3 and 4 in equation 2.

$$\frac{d\langle x\rangle}{dt} = \int_{-\infty}^{\infty} x \left[\Psi^* \frac{1}{i\hbar}\left(V\Psi - \frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}\right) + \Psi\frac{1}{-i\hbar}\left(V\Psi^* - \frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\right)\right] dx$$

$$= \frac{1}{i\hbar}\int_{-\infty}^{\infty} x\left[\left(\Psi^* V\Psi - \Psi^*\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}\right) - \left(\Psi V\Psi^* - \Psi\frac{\hbar^2}{2m}\frac{\partial^2\Psi^*}{\partial x^2}\right)\right] dx$$

$$= \frac{1}{i\hbar}\frac{\hbar^2}{2m}\int_{-\infty}^{\infty} x\left[\left(-\Psi^*\frac{\partial^2\Psi}{\partial x^2}\right) + \left(\Psi\frac{\partial^2\Psi^*}{\partial x^2}\right)\right] dx$$

$$= -\frac{\hbar}{i\,2m}\int_{-\infty}^{\infty} x\frac{\partial}{\partial x}\left[\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right] dx$$

Integration by parts,

$$\int uv\,dx = u\int v\,dx - \int \frac{du}{dx}\left(\int v\,dx\right) dx$$

$$\frac{d}{dt}\langle x\rangle = \frac{i\hbar}{2m}\left[x\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right)\right]_{-\infty}^{\infty} - \int 1.\int_{-\infty}^{\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right) dx$$

At $x\to\infty$, Ψ and $\frac{\partial\Psi}{\partial x}$ $\to zero$. Therefore first term becomes 0.

$$\frac{d}{dt}\langle x\rangle = -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \Psi\frac{\partial\Psi^*}{\partial x}\right) dx - - - - - -5$$

$$Momentum\ Operator\ \hat{p} = -i\hbar\nabla = \frac{\hbar}{i}\nabla$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$The\ expectation\ value\ of\ p_x\ is\ \langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^* \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\Psi dx$$

Therefore,

$$\int_{-\infty}^{\infty} \Psi^* \frac{\partial\Psi}{\partial x}\,dx = \frac{i}{\hbar}\langle p_x \rangle -------6$$

Complex conjugate is,

$$\int_{-\infty}^{\infty} \Psi \frac{\partial\Psi^*}{\partial x}\,dx = -\frac{i}{\hbar}\langle p_x \rangle -------7$$

Substitute equations 6 and 7 in equation 5. Then we get,

$$\frac{d}{dt}\langle x \rangle = -\frac{i\hbar}{2m}\left[\frac{i}{\hbar}\langle p_x \rangle - \left(-\frac{i}{\hbar}\langle p_x \rangle\right)\right]$$

$$\frac{d}{dt}\langle x \rangle = -\frac{i\hbar}{2m}\left[\frac{i}{\hbar}\langle p_x \rangle + \frac{i}{\hbar}\langle p_x \rangle\right]$$

$$\frac{d}{dt}\langle x \rangle = -\frac{i\hbar}{2m}\left(\frac{2i\langle p_x \rangle}{\hbar}\right)$$

$$\frac{d}{dt}\langle x \rangle = -\frac{i^2\langle p_x \rangle}{m} = \frac{\langle p_x \rangle}{m}$$

Thus,

$$\frac{d}{dt}\langle x \rangle = \frac{\langle p_x \rangle}{m}$$

Ehrenfest's theorem is proved.

Operator Formalism

"An operator is a rule that transforms a given function into another function". For example the operator $\partial/\partial x$ represents differentiation with respect to x. when it operates,

$$f(x) = x^n$$

$$then, \frac{df}{dx} = nx^{n-1}$$

An operator $\hat{A}$ when operates on a function f(x) then,

$$\hat{A} f(x) = a f(x) -----\to Eigen\ Value\ equation$$

$$\hat{A} \quad \to \quad operator$$

$$f(x) \quad \to \quad Eigen\ function$$

$$a \quad \to \quad Eigen\ value$$

In quantum mechanics all physical observables (position, momentum, energy, etc.) are represented by Operator's. The outcomes of any measurement of the observable associated with the operator $\hat{A}$ are the Eigen values 'a' that satisfy the Eigen value equation. The symbol $^\wedge$ (hat) is used to distinguish the operator from physical quantities. Example, momentum operator for x-component is

$$\hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

The Eigen value of momentum operator,

$$\hat{p}_x \Psi = \lambda \Psi \quad (or) \quad \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} = \lambda \Psi$$

The total energy operator is denoted by $\hat{H}$ called as Hamiltonian operator.

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V \quad (Time\ Independent\ form)$$

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

The Eigen value equation of Hamiltonian operator is $\hat{H} \Psi = \hat{E} \Psi$

Hermitian Operators

An operator is said to be Hermitian if it satisfies $A^+ = A$, A is an operator. (Simply saying self- adjoint).

In quantum mechanics all observables are represented by Hermitian operators. Condition for Hermitian for an Eigen value equation $\hat{A}\,\Psi = \lambda\,\Psi$ is

$$\int \Psi^* \hat{A}\,\Psi\,d\tau = \int \Psi\,\hat{A}^*\,\Psi^*\,d\tau$$

For two different Eigen functions, Ψ_1 and Ψ_2, the condition is.

$$\int \Psi_1^* \hat{A}\,\Psi_2\,d\tau = \int \hat{A}^*\,\Psi_1^*\,\Psi_2\,d\tau$$

Properties of Hermitian Operators

1. Hermitian operators have only real eigen values.
2. Hermitian operators eigen functions are orthogonal if they have different eigen values.
3. The sum of two Hermitian operators is Hermitian.
4. The product of Hermitian operators is Hermitian if and only if they commute.

If $\hat{a}$ and $\hat{b}$ are commuting operators then, $\hat{a}\,.\,\hat{b} = \hat{b}\,.\,\hat{a}$

Show that Eigen values of Hermitian Operators are real.

$$\hat{A}\,\Psi = \lambda\,\Psi$$

$\Psi \rightarrow Eigen\ function, \lambda \rightarrow Eigen\ value\ and\ \hat{A} \rightarrow operator.$

$Taking\ complex\ conjugate, \quad \hat{A}^*\,\Psi^* = \lambda^*\Psi^*$

Condition for Hermitian,

$$\int \Psi^* \hat{A}\,\Psi\,d\tau = \int \Psi\,\hat{A}^*\,\Psi^*\,d\tau$$

Now,
$$\int \Psi^* \lambda\Psi\,d\tau = \int \Psi\,\lambda^*\,\Psi^*\,d\tau$$

$$\lambda \int \Psi^*\,\Psi\,d\tau = \lambda^* \int \Psi\,\Psi^*\,d\tau$$

$$\lambda.1 = \lambda^*.1$$

$$\lambda = \lambda^*$$

This is possible if λ is real. Thus Eigen value of Hermitian operator is real.

