$H_{ii} \Rightarrow H_{11} = H_{22} = H_{33} = \alpha$ = coulomb integral

$$\boxed{\int \phi_i H \phi_i d\tau = \alpha}$$

$H_{ij} \Rightarrow H_{12} = H_{21} = H_{23} = H_{32} ..... = \beta$

Exchange integral $= H_{ij} = \boxed{\int \phi_i H \phi_j d\tau = \beta}$

It represent the interaction of eleetron in the atom i and j.

Overlap integral: $S_{ij} = \int \phi_i \phi_j d\tau$

It represent the overlap of the orbitals centered on atom i and j and generally atomic orbital is normalised so, if

$i = j, S_{ij} = \int \phi_i \phi i d\tau = 1$

Q. (a) Using the Huckel approximations, show that for the allyl radical ($\overset{1}{C}H_2 - \overset{2}{C}H = \overset{3}{C}H_2$) the wave functions and the corresponding energies are given by,

$$\psi_1 = \frac{1}{2}\psi_{2p_z(1)} + \frac{1}{\sqrt{2}}\psi_{2p_z(2)} + \frac{1}{2}\psi_{2p_z(3)};\ E_1 = \alpha + \sqrt{2}\beta$$

$$\psi_2 = \frac{1}{\sqrt{2}}\psi_{2p_z(1)} - \frac{1}{\sqrt{2}}\psi_{2p_z(3)};\ E_2 = \alpha$$

$$\psi_3 = \frac{1}{2}\psi_{2p_z(1)} - \frac{1}{\sqrt{2}}\psi_{2p_z(2)} + \frac{1}{2}\psi_{2p_z(3)};\ E_2 = \alpha - \sqrt{2}\beta$$

(b) Calcualte the electron densities and bond orders for (i) allyl cation and (ii) allyl anion.

Soln. (a) The secular determinant for allyl radical is given by.

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Dividing each element of the above determinant by β and then setting $(\alpha - E)/\beta = x$, we get.

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

Which on expanding gives

$$x^3 - 2x = 0$$

The three roots of the above equation are

$$-\sqrt{2},\ 0,\ \sqrt{2}$$

The correspinding three values of energies are;

$$E_1 = \alpha + \sqrt{2}\beta$$

$$E_2 = \alpha$$

$$E_3 = \alpha - \sqrt{2}\beta$$

The secualr equations are.

$$C_1 x + C_2 = 0;\ C_1 + C_2 x + C_3 = 0;\ C_2 + C_3 x = 0$$

For $x = -\sqrt{2}$, we will hve,

$$-\sqrt{2}C_1 + C_2 = 0 \quad ...(1)$$

$$C_1 - \sqrt{2}C_2 + C_3 = 0 \quad ...(2)$$

$$C_2 - \sqrt{2}C_3 = 0 \quad ...(3)$$

Equation (1) and (2) suggest that,

$$C_1 = \frac{C_2}{\sqrt{2}} \text{ and } C_3 = \frac{C_2}{\sqrt{2}}$$

Using the normalization criterion.

$$C_1^2 + C_2^2 + C_3^2 = 1$$

We get, $\left(\frac{C_2}{\sqrt{2}}\right)^2 + C_2^2 + \left(\frac{C_2}{\sqrt{2}}\right)^2 = 1$

$$C_2 = \pm\frac{1}{\sqrt{2}}$$

Thus the first wave functions is given by

$$\psi_1 = \frac{1}{2}\psi_{2pz(1)} + \frac{1}{\sqrt{2}}\psi_{2pz(2)} + \frac{1}{2}\psi_{2pz(3)} \text{ ; (Bonding)}$$

Working out similarly with $x = 0$ and $x = \sqrt{2}$, we get.

$$\psi_2 = \frac{1}{\sqrt{2}}\psi_{2pz(1)} \frac{1}{\sqrt{2}}\psi_{2pz(3)} \text{ ; (Non bonding)}$$

$$\psi_3 = \frac{1}{2}\psi_{2pz(1)} - \frac{1}{2}\psi_{2pz(2)} + \frac{1}{2}\psi_{2pz(3)} \text{ ; (Antibonding)}$$

(b) Allyl cation.

$$q_1 = 2C_{11}^2 = 2\left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$q_2 = 2C_{12}^2 = 2\left(\frac{1}{\sqrt{2}}\right)^2 = 1$$

$$q_3 = 2C_{13}^2 = 2\left(\frac{1}{2}\right)^2 = \frac{1}{2}$$

$$q_{12} = 2C_{11}C_{12} = 2\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) = \frac{1}{\sqrt{2}}$$

$$q_{23} = 2C_{12}C_{13} = 2\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) = \frac{1}{\sqrt{2}}$$

(c) Allyl anion :

$$q_1 = 2C_{11}^2 + 2C_{21}^2 = 2\left(\frac{1}{2}\right)^2 + \left(\frac{1}{\sqrt{2}}\right)^2 = 1.5, \qquad q_2 = 2C_{12}^2 + 2C_{22}^2 = 2\left(\frac{1}{\sqrt{2}}\right)^2 + 0 = 1$$

$$q_3 = 2C_{13}^2 + 2C_{23}^2 = 2\left(\frac{1}{2}\right)^2 + 2\left(-\frac{1}{\sqrt{2}}\right)^2 = 1.5, \qquad p_{12} = 2C_{11}C_{12} + 2C_{21}C_{22} = 2\left(\frac{1}{2}\right)\left(\frac{1}{\sqrt{2}}\right) + 0 = \frac{1}{\sqrt{2}}$$

$$p_{23} = 2C_{12}C_{13} + 2C_{22}C_{23} = 2\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{2}\right) + 0 = \frac{1}{\sqrt{2}}$$

THE HYDROGEN ATOM

Quantization of Electronic Energy:

Necessity of Replacing Bohr's Theory :

The mathematical framework of the Bohr's theory was based on the basic assumption of quantization of orbital angular momentum of the electron. It was seen earlier that this theory led to the quantization of electronic energies which formed the basis for explaining the experimental spectra of hydrogen like species such as H, He^+, Li^{2+} and Be^{3+}. However, this theory was not entirely stisfactory as it failed to provide an interpretation of relative line intensities in the hydrogen spectrum and also failed completely when it was applied to explain the energies and spectra of more complex atoms. In this section, we consider the application of Schrodinger's wave theory to one-electron atom. In the subsequent section, it will be shown how the principles of this theory can be applied, in a more approximate way, to many electron atoms.

Setting of Shrodinger Equation :

The time independent form of Schrodinger equation is

$$H_{op}\,\psi_{total} = E_{total}\,\psi_{total} \qquad ...(1)$$

where H_{op} is the Hamiltonian operator, E_{total} is the total nonrelativistic energy and ψ_{total} is the wave function for the total system. Since the hydrogen like system contain two particles, namely, nucleus and electron, it is obvious that the wave function ψ_{total} depends on the six coodinate variables, three for the electron (x_e, y_e, z_e) and three for the nucleus (x_n, y_n, z_n), both sets of coordinates refer to the common origin. The Hamiltonian operator consists of two terms, viz. the kinetic and potential energy terms. The kinetic energy operator will contain two terms, one for the electron and one for the nucleus. Thus, we have

$$\begin{aligned} H_{op} &= T_{op} + V_{op} \\ &= \left(-\frac{h^2}{8\pi^2 m_e}\nabla_e^2 - \frac{h^2}{8\pi^2 m_n}\nabla_n^2\right) - \frac{Ze^2}{(4\pi\varepsilon_o)r} \end{aligned} \qquad ...(2)$$

All symbols have their usual meanings. Substituting Eq. 2 in Eq. 1, we have

$$\left[-\frac{h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right) - \frac{h^2}{8\pi^2 m_n}\left(\frac{\partial^2}{\partial x_n^2}+\frac{\partial^2}{\partial y_n^2}+\frac{\partial^2}{\partial z_n^2}\right)\right] - \frac{Ze^2}{(4\pi\varepsilon_0)r}\Bigg]\psi_{total} = E_{total}\,\psi_{total} \qquad ...(3)$$

Equation 3 can be broken into two simpler equations, one involving the free movement of the centre of mass of the atom in space and the other involving the relative motion of the electron with respect to the nucleus within the atom. The two equations are

$$-\frac{h^2}{8\pi^2(m_e+m_n)}\left(\frac{\partial^2}{\partial x_c^2}+\frac{\partial^2}{\partial y_c^2}+\frac{\partial^2}{\partial z_c^2}\right)\psi_M = E_{trans}\psi_M \qquad ...(4)$$

and

$$\left[-\frac{h^2}{8\pi^2\mu_e}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi_e = E\psi_e \qquad ...(5)$$

with $E_{trans} + E = E_{total}$

Equation 4 is simply the Schrodinger equation for a free particle of mass $(m_e + m_n)$, E_{trans} is the translational kinetic energy associated with the free movement of the centre of mass of the atom through space.
Equation 5 is the Shrodinger equation which represents the system in which an electron of reduced mass μ is revolving around the stationary nucleus of positive charge Z at a distance of r. The behaviour of this electron can be described by the function ψ_e and E is the corresponding energy of the electron. The allowed values of electronic energies can be obtained by solving Eq. 5 Equation 4 which describes the motion of the centre of mass is of the same form as that of the particle in a three dimensional box.

Sehrodinger Equation in Terms of Spherical Polar Coordinates:
The solution of Schrodinger equation becomes very much simplified if the equation is expressed in the coordinate system that reflects the symmetry of the system. In the present case the potential energy field is spherical symmetry(V depends only on r), and thus, it is convenient to transform the Schrodinger equation 5 into the spherical polar coordinates r, θ and φ by using the relations

$$x = r\sin\theta\cos\varphi;\quad y = r\sin\theta\sin\varphi;\quad z = r\cos\theta$$

The transformation is lengthly and tedious process, and only the transformed expression is given below :

$$\left[-\frac{h^2}{8\pi^2\mu r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi = E\psi$$

where ψ is a function of r, θ and φ

Splitting of Schrodinger Equation: Rearranging the above expression, we get

$$\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\psi + \frac{8\pi^2\mu}{h^2}\left(\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right)\psi = 0$$

Multiplying throughout by r^2 and rearranging the resultant expression, we get

$$\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi = 0 \quad ...(6)$$

Since the operator is made up of two terms, one depending on the variable r and the other on the variables θ and φ taken together, we can write the wave function ψ as the product of two functions– one depending on r and the other on θ and φ. Hence, we can write

$$\psi_{r,\theta,\varphi} = R_r Y_{\theta,\varphi} \quad ...(7)$$

The function Y is known as spherical harmonics. Substituting Eq. 7 in eq. 6 we get

$$Y_{\theta,\varphi}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left[\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right]R_r Y_{\theta,\varphi}$$

$$+R_r\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi} = 0 \quad ...(8)$$

Dividing throghout by $R_r Y_{\theta,\varphi}$, we get

$$\left[\frac{1}{R_r}\frac{d}{dr}\left(r^2\frac{d}{dr}R_r\right)+\frac{8\pi^2\mu r^2}{h^2}\left\{\frac{Ze^2}{(4\pi\varepsilon_0)r}+E\right\}\right]$$

$$= -\left[\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}\right] \quad ...(9)$$

Equality shown in Eq. (9) holds good only when both sides are equal to a constant say, $\iota(\iota+1)$. Thus Eq. 9 separates into two equations, one depending only on r and the other on θ and φ. These are :

Equation involving the variable r

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=\iota(\iota+1) \qquad ...(10)$$

Equation involving the angles θ and φ

$$\frac{1}{Y_{\theta,\varphi}}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\theta,\varphi}=-\iota(\iota+1) \qquad ...(11)$$

Multiplying Eq. 1 by $\sin^2\theta$ and rearranging the resultant expression, we get

$$\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\iota(\iota+1)\sin^2\theta+\frac{\partial^2}{\partial\varphi^2}\right]Y_{\theta,\varphi}=0 \qquad ...(12)$$

Since the operator in Eq. 11 consists of two terms. one depending on θ and the other on φ, we can write the wave function $Y_{\theta,\varphi}$ as $Y_{\theta,\varphi}=\Theta_\theta\,\Phi_\varphi$

With this, Eq. (12) becomes

$$\Phi_\varphi\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\iota(\iota+1)\sin^2\theta\,\Theta_\theta\Phi_\varphi+\Theta_\theta\frac{d^2}{d\varphi^2}\Theta_\theta=0$$

Dividing throughout by $\Theta_\theta\,\Phi_\varphi$ and rearranging, we get

$$\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\iota(\iota+1)\sin^2\theta=-\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2} \qquad ...(13)$$

The two sides of Eq. 12 must be equal to a constant, say m^2. Thus, we have

$$\frac{\sin\theta}{\Theta_\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta_\theta}{d\theta}\right)+\iota(\iota+1)\sin^2\theta=m^2 \qquad ...(14)$$

and

$$\frac{1}{\Phi_\varphi}\frac{d^2\Phi_\varphi}{d\varphi^2}=-m^2 \qquad ...(15)$$

Three Split Expressions of the Schrodinger Equation :

Thus, the Schrodinger equation (6) for the hydrogen like species can be separated into three equations. These are :

- Equation involving only r

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{Ze^2}{(4\pi\varepsilon_0)r}\right)=\iota(\iota+1) \qquad ...(16)$$

- Equation involving only θ

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\iota(\iota+1)\sin^2\theta=m^2 \qquad ...(17)$$

- Equation involving only φ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2 \qquad ...(18)$$

We now consider the acceptable solutions of Eqs 16, 17 and 18.

Solutions of φ Dependent Equation :

Equation 17 has already been solved in conection with the rigid rotator system. Its solution is

$$\Phi_m = \frac{1}{\sqrt{2\pi}}\exp(im\varphi); \quad m = 0, \pm 1, \pm 2, \ldots \qquad \ldots(19)$$

The constant m is called the magnetic quantum number and it represents the quantization of the z-component of the angular momentum since

$$\hat{L}_z\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\} = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\}$$

$$= m\frac{h}{2\pi}\left\{\frac{1}{\sqrt{2\pi}}\exp(im\varphi)\right\} \qquad \ldots(20)$$

Thus, the permitted values of z-component of the angular momentum of the electron are given by the expression m(h/2π).