Show that Eigen functions of Hermitian Operators are orthogonal if they have different Eigen values.

$$\hat{A}\ \Psi_1 = \lambda_1\ \Psi_1$$
$$\hat{A}\ \Psi_2 = \lambda_2\ \Psi_2$$

Eigen value equations

Complex conjugate is,

$$\hat{A}^*\ \Psi_1^* = \lambda_1^*\ \Psi_1^* = \lambda_1\ \Psi_1^*$$
$$\hat{A}^*\ \Psi_2^* = \lambda_2^*\ \Psi_2^* = \lambda_2\ \Psi_2^*$$

$$\boxed{\begin{array}{c} \lambda_1 = \lambda_1^* \\[4pt] \lambda_2 = \lambda_2^* \end{array}}$$

Condition for Hermitian,

$$\int \Psi_1^*\ \hat{A}\ \Psi_2\ d\tau = \int \hat{A}^*\ \Psi_1^*\ \Psi_2\ d\tau$$

Now,

$$\int \Psi_1^*\ \lambda_2\ \Psi_2\ d\tau = \int \lambda_1\ \Psi_1^*\ \Psi_2\ d\tau$$

$$\lambda_2 \int \Psi_1^*\ \Psi_2\ d\tau = \lambda_1 \int \Psi_1^*\ \Psi_2\ d\tau$$

$$(\lambda_2 - \lambda_1) \int \Psi_1^*\ \Psi_2\ d\tau = 0$$

as $\lambda_2 \neq \lambda_1$, *we have* $\int \Psi_1^*\ \Psi_2\ d\tau = 0$, indicating Ψ_1 *and* Ψ_2 are orthogonal functions.

Heisenberg's uncertainty relation

- In 1927 Werner Heisenberg stated that it is impossible to know precisely where an electron is and what path it follows – a statement called the Heisenberg uncertainty principle.
- That is if momentum of a particle is precisely known the location of the same particle is completely unknown.
- Heisenberg uncertainty principle states that, **"It is impossible to measure both the position and momentum at the same time with accuracy".**

$$\Delta x . \Delta p \geq \hbar$$

Δx is uncertainty in position, Δp is uncertainty in momentum and $\hbar = {}^h/_{2\pi}$

(OR)

$$\Delta x . \Delta p \sim \hbar$$

- Uncertainty principle also applies to simultaneous measurements of *energy* and *time*

$$\Delta E . \Delta t \sim \hbar$$

UNIT – II   EXACTLY SOLVABLE SYSTEMS

LINEAR HARMONIC OSCILLATOR- SOLVING THE ONE DIMENSIONAL SCHRODINGER EQUATION.

In the case of a liner harmonic oscillator the force $F = - Kx$ can be represented by the potential energy function $V(x) = 1/2Kx^2$

From the Schroedinger equation,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}Kx^2\right)\psi = 0.$$

(2.1)

Introducing a variable $\xi = \alpha x$, where α is constant, we can write,

$$\frac{d\psi}{dx} = \frac{d\psi}{d\xi}\frac{d\xi}{dx} = \frac{d\psi}{d\xi}\alpha$$

and
$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{d\xi}.\alpha\right) = \frac{d}{d\xi}.\frac{d\xi}{dx}\left(\frac{d\psi}{d\xi}.\alpha\right) = \alpha^2\frac{d^2\psi}{d\xi^2}$$

Therefore eq. (2.1) becomes

$$\alpha^2\frac{d^2\psi}{d\xi^2} + \left[\frac{2mE}{\hbar^2} - \frac{mK}{\hbar^2}\frac{\xi^2}{\alpha^2}\right]\psi = 0.$$

(2.2)

or
$$\frac{d^2\psi}{d\xi^2} = \left[\frac{2mE}{\hbar^2\alpha^2} - \frac{mK\xi^2}{\alpha^4\hbar^2}\right]\psi = 0.$$

(2.3)

Let us choose α such that $\dfrac{mK}{\hbar^2\alpha^4} = 1$ and $\lambda = \dfrac{2mE}{\hbar^2\alpha^2}$

Therefore equation (2.3) assumes the dimensionless form

$$\frac{d^2\psi}{d\xi^2} = +(\lambda - \xi^2)\psi = 0.$$

(2.4)

Let the solution is of the form

$$\psi(\xi) = H(\xi)e^{-\xi^2/2}$$

(2.5)

where H(ξ) is a polynomial of finite order in ξ. If we consider the positive sign in the exponent, then ψ will diverge as $\xi \to \infty$. From eqn. (2.5)

$$\frac{d\psi}{d\xi} = H'(\xi)\exp\left[\frac{-\xi^2}{2}\right] - H(\xi)\xi\exp\left[\frac{-\xi^2}{2}\right]$$

and

$$\frac{d^2\psi}{d\xi^2} = H^{\cdot}(\xi)\exp\left[\frac{-\xi^2}{2}\right] - H'(\xi)\xi\exp\left[\frac{-\xi^2}{2}\right]$$

$$- H(\xi)\exp\left[\frac{-\xi^2}{2}\right] - \xi H'(\xi)\exp\left[\frac{-\xi^2}{2}\right] + \xi^2 H(\xi)\exp\left[\frac{-\xi^2}{2}\right]$$

$$= - H''(\xi)\exp\left[\frac{-\xi^2}{2}\right] - 2\xi H'(\xi)\exp\left[\frac{-\xi^2}{2}\right] + (\xi^2 - 1)H(\xi)\exp\left[\frac{-\xi^2}{2}\right]$$

Substituting the value of $\psi(\xi)$ and $\frac{d^2\psi}{d\xi^2}$ in equation (2.4) we get

$$\exp\left[\frac{-\xi^2}{2}\right]\left\{H''(\xi) - 2\xi H'(\xi) + \xi^2 H(\xi) - H(\xi) + (\lambda - \xi^2)H(\xi)\right\} = 0$$

$$H''(\xi) - 2\xi H'(\xi) + (\lambda - 1)H(\xi) = 0$$

or

(2.6)

Energy Levels.
Using power series, we can solve equation (2.6)
Let

$$H(\xi) = \xi^s(a_0 + a_1\xi + a_2\xi^2 + ...),$$

$$a_0 \neq 0, s \geq 0$$

$$= \xi^s \sum_{v=0}^{\infty} a_v \xi^v = \sum_{v=0}^{\infty} a_v \xi^{s+v}$$

On differentiation, $$\frac{dH}{d\xi} = \sum_v a_v(s+v)\xi^{s+v-1}$$

and $$\frac{d^2H}{d\xi^2} = \sum_v a_v(s+v)(s+v-1)\xi^{s+v-2}$$

Substituting these values in equation (2.6), we get,

$$\sum_v a_v(s+v)(s+v-1)\xi^{s+v-2} - 2\xi\sum_v a_v(s+v)\xi^{s+v-1} + (\lambda-1)\sum_v a_v\xi^{s+v} = 0$$

or $\quad \sum_v a_v (s+v)(s+v-1) \, \xi^{s+v-2} - 2\sum_v a_v (s+v) \, \xi^{s+v} + (\lambda-1)\sum_v a_v \, \xi^{s+v} = 0$

$$(2.7)$$

For $H(\xi)$ to be a solution for all values of ξ, the coefficient of the individual powers of ξ must vanish separately, i.e., equating to zero the coefficients of various powers of ξ we get

$$s(s\text{-}1) \, a_0 = 0$$

$$(s+1)(s) \, a_1 = 0$$

$$(s+2)(s+1) \, a_2 - (2s+1-\lambda) \, a_0 = 0$$

$$(s+3)(s+2) \, a_3 - (2s+3-\lambda) \, a_1 = 0$$

... ...

... ...

$$(s+v+2)(s+v+1) \, a_{v+2} - (2s+2v+1-\lambda) \, a_v = 0 \qquad (2.8)$$

From these expressions we can write,

$$a_{v+2} = \frac{2s+2v+1-\lambda}{(s+v+1)(s+v+2)} a_v \qquad (2.9)$$

where v is an integer. Since a_0 cannot be equal to zero, from the first of equations (2.8), $s = 0$ or 1. If a_0 is equal to zero, only odd powers appear. With a_1 equals to zero, the series contains even powers only. If we examine the convergence of the power series solution defined by equation (2.9), we find that as $v \to \infty$, $(a_{v+2})/a_v \to 2/v$, so that the series converges for all finite values of ξ.

Considering the series expansion of $e^{+\xi^2}$, we have

$$e^{+\xi^2} = 1 + \xi^2 + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + ... + \frac{\xi^v}{(v/2)!} + \frac{\xi^{v+2}}{(v/2+1)!} + ...$$

$$= b_0 + b_2\,\xi^2 + b_4\,\xi^4 + b_v\,\xi^v + b_{v+2}\xi^{v+2} + ...$$

$$\frac{b_{v+2}}{b_v} = \frac{\dfrac{1}{(v/2+1)!}}{\dfrac{1}{(v/2)!}} = \frac{2}{2+v} \qquad \text{or} \qquad \underset{v \to \infty}{\text{Lim}} \quad \frac{b_{v+2}}{b_v} = \frac{2}{v}$$

This shows that H(ξ) diverges approximately as e^{ξ^2} and the product $H(\xi)e^{-\xi^2/2}$ will behave like $e^{+\xi^2/2}$ in this region which tends to ∞, $as\ \xi \to \infty$. So this is not an acceptable solution. This situation can be avoided by coosing λ in such a way that the power series for H(ξ) cuts off at some term, making H (ξ) a polynomial.

From eqn (2.9), by making

$$\lambda = 2s + 2v + 1.$$

we can make the series cut off. The index s can still be either 0 or 1, and corresponding to these values, λ is equal to $2v + 1$ or $2v+3$ where $2v$ is an even integer. Or,

$$\lambda = (2n+1). \qquad\qquad n=0,1,2...$$
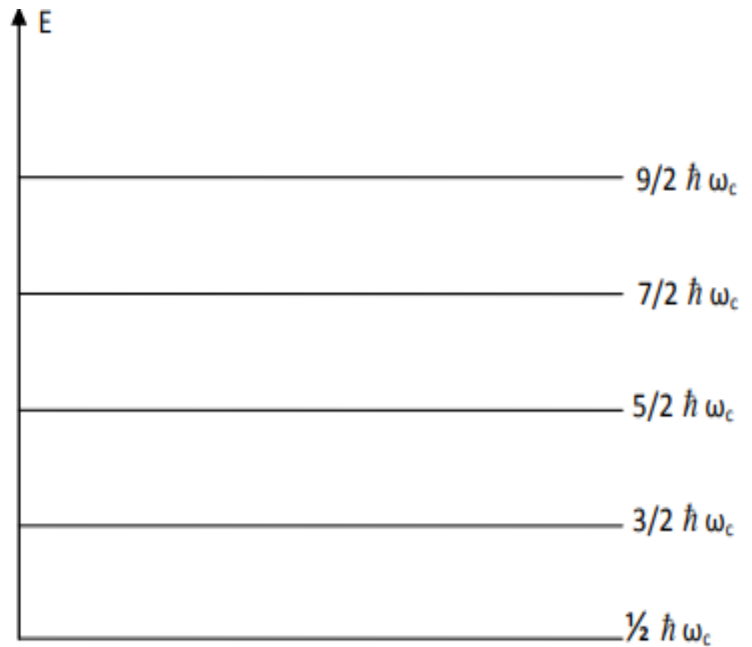
Then $\quad \dfrac{2E_n}{\hbar}\sqrt{\dfrac{m}{K}} = (2n+1)$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_c.$$

or

$n = 0,1,2...$ ...(2.9A)

where $\omega_c = \sqrt{\dfrac{K}{m}}$ is the classical

angular frequency of the

oscillator.

```
                                                          E
                                                          │
                                                          │
                                          ──────────────────  9/2 ℏ ωc
                                                          │
                                          ──────────────────  7/2 ℏ ωc
                                                          │
                                          ──────────────────  5/2 ℏ ωc
                                                          │
                                          ──────────────────  3/2 ℏ ωc
                                                          │
                                          ──────────────────  ½ ℏ ωc
```

Zero point energy. The energy levels given by equations (2.9A) are discrete and have equal spacings. When $n=0$, the finite value of lowest energy or ground state energy is $(1/2)\hbar\omega_c$. Hence zero point energy is given by,

$$E_0 = \frac{1}{2}\hbar\omega_c$$

and all higher energy levels are separated by an amount equal to $\hbar\omega_c$. Zero point energy is characteristic of quantum mechanics and is related to the uncertainty principle.

$$(s+v+2)(s+v+1)a_{v+2} - (2s+2v+1-\lambda)a_v = 0 \tag{2.8}$$

From these expressions we can write,

$$a_{v+2} = \frac{2s+2v+1-\lambda}{(s+v+1)(s+v+2)}a_v$$

(2.9)

where v is an integer. Since a_0 cannot be equal to zero, from the first of equations (2.8), $s = 0$ or 1. If a_0 is equal to zero, only odd powers appear. With a_1 equals to zero, the series contains even powers only. If we examine the convergence of the power series solution defined by equation (2.9), we find that as $v \rightarrow \infty$, $(a_{v+2})/a_v \rightarrow 2/v$, so that the series converges for all finite values of ξ.

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$$e^{+\xi^2} = 1+\xi^2+\frac{\xi^4}{2!}+\frac{\xi^6}{3!}+...+\frac{\xi^v}{(v/2)!}+\frac{\xi^{v+2}}{(v/2+1)!}+...$$

$$= b_0 + b_2\,\xi^2 + b_4\,\xi^4 + b_v\,\xi^v + b_{v+2}\xi^{v+2} + ...$$

$$\frac{b_{v+2}}{b_v} = \frac{\dfrac{1}{(v/2+1)!}}{\dfrac{1}{(v/2)!}} = \frac{2}{2+v} \qquad \text{or} \qquad \underset{v\rightarrow\infty}{\text{Lim}}\quad \frac{b_{v+2}}{b_v} = \frac{2}{v}$$

This shows that H(ξ) diverges approximately as e^{ξ^2} and the product $H(\xi)e^{-\xi^2/2}$ will behave like $e^{+\xi^2/2}$ in this region which tends to ∞, as $\xi \rightarrow \infty$. So this is not an acceptable solution. This situation can be avoided by coosing λ in such a way that the power series for H(ξ) cuts off at some term, making H (ξ) a polynomial.