Solutions of θ-Dependent Equation:

Equation 17 has also been solved in the rigid rotator system. The solution is

$$\Theta_{l,|m|} = \left[\frac{(2l+1)}{2}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|} \qquad \ldots(21)$$

where $P_l^{|m|} = (1-\xi^2)^{|m|/2}\frac{d^{|m|}P_l}{d\xi^{|m|}}$: Associated Legendre Polynomials ...(22)

$$P_l = \frac{1}{2^l l!}\frac{d^l}{d\xi^l}(\xi^2-1)^l \quad : \text{Legendre polynomials} \qquad \ldots(23)$$

and $\xi = \cos\theta$

These solutions are obtained provided the following conditions are satisfied.

$l = 0, 1, 2, 3, \ldots\ldots\ldots$

$m = 0, \pm 1, \pm 2, \ldots, \pm l$

The quantum number l is called the azimuthal quantum number or the subsidiary quantum number and it represents the quantization of the square of total angular momentum according to the equation

$$\hat{L}^2\Theta_{l,|m|} = l(l+1)\left(\frac{h}{2\pi}\right)^2\Theta_{l,|m|} \qquad \ldots(24)$$

Solution of r-Dependent Equation :

With the help of a suitable transformation of independent variable and from the forms of solutions as the variable approaches zero and infinity, it is possible to write in the following more familiar form, known as associated Laguerre equation.

$$\rho^2\frac{d^2L}{d\rho^2} + (j+1-\rho)\frac{dL}{d\rho} + (K-j)L = 0 \qquad \ldots(25)$$

where the function R is related to the function L through the following transformation scheme.

$$R(r) = s(\rho) = e^{-\rho/2}F(\rho) = e^{-\rho/2}\rho^l L(\rho) \qquad \ldots(26)$$

The terms ρ, j and k are given by

$$\rho = 2\alpha r \qquad \ldots(27)$$

$$k = \lambda + 1 \qquad ...(29)$$

where $$\alpha^2 = -\frac{8\pi^2\mu E}{h^2} \qquad ...(30)$$

$$\lambda = \frac{4\pi^2\mu Z e^2}{(4\pi\varepsilon_0)h^2\alpha} \qquad ...(31)$$

The solution of Eq. (25), as determined by the power series method, is the associated Laguerre polynomial of degree (k–j) and order j, and is given by

$$L_k^j = \frac{d^j}{d\rho^j} L_k \qquad ...(32)$$

where L_k, the Laguerre polynomial of degree k, is given by

$$L_k = e^{\rho}\frac{d^k}{d\rho^k}\left(\rho^k e^{-\rho}\right) \qquad ...(33)$$

In order that the associated Laguerre polynomial is the acceptable solution of Eq. (25) the following quantum restriction has to be satisfied.

$$k = 1, 2, 3, \ldots\ldots, \infty \qquad ...(34)$$

Acceptable solutions, as usual, means that the wave function L(ρ) should be a well-behaved function and should vanish as $\rho \to \infty$. The latter condition requires that the polynomial must be restricted to a finite number of terms.

This quantum restriction leads to the fact that λ which is equal to $k - 1$ (Eq.29) must also be an integer. Let λ be written as n, so that

$$k = n + 1 \qquad ...(35)$$

Expression of the Normalized R Functions:

Thus, the function R as given by Eq. (26) is

$$R = \rho^l e^{-\rho/2} L_{n+l}^{2l+1} \qquad ...(36)$$

Normalizing the above solution through the expression

$$\int_0^{\infty} R^* R\, r^2 dr = 1$$

we get $$R = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}\right\}^{1/2} \cdot \rho^l e^{-\rho/2} L_{n+l}^{2l+1} \qquad ...(37)$$

where $$\rho = (2\alpha r) = 2\left(\frac{4\pi^2\mu Z e^2}{nh^2(4\pi\varepsilon_0)}\right) r = \left(\frac{2Z}{na_0}\right) r \qquad ...(38)$$

and $$a_0 = \frac{h^2(4\pi\varepsilon_0)}{4\pi^2\mu e^2} \qquad ...(39)$$

Allowed Values of n and its Relation with l:

The constant n is referred to as the principal quantum number. If the associated Laguerre polynomial (Eq 32) is not to vanish, we must have

$$j \le k \qquad ...(40)$$

Since $j = 2l + 1$ and $k = n + l$, we have

$$(2l+1) \le (n+l)$$

or $\iota+1 \le n$ or $\iota \le n-1$ ... (41)

Since the allowed values of ι are 1, 2, 3, ..., it is obvious that the pricipal quantum number n cannot have a zero value. The allowed values of n are only positive integers. Thus, we have

$n = 1, 2, 3, 4, ...$

$\iota = 0, 1, 2, 3, ..., (n-1)$ ... (42)

Expressions for the Function $R_{n,\iota}$:

The exact form of the function $R_{n,\iota}(r)$ for the given values of n and ι can be determined from Eqs. (37), (32) and (33). These equations are

$$R_{n,\iota} = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-\iota-1)!}{2n[(n+\iota)!]^3}\right\}^{1/2} \rho^{\iota} e^{-\rho/2} L_{n+\iota}^{2\iota+1} \quad \text{... (43)}$$

$$L_{n+\iota}^{2\iota+1} = \frac{d^{2\iota+1}}{d\rho^{2\iota+1}} L_{n+\iota} \quad \text{... (44)}$$

and $$L_{n+\iota} = e^{\rho} \frac{d^{n+\iota}}{d\rho^{n+\iota}}\left(\rho^{n+\iota} e^{-\rho}\right) \quad \text{... (45)}$$

where $\rho = \left(\frac{2Z}{na_0}\right) r$

Hydrogen Atom Problem:

Q. Calculate the probability of finding of electron in 1s-orbital of H-atom between 0 to a_0.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$$

Probability of finding an electron between 0 to a_0.

$$\int_0^{a_0} \psi.\psi^* d\tau = \int_0^{a_0} \frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0} \frac{e^{-r/a_0}}{\sqrt{\pi}.a_0^{3/2}} 4\pi r^2 dr$$

$$= \frac{4\cancel{\pi}}{\cancel{\pi} a_0^3} \int_0^{a_0} r^2 . e^{-2r/a_0} dr \quad \text{... (1)}$$

Now, $$\int_0^{a_0} r^2 e^{-2r/a_0} dr = r^2 \int_0^{a_0} e^{-2r/a_0} dr - \int_0^{a_0}\left[\frac{d}{dr}(r^2) \int e^{2r/a_0} dr\right] dr \Rightarrow \frac{\left[r^2 e^{-2r/a_0}\right]_0^{a_0}}{-\frac{2}{a_0}} - \int_0^{a_0} 2r \frac{e^{-2r/a_0}}{-\frac{2}{a_0}} dr$$

$$= -\frac{a_0}{2}\left[r^2 e^{-2r/a_0}\right]_0^{a_0} + a_0 \int_0^{a_0} r\, e^{-2r/a_0} dr$$

Let, $M = -\frac{a_0}{2}\left[r^2 e^{-2r/a_0}\right]_0^{a_0}$

For simplicity $= -\frac{a_0}{2}\left[a_0^2 e^{-2\frac{a_0}{a_0}} - 0\right]$

$$= M + a_0\left[r\int_0^{a_0} e^{-2r/a_0}dr - \int_0^{a_0} e^{-2r/a_0}dr\right]dr \quad \Rightarrow M + a_0\left[\left[r.\frac{e^{-2r/a_0}}{-2/a_0}\right]_0^{a_0} - \int_0^{a_0}\left[\frac{e^{-\frac{2r}{a_0}}}{-\frac{2}{a_0}}dr\right]\right]$$

$$= M + a_0\left[-\frac{a_0}{2}\left[r.e^{-2r/a_0}\right]_0^{a_0} - \left(-\frac{a_0}{2}\right)\frac{\left[e^{-2r/a_0}\right]_0^{a_0}}{-2/a_0}\right] = M + a_0\left[-\frac{a_0}{2}\left[r.e^{-2r/a_0}\right]_0^{a_0} - \frac{a_0^2}{4}\left[e^{-2r/a_0}\right]_0^{a_0}\right]$$

$$= -\frac{a_0}{2}\left[a_0^2.e^{-2}\right]a_0\left[\left\{-\frac{a_0^2}{2}e^{-2} - 0\right\} - \frac{a_0^2}{4}\left\{e^{-2} - 1\right\}\right]$$

$$= -\frac{a_0^3}{2e^2} - \frac{a_0^3}{2e^2} - \frac{a_0^3}{4e^2} + \frac{a_0^3}{4} \quad \Rightarrow \frac{-2a_0^3 - 2a_0^3 - a_0^3 + a_0^3e^2}{4e^2} \quad \Rightarrow \frac{a_0^3}{4} - \frac{5a_0^3}{4e^2}$$

From equation (1),

$$\therefore \quad \int_0^{a_0}\psi\psi^*d\tau = \frac{4}{a_0^3}\left(\frac{a_0^3}{4} - \frac{5a_0^3}{4e^2}\right) = \left(\frac{\cancel{4}}{\cancel{a_0^3}}\cdot\frac{\cancel{a_0^3}}{\cancel{4}} - \frac{\cancel{4}}{\cancel{a_0^3}}\cdot\frac{5\cancel{a_0^3}}{\cancel{4}e^2}\right) = 1 - \frac{5}{e^2}$$

$$\boxed{\int_0^{a_0}\psi\psi^*d\tau = \left(1 - \frac{5}{e^2}\right) \approx 32\%}$$

value of $e = 2.718$ $\quad \therefore \quad \int_0^{a_0}\psi\psi^*d\tau = 32\%$

Q. Calculate the average potential energy of H-atom for 1s orbital.

Soln. $$\psi_{1s} = \frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$$

For H-atom potential energy $V = -\frac{e}{r^2} = -\frac{ze^2}{r}$

$$\langle v\rangle = \int_0^{\infty}\frac{1}{\sqrt{\pi}\,a_0^{3/2}}\,e^{-r/a_0}\left(-\frac{Ze^2}{r}\right)\frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}4\pi r^2dr$$

$$= \left(-Ze^2\right)\frac{4\cancel{\pi}}{\cancel{\pi}\,a_0^3}\int_0^{\infty}e^{-r/a_0}\,e^{-r/a_0}\frac{1}{r}r^2dr$$

$$= -\frac{4Ze^2}{a_0^3}\int_0^{\infty}r\,e^{-2r/a_0}dr = -\frac{4Ze^2}{a_0^3}\frac{1!}{\left(\frac{2}{a_0}\right)^2} = -\frac{\cancel{4}Ze^2\times\cancel{a_0^2}}{a_0^{\cancel{3}}\times\cancel{2}\times\cancel{2}} = -\frac{Ze^2}{a_0}$$

$$\langle v\rangle = -Ze^2\left\langle\frac{1}{r}\right\rangle$$

$$= -Ze^2\frac{1}{a_0}$$

$$= -\frac{Ze^2}{a_0}$$

$$\langle v\rangle = \int_0^{\infty}\psi\left(-\frac{Ze^2}{r}\right)\psi^*d\tau$$

$$= -Ze^2\int_0^{\infty}\psi\left(\frac{1}{r}\right)\psi d\tau$$

$$= -Ze^2\left\langle\frac{1}{r}\right\rangle = -\frac{Ze^2}{a_0}$$

Q. Show that the 1s and 2s wave-functions of hydrogen atom given by

$$\psi_{1s} \equiv \psi_{1,0,0} = \frac{1}{\sqrt{\pi} a_0^{3/2}} \exp(-r/a_0) \text{ and } \psi_{2s} \equiv \psi_{2,0,0} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) \exp(-r/2a_0) \text{ are}$$

orthogonal to each other :

Soln. For the given wave function to be orthogonal, they should satisfy the following condition :

$$\int \psi_{1s}\, \psi_{2s}\, d\tau = 0$$

Since in polar coordinates, $d\tau = r^2\, dr \sin\theta\, d\theta\, d\phi$. we have, after integrating between appropriate limits,

$$\int \psi_{1s}\psi_{2s} d\tau = \frac{1}{4\sqrt{2\pi a_0^3}} \left[2\int_0^\infty r^2 e^{-3r/2a_0} dr - \frac{1}{a_0} \int_0^\infty r^3 e^{-3r/2a_0} dr \right] \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

Now, $\int_0^\pi \sin\theta\, d\theta [-\cos\theta]_0^\pi = -(-1) - (-1) = 2 \int_0^{2\pi} d\phi = 2\pi$

Using the standard result $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$, we have

$$\int_0^\infty r^2 e^{-3r/2a} a_0 dr = \frac{2!}{(3/2a_0)^3} = \frac{16a_0^3}{27} \text{ and } \int_0^\infty r^3 e^{-3r/2a_0} dr \frac{31}{(3/2a_0)^4} = \frac{32a_0^4}{27}$$

Using the above values of the var ious integrals we find that

$$\int \psi_{1s}\psi_{2s} d\tau = 0$$

Q. Using the normalized wave function

$$\psi_{1s} = \left(1/\pi a_0^3\right)^{1/2} \exp(-ra_0)$$

for the ground state of hydrogen atom, calculate the probability for the electron to be confined in a sphere of radius $r = a_0$, the Bohr radius.