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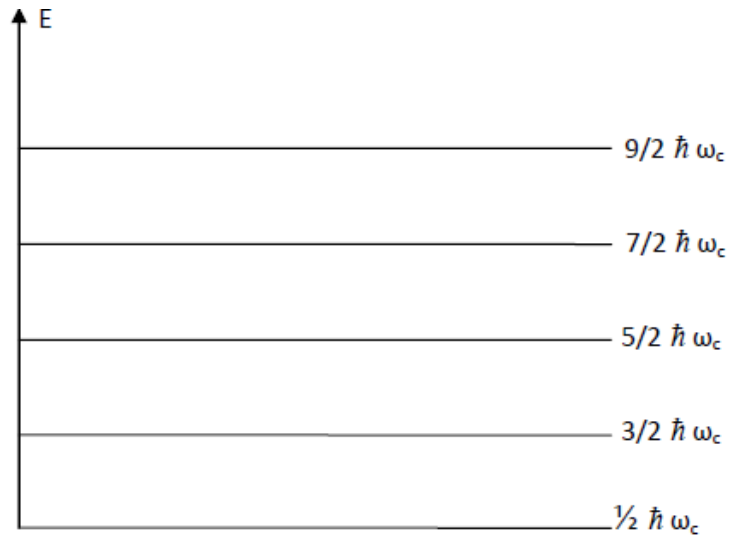
$$\lambda = (2n+1). \qquad\qquad n=0,1,2...$$

Then $\dfrac{2E_n}{\hbar}\sqrt{\dfrac{m}{K}} = (2n+1)$

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_c.$$

or

$n = 0, 1, 2...$ ...(2.9A)

where $\omega_c = \sqrt{\dfrac{K}{m}}$ is the classical

angular frequency of the

oscillator.

— 9/2 $\hbar$ ω_c

— 7/2 $\hbar$ ω_c

— 5/2 $\hbar$ ω_c

— 3/2 $\hbar$ ω_c

— ½ $\hbar$ ω_c

Zero point energy. The energy levels given by equations (2.9A) are discrete and have equal spacings. When $n=0$, the finite value of lowest energy or ground state energy is $(1/2)$ $\hbar\omega_c$. Hence zero point energy is given by,

$$E_0 = \frac{1}{2}\hbar\omega_c$$

and all higher energy levels are separated by an amount equal to $\hbar\omega_c$. Zero point energy is characteristic of quantum mechanics and is related to the uncertainty principle.

Infinitely deep potential well or particle in one-dimensional box

Consider a square potential well with infinitely high sides, as indicated in figure (2.1). The particle is bounded by impenetrable rigid walls of width $2a$ as shown. The potential of the well is represented by,

$V(x) = 0$ for $-a < x < a$ and

$V(x) = \pm \infty,$ for $|x| \geq a$

The boundary condition on the wavefunction is, it vanishes at the wall. That is

The boundary condition on the wavefunction is, it vanishes at the wall. That is

$$\psi_{x=a} = \psi_{x=-a} = 0$$

The wave equation for $|x| < a$ is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0 \qquad [\because V = 0]$$

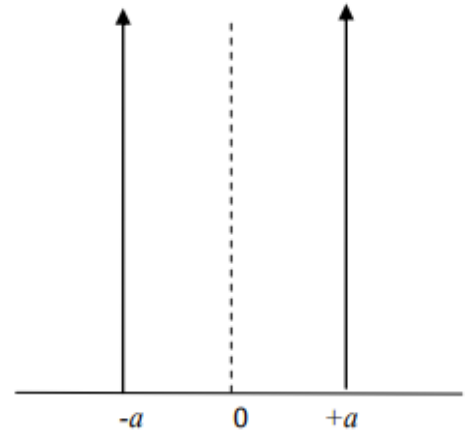$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad \text{where} \quad \alpha^2 = \frac{2mE}{\hbar^2}$$

The general solution of this eqn can be written as,

$$\psi = A \cos \alpha x + B \sin \alpha x. \quad (2.10)$$

Applying the boundary conditions,

$$\psi = 0 \text{ at } x = a \text{ and } \psi = 0 \text{ at } x = -a$$

We get, $A \cos \alpha a + B \sin \alpha a = 0.$ (2.11)

and $A \cos \alpha a - B \sin \alpha a = 0.$ (2.12)

Adding and subtracting equations (2.11) and (2.12), we get,

$$2A \cos \alpha a = 0 \qquad \text{and} \qquad 2B \sin \alpha a = 0.$$

There are two possible solutions namely,

(i) $A = 0$ or $\cos \alpha a = 0.$

(ii) $B = 0$ or $\sin \alpha a = 0.$

For $\sin \alpha a = 0$, $\alpha a = \pi, 2\pi, 3\pi \ldots\ldots n \pi/2$ where n is even

And for $\cos \alpha a = 0$, $\alpha a = \pi/2, 3\pi/2, \ldots = n\pi/2$,   where n is an odd integer.

We have, $\alpha^2 = \frac{2mE}{\hbar^2}$ or $E = \frac{\alpha^2 \hbar^2}{2m}$ (2.13)

or in general, $E_n = \frac{n^2\pi^2\hbar^2}{8ma^2}$ since, $\alpha = n\pi/2a.$ (2.14)

There are an infinite sequence of discrete energy levels that correspond to all positive integral values of n.

Wave function. The general form of wave functions may be written as

$$\psi_n = A\cos\frac{n\pi x}{2a} \qquad \text{when } n \text{ is odd} \qquad (2.15)$$

$$\psi_n = B\sin\frac{n\pi x}{2a} \qquad \text{when } n \text{ is even} \qquad (2.16)$$

To normalise the wave function ψ_n :

From eqn (2.15),

$$|\psi_n|^2 = \int_{-a}^{a} A^2 \cos^2\frac{n\pi x}{2a} dx = 1$$

$$\int_{-a}^{a} \frac{A^2}{2}\left(1+\cos\frac{2n\pi x}{2a}\right) dx = 1$$

On simplifying the above integral we get,

$$A^2 = \frac{1}{a} \qquad or \qquad A = \sqrt{(1/a)}.$$

Similarly we can show, $\qquad B = \sqrt{(1/a)}.$

Hence the normalized wavefunctions are,
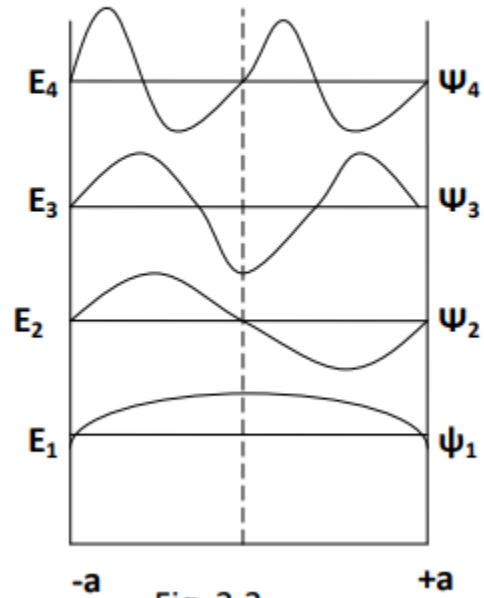
Fig. 2.2

$$\psi_n = \frac{1}{\sqrt{a}} \cos \frac{n\pi x}{2a} \qquad (n = 1, 3, 5,...). \qquad (2.17)$$

$$\psi_n = \frac{1}{\sqrt{a}} \sin \frac{n\pi x}{2a} \qquad (n = 2, 4, 6,...). \qquad (2.18)$$

The energy levels and wavefunctions are shown in fig. (2.2) The successive energy states differ by half wavelength. The lowest energy level has only half wavelength. The points between $a \leq x \leq -a$, where the wave function vanishes are called a *node*. For a particular energy state, characterised by the quantum number n, the number of intermediate nodes is *(n-1)*. Wavefunctions $\psi_n(x)$ for odd n are even functions of x. Such functions are said to have an even parity (symmetric). Similiary $\psi_n(x)$ for even n are odd functions (antisymmetric) and have an odd parity.