Soln. We have that from Born's interpretation of the wave function, the probability is given by

$$P(r)\, dr = \psi^*\, \psi d\tau$$

∴ Integrating, we obtain

$$\int P(r) dr = \int \psi^* \psi d\tau, \text{ where } d\tau = r^2 dr \sin\theta\, d\theta\, d\phi$$

Or $$P = \frac{1}{\pi a_0^3} \int_0^{a_0} r^2 e^{-2r} dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi = \frac{4}{a_0^3} \int_0^{a_0} r^2 e^{-2r} dr$$

Carrying out integration by parts, we obtain

$$P = \frac{4}{a_0^3} \left\{ \left[\frac{a_0}{2} r^2 e^{-2r/a_0} \right]_0^{a_0} + \left[-\frac{a_0^2}{2} r e^{-2r/a_0} \right]_0^{a_0} + \left[-\frac{a_0^3}{4} e^{-2r/a_0} \right]_0^{a_0} \right\} = 5e^{-2} + 1 = 0.323$$

Q. Calculate the most probable distance, r_{mp} of the electron from the nucleus in the ground state of hydrogen atom, given that the normalized ground state wave function is

$$\psi_{1s} = \frac{1}{\sqrt{\pi} a_0^{3/2}} \exp(-r/a_0)$$

Soln. Quantum mechanically, the probability of finding the electron in a spherical shell of thickness dr at a distance r from the nucleus(in figure..) is given by

$$P(r) dr = 4\pi |\psi_{1s}|^2\, r^2 dr = 4\pi r^2 \left(1/\pi a_0^3\right) e^{-2r/a_0} dr$$

For the probability to be a maximum,

$dP(r)/dr = 0$. Thus,

$$\frac{dP(r)}{dr} = \frac{4}{a_0^3}\left(-\frac{2r^2}{a_0} + 2r\right)e^{-2r/a_0} = 0$$

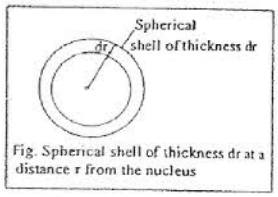


Fig. Spherical shell of thickness dr at a distance r from the nucleus

Since the Bohr radius $a_0 \neq 0$ and the exponential is also $\neq 0$, hence $-\frac{2r^2}{a_0} + 2r = 0$ $\therefore r = r_{mp} = a_0$

Q. Calculate the average distance of the electron from the nucleus in the ground state of hydrogen atom; given that the normalized ground state wave function is $\psi_{1s} = \frac{1}{\sqrt{\pi a_0^{3/2}}} \exp(-r/a_0)$

Soln. In quantum mechanics, the average (or expectation) value of dynamical variable r is given by

$$\langle r \rangle = \int \psi_n^* \, r \, \psi_n \, d\tau$$

In the present case, the average distance of the electron from the nucleus is given by

$$\langle r \rangle = \int \psi_{1s}^* \, r \, \psi_{1s} \, d\tau$$

Since $d\tau = dr \sin\theta \, d\theta \, d\phi$ hence, integrating between appropriate limits, we get

$$\langle r \rangle = \frac{1}{\pi a_0^3}\int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{1}{\pi a_0^3}\left(\frac{3!}{(2/a_0)^4}(2)(2\pi)\right) = \frac{3}{2}a_0$$

Note : The results of the last two examples are quite instructive. According to Bohr's theory of hydrogen atom, the distance of the electron from the nucleus in the ground state is exactly equal to a_0, the Bohr radius. That according to Heisenberg's uncertainty principle, the electron cannot be exactly located in its orbit. Hence, quantum mechanically, while the most probable distance is a_0 the average distance is $3a_0/2$ i.e. the average distance is 50% greate than the Bohr theory result! The inescapable conclusion we draw from this is that we really do not know where the electron is located in its orbit at a given moment.

Q. Show that the average value of 1/r for an electron in the 1s orbital of hydrogen atom is $1/a_0$, where a_0 is the Bohr radius; given that $\psi_{1s} = \frac{1}{\sqrt{\pi a_0^{3/2}}} \exp(-r/a_0)$

Soln. $\langle 1/r \rangle = \int \psi_{1s}^* (1/r) \psi_{1s} d\tau$

Since : $d\tau = r^2 \, dr \sin\theta \, d\theta \, d\phi$, hence, integrating between appropriate limits.

$$\langle 1/r \rangle = \frac{1}{\pi a_0^3}\int_0^\infty r \, e^{-2r/a_0} dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{1}{\pi a_0^3}\left(\frac{1}{(2/a_0)^2}(2)(2\pi)\right) = \frac{1}{a_0}$$

Q. Show that the 1s wave function of hydrogen atom given by

$\psi_{1s} = \psi_{1,0,0} = \frac{1}{\sqrt{\pi a_0^{3/2}}} \exp(-r/a_0)$, **is normalized;** a_0 **is the Bohr radius.**

Soln. For the wave function to be normalized the following condition helds :

$$\int \psi_{1s}^* \, \psi_{1s} \, d\tau = 1$$

In polar coordinates (r, θ, ϕ), the volume element $d\tau = r^2 \, dr \sin\theta \, d\theta \, d\phi$. Using this expression for $d\tau$ and integrating between appropriate limits, we have

$$\int \psi_{1s} \, \psi_{1s} d\tau = \frac{1}{\pi a_0^3} \int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin\theta \; d\theta \int_0^{2\pi} d\phi$$

Each of these integrals can be evaluated separately as follows :

$$\int_0^{2\pi} d\phi = 2\pi \text{ and } \int_0^\pi \sin\theta \, d\theta = [-\cos\theta]_0^\pi = -(-1) - (-1) = 2$$

The first integral is evaluated by using the result

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^n + 1}, \; n \text{ is a positive integer : } a > 0$$

Thus, $\int r^2 e^{-2r/a_0} dr = \dfrac{2}{(2/a_0)^3} = \dfrac{a_0^3}{4}$

$$\therefore \int \psi_{1s} \, \psi_{1s} d\tau = \left(\frac{1}{\pi a_0^3}\right)\left(\frac{a_0^3}{4}\right)(2)(2\pi) = 1$$

Hence, ψ_{1s} is normalized.

Q. **The un-normalized 1s wave function for hydrogen atom is given by**

$\psi_{1s} \equiv \psi_{1,0,0} = N \exp(-r/a_0)$ where a_0 is the Bohr radius.

Determine the normalized wave function

Soln. Here we have to determine the normalization constant, N. For the wave function to be normalized, the following condition holds.

$$\int \psi_{1s} \, \psi_{1s} d\tau = 1$$

In polar coordinates (r, θ, ϕ), the volume element $d\tau = r^2 \sin\theta d\theta d\phi$. Using this expression for $d\tau$ and integrating between appropriate limits, we have

$$\int \psi_{1s} \psi_{1s} d\tau = N^2 \int e^{-2r/a_0} d\tau = N^2 \int_0^\infty r^2 e^{-2r/a_0} dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi = 1$$

Each of these integrals can be evaluated separately as follows:

$$\int_0^{2\pi} d\phi = 2\pi \text{ and } \int_0^\pi \sin\theta \, d\theta = [-\cos\theta]_0^\pi = -(-1) - (-1) = 2$$

Using the result

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}; \; n \text{ is a positive integer ; } a > 0, \text{ we obtain}$$

$$\int_0^\infty r^2 e^{-2r/a_0} dr = \frac{2!}{(2/a_0)^3} = \frac{a_0^3}{4}$$

Hence, $N^2 \left(a_0^3/4\right)(2)(2\pi) = 1$

$$\therefore \quad N = 1/\sqrt{\pi} a_0^{3/2}$$

Hence, the normalized ground state wave function is

$$\psi_{1s} = 1/\sqrt{\pi} \, a_0^{3/2} \; e^{-(r/a_0)}$$

Note : this example is the reverse of the last example.

THE RIGID ROTOR

A diatomic molecule rotating about an axis perpendicular to the internuclear axis and passing through the centre of gravity of the molecule, constitutes an example of a rigid rotor, it being assumed that the internuclear distance does not change during rotation. The kinetic energy (K.E.) of the molecule is given by

$$K.E. \equiv T = \frac{1}{2} I\omega^2 = L^2/2I \qquad ...(1)$$

where ω is the angular velocity and I is the moment of intertia of the roating molecule. The angular momentum $L = I\omega$. If no force acts on the rotor, we can set the potential energy $V = 0$. Hence, the Hamiltonian is expressed as

$$H = T + V = L^2/2I \qquad ...(2)$$

The expression for L^2 in spherical polar coordinates (r, θ, ϕ) is given by

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad ...(3)$$

The Schorodinger equation $\hat{H}\psi = E\psi$ may thus be written as

$$\frac{1}{2I}\left[-\hbar^2\left\{\frac{1}{\sin\theta}\frac{1}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}\right] = E\psi \qquad ...(4)$$

The above equation may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2}E\psi = 0 \qquad ...(5)$$

Eq. 5 contains two angular variable θ and ϕ. It can be solved by the method of separation of variable, i.e., we look for a solution of the form

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi) \qquad ...(6)$$

Substituting Eq. 6 into Eq.5 we obtain

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{8\pi^2 IE}{h^2}\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \qquad ...(7)$$

We can set both sides of Eq.....equal to a constant, say m^2, there by obtaining two differential equations each in one variable. These equations are :

$$\frac{\partial^2\Phi}{\partial\phi^2} + m^2\Phi = 0 \text{ and} \qquad ...(8)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 \qquad ...(9)$$

where $\because \cos 2\pi m + i\sin 2\pi m = 1$

Eq. 8 has the solution

$$\Phi(\phi) = N\exp(\pm im\phi). \quad i = \sqrt{-1} \qquad ...(10)$$

where N is the normalization constant.

This wave function is acceptable provided m is an integer. This condition arises because Φ must be single valued. Thus,

$$\Phi(\phi) = \Theta(\phi + 2\pi) \qquad ...(11)$$

If follows, therefore, that $\exp(2\pi mi) = 1$ ...(12)

Since $e^{x} = \cos x + i \sin x$ (Euler's relation) ...(13)

$\therefore \cos 2\pi m + i \sin 2\pi m = 1$ ...(14)

This can be true only if m= 0, ± 1, ± 2, ± 3,.....etc. Let us now normalize the wave function $\Theta(\phi)$ to determine the normalization constant N.

$$\int_0^{2\pi} \Phi^{*} \Phi \, d\phi = 1 \quad (0 \le \phi \le 2\pi) \qquad ...(15)$$

$$\text{or} \quad N^2 \int_0^{2\pi} e^{im\phi} \times e^{-im\phi} d\phi = 1 \qquad ...(16)$$

$$\text{or} \quad N^2 \int_0^{2\pi} d\phi = 1, \text{ i.e., } N^2 (2\pi) = 1$$

So that $N = (2\pi)^{-1/2}$ ...(17)

Hence, the normalized wave function become

$\Phi_{\pm m}(\phi) = (2\pi)^{-1/2} \exp(\pm im\phi)$; m = 0, 1, 2, 3,... ...(18)

We shal not attempt to give a complete solution of Eq. 9 but will merely state that if $\beta = l(l+1)$ where l is the rotational quantum number, then this equation becomes a standard mathematical equation whose solutions are known to be associated legendre polynomials $P_l^{|m|}(\cos\theta)$ where l is either zero or a positive integer and $l > |m|$

The normalized solutions are givey by :

$$\Theta(\theta) = \Theta_{l,\pm m}(\theta) = \left[\frac{2l+1}{2} \times \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l^{|m|} \cos\theta \qquad ...(19)$$

The energy eigenvalues of the rigid rotor are obtained as follows :

$$\beta = 8\pi^2 IE / h^2 = l(l+1) \qquad ...(20)$$

$$\text{Thus,} \quad E = \frac{l(l+1)h^2}{8\pi^2 I}; \; l = 0, 1, 2, 3 \qquad ...(21)$$

In spectroscopy it is customary to use the symbol J rather than l for the rotational quantum number so that the rotational energy levels are given by the expression.

$$E_J = \frac{J(J+1)}{8\pi^2 I}; \; J = 0, 1, 2, 3.... \qquad ...(22)$$

The Schrodinger Equation for Hydrogen Atom : Hydrogen atom is the simplest of all atoms. It is a three dimensional system and the schrodinger equation for this system is

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

$$\text{where} \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)$$

and where the Laplacian operator in Cartesian coordinates is givey by

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

The potential energy of interaction between the electron and the nucleus is given by

$$V(r) = Ze^2 / 4\pi\varepsilon_0 r$$

Since this attractive potential has spherical symmetry depending only upon r, it is convenient to express the Schrodinger equation in terms of polar coordinates (r, θ, ϕ), rather than Cartesian coordinates (x, y, z). The Cartesian coordinates are related to polar coordinates as follows :

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

Q. **Normalise the wave function** $\Phi = e^{im\phi}$

Soln. $\int_0^{2\pi} \Phi^* \Phi \, d\phi = 1 \; (0 \le \phi \le 2\pi)$ ....(1)

or $N^2 \int_0^{2\pi} e^{im\phi} \times e^{-im\phi} d\phi = 1$ ...(2)

or $N^2 \int_0^{2\pi} d\phi = 1$, i.e., $N^2(2\pi) = 1$ so that

$N = (2\pi)^{-1/2}$ ...(3)

Hence, the normalized wave functions become

$\Phi_{\pm m}(\phi) = (2\pi)^{-1/2} \exp(\pm im\phi)$; m = 0, 1, 2, 3,... ...(4)

Q. Normalise the wave function for rigid rotor $\phi_M(\phi) = e^{iM\phi}$.

Soln. Let, normalised function is $\phi' = A.e^{-iM\phi}$

$\therefore \quad \int_0^{2\pi} A.e^{iM\phi} \; A\, e^{-iM\phi} d\phi = 1$

$\Rightarrow \quad A^2 \int_0^{2\pi} 1.d\phi = 1$

$\Rightarrow \quad A^2 = \frac{1}{(2\pi - 0)} = \frac{1}{2\pi}$

$\therefore \quad A = \sqrt{\frac{1}{2\pi}}$

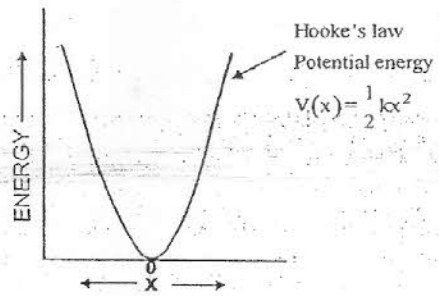
$\therefore \quad \boxed{\psi' = \sqrt{\frac{1}{2\pi}} e^{im\phi}}$ → Normalised wave function for rigid rotor.