Rectangular potential barrier

Let us consider the one-dimensional problem where the potential is defined as in fig.2.5.

$$\left\{ \begin{array}{l} V(x) = 0 \quad for \quad x < 0 \\ \quad = V_0 for\ 0<x<a \\ \quad = 0\ for\ x > a \end{array} \right\}$$

$$(2.31)$$

Fig. 2.5

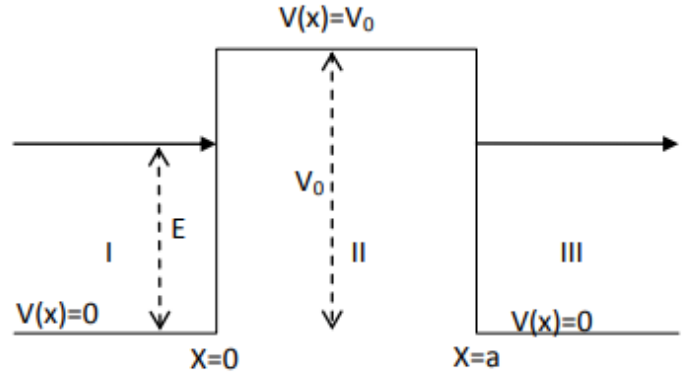Here we have a potential barrier between $x=0$ and $x=a$. If a particle having energy less than

$V_0, i.e., E < V_0$, approaches this barrier from the left, i.e., from 1st region, classically the particle will always be reflected and hence will not penetrate the barrier. However, wave mechanics predicts that the particle has some probability of penetrating to region 3rd, the probability of penetration being greater if $E > V_0$ classical mechanics predicts that the particle will always be transmitted ; while according to wave-mechanics, the particle has a finite probability of transmission and hence it is not certain that the particle will penetrate the barrier.

The Schroedinger equation for region-I is

$$\frac{\partial^2 \psi_1}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \text{ (since } V=0). \qquad (2.32)$$

The Schroedinger equation for II region is

$$\frac{\partial^2 \psi_2}{\partial x^2} + \frac{2m}{\hbar^2}(E - V_0)\psi_2 = 0. \qquad (2.33)$$

The Schroedinger equation for III region is

$$\frac{\partial^2 \psi_3}{\partial x^2} + \frac{2m}{\hbar^2} E\psi_3 = 0. \qquad (2.34)$$

Here ψ_1, ψ_2 and ψ_3 are the wave-functions for I, II and III regions respectively.

The general solutions of equations (2.32) (2.33) and (2.34) may be written as

$$\psi_1 = A_1 e^{ip_1 x/\hbar} + B_1 e^{-ip_1 x/\hbar} \qquad (2.35)$$

$$\psi_2 = A_2 e^{ip_2 x/\hbar} + B_2 e^{-ip_2 x/\hbar} \qquad (2.36)$$

$$\psi_3 = A_3 e^{ip_1 x/\hbar} + B_3 e^{-ip_1 x/\hbar} \qquad (2.37)$$

where p_1 and p_2, are the momenta of particle in the corresponding regions, which are given by

$$\left\{ \begin{array}{l} P_1 = \sqrt{2mE} \\ p_2 = \sqrt{2m(E - v_0)} \end{array} \right\} \tag{2.38}$$

A_1, B_1, A_2, B_2 and B_3 are constants to be determined by boundary conditions.

In equation (2.35) the first term represents the wave travelling along +ve x-axis in the I region, i.e., the incident wave and second term represents the wave travelling along negative X-axis i.e., wave reflected at $x=0$.

In equation (2.36), the first term represents the wave travelling along (+) ve X-axis in the II region, i.e., the wave transmitted at $x=0$ and second term represents the wave travelling along (-) ve X-axis in the II region, i.e., the wave reflected at $x=a$.

In equation (2.37) the first term represents the wave travelling along (+)ve X-axis in the III region, i.e., the wave transmitted $x=a$ and the second term represents the wave travelling along (-)ve X-axis in the III region; but no wave travels back from infinity in III region. Consequently $B_3 = 0$, so that the solution of equation (2.34), i.e., equation (2.37) can be written as

$$\psi_3 = A_3 e^{ip_1 x/\hbar} \tag{2.39}$$

For the evaluation the constants A_1, B_1, A_2, B_2 and A_3 we shall apply the conditions at the two boundaries $x=0$ and $x=a$.

One conditions is that ψ must be continuous at the boundaries, i.e.,

$$\left\{ \begin{array}{l} \psi_1 = \psi_2 \ \ at \ x{=}0 \ \ ....(\ A \ ) \\ \psi_2 = \psi_3 \ \ at \ x{=}a \ \ ....(\ B \ ) \end{array} \right\} \tag{2.40}$$

The other condition is $\partial \psi / \partial x$ must be continuous at the boundaries i.e.,

$$\left.\begin{array}{l} \dfrac{\partial \psi_1}{\partial x} = \dfrac{\partial \psi_2}{\partial x} \, at \, x=0 \quad ....(A) \\ \dfrac{\partial \psi_2}{\partial x} = \dfrac{\partial \psi_3}{\partial x} \, at \, x=a \quad ....(B) \end{array}\right\}$$ (2.41)

Applying boundary condition (2.40A) to equations (2.35) and (2.36), we have

$$A_1 + B_1 = A_2 + B_2$$ (2.42)

Applying boundary condition (2.40B) to equations (2.36) and (2.39), we get

$$A_2 e^{\,ip_2 a/\hbar} + B_2 e^{\,-ip_2 a/\hbar} = A_3 e^{\,ip_1 a/\hbar}$$ (2.43)

Differentiating equations (2.35), (2.36) and (2.39), we get

$$\frac{\partial \psi_1}{\partial x} = \frac{ip_1}{\hbar}\left[A_1 e^{\,ip_1 x/\hbar} + B_1 e^{\,-ip_1 x/\hbar} \right]$$ (2.44)

$$\frac{\partial \psi_2}{\partial x} = \frac{ip_2}{\hbar}\left[A_2 e^{\,ip_2 x/\hbar} + B_2 e^{\,-ip_2 x/\hbar} \right]$$ (2.45)

$$\frac{\partial \psi_3}{\partial x} = \frac{ip_1}{\hbar} A_3 e^{\,ip_1 x/\hbar}$$ (2.46)

Applying boundary conditions (2.41) to these equations, we get

$$p_1[A_1 - B_1] = p_2[A_2 - B_2]$$

and

$$p_2\left[A_2 e^{\,ip_2 a/\hbar} - B_2 e^{\,-ip_2 a/\hbar} \right] = p_1\left[A_3 e^{ip_1 a/\hbar} \right]$$

or

$$A_1 - B_1 = \frac{p_2}{p_1}(A_2 - B_2)$$ (2.47)

$$\left[A_2 e^{\,ip_2 a/\hbar} - B_2 e^{\,-ip_2 a/\hbar} \right] = \frac{p_1}{p_2} A_3 e^{\,ip_1 a/\hbar}$$ (2.48)