ONE-DIMENSIONAL SIMPLE HARMONIC OSCILLATOR

A diatomic vibrating molecule can be represented by a simple model, the so-called simple harmonic oscillator. (S.H.O.). The force acting on the molecule is given by f = –kx, where x is the displacement from the equilibrium position and k is a constant called the force constant. The potential energy V(x) of this molecule is given by

$$V(x) = -\int_0^x f\,dx = \int_0^x kx\,dx = \frac{1}{2}kx^2 \qquad \text{... (1)}$$

Eq. 1. is the equation of a parabola. Thus, if we plot potential energy of a particle executing simple harmonic oscillations as a function of displacement from the equilibrium position, we get a curve as shown in figure.



potential energy diagram
for a simple harmonic oscillator

The vibrational frequency of the oscillator of mass m is given by

$$\upsilon = \frac{1}{2\pi}\left(\frac{k}{m}\right)^{1/2} \qquad \text{...(2)}$$

It is more accurate to define the vibrational frequency as

$$\upsilon = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2} \qquad \text{...(3)}$$

where μ is the reduced mass of the diatomic molecule defined as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \text{...(4)}$$

where m_1 and m_2 are the atomic masses of the two atoms.

Using the potential energy given by Eq. 1, for one dimensional S.H.O , the schrodinger equation is represented as

$$\left[-\frac{h^2}{2m}\left(\frac{d^2}{dx^2}\right) + \frac{1}{2}kx^2\right]\psi(x) = E\psi(x) \qquad \text{...(5)}$$

Mathematically, Eq. 5 may be written as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0 \qquad \text{...(6)}$$

Defining α and β as $\alpha = 2mE/\hbar^2$ and $\beta = (mk)^{1/2}/\hbar$. ...(7)

Eq. 6 becomes $\frac{d^2\psi}{dx^2} + \left(\alpha - \beta^2 x^2\right)\psi = 0$ ...(8)

Defining a new variable $\xi = \beta^{1/2}x$, the above equation becomes

$$\frac{d^2\psi}{d\xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0 \qquad ...(9)$$

Eq. 9 has a solution of the form

$$\psi(\xi) = \phi(\xi)e^{-\xi^2/2} \qquad ...(10)$$

Using this solution Eq. 9 becomes

$$\frac{d^2\phi}{d\xi^2} - 2\xi\frac{d\phi}{d\xi} + \left(\frac{\alpha}{\beta} - 1\right)\phi = 0 \qquad ...(11)$$

Eq. 11 is identical in form to a well known second order differential equation, called the Hermite equation., viz.,

$$\frac{d^2\phi}{d\xi^2} - 2\xi\frac{d\phi}{d\xi} + 2n\phi = 0 \qquad ...(12)$$

The Hermite equation has solutions which depend upon the value of n. These solutions are called Harmite polynomials, $H_n(\xi) \equiv H_n(\xi)$.

The Hermite Polynomial of degree n is defined as

$$H_n(\xi) = (-1)^n e^{\xi^2}\left\{\frac{\partial^n\left(e^{-\xi^2}\right)}{\partial\xi^2}\right\} \qquad ...(13)$$

A few Hermite polynomials are given below :

$H_0(\xi) = 1$ $\qquad$ $H_3(\xi) = 8\xi^3 - 12\xi$

$H_1(\xi) = 2\xi$ $\qquad$ $H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$

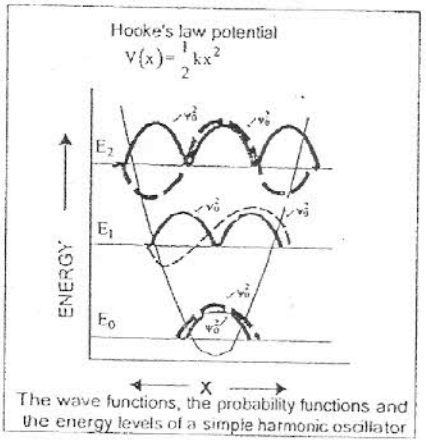
$H_2(\xi) = 4\xi^2 - 2$

The normalized wave functions of the one-dimensional S.H.O. are then written as

$$\psi_n(\xi) = \left[\frac{\beta^{1/2}}{2^n n!\sqrt{\pi}}\right]^{1/2} e^{-\xi^2/2}H_n(\xi) \quad \text{where } n = 0, 1, 2, 3, \ldots$$

...(14)

The first three wave functions (with n = 0, 1, 2), the corresponding energy levels and the probability finctions ψ_n^2 fofr the S.H.O, are shown in Figure.



The wave functions, the probability functions and the energy levels of a simple harmonic oscillator

Energy of S.H.O. The energy of the S.H.O. is obtained by comparing Eqs. 11 and 12, whence we find that

$$\alpha/\beta = 2n+1 \qquad ...(15)$$

Substituting for α and β Eq. 7, we have

$$\left(2mE/\hbar^2\right)(mk)^{1/2}/\hbar = 2n+1 \qquad ...(16)$$

or $$E = \left(n+\frac{1}{2}\right)\hbar(k/m)^{1/2} \qquad ...(17)$$

From Eq. 2 $(k/m)^{1/2} = 2\pi\upsilon$ ...(18)

Combining Eqs. 17 and 18, we have

$$E \equiv E_n = \left(n+\frac{1}{2}\right)\hbar(2\pi\upsilon)$$
$$= \left(n+\frac{1}{2}\right)h\upsilon \; ; \; n = 0,1,2,3,...(\hbar = h/2\pi) \qquad ...(19)$$

The energy state with $n = 0$ is the vibrational ground state with energy

$$E_0 = \frac{1}{2}h\upsilon$$

This energy is called the zero point energy of the oscillator. Classical mechanics predicts that the zero-point energy of the oscillator is zero whereas quantum mechanics predicts that the zero-point energy is non-zero. The occurrence of the zero-point energy is consistent with the Heisenberg uncertainty principle.

PROBLEMS

Q. **"According to the virial theorem for a diatomic S.H.O. the expectation (average) value of the kinetic energy, $< T >$, is equal to the expectation value of the potential energy, $< V >$".** Verify this statement for the ground state of the S.H.O. given that the ground state wave function is

$$\psi_0(x) = (\beta/\pi)^{1/4}\exp\left(-\beta x^2/2\right)$$

where $\beta = (mk)^{1/2}/\hbar$ and $k = m\omega^2$; $\omega = 2\pi\upsilon$ where υ is the vibrational frequancy of the S.H.O.

Soln. Let us calculate $<\hat{T}>$ and $<\hat{V}>$.

Here, the kinetic energy operator is $-\frac{\hbar^2}{2m}\frac{\partial^2}{dx^2}$ and potential energy $V(x) = \frac{1}{2}kx^2$ where k is the force constant and x is the displacement of the S.H.O. from the equilibrium position.

$$<\hat{T}> = \int_{-\infty}^{\infty}\psi_0^*\hat{T}\,dx = \int_{-\infty}^{\infty}(\beta/\pi)^{1/4}e^{-\beta x^2/2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)(\beta/\pi)^{1/4}e^{-\beta x^2/2}\,dx$$

$$= (\beta/\pi)^{1/2}\left(-\hbar^2/2m\right)\int_{-\infty}^{\infty}e^{-\beta x^2/2}\left(\frac{d^2}{dx^2}\right)e^{-\beta x^2/2}dx$$

$$= (\beta/\pi)^{1/2}\left(-\hbar^2/2m\right)\int_{-\infty}^{\infty}e^{-\beta x^2/2}\left(\frac{d}{dx}\right)\left(-\beta x\,e^{-\beta x^2/2}\right)dx$$

$$= (\beta/\pi)^{1/2}\left(-\hbar^2/2m\right)(-\beta)\int_{-\infty}^{\infty}e^{-\beta x^2/2}\left[1-\beta x^2\right]e^{-\beta x^2/2})dx$$

$$= = (\beta/\pi)^{1/2}\left(\hbar^2/2m\right)\left[\beta\int_{-\infty}^{\infty}e^{-\beta x^2/2}dx - \beta^2\int_{-\infty}^{\infty}x^2\,e^{-\beta x^2}dx\right]$$

Using the standard integrals

$$\int_{-\infty}^{\infty} e^{-ax^2}dx = (\pi/a)^{1/2} \quad \text{and} \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2}dx = \frac{1}{2a}(\pi/a)^{1/2}$$

we obtain $$\langle \hat{T} \rangle = (\beta/\pi)^{1/2}\left(\hbar^2/2m\right)\left[(\beta)(\pi/\beta)^{1/2} - \left(\beta^2\right)(1/2\beta)(\pi/\beta)^{1/2}\right]$$

$$= \frac{\beta\hbar^2}{2m} - \frac{\beta\hbar^2}{4m} = \frac{\beta\hbar^2}{4m} = \frac{\hbar\omega}{4} = \frac{h\upsilon}{4} \quad \left(\text{since } \beta = (mk)^{1/2}/h\,;\, k = m\omega^2 \text{ and } \omega = 2\pi\upsilon\right)$$

Again $$\langle \hat{V} \rangle = \int_{-\infty}^{\infty} \psi_0^* \hat{V} \psi_0 \, dx = \int_{-\infty}^{\infty} (\beta/\pi)^{1/4} e^{-\beta x^2/2}\left(\frac{1}{2}kx^2\right)(\beta/\pi)^{1/4} e^{-\beta x^2/2}dx$$

$$\Rightarrow (\beta/\pi)^{1/2}\left(\frac{1}{2}k\right)\int_{-\infty}^{\infty} x^2 e^{-\beta x^2}dx = (\beta/\pi)^{1/2}(k/2)\left(\frac{1}{2\beta}\right)(\pi/\beta)^{1/2} = \frac{k}{4\beta} = \frac{m\omega^2}{4(mk)^{1/2}/\hbar} = \frac{m\omega^2\hbar}{4m\omega} = \frac{\hbar\omega}{4} = \frac{h\upsilon}{4}$$

From Eqs. (i) and (ii) we see that $\langle \hat{T} \rangle = \langle \hat{V} \rangle$, which is the virial theorem.

Q. **Verify the Heisenberg uncertainty principle for the ground state of a one-dimensional S.H.O.**

Soln. We know that $\Delta x = \left[\langle x^2 \rangle - \langle x \rangle^2\right]^{1/2}$; $(\Delta p_x) = \left[\langle p_x^2 \rangle - \langle p_x \rangle^2\right]^{1/2}$

For an S.H.O. $\psi_0(x) = (\beta/\pi)^{1/4} e^{-\beta x^2/2}$

Now, $$\langle x \rangle = \int_{-\infty}^{\infty} \psi_0^* \hat{x} \, dx = \int_{-\infty}^{\infty} (\beta/\pi)^{1/4} e^{-\beta x^2/2} \hat{x} (\beta/\pi)^{1/4} e^{-\beta x^2/2} \, dx$$

$$= (\beta/\pi)^{1/2}\int_{-\infty}^{\infty} x e^{-\beta x^2}dx = 0 \quad \text{(Integrand is zero is power of x is odd)} \qquad ...(i)$$

Again $$\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0^* x^2 \psi_0 dx$$

Proceeding as in Example 27, we find that

$$\langle x^2 \rangle = 1/2\beta \qquad ...(ii)$$

$$\langle \hat{p}_x \rangle = \int_{-\infty}^{\infty} (-i\hbar d/dx)\psi_0 dx = (\beta/\pi)^{1/2}(-i\hbar)\int_{-\infty}^{\infty} e^{\beta x^2/2}\left[-\beta x\, e^{-\beta x^2/2}\right]dx$$

$(\beta/\pi)^{1/2}\int_{-\infty}^{\infty} x e^{-\beta x^2}dx = 0$ (Integrand is zero is power of x is odd) ...(i)

Again $\langle x^2 \rangle = \int_{-\infty}^{\infty} \psi_0^* x^2 dx$

Proceeding as in Example original we find that

$$\langle x^2 \rangle 1/2\beta$$

$$\langle p_x \rangle \int_{-\infty}^{\infty} \psi_0^*(-i\hbar d/dx)\psi_0 dx = (\beta/\pi)^{1/2}(-i\hbar)\int_{-\infty}^{\infty} e^{\beta x^2/2}\left[-\beta x\, e^{-\beta x^2/2}\right]dx \qquad ...(ii)$$

$$= (\beta/\pi)^{1/2}(-i\hbar)(-\beta)\int_{-\infty}^{\infty} x\, e^{-\beta x^2}dx$$

$= 0$ (because the integrand is odd) ...(iii)

Again, $$\langle p_x^2 \rangle = \int_{-\infty}^{\infty} \psi_0^*\left(-\hbar^2 d^2/dx^2\right)\psi_0 dx = \left(-\hbar^2\right)(\beta/\pi)^{1/2}\int_{-\infty}^{\infty} e^{-\beta x^2/2}\left(d^2/dx^2\right)e^{-\beta x^2/2}dx$$

Proceeding as in Example original where we have evaluated $\langle \hat{T} \rangle$, we find that

$$\langle p_x^2 \rangle = \beta\hbar^2/2 \qquad ...(iv)$$

From Eqs. (i), (ii), (iii), and (iv) we find on simplification that

$$\Delta x.\Delta p_x = \hbar/2,$$

which is the Heisenberg uncertainty principle. A rigorous mathematical derivation gives the inequality

$$\Delta x, \Delta p_x \geq \hbar/2$$

ANGULAR MOMENTUM

The classical definition of angular momentum $L = r \times p$ depends on six numbers r_x, r_y, r_z, p_x, p_y and p_z. Translating this into quantum mechanical terms, the heisenberg uncertainty principle tells us that it is not possible for all six of these numbers to be measured simultaneously with arbitrary precision. Therefore, there are limits to what can be known or measured about a particles angular momentum. It turns out that the best that one can do is to simultaneously measure both the angular momentum vectors magnitude and its component along one axis.

Mathematically, angular momentum in quantum mechanics is defined like momentum not as a quantity but as an operator on the wave function.

$$L = r \times p$$

where r and p are the position and momentum operators respectively.

$$L = L_x i + L_y j + L_z k$$

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{p} = p_x\hat{i} + p_y\hat{j} + p_z\hat{k}$$

$$L = \begin{bmatrix} i & j & k \\ x & y & z \\ p_x & p_y & p_z \end{bmatrix}$$

$$L = i(ypz - pyz) - \hat{j}(xpz - pxz) + k(xpy - ypx)$$

$$L = i(yp_z - p_y z) + \hat{j}(zp_x - xp_z) + k(xp_y - yp_x)$$

$L_x = yp_z - zp_y$

$$= y\left(-i\hbar\frac{\delta}{\delta z}\right) - z\left(-i\hbar\frac{\delta}{\delta y}\right)$$

$$= -i\hbar\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right)$$

$L_y = zp_x - zp_z$

$$= z\left(-i\hbar\frac{\delta}{\delta x}\right) - x\left(-i\hbar\frac{\delta}{\delta z}\right)$$

$$= -i\hbar\left(z\frac{\delta}{\delta x} - x\frac{\delta}{\delta z}\right)$$

$L_z = xp_y - yp_x$

$$= x\left(-\hbar\frac{\delta}{\delta y}\right) - y\left(-\hbar\frac{\delta}{\delta x}\right)$$

$$= -i\hbar\left(x\frac{\delta}{\delta y} - y\frac{\delta}{\delta x}\right)$$

Q. Prove that: $[L_x, L_y] = i\hbar L_z$

Proof: L.H.S. $= [L_x, L_y] = L_x L_y - L_y L_x$

$$= i^2\hbar^2\left(y\frac{\delta}{\delta x}\right) - i^2\hbar^2\left(x\frac{\delta}{\delta y}\right)$$

$$= (-i\hbar)(-i\hbar)\left(y\frac{\delta}{\delta x}\right) - (i\hbar)(-i\hbar)\left(x\frac{\delta}{\delta y}\right)$$

$$= -i\hbar\left[-i\hbar\left\{y\frac{\delta}{\delta x} - x\frac{\delta}{\delta y}\right\}\right] = -i\hbar(-Lz) = i\hbar Lz \text{ Ans.}$$

Q. Show that $[L_x, y] = i\hbar z$

Proof: L.H.S. $= [L_x, y] = L_x y - y L_x$

$$= -i\hbar\left[y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right]y - y(-i\hbar)\left[y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right] = -i\hbar y\frac{\delta y}{\delta z} + i\hbar z\frac{\delta y}{\delta y} + i\hbar y\left[y\frac{\delta}{\delta z} - z\frac{\delta}{\delta z}\right]$$

The IInd term become zero because the operator is commute. A function that are dependent on three co-ordinates x, y, z is always given the value zero because commutation is possible in three inter dependent co-ordinate.

$$= -i\hbar\, y\frac{\delta y}{\delta z} + i\hbar\, z\frac{\delta y}{\delta y}$$

$[L_x, y] = i\hbar\, z$ Ans.

Q. **Prove that:** $[L_x, x] = 0$

Proof: L.H.S. $= [L_x, x] = L_x\, x - xL_x = -i\hbar\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right)x - x\left[-i\hbar\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right)\right]$

$$= -i\hbar\, y\frac{\delta x}{\delta z} + i\hbar\, z\frac{\delta x}{\delta y} - (-i\hbar)x\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right) = i\hbar\, x\left(y\frac{\delta}{\delta z} - z\frac{\delta}{\delta y}\right) = 0 \text{ Ans.}$$

RELATION:

$[L_x\, L_y] = i\hbar L_z$	$[L_x, y] = i\hbar z$	$[L_x, x] = 0$
$[L_y\, L_z] = i\hbar L_x$	$[L_y, z] = i\hbar x$	$[L_y, y] = 0$
$[L_z\, L_x] = i\hbar\, L_y$	$[L_z, x] = i\hbar y$	$[L_z, z] = 0$

We can't determine LxLy simultaneously. Hence the two different component of the angular momentum don't commute. It will not be possible to measure Lx, Ly and Lz simultaneously because product of the uncertainty of two quantities is not zero.

$[L_x\, L_y] \neq 0 \quad [L_y\, L_z] \neq 0 \quad [L_z\, L_x] \neq 0$

$[ab, c] = a[b, c] + [a, c]b$; $\left[L_x^2, L_x\right] = \left[\underset{a}{L_x}\,\underset{b}{L_x}\,\underset{c}{L_x}\right]$

Q. $\left[L_x^{\,2}, L_x\right] = 0$, show.

$[L_xL_x, L_x] = L_x[L_x, L_x] + [L_x, L_x]L_x = 0$ Ans.

Q. Prove that $[L^2, L_x] = 0$

(I) $\left[L_x^{\,2} + L_y^{\,2} + L_z^{\,2}, L_x\right] = \underset{\text{I}}{\left[L_x^{\,2}, L_x\right]} + \underset{\text{II}}{\left[L_y^{\,2}, L_x\right]} + \underset{\text{III}}{\left[L_z^{\,2}, L_x\right]}$

(II) $\left[L_y^{\,2}, L_x\right] = [L_y, L_y, L_x] = L_y\left[L_y, L_x\right] + \left[L_y, L_x\right]L_y$

$L_y[-i\hbar\, L_z] + [-i\hbar\, L_z]L_y$; $-i\hbar\left[L_y\, L_z\right] - i\hbar\left[L_z\, L_y\right]$; $-i\hbar[i\hbar\, L_x] - i\hbar\left[-i\hbar\, L_x\right]$

$-i^2\hbar^2\, L_x + i^2\hbar^2\, L_x = 0$

(III) $\left[L_z^{\,2}, L_x\right] = [L_z, L_z, L_x] = L_z\left[L_z, L_x\right] + \left[L_z, L_x\right]L_z = L_z\left[i\hbar\, L_y\right] + \left[i\hbar\, L_y\right]L_z$

$= i\hbar\left[L_z\, L_y\right] + i\hbar\left[L_y\, L_z\right] = i\hbar\left[-i\hbar\, L_x\right] + i\hbar[i\hbar\, L_x] = -i^2\hbar^2\, L_x + i^2\hbar^2\, L_x = 0$

$\left[L^2, L_x\right] = \left[L_x^{\,2}, L_x\right] + \left[L_y^{\,2}, L_x\right] + \left(L_z^{\,2}, L_x\right)$

$\left[L^2, L_x\right] = 0$

HARTREE

Hartree's method of self-consistent fields: An important method for obtaining a suitable central field is due to Hartree. In this method, a suitable function $\bar{V}(r_i)$ is first chosen with property close to that given by equation

$$\left.\begin{aligned} \bar{V} &= -\frac{Ze^2}{r_i} + \text{constant} \quad (\text{for small } r_i) \\ \text{And} \quad \bar{V} &= -\frac{e^2}{r_i} \quad (\text{for large } r_i) \end{aligned}\right\} \quad \ldots (1)$$

The single particle states ψ_i are then obtained by solving the Schrodinger equation. Now, the part of the potential due to all electrons other than the ith is calculated by assuming that each of these electrons yields a charge distribution as given by their wavefunctions already worked out.

Consider the jth electron, $j \neq i$. The average charge in a volume element $d\tau_j$ due to this electron is $e\, d\tau_j |\psi(r_j)|^2$ and the potential energy of interaction with the ith electron is

$$e^2 \int d\tau_j \frac{|\psi_j(r_j)|^2}{|r_i - r_j|} \quad \ldots (2)$$

Thus, the ith electron moves in a potential generated by all the other electrons,

Namely, $$e^2 \sum_{j \neq i} \int d\tau_j \frac{|\psi_j(r_j)|^2}{|r_i - r_j|}$$

So, that the full potential is,

$$\bar{V}(r_i) = -\frac{Ze^2}{r_i} + e^2 \sum_{j=1}^{Z-1} \int d\tau_j \frac{|\psi_j(r_j)|^2}{|r_i - r_j|} \quad \ldots (3)$$

where the first term is due to the nucleus. With this potential, we can repeat the whole process, i.e. calculate the wavefunctions (in general, numerically), etc. The process is repeated until two successive iterations yield the same $\bar{V}(r_i)$ to the desired accuracy. In other words, the electrons are supposed to move in a potential which they themselves generate. This is why the method is called "self consistent'.

The numerical calculations necessary are possible only with high speed computers and that too with a great deal of technical expertise. We shall, however, illustrae the method with an elementary calculation for helium. Hartree's method is designed for heavier atoms than helium but the purpose here is to clarify the general technique. We have used a small programmable calculator for this purpose and would strongly advise the student to try this calculation himself.

Application to helium atom:

We start by assuming a potential[2]

$$V_0(r) = -2/r \quad \ldots (4)$$

This is the potential either electron moves in if the other were absent. [In practice, it would save considerable labour to start with a more realistic potential in accordance with equation (1). The radial function for the ground state is

$$R_{10}(r) = 2^{3/2} e^{-2r} \quad \ldots (5)$$

So, that

$$\psi_{100}(r_2) = R_{10}(r_2) Y_{00} = \frac{1}{\sqrt{4\pi}} R_{10}(r_2) \quad \ldots (6)$$

The suffix 2 indicates that it is in the field of the second electron that the first one moves. Next, we calculate the integral.

$$S = \int d\tau_2 \frac{|\psi_{100}(r_2)|^2}{|r_1 - r_2|} \qquad \ldots (7)$$

The result is

$$S = \frac{1}{r_1}\left\{1 - \left(1 + 4r_1 + 8r_1^2\right)e^{-4r_1}\right\} + 2\left(1 + 4r_1\right)e^{-4r_1} \qquad \ldots (8)$$

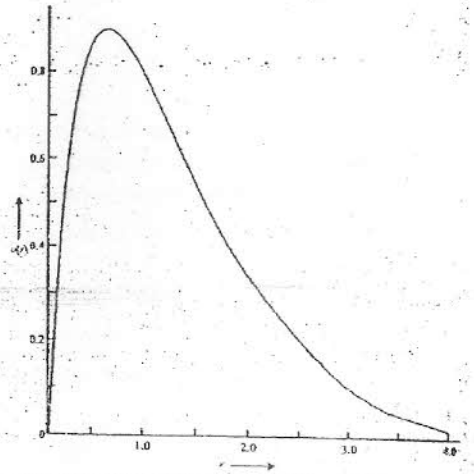


Fig: The normalized wave function u(r) corresponding to an eigenvalue $E \approx 0.82$

Adding the term $-Z/r_1$ [See equation (3)], we obtain

$$\bar{V}_1(r_1) = -\left\{\frac{1}{r_1} + \left(\frac{1}{r_1} + 2\,e^{-4r_1}\right)\right\} \qquad \ldots (9)$$

the suffix on $\bar{V}_1$ indicating that we have now worked out the first iteration. Note that this function already has the correct limiting behaviour for $r_1 << 1$ and $r_1 >> 1$.

We can solve the radial equation numerically to obtain the ground state wavefunction. The normalized wavefunction u(r), corresponding to an eigenvalue $E \approx 0.82$, is plotted in figure above. Here $u(r) = rR(r)$ is the more convenient function to use. The radial equation is then

$$\frac{d^2u}{dr^2} = -2\left[E - V\right]u = F(r)\,u \qquad \ldots (10)$$

and u is normalized to give

$$\int_0^\infty |u|^2\, dr = 1 \qquad \ldots (11)$$

The energy of each electron corresponding to this function is

$$\langle H \rangle = \left\langle -\frac{1}{2}\nabla^2 - \frac{2}{r} + \frac{1}{r_{12}} \right\rangle \qquad \ldots (12)$$

where the three terms are the kinetic energy, the potential energy due to the nucleus and the energy of repulsion between the electrons. We write

$$\langle H \rangle = \langle t \rangle + \langle v \rangle + \langle v_{12} \rangle \qquad \ldots (13)$$

Since there is no angular dependence for the 's' wavefunctions, we have

$$\langle \nabla^2 \rangle = \int_0^\infty u \cdot \frac{d^2u}{dr^2}\, dr \qquad \ldots (14)$$

The simplest way to evaluate this is two use equation (10) and write

$$\langle t\rangle = -\frac{1}{2}\int_0^\infty F(r)\,u^2 dr \qquad \ldots(15)$$

Similarly, $$\langle v\rangle = \int_0^\infty \frac{u^2}{r} dr \qquad \ldots(16)$$

To evaluarte, $\langle v_{12}\rangle$, we write

$$\left.\begin{aligned}\frac{1}{r_{12}} &= \frac{1}{r_1}\sum_{i=0}^{\infty}\left(\frac{r_2}{r_1}\right)^{\ell} P_\ell(\cos\theta) \quad \text{for } r_2 < r_1\\ &= \frac{1}{r_2}\sum_{i=0}^{\infty}\left(\frac{r_1}{r_2}\right)^{\ell} P_\ell(\cos\theta) \quad \text{for } r_2 > r_1\end{aligned}\right\} \qquad \ldots(17)$$

Since for the 's' wavefunctions only the $l = 0$ terms survive on integration over angles, we have

$$\left\langle \frac{1}{r_{12}}\right\rangle = \int_0^\infty |u(r_1)|^2 dr_1 \left\{\frac{1}{r_1}\int_0^{r_1} |u(r_2)|^2 dr_2 + \int_{r_1}^{r_2}\frac{|u(r_2)|^2}{r_2} dr_3\right\} \qquad \ldots(18)$$

Each of the integrals in equations (15), (16) and)17) has to be evaluated numerically. For the wavefunction in figure above.
We obtain,

$$\left.\begin{aligned}\langle t\rangle &= 1.29\\ \langle v\rangle &= -3.20\\ \text{and}\quad \langle v_{12}\rangle &= 0.97\end{aligned}\right\} \qquad \ldots(19)$$

The total energy of helium atom (ground state) is not twice the sum of the above values. We must remember that the electrostatic energy of the two electrons must be added just once. Thus,

$$E_0 = 2(\langle t\rangle + \langle v\rangle) + \langle v_{12}\rangle \approx -2.85 \qquad \ldots(20)$$

which turns out to be -77.6 eV; somewhat larger than the observed value of -79 eV.