Solving (2.42) and (2.47) for A_1 and B_1, we get

$$A_1 = \frac{A_2}{2}\left(1+\frac{p_2}{p_1}\right)+\frac{B_2}{2}\left(1-\frac{p_2}{p_1}\right)$$

(2.49)

$$B_1 = \frac{A_2}{2}\left(1-\frac{p_2}{p_1}\right)+\frac{B_2}{2}\left(1+\frac{p_2}{p_1}\right)$$

(2.50)

Solving (2.43) and (2.48) for A_2 and B_2, we get

$$A_2 = \frac{A_3}{2}\left(1+\frac{p_1}{p_2}\right)e^{i(p_1-p_2)a/\hbar}$$

(2.51)

$$B_2 = \frac{A_3}{2}\left(1-\frac{p_1}{p_2}\right)e^{i(p_1+p_2)a/\hbar}$$

(2.52)

Substituting values of A_2 and B_2 from these equations in (2.49) and (2.50), we get

$$A_1 = \frac{A_3}{4}e^{ip_1a/\hbar}\left[\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{-p_2a/\hbar}\right]$$

(2.53A)

$$B_1 = \frac{A_3}{4}e^{ip_1a/\hbar}\left[\left(1-\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1+\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{-p_2a/\hbar}\right]$$

(2.53B)

Equation (2.53A) may be written as

$$\frac{A_3}{A_1}=\frac{4e^{-ip_1a/\hbar}}{\left\{\left(1+\frac{p_2}{p_1}\right)\left(1+\frac{p_1}{p_2}\right)e^{-ip_2a/\hbar}+\left(1-\frac{p_2}{p_1}\right)\left(1-\frac{p_1}{p_2}\right)e^{ip_2a/\hbar}\right\}}$$

$$=\frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1+p_2)^2e^{-ip_2a/\hbar}-(p_1-p_2)^2e^{-ip_2a/\hbar}}$$

$$=\frac{4p_1p_2e^{-ip_1a/\hbar}}{(p_1^2+p_2^2)(e^{-ip_2a/\hbar}-e^{ip_2a/\hbar})+2p_1p_2(e^{-ip_2a/\hbar}+e^{ip_2a/\hbar})}$$

$$= \frac{2p_1 p_2 e^{-ip_1 a/\hbar}}{(p_1^2 + p_2^2)\left(\dfrac{e^{-ip_2 a/\hbar} - e^{-ip_2 a/\hbar}}{2}\right) + 2p_1 p_2 \dfrac{(e^{-ip_2 a/\hbar} + e^{-ip_2 a/\hbar})}{2}}$$

Dividing equation (2.53B) by (2.53A), we get,

$$\frac{B_1}{A_1} = \frac{\left(1 - \dfrac{p_2}{p_1}\right)\left(1 + \dfrac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1 + \dfrac{p_2}{p_1}\right)\left(1 - \dfrac{p_1}{p_2}\right)e^{ip_2 a/\hbar}}{\left(1 + \dfrac{p_2}{p_1}\right)\left(1 + \dfrac{p_1}{p_2}\right)e^{-ip_2 a/\hbar} + \left(1 - \dfrac{p_2}{p_1}\right)\left(1 - \dfrac{p_1}{p_2}\right)e^{ip_2 a/\hbar}}$$

$$= \frac{(p_1^2 - p_2^2)(e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}{(p_1 + p_2)^2 (e^{-ip_2 a/\hbar} - (p_1 - p_2)^2 e^{ip_2 a/\hbar}}$$

$$= \frac{(p_1^2 - p_2^2)(e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}{(p_1^2 + p_2^2)(e^{ip_2 a/\hbar} - e^{ip_2 a/\hbar}) + 2p_1 p_2 (e^{-ip_2 a/\hbar} - e^{ip_2 a/\hbar})}$$

Case (i) $E > V_0$; in this case $p_1 = \sqrt{2mE}$, $p_2 = \sqrt{2m(E - V_0)}$, both are real so

$$\frac{A_3}{A_1} = \frac{4p_1 p_2 e^{-ip_1 a/\hbar}}{(p_1^2 + p_2^2)\left\{-2i \sin \dfrac{p_2 a}{\hbar}\right\} + 2p_1 p_2 \left(-2\cos \dfrac{p_2 a}{\hbar}\right)}$$

$$= \frac{2p_1 p_2 e^{-ip_1 a/\hbar}}{i(p_1^2 + p_2^2)\sin \dfrac{p_2 a}{\hbar} + 2p_1 p_2 \cos \dfrac{p_2 a}{\hbar}}$$

$$\frac{A_3*}{A_1*} = \frac{2p_1 p_2 e^{ip_1 a/\hbar}}{-i(p_1^2 + p_2^2)\sin \dfrac{p_2 a}{\hbar} + 2p_1 p_2 \cos \dfrac{p_2 a}{\hbar}}$$

$\therefore$ Transmission coefficient $T = \dfrac{\text{Transmitted flux}}{\text{Incident flux}}$

$$R = \frac{\text{Reflected flux}}{\text{Incident flux}} = \frac{B_1 B_1* \dfrac{p_1}{m}}{A_1 A_1* \dfrac{p_1}{m}} = \frac{B_1 B_1*}{A_1 A_1*}$$

Rigid Rotator

The system, consisting of two spherical particles attached together, separated by finite fixed distance and capable of rotating about an axis passing through the centre of mass and normal to the plane containing the two particles, constitutes, a rigid rotator. If these two particles are constrained, to remain in one plane, then the direction of the axis of rotation is fixed and so the system is called the rigid rotator with fixed axis. If the plane of these two particles can move, then the axis of rotation is free to take any position in space and so the system is called the rigid rotator with free axis. In a diatomic molecule the atoms vibrate with respect to each other and so the distance between atoms will not be always constant ; while the distance apart of the equilibrium position is constant. Thus the system of diatomic molecules is not really
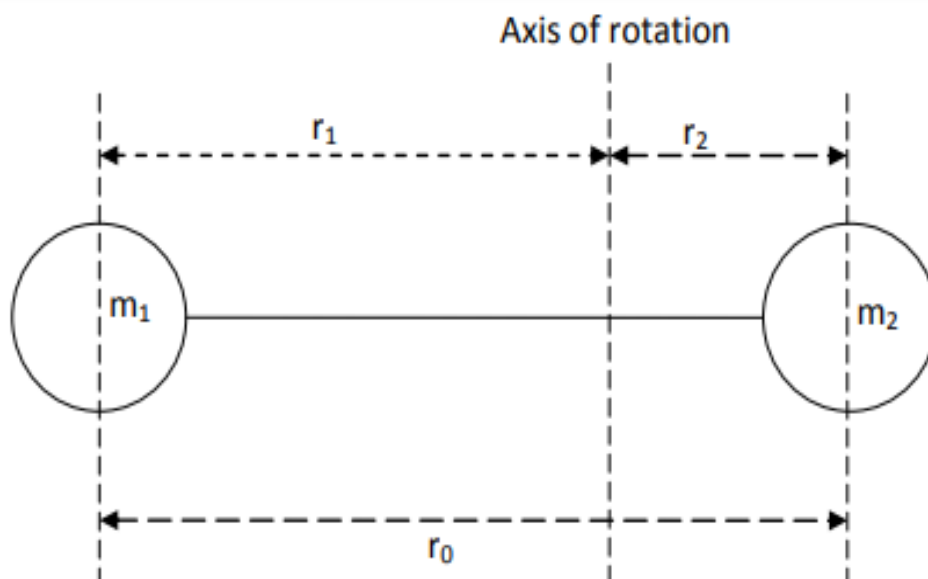
Energy for the rotator