The above calculation, chosen for its simplicitly, misses some of the subtler points. For example, the two electrons in the ground state are both in the 1s state so that the self-consistent potential for them is the same. This, however, is not true in general. For the potential of one of the electrons due to other,

$$V_1(r_1) = -\frac{2}{r_1} + \int d\tau_2 \frac{|\psi_{2s}(r_2)|^2}{|r_1 - r_2|} \qquad \ldots(21)$$

and $$V_2(r_2) = -\frac{2}{r_2} + \int d\tau_1 \frac{|\psi_{1s}(r_1)|^2}{|r_1 - r_2|} \qquad \ldots(22)$$

showing explicitly that $V_1(r_1)$ and $V_2(r_2)$ are different functions. (Hence the suffixes on V_1 and V_2). One can use these to calculate the energies as before.

Since the effective Hamiltonian for the various electrons are different, the resulting solutions of the wave equations for the electrons will not, in general, be orthogonal. Moreover, the wavefunctions used will have to satisfy the exclusion principle. These features are incorporated in the Hartree-Fock method.

APPROXIMATION TECHNIQUE

A. PERTURBATION THEOREM:

First Order Perturbation: Perturbation theory is an approximation method to find out the exact solution of any system with great accuracy. We disturb the operator in a specific order. to break the energy correction in a particular energy level. Perturbation are of two type.

1. Slow Perturbation 2.Sudden

The energy correction. $\boxed{\Delta E = \int \psi_0^* H^1 \psi_0 d\tau}$; H^1 = Perturbed value in operator.

Let us take a problem $H\psi_0 = E\psi_0$.

where H = operator ψ = function, E = energy.

$$H = H_0 + H_1,\ E = E_0 + \Delta E$$

The ground state. problem is $H_0\psi_0 = E_0\psi_0$; ψ_0 and E_0 are known & effect of H^1 is not more because it is a Ist order effect, $H\psi = E\psi$; $(H_0 + H^1)\psi_0 = (E_0 + \Delta E)\psi$.

The effect of perturbation may be seen all function, but a slighlty effect so ψ_0 may be turn is to $\psi_0 + \Delta\psi$ but $\Delta\psi$ and ΔE is very small.

$$= (H_0 + H^1)(\psi_0 + \Delta\psi) = (E_0 + \Delta E)(\psi_0 + \Delta\psi)$$

$$= H_0\psi_0 + H^1\psi_0 + H_0\Delta\psi + H^1\Delta\psi = E_0\psi_0 + \Delta E\psi_0 + E_0\Delta\psi + \Delta E\Delta\psi$$

$$[H_0\psi_0 = E_0\psi_0] \qquad \text{...(i)}$$

The Ist term cancel because of equation Ist

$H^1\Delta\psi$ & $\Delta E\Delta\psi$. In addition to it we shall neglect the last term of each side may be neglected because multiplication of these two small term is further small.

$$H^1\psi_0 + H_0\Delta\psi = \Delta E\psi_0 + E_0\Delta\psi$$

realised that ΔE & $\Delta\psi$ are unknown quantity and the order of the equation is same. Because each term is the product of unperturbed term and a small quantity.

This equation in which unperturbed and another small quantity is present may be called as Ist order perturbation. The two term that we've neglected are IInd order term.

$$H_1\psi_0 + (H_0 - E_0)\Delta\psi = \Delta E\psi_0 \qquad \text{...(ii)}$$

Multiplying both sides by ψ_0^* from left and then integrating both sides w.r.t. volume element τ.

$$\int \psi_0^*(H_0 - E_0)\Delta\psi d\tau + \int \psi_0^* H_1\psi_0 d\tau = \int \psi_0^* \Delta E\psi_0 d\tau$$

$$\int \psi_0^*(H_0 - E_0)\Delta\psi d\tau + \int \psi_0^* H_1\psi_0 d\tau = \Delta E \int \psi_0^* \psi_0 d\tau = \Delta E$$

$$\Delta E = \int \psi_0^*(H_0 - E_0)\Delta\psi d\tau + \int \psi_0^* H_1\psi_0 d\tau \qquad \text{... (iii)}$$

Ist term on the R.H.S is zero because every operator in quantum mechanics is Hermitian operator. It means

$$\int \psi_0^*(H_0 - E_0)\Delta\psi d\tau = \int \Delta\psi (H_0 - E_0)^* \psi_0^* d\tau$$

$$\text{- - - - - } = \int \Delta\psi [H_0\psi_0 - E_0\psi_0]^* d\tau = \int \Delta\psi \times 0\, d\tau = 0 \qquad (\text{using equation (i)})$$

Therefore, the equation (3) gives,

$$\boxed{\Delta E = \int \psi_0^* H_1\psi_0 d\tau}$$

PROBLEM ON PERTURBATION:

Q. If a value of $\frac{v}{a}x$ is perturbed in a 1D box having length 0 to a. What is the total energy of the system.

$$\psi = \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a} \qquad H' = \frac{v}{a}x$$

$$\therefore \quad \Delta E = \int_0^a \sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}\frac{v}{a}x\sqrt{\frac{2}{a}}\sin\frac{n\pi x}{a}dx = \frac{2}{a}\cdot\frac{v}{a}\int_0^a x\sin^2\frac{n\pi x}{a}dx = \frac{2v}{\cancel{4}}\cdot\frac{\cancel{4}}{4} = \frac{v}{2}$$

$\therefore$ Perturbed total energy is always greater than ground state energy $\frac{n^2h^2}{8m\ell^2}$

$\therefore$ The corrected total energy $= \left(\frac{n^2h^2}{8m\ell^2} + \frac{v}{2}\right)$

Q. The quantum state of a particle moving in a cicular path in a plane is given by: **[GATE-2007]**

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{iM\phi}$$

when perturbation $H' = P\cos\phi$ (P=constant) is applied, what will be the 1st order energy correction?

Soln. $$\Delta E = \int_0^{2\pi}\psi_m^*(\phi)H'\psi_m(\phi)d\tau = \int_0^{2\pi}\frac{1}{\sqrt{2\pi}}e^{iM\phi}\,P\cos\phi\,\frac{1}{\sqrt{2\pi}}e^{iM\phi}d\phi$$

$$= \frac{P}{2\pi}\int_0^{2\pi}\cos\phi\,d\phi = \frac{P}{2\pi}[\sin\phi]_0^{2\pi} = \frac{P}{2\pi}[\sin 2\pi - \sin 0] = \frac{P}{2\pi}\times 0 = 0$$

Q. A perturbation $V = \delta\left(x - \frac{a}{2}\right)$ is introduced in the box, the first what energy correction is ?
(limit –a to +a and first excited state)

Soln. $$\psi = \frac{1}{\sqrt{a}}\sin\frac{n\pi x}{2a} = \frac{1}{\sqrt{a}}.\sin\frac{2\pi x}{2a} = \frac{1}{\sqrt{a}}.\sin\frac{\pi x}{a}$$

$$\Delta E = \int_{-a}^{+a}\frac{1}{\sqrt{a}}.\sin\frac{\pi x}{a}\delta\left(x - \frac{a}{2}\right)\frac{1}{\sqrt{a}}\sin\frac{\pi x}{a}dx = \frac{1}{\sqrt{a}}\sin\frac{\pi\frac{a}{2}}{a}\times\frac{1}{\sqrt{a}}\sin\frac{\pi\frac{a}{2}}{a}$$

$$= \frac{1}{\sqrt{a}}\sin\frac{\pi}{2}\frac{1}{\sqrt{a}}\sin\frac{\pi}{2} \qquad \left(\because \sin\frac{\pi}{2} = 1\right) \qquad \Rightarrow \frac{1}{a}$$

Q. Consider an anharmonic oscillator whose potential is $\frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3$. Calculate the 1st correction to the harmonic oscillator energy.

Soln. As we know, $$\Delta E = \int_{-\infty}^{+\infty}\psi_0\frac{1}{6}\gamma x^3\psi_0 = 2\int_0^{\infty}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}\frac{1}{6}\gamma x^3\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2} = 2\times\frac{1}{6}\gamma\times\frac{\sqrt{\beta}}{\sqrt{\pi}}\int_0^{\infty}e^{-2\beta x^2/2}x^3dx$$

Compare this equation with the formula $\int_{-\infty}^{+\infty}x^n e^{-\alpha x^2}dx$, if n is odd (n=3 in the given problem) then it becomes equal to zero. So energy change is zero.

Q. Calculate the 1st order correction to the ground state slightly energy of an anharmonic oscillator whose potential energy is $\frac{1}{2}kx^2+\frac{\gamma}{6}x^3+bx^4$

Soln. $\Delta E=\int_{-\infty}^{+\infty}\left(\frac{\beta}{\pi}\right)^{\frac{1}{4}}e^{-\beta x^2/2}+\frac{\gamma}{6}x^3+bx^4+\left(\frac{\beta}{\pi}\right)^{\frac{1}{4}}e^{-\beta x^2/2}dx=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2\int_0^{\infty}e^{-\beta x^2}+0+bx^4$

$=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2\times b\int_0^{\infty}x^4+e^{-\beta x^2}$ [where, $n=4$ & $\alpha=\beta$]

$=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2b\times\frac{1}{2\beta^{\frac{4+1}{2}}}\Gamma\left(\frac{4+1}{2}\right)=\frac{\sqrt{\beta}}{\sqrt{\pi}}\times 2b\times\frac{1}{2\beta^{\frac{4+1}{2}}}\times\frac{3}{2}\times\frac{1}{2}\times\sqrt{\pi}=\sqrt{\beta}\times b\times\frac{3}{2}\times\frac{1}{2}$

$=\frac{3b}{4\beta^2}$ where $\beta=\frac{\sqrt{mk}}{\hbar}\Rightarrow\frac{3b}{4\left(\frac{\sqrt{mk}}{\hbar}\right)^2}$

Q. Calculate the I[a] order energy correction for 1D Harmonic oscillator whose Hamiltonian is $\frac{P^2}{2m}+\frac{1}{2}kx^2+ax^4$

$\psi_0=\left(\frac{k}{\pi\hbar\omega}\right)^{1/4}e^{-\left(\frac{kx^2}{2\hbar\omega}\right)}$ further show the value of ground state energy can be written as $E=\frac{\hbar\omega}{2}\left(1+\frac{3}{2}\frac{\hbar\omega}{k^2}\right)$

Soln. As we know as $E=\int_{-\infty}^{+\infty}\psi H\,\psi\,dx$

$\Delta E=\int_{-\infty}^{+\infty}\psi\frac{1}{2}ax^2\psi dx=2\int_0^{a}\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}\frac{1}{2}ax^2\left(\frac{\beta}{\pi}\right)^{1/4}e^{-\beta x^2/2}dx$

$=\frac{2\sqrt{\beta}}{\sqrt{\pi}}\times\frac{a}{2}\int_0^{a}e^{-2\beta x^2/2}x^2\Rightarrow\frac{a\sqrt{\beta}}{\sqrt{\pi}}\times\frac{1}{2\beta^{3/2}}\times\frac{1}{2}\sqrt{\pi}$

$\Rightarrow\frac{a\sqrt{\beta}}{\sqrt{\pi}}\times\frac{1}{2\beta^{3/2}}\times\frac{1}{2}\sqrt{\pi}=\frac{a}{4\beta}$ Ans.

(B) VARIATION THEOREM AND SECULAR EQUATION

When the system contains only a single electron the exact solution of Schrodinger wave equation is possible, as in case of H-like atom.

However if several electrons are involved the exact solution is not possible and approximations are used. There are a number of such methods

- Perturbation method.
- Variation method.

We guess a wave function and calculate the energy fortunately, if the guess is correct, the energy of the system is correct. On the other hand for a poor wave function, the energy will be poor.

According to variation principle it can be shown that, if ψ_0 is the correct wave function for a system, whose correct energy is E_0 than any other acceptable wave function ψ_i will give energy greater than E_0.

Energy for any trial wave function can be calculated by using conventional formula.

$$E_i = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau}$$ (Because we don't know that the trial wavefunction is normalised or not)

$$E_i \geq 0$$

Secular Equation:

In most instances, the variation function can be expressed in terms of,

$$\psi = a_1\phi_1 + a_2\phi_2 + \ldots\ldots\ldots\ldots a_i\phi_i$$

Where $a_1, a_2 \ldots\ldots a_i$ are arbitrary parameters that can be varied to a minimum in the energy.

For the convience, we express it,

$$\psi = a_1\phi_1 + a_2\phi_2$$

$$\therefore \quad E = \frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} = \frac{\int (a_1\phi_1 + a_2\phi_2)^* H (a_1\phi_1 + a_2\phi_2) d\tau}{\int (a_1\phi_2 + a_2\phi_2)^* (a_1\phi_1 + a_2\phi_2) d\tau}$$

$$= \frac{\int (a_1 + \phi_1 + a_2\phi_2)\left[H(a_1\phi_1) + H(a_2\phi_2)\right] d\tau}{\int (a_1\phi_1 + a_2\phi_2)^* (a_1\phi_1 + a_2\phi_2) d\tau}$$

$$= \frac{\int (a_1\phi_1 + a_2\phi_2)\left[a_1 H\phi_1 + a_2 H\phi_2\right] d\tau}{\int (a_1\phi_1 + a_2\phi_2)^* (a_1\phi_1 + a_2\phi_2) d\tau}$$

$$\left|\begin{array}{l} \int \phi_i^* H \phi_i d\tau = H_{ii} \\ \int \phi_i^* H \phi_j d\tau = H_{ij} \\ \int \phi_i^* \phi_i d\tau = S_{ii} \\ \int \phi_i^* \phi_j d\tau = S_{ij} \end{array}\right.$$

$$= \frac{\int\int \left[a_1^2\phi_1 H\phi_1 + a_1a_2\phi_1 H\phi_2 + a_1a_2\phi_2 H\phi_1 + a_2^2\phi_2 H\phi_2\right] d\tau}{\int\int \left[a_1^2\phi_1^*\phi_1 + a_1a_2\phi_1^*\phi_2 + a_1a_2\phi_2^*\phi_1 + a_2^2\phi_2^*\phi_2\right] d\tau}$$

$$= \frac{\int a_1^2\phi_1 H\phi_1 d\tau + a_1a_2\int \phi_1 H\phi_2 d\tau + a_1a_2\int \phi_2 H\phi_1 d\tau + a_2^2\int \phi_2 H\phi_2 d\tau}{a_1^2\int \phi_1^*\phi_1 d\tau + a_1a_2\int \phi_1^*\phi_2 d\tau + a_1a_2\int \phi_2^*\phi_1 d\tau + a_2^2\int \phi_2^*\phi_2 d\tau}$$

$$= \frac{a_1^2 + H_{11} + a_1a_2H_{12} + a_1a_2H_{21} + a_2^2H_{22}}{a_1^2S_{11} + a_2^2S_{22} + a_1a_2S_{12} + a_1a_2S_{21}} = \frac{a_1^2H_{11} + a_2^2H_{22} + a_1a_2H_{12}}{a_1^2S_{11} + a_2^2S_{22} + a_1a_2S_{12}}$$

$$\therefore \quad a_1^2H_{11} + a_2^2H_{22} + a_1a_2H_{12} = E\left(a_1^2S_{11} + a_2^2S_{22} + a_1a_2S_{12}\right)$$

Since we desire the minimum value of E (energy), it is necessary to minimize E with respect to both a_1 and a_2.

Using the differentiation w.r.to a_1 and a_2.

$$\left.\begin{array}{l} (H_{11} - ES_{11})a_1 + (H_{12} - ES_{12})a_2 = 0 \\ (H_{21} - ES_{21})a_1 + (H_{22} - ES_{22})a_2 = 0 \end{array}\right\}$$

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix} \rightarrow \text{secular determinant.}$$

Differentiation:

$$E\left(a_1^2S_{11}+a_2^2S_{22}+a_1a_2S_{12}\right)=a_1^2H_{11}+a_2^2H_{22}+a_1a_2H_{12}$$

Differentiating both sides w.r.to a,

$$\therefore \quad E\frac{\partial}{\partial a_1}\left(a_1^2S_{11}+a_2^2S_{22}+a_1a_2S_{12}\right)=\frac{\partial}{\partial a_1}a_1^2H_{11}+a_2^2H_{22}+a_1a_2H_{12}$$

$$\Rightarrow \quad E.\left[2a_1S_{11}+0+2a_2S_{12}\right]=\left[2a_1H_{11}+0+2a_2H_{12}\right]$$

$$\Rightarrow \quad E\left(a_1S_{11}+a_2S_{12}\right)=\left(a_1H_{11}+a_2H_{12}\right)$$

$$\Rightarrow \quad Ea_1S_{11}+Ea_2S_{12}=a_1H_{11}+a_2H_{12}$$

$$\therefore \quad -a_2\left(H_{12}-ES_{12}\right)=a_1\left(H_{11}-ES_{11}\right)$$

$$\therefore \quad \left(H_{11}-ES_{11}\right)a_1+\left(H_{12}-ES_{12}\right)a_2=0$$

$$E\left(a_1^2S_{11}+a_2^2S_{22}+2a_1a_2S_{12}\right)=\left(a_1^2H_{11}+a_2^2H_{22}+2a_1a_2H_{12}\right)+\left(a_1^2S_{11}+a_2^2S_{22}+a_1a_2S_{12}\right)\frac{\partial E}{\partial a_1}$$

Differentiating both sides w.r.to a_2,

$$\Rightarrow \quad E\left[0+2a_2S_{22}+2a_1S_{12}\right]+\left(a_1^2S_{11}+a_2^2S_{22}+a_1a_2S_{12}\right)\frac{\partial E}{\partial a_2}=\left(0+2a_2H_{22}+2a_1H_{12}\right)$$

$$\Rightarrow \quad E\left(a_2S_{22}+a_1S_{12}\right)=\left(a_2H_{22}+a_1H_{12}\right)$$

$$\Rightarrow \quad Ea_2S_{22}-a_2H_{22}=a_1H_{12}-Ea_1S_{12}$$

$$\Rightarrow \quad a_2\left(ES_{22}-H_{22}\right)=a_1\left(H_{12}-ES_{12}\right)$$

$$\therefore \quad a_1\left(H_{12}-ES_{12}\right)+a_2\left(H_{22}-ES_{22}\right)=0$$

Q. Use the variation method to calculate the ground state energy of a particle confined to move with in the region $0\le x\le a$ in a potential giving by $U(x)=V_1x, \quad 0\le x\le a/2$

$$U(x)=V_1(a-x_1),\ a/2\le x\le a$$

As a trial function, use a function

$$\phi=C_1\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}+C_2\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$ and represent the secular representation.

Soln. $H_{11}\int\phi_1H\phi_1d\tau$

$$=\int_0^{a/2}\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\left(-\frac{h^2}{2m}\frac{d^2}{dx^2}+V_1x\right)\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}+\int_{a/2}^{a}\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}\left(-\frac{\hbar^2}{2m}.\frac{d^2}{dx^2}+V_1(a-x_1)\right)\sqrt{\frac{2}{a}}\sin\frac{\pi x}{a}$$

$$=\frac{2}{a}\int_0^{a/2}\sin\frac{\pi x}{a}\left[-\frac{h^2}{2m}.\frac{d^2}{dx^2}.\sin\frac{\pi x}{a}+V_1x.\sin\frac{\pi x}{a}\right]+\frac{2}{a}\int_{a/2}^{a}\sin\frac{\pi x}{a}.\left[-\frac{\hbar^2}{2m}.\frac{d^2}{dx^2}.\sin\frac{\pi x}{a}+V_1(a-x_1).\sin\frac{\pi x}{a}\right]$$

$$=\boxed{\frac{h^2}{8ma^2}+V_1a\left(\frac{1}{4}+\frac{1}{\pi^2}\right)}$$

$$\begin{vmatrix}S_{11}=S_{22}=1\\S_{12}=S_{21}=0\\H_{12}=H_{21}=0\end{vmatrix}$$

$$H_{22} = \int \phi_2 H \phi_2 d\tau$$

$$= \int_0^{a/2} \sqrt{\frac{2}{a}} \sin\frac{2\pi x}{a}\left(-\frac{\hbar^2}{2m}\cdot\frac{d^2}{dx^2} + V_1 x\right)\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a} + \int_{a/2}^{a} \sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}\left[-\frac{\hbar^2}{2m}\cdot\frac{d^2}{dx^2} + V_1(a-x_1)\right]\sqrt{\frac{2}{a}}\sin\frac{2\pi x}{a}$$

$$= \boxed{\frac{h^2}{2ma^2} + \frac{V_1 a}{4}}$$

So, secular Determinant $= \begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{bmatrix}$

$$\begin{bmatrix} \frac{h^2}{8ma^2} + V_1 a\left(\frac{1}{4} + \frac{1}{\pi^2}\right) - E & 0 \\ 0 & \frac{h^2}{2ma^2} + \frac{V_1 a}{4} - E \end{bmatrix}$$

APPLICATION:

1. % error in energy by using variation principle and cross check of the function's validity.

$$\% \text{ error} = \frac{E_1 - E_0}{E_0} \times 100\%$$

If % error is –ve, function is not acceptable.

Q. Apply the variation function. Check their validity also.

(i) x (ii) x^2 (iii) $x(1-x)$ (iv) $x^2(1-x)^2$ (v) $\sin\frac{\pi x}{\ell}$

to the particle in 1-D box: $v = 0 \quad 0 \le x \le \ell$

$v - \alpha$

Soln. (i) $E_1 = \dfrac{\int_0^{\ell} x\left(-\frac{\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}(x)\right)dx}{\int_0^{\ell} x^2 dx} = 0$

So, this function is unacceptable.

(ii) $E_1 = \dfrac{-\int_0^{\ell} x^2 \cdot \frac{\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2}(x^2)\,dx}{\int_0^{\ell} x^4 dx}$

$$\left|\frac{\partial^2}{\partial x^2}(x^2) = \frac{\partial}{\partial x}.2x = 2\right.$$

$$= \frac{-\frac{\hbar^2}{m}\int_0^{\ell} x^2 dx}{\int_0^{\ell} x^4 dx} = -\frac{\hbar^2}{m}\cdot\frac{\frac{\ell^3}{3}}{\frac{\ell^5}{5}} = -\frac{5\hbar^2}{3m\ell^2}$$

$$\therefore \quad \%\ \text{error} = \frac{-\frac{5\hbar^2}{3m\ell^2}\times 100}{\frac{h^2}{8m\ell^2}} = -\text{ve}$$

% error $\neq$ -ve, so it is also unacceptable wave function.

(iii) $$E_i = \frac{\int_0^\ell x(\ell-x).(-)\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x}[x(\ell-x)]dx}{\int_0^\ell x(\ell-x)\cdot x(\ell-x)dx}$$

$$= \frac{-\frac{\hbar^2}{2m}\int_0^\ell x(\ell-x)\frac{\partial}{\partial x}(\ell-2x)dx}{\int_0^\ell x^2(\ell-x)^2dx} \qquad \Rightarrow \frac{\frac{-\hbar^2}{2m}\int_0^\ell x(\ell-x).(-2).dx}{\int_0^\ell x^2(\ell^2-2x\ell+x^2)dx}$$

$$= +\frac{\hbar^2}{m}\frac{\ell\int_0^\ell xdx - \int_0^\ell x^2dx}{\int_0^\ell x^2\ell^2dx - 2\ell\int_0^\ell x^3dx + \int x^4dx} \qquad \Rightarrow +\frac{\hbar^2}{m}\frac{\ell\frac{\ell^2}{2}-\frac{\ell^3}{3}}{\frac{\ell^5}{3}-2\frac{\ell^5}{4}+\frac{\ell^5}{5}}$$

$$= +\frac{\hbar^2}{m}\frac{\frac{\ell^3}{6}}{\frac{1}{30}\ell^5} \qquad \Rightarrow \frac{\hbar^2}{m}\frac{5}{\ell^2} = \frac{5h^2}{4\pi^2m\ell^2}$$

$$\therefore \quad \%\ \text{error} = \frac{E_i - E_0}{E_0}\times 100$$

$$\Rightarrow \frac{\frac{5h^2}{4\pi^2m\ell^2}-\frac{h^2}{8m\ell^2}}{\frac{h^2}{8m\ell^2}}\times 100 = \left(\frac{2\times 5}{\pi^2}-1\right)\times 100 = 0.0142\times 100 = 1.42\,\%$$

$$\therefore \quad \%\ \text{error} = 1.42\,\%$$

(v) $\psi = \sin\frac{\pi x}{\ell}$ $$\therefore \quad E_i = \frac{-\frac{\hbar^2}{2m}\int_0^\ell \sin\frac{\pi x}{\ell}\cdot\frac{\partial^2}{\partial x^2}\sin\frac{\pi x}{\ell}dx}{\int_0^\ell \sin\frac{\pi x}{\ell}\cdot\sin\frac{\pi x}{\ell}dx}$$

$$= \frac{+\frac{\hbar^2}{2m}\int_0^\ell \sin\frac{\pi x}{\ell}\left(\frac{\pi}{\ell}\right)^2\sin\frac{\pi x}{\ell}}{\int_0^\ell \sin\frac{2\pi x}{\ell}dx} = \frac{\frac{\hbar^2}{2m}\cdot\frac{\pi^2}{\ell^2}\int_0^\ell \sin^2\frac{\pi x}{\ell}dx}{\int\sin^2\frac{\pi x}{\ell}dx} = \frac{\hbar^2\pi^2}{2m\ell^2} = \frac{h^2\pi^2}{4\pi^2.2m\ell^2} = \frac{h^2}{8m\ell^2}$$

$$\therefore \quad \%\ E = \left(\frac{\frac{h^2}{8m\ell^2}}{\frac{h^2}{8m\ell^2}}-1\right)\times 100 = 0 \qquad \therefore \quad \%\ \text{error} = 0$$

The function x and x^2 cannot be used as variation function, since they do not satisfy the concept of variation theorem, according to which the energy calculated by a well behaved approximate wave function will always be equal to or greater the true energy of the system. So, function (iii), (iv) and (v) are well behaved function (come out to be larger) for (iii) and (iv) and (equal to) for (v). Hence the variation theorem is satisfied by these wave function.

Q. Using a trial wave function e^{-ax^2}, calculate ground state energy and minimum energy or zero point energy by using variation principle.