The kinetic energy of a particle of mass m can be expressed as

$$T = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \tag{2.57}$$

where $\dot{x}, \dot{y}, \dot{z}$ are the components of the velocity of a particle along X, Y and z axes respectively. The transformation between Cartesian co-ordinates (x, y, z) and spherical co-ordinates (r, θ, φ) are given by

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi \tag{2.58}$$
$$z = r \cos\theta$$

so that the kinetic energy in spherical co-ordinates is expressed as

$$T = \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\phi}^2) \tag{2.59}$$

If the distance r of the particle from the origin is fixed, its derivative $\dot{r}$ will be zero ; then from equation (2.59) the kinetic energy would be

$$T = \frac{1}{2}mr^2(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2) \tag{2.60}$$

Taking O, the centre of mass of the rotator, as origin, the K.E. of the particle of mass m_1 is given by

$$T_1 = \frac{1}{2}m_1r_1^2(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

Similarly the K.E of the particle of mass m_2 is

$$T_2 = \frac{1}{2}m_2r_2^2(\dot{\theta}^2 + \sin^2\theta\,\dot{\phi}^2)$$

Hence the total kinetic energy of the rotator will be

$$T = T_1 + T_2 = \frac{1}{2} m_1 r_1^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) + \frac{1}{2} m_2 r_2^2 (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 \right)(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \qquad (2.61)$$

As there is no potential energy of the rotator, total energy is given by

$$E = T + V = T \qquad (\text{since } V = 0)$$

$$= \left(\frac{1}{2} m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 \right)(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \qquad (2.62)$$

But $m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 = I$, the moment of interia of the system about the axis passing through the

centre of mass and perpendicular to the line joining the two masses.

$$E = T = \frac{1}{2} I (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \qquad (2.63)$$

The moment of inertia of the rotator may be expressed in a more convenient form as follows :

According to definition of centre of mass, $r_{cm} = \dfrac{m_1 r_1 + m_2 r_2}{m_1 + m_2}$, we have

$$0 = \frac{-m_1 r_1 + m_2 r_2}{m_1 + m_2} \quad ie. \ m_1 r_1 = m_2 r_2 \qquad (2.64)$$

But $r_0 = r_1 + r_2 \qquad \text{or} \qquad r_2 = r_0 - r_1$

Substituting this in eqn. (2.64) we get

$$m_1 r_1 = m_2 (r_0 - r_1)$$

$$\therefore \qquad r_1 = \frac{m_2}{m_1 + m_2} r_0 \qquad (2.65)$$

Similarly
$$r_2 = \frac{m_1}{m_1 + m_2} r_0 \qquad (2.66)$$

Then the moment of intertia of the rotator may be expressed as

$$I = m_1 r_1^2 + \frac{1}{2} m_2 r_2^2 = m_1 \left(\frac{m_2}{m_1 + m_2} r_0 \right)^2 + m_2 \left(\frac{m_1}{m_1 + m_2} r_0 \right)^2$$

$$= \frac{m_1 m_2}{m_1 + m_2} r_0^2 \qquad \text{since,} \quad I = \mu r_0^2 \qquad (2.67)$$

$$\text{where} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (2.68)$$

is called the reduced mass of the system.

From equations (2.60) and (2.63) it is evident that the rigid rotator behaves like a single particle of mass μ given by eqn. (2.68) placed at a fixed distance, equal to unity (since $r=1$) from the origin, which in this case is the centre of mass of the system.

Wave equation for the rotator : The Schroedinger wave equation in three dimensions in spherical co-ordinates is given by

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0 \qquad (2.69)$$

For a rigid rotator we have seen that potential energy is zero. $r=1$ and the mass m may be replaced by the moment of inertia I. Therefore the Schroedinger wave equation for a rigid rotator becomes

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{2I}{\hbar^2} E\psi = 0. \qquad (2.70)$$

This equation consists of two variables θ and ϕ which represent the precessional motion of the rotator's free axis and the rotation of the system respectively.

Eigen values or energy levels of the rigid rotator.

$$\frac{2IE}{\hbar^2}=l(l+1)$$

or $$E=E_l=\frac{l(l+1)\hbar^2}{2I} \qquad l=0,1,2,3....$$

This equation gives allowed values for the energy (i.e. eigen values) of a rigid rotator with free axis.

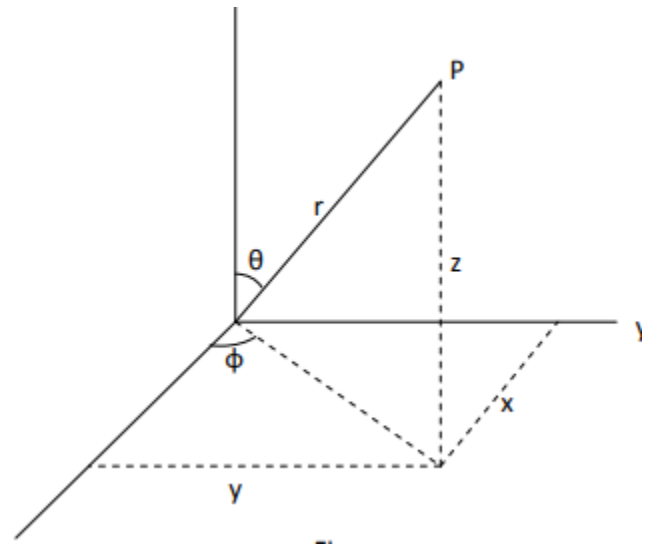## The Hydrogen atom

The Schroedinger wave equation is written as

$$\nabla^2\psi+\frac{2\mu}{\hbar^2}[E-V]\psi=0.$$

In spherical polar coordinates (fig 2.8)

$$x=r \sin \theta \cos \phi$$
$$y=r \sin \theta \sin \phi$$
$$z=r \cos \theta$$

The expression for ∇^2 in spherical

polar coordinates is expressed as,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Hence the Schroedinger wave equation in a spherically symmetric potential may be written in the spherical coordinates as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2\mu}{\hbar^2}[E - V(r)]\psi = 0.$$

The solution of the above equation can be separated in different variables of r, θ and ϕ by writing.

$$\psi\ (r,\theta,\phi) = R(r)\ \Theta\ (\theta)\ \Phi\ (\phi)$$

and differentiating, dividing throughout by $\psi = R\ \Theta\ \Phi$ and multiplying by $r^2\sin^2\theta$ we get,

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta} + \right) + \frac{2\mu r^2\sin^2\theta}{\hbar^2}\{E - V(r)\} = 0.$$

(2.107A)

The second term of this equation depends only on ϕ and the rest is independent of ϕ. Hence the second term should be equal to a constant. Let the constant is equal to $-m^2$

That is,
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$

$$\frac{d^2\Phi}{d\phi^2} = +m^2\Phi = 0.$$

(2.108)

With this value for the second term, equation (2.107a) now can be written as,

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\sin\theta}\frac{1}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta} + \right) - \frac{m^2}{\sin^2\theta} + \frac{2\mu r^2}{\hbar^2}\{E - V(r)\} = 0.$$

(2.109)

The I and IV terms of this equation depend only on r and the II and III terms only on θ; therefore each part must be equal to a constant, (say) λ.

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(E - V) = \frac{m^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = \lambda.$$

so that we have

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)=\left(\lambda-\frac{m^2}{\sin^2\theta}\right)\Theta=0.$$

(2.110)

and
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2\mu}{\hbar^2}\{E-V(r)\}-\frac{\lambda}{r^2}\right]R=0.$$

(2.111)

Equation (2.108), (2.110) and (2.111) are known as ϕ, θ and r equations respectively.

(b) Solution of ϕ equation :

The ϕ equation is $\qquad \dfrac{d^2\Phi}{d\phi^2}=+m^2\Phi=0$

This is a second order differential equation whose solution is given by

$$\Phi = A\,e^{\pm i\,m\,\phi}$$

(2.112)

where A is an arbitrary constant. The constant may be evaluated by normalizing Φ, i.e.,

$$\int_0^{2\pi}\Phi*\Phi\,d\phi=1$$

$$\int_0^{2\pi}A^2d\phi\;=\;1$$

or $\qquad A=\dfrac{1}{\sqrt{2\pi}}$ (2.113)

therefore the solution becomes

$$\Phi=\frac{1}{\sqrt{2\pi}}e^{\pm i m\phi}$$

(2.114)

The single valuedness of the function Φ indicates that it should have the same value at $\phi = 0$ and $\phi = 2\pi$; hence

$$\Phi = A = A e^{\pm 2\pi i m}$$

$$e^{\pm 2\pi i m} = \cos 2\pi m \pm i \sin 2\pi m = 1$$

or   (2.115)

This is true only when m is zero or an integer (positive or negative). Thus we write

$$\Phi = \frac{1}{\sqrt{2\pi}} e^{im\phi}, \quad m = 0, \pm 1, \pm 2, ...$$ (2.116)

The quantity m is called the magnetic quantum number .

Energy of atomic levels and degeneracy.

We have assumed that

$$\lambda' = \frac{Ze^2}{\hbar} \left[\frac{\mu}{2|E|} \right]^{1/2}$$

or

$$\lambda'^2 = \frac{Z^2 e^4}{\hbar^2} \frac{\mu}{2|E|}$$

Replacing λ' by n

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}$$ (2.137)

Equation (2.137) is the expression for energy of an atomic state of a hydrogen – like atom defined by the principal quantum number n.

Now consider the equation

$$n = n_r + l + 1$$

can be satisfied for a given n for several combinations of n_r and l. This implies that there are several possible wave functions for a given energy value (n fixed). When this happens the state is said to be degenerate. This holds good for every value of $n > 1$.

To determine the degeneracy

From equation (2.137) it is clear that energy eigen –values depend upon n and so are degenerate with respect to both l and m. Thus for each value of n, l can vary from 0 to $n - 1$ and for each of these l values, m can vary from $- l$ to $+l$. So, the total degeneracy is

$$\sum_{l=0}^{n-1}(2l+1)=\frac{2(n)(n-1)}{2}+n=n^2 \tag{2.138}$$

so that for $n=2$, we have $l=0$, $m=0$, and $l=1$, $m=0,+1,-1$ giving four wave functions or quantum states etc. Fig. (2.10) shows the different eigen – states in case of hydrogen – like atom.

The solution for radial wave function is found as

$$R(r) = \sqrt{\left[\left(\frac{2z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\{(n+l)!\}^3}\right]}\exp\left(-\frac{zr}{na_0}\right)\left(\frac{2zr}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2zr}{na_0}\right)$$

The complete solution for the problem of hydrogen atom is obtained by multiplying the solutions $R(r), \Theta(\theta) and \Phi(\phi)$
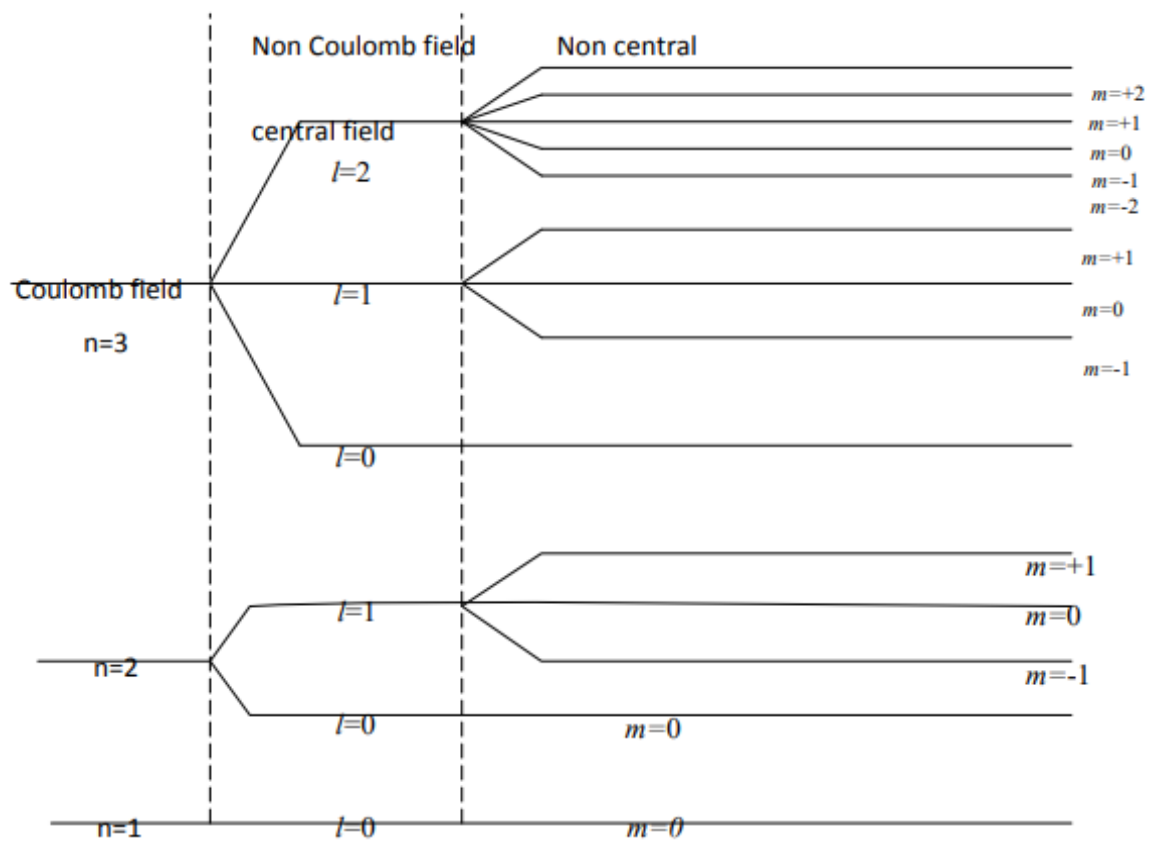
Fig. 2.9

In particular

$$m = 0, \pm 1, \pm 2, \ldots \pm l$$
$$l = 0, 1, 2 \ldots (n-1)$$

In particular

$$m = 0, \pm 1, \pm 2, \ldots \pm l$$
$$l = 0, 1, 2 \ldots (n-1)$$

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