Soln. For simple harmonic oscillator,

$$\hat{H} = \underbrace{\left(\frac{-\hbar^2}{2m}\right)\frac{d^2}{dx^2}}_{P.E.} + \underbrace{\frac{1}{2}kx^2}_{K.E.} \qquad \Rightarrow E = \frac{\int_{-\infty}^{+\infty} \psi\, H\psi d\tau}{\int_{-\infty}^{+\infty} \psi\,\psi d\tau}$$

$$= \frac{\int_{-\infty}^{+\infty} e^{-ax^2}\left[\left(-\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]e^{-ax^2}dx}{\int_{-\infty}^{+\infty} e^{-ax^2}\, e^{-ax^2}dx} \Rightarrow \frac{\overbrace{\int_{-\infty}^{+\infty}\left(-\frac{\hbar^2}{2m}\right)e^{-ax^2}\frac{d^2}{dx^2}e^{-ax^2}dx}^{I} + \overbrace{\int_{-\infty}^{+\infty} e^{-ax^2}\frac{1}{2}kx^2 e^{-ax^2}dx}^{II}}{\underbrace{\int_{-\infty}^{+\infty} e^{-2ax^2}dx}_{m}}$$

Part - I: **Kinetic Energy:**

$$\left(-\frac{\hbar^2}{2m}\right)\int_{-\infty}^{+\infty} e^{-ax^2}\cdot\frac{d}{dx}\cdot\frac{d}{dx}\left(e^{-ax^2}\right)dx \qquad \Rightarrow -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} e^{-ax^2}\frac{d}{dx}\left[-2ax.e^{-ax^2}\right]dx$$

$$= -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} e^{-ax^2}\left[(-2a)\left\{e^{-ax^2} + x.(-2ax)\,e^{-ax^2}\right\}\right]dx = -\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} e^{-ax^2}\left\{-2ae^{-ax^2} + 4a^2x^2\, e^{-ax^2}\right\}dx$$

$$= +\frac{\hbar^2}{2m}\int_{-\infty}^{+\infty} e^{-2ax^2}2a - \frac{\hbar^2}{2m}4a^2\int_{-\infty}^{+\infty} x^2\, e^{-2ax^2}dx = \frac{\hbar^2}{2m}2a\,2\frac{1}{2(2a)^{1/2}}\Gamma\left(\frac{1}{2}\right) - \frac{\hbar^2}{2m}\cancel{4}a^2\,2\frac{1}{\cancel{2}(2a)^{1/2}}\Gamma\left(\frac{3}{2}\right)$$

$$= \frac{\hbar^2 a}{m}\frac{\sqrt{\pi}}{\sqrt{2a}} - \frac{\hbar^2\cancel{2}a^2}{m}\frac{1}{(2a)^{3/2}}\frac{1}{\cancel{2}}\sqrt{\pi} \Rightarrow -\frac{\hbar^2}{2m}\left[-\sqrt{2a\pi} + \frac{1}{2}\sqrt{2a\pi}\right] \Rightarrow \frac{\hbar^2}{4m}\sqrt{2a\pi}$$

Part - II:

$$\int_{-\infty}^{+\infty} e^{-ax^2}\frac{1}{2}kx^2.e^{-ax^2}dx \Rightarrow \frac{1}{\cancel{2}}k\cancel{2}\int_{0}^{+\infty} x^2\, e^{-2ax^2}dx \Rightarrow k\frac{1}{2(2a)^{3/2}}\Gamma\left(\frac{3}{2}\right)$$

$$= \frac{k}{2}\frac{\frac{1}{2}\sqrt{\pi}}{(2a)^{3/2}} \Rightarrow \frac{k}{4(2a)^{3/2}}\sqrt{\pi}$$

Part III:

$$\int_{-\infty}^{+\infty} e^{-2ax^2}dx \Rightarrow 2\int_{0}^{\infty} e^{-2ax^2}dx \Rightarrow \cancel{2}\frac{1}{\cancel{2}(2a)^{1/2}}\sqrt{\pi} = \frac{\sqrt{\pi}}{(2a)^{1/2}}$$

$$\therefore \quad E = \frac{\frac{\hbar^2}{4m}\sqrt{2a\pi} + \frac{k}{4(2a)^{3/2}}\sqrt{\pi}}{\frac{\sqrt{\pi}}{(2a)^{1/2}}} \qquad \Rightarrow \frac{\hbar^2}{4m}\frac{\sqrt{2}\sqrt{a\pi}(2a)^{1/2}}{\sqrt{\pi}} + \frac{\frac{k\sqrt{\pi}}{4(2a)^{3/2}}}{\frac{\sqrt{\pi}}{(2a)^{1/2}}}$$

$$\Rightarrow \frac{\hbar^2}{4m}2a + \frac{k}{4}\frac{1}{2a} \quad \Rightarrow \frac{\hbar^2 a}{2m} + \frac{k}{8a}$$

E_{min} : $\frac{dE}{da} = 0 \quad \Rightarrow \frac{\hbar^2}{2m} - \frac{k}{8}\frac{1}{a^2} = 0 \quad \Rightarrow \frac{k}{8a^2} = \frac{\hbar^2}{2m} \quad \Rightarrow a = \frac{\sqrt{mk}}{2\hbar}$

$$\therefore \quad E_{min} = \frac{\hbar^2\sqrt{mk}}{4m.\hbar} + \frac{k.2\hbar}{8\sqrt{mk}}$$

$$= \frac{1}{4}.\frac{\hbar}{2}\sqrt{\frac{k}{m}} + \frac{1}{4}.\frac{\hbar}{2}\sqrt{\frac{k}{m}} \quad \Big| \upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \Rightarrow \frac{1}{4}.\frac{h}{2\pi}\sqrt{\frac{k}{m}} + \frac{1}{4}.\frac{h}{2\pi}\sqrt{\frac{k}{m}} \quad \Rightarrow \frac{h\upsilon}{4} + \frac{h\upsilon}{4} = \frac{1}{2}h\upsilon$$

LADDER OPERATOR

There are two types of Ladder Operators.

1. $L_+ = L_x + iL_y$ 2. $L_- = L_x - iL_y$

Q. Show that both ladder operator do not commute.

Soln. $[L_+, L_-] = \left[\left(L_x + iL_y\right), \left(L_x - iL_y\right)\right]$

$$= [L_x, \underset{0}{L_x}] - i[L_x, L_y] + i[L_y, L_x] - i^2[\underset{0}{L_y, L_y}]$$

$$= 0 - i^2\hbar L_z + i\left(-i\hbar L_z\right) = -2i^2\hbar L_z = 2\hbar L_z$$

Q. Show that $[L_z, L_+] = \hbar L_+$

Soln. $[L_z, L_+] = \left[L_z, \left(L_x + iL_y\right)\right] = [L_z L_x] + i[L_z L_y] = i\hbar L_y + i\left(-i\hbar L_x\right)$

$$= i\hbar L_y - i^2\hbar L_x = i\hbar L_y + \hbar L_x = \hbar\left(L_x + iL_y\right) = \hbar L_+$$

Q. Show that $[L_z, L_-] = -\hbar L_-$

Soln. $[L_z, L_-] = \left[L_z, \left(L_x - iL_y\right)\right] = [L_z L_x] - i[L_z L_y] = i\hbar L_y - i\left(-i\hbar L_x\right) = i\hbar L_y + i^2\hbar L_x$

$$= i\hbar L_y - \hbar L_x$$

$$= -\hbar\left(L_x - iL_y\right) = -\hbar L_-$$

Angular momentum matriees corresponding to j = 1/2 and the Pauli spin matrices:

We will consider the matrix representation of the components of the angular momentum operator (corresponding to j = 1/2) in a system in which J^2 and J_z are diagonal, i.e. we will choose as basis vectors the simultaneous eigenfunctions of J^2 and J_z. Now, corresponding to j = 1/2 we have m = 1/2 and –1/2; thus we have two base states which we denote by $|1\rangle$ and $|2\rangle$

$$|1\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle = \left|j = \frac{1}{2}, m = \frac{1}{2}\right\rangle \quad \ldots (1)$$

And $$|2\rangle = \left|\frac{1}{2}, -\frac{1}{2}\right\rangle = \left|j = \frac{1}{2}, m = -\frac{1}{2}\right\rangle \quad \ldots (2)$$

Obviously,
$$\left.\begin{aligned} J_z|1\rangle &= \frac{1}{2}\hbar|1\rangle,\ J_z|2\rangle = -\frac{1}{2}\hbar|2\rangle \\ J^2|1\rangle &= \frac{3}{4}\hbar^2|1\rangle,\ J^2|2\rangle = \frac{3}{4}\hbar^2|2\rangle \end{aligned}\right\} \quad \ldots (3)$$

The (i j)th matrix element of an operator 'O' is defined by

$$O_{ij} = \langle i|O|j\rangle$$

Consequently,

$$(J_z)_{12} = \langle 1|J_z|2\rangle = 0 = \langle 2|J_z|1\rangle = (J_z)_{21}$$

$$(J_z)_{11} = \langle 1|J_z|1\rangle = \frac{1}{2}\hbar,\ (J_z)_{22} = \langle 2|J_z|2\rangle = -\frac{1}{2}\hbar$$

Similarly, $(J^2)_{12} = (J^2)_{21} = 0$ And $(J^2)_{11} = (J^2)_{22} = \frac{3}{4}\hbar^2$

Now,
$$\langle j, m|J_x|j, m\rangle = \left\langle j, m\left|\frac{1}{2}[J_+ + J_-]\right|j, m\right\rangle$$

$$= \frac{1}{2}\left[(j+m+1)(j-m)\right]^{\frac{1}{2}}\hbar\langle j, m'|j, m+1|\rangle$$

$$+ \frac{1}{2}\left[(j+m)(j-m+1)\right]^{\frac{1}{2}}\hbar\langle j, m'|j, m-1|\rangle$$

$$= \frac{1}{2}\left[(j+m+1)(j-m)\right]^{1/2}\hbar\delta_{m',m+1} + \frac{1}{2}\left[(j+m)(j-m+1)\right]^{1/2}\hbar\delta_{m',m-1}$$

i.e. the matrix element is zero unless $m' = m+1$ or $m' = m-1$. Thus

$$(J_x)_{11} = \langle 1|J_x|1\rangle = \left\langle \frac{1}{2}, \frac{1}{2}\middle|J_x\middle|\frac{1}{2}, \frac{1}{2}\right\rangle = 0$$

and similarly $(J_x)_{22} = 0$. However,

$$(J_x)_{12} = \langle 1|J_x|2\rangle = \left\langle \frac{1}{2},\frac{1}{2}|J_x|\frac{1}{2},-\frac{1}{2}\right\rangle$$

Similarly, $(J_y)_{11} = (J_y)_{22} = 0$

$$(J_y)_{12} = -\frac{1}{2}h \text{ and } (J_y)_{21} = \frac{i}{2}\hbar$$

Thus the angular momentum matrices for $j = \frac{1}{2}$ are

$$\left.\begin{aligned} J_x &= \frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, \qquad J_y = \frac{1}{2}\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}\\ J_z &= \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \qquad J^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix}\end{aligned}\right\} \quad \ldots (4)$$

We can also write

$$J = \frac{1}{2}\hbar\sigma \quad \ldots (5)$$

Where $\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$ ... (6)

$$\sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \quad \ldots (7)$$

And $\sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ ... (8)

are known as Pauli spin matrices. Further σ_x^2, σ_y^2 and σ_z^2 are all unit matrices. It may be noted that the Pauli spin matrices as well as J_x, J_y, J_z and J^2 are all Hermitian. Further, the eigenvalues of J_x, J_y and J_z are $+\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$. Thus, if we make a measurement of J_x $(\text{or } J_y \text{ or } J_z)$ we will either get $+\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$.

Now, $|1\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle = \begin{pmatrix}1\\ 0\end{pmatrix}$ ... (9)

And $|2\rangle = \left|\frac{1}{2},-\frac{1}{2}\right\rangle = \begin{pmatrix}0\\ 1\end{pmatrix}$ ... (10)

which are known as the spin up $\left(|\uparrow\rangle\right)$ and spin down $\left(|\downarrow\rangle\right)$ states. They are also denoted by $|\hat{z}\uparrow\rangle$ and $|\hat{z}\downarrow\rangle$ states implying that if the electron is in the state (say) $|\hat{z}\downarrow\rangle$ and if the z-component of the spin angular momentum is measured then the measurement will yield $-\frac{1}{2}\hbar$.

From the matrices representing J_x and J_y, one can calculate the corresponding eigenvalues and eigenvectors and one can immediately see that

$$|\hat{x}\uparrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{z}\uparrow\rangle + \frac{1}{\sqrt{2}}|\hat{z}\downarrow\rangle \qquad \ldots(11)$$

$$|\hat{x}\downarrow\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{z}\uparrow\rangle - \frac{1}{\sqrt{2}}|\hat{z}\downarrow\rangle \qquad \ldots(12)$$

We also have, $$|\hat{z}\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{x}\uparrow\rangle + \frac{1}{\sqrt{2}}|\hat{x}\downarrow\rangle \qquad \ldots(13)$$

And $$|\hat{z}\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix} = \frac{1}{\sqrt{2}}|\hat{x}\uparrow\rangle - \frac{1}{\sqrt{2}}|\hat{x}\downarrow\rangle \qquad \ldots(14)$$

Thus if a system is in the $|\hat{z}\uparrow\rangle$ state and if one makes a measurement of Jx, then the probability of obtaining the value $+\frac{1}{2}\hbar$ is $\frac{1}{2}$ and the value $-\frac{1}{2}\hbar$ is also $\frac{1}{2}$.

Similarly, one can write down for the $|\hat{y}\uparrow\rangle$ and $|\hat{y}\downarrow\rangle$ states in terms of $|\hat{x}\uparrow\rangle$ and $|\hat{x}\downarrow\rangle$ and $|\hat{z}\uparrow\rangle$ and $|\hat{z}\downarrow\rangle$ states.

Angular momentum matrices for j = 1:

In this section we will derive the angular momentum matrices corresponding to j = 1; the procedure will be similar to that in the previous section. Now, for j=1 we have m = 1, 0 and –1; thus we have three base states which we denoted by $|1\rangle, |2\rangle$ and $|3\rangle$.

$$|1\rangle = |j=1, m=1\rangle = |1,1\rangle;\ |2\rangle = |j=1, m=0\rangle = |1,0\rangle;\ |3\rangle = |j=1, m=-1\rangle = |1,-1\rangle$$

Obviously, $$J_z|1\rangle = \hbar|1\rangle;\ J_z|2\rangle = 0;\ J_z|3\rangle = -\hbar|1\rangle$$

And $$J^2|1\rangle = 2\hbar^2|1\rangle;\ J^2|2\rangle = 2\hbar^2|2\rangle;\ J^2|3\rangle = 2\hbar^2|3\rangle$$

Thus, when the base kets are $|1\rangle, |2\rangle$ and $|3\rangle$ the matrices representig J^2 and J_z are diagonal and are given by

Matrix representing J_z, $$J_z = \hbar\begin{pmatrix}1 & 0 & 0\\0 & 0 & 0\\0 & 0 & -1\end{pmatrix} \qquad \ldots(15)$$

And matrix representing J^2, $J^2 = 2\hbar\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$ ... (16)

Further, $J_+|1\rangle = 0$ ... (17)

$J_+|2\rangle = \sqrt{2}\hbar|1\rangle$ ... (18)

$J_+|3\rangle = \sqrt{2}\hbar|2\rangle$ ... (19)

And $J_-|1\rangle = \sqrt{2}\hbar|2\rangle$ ... (20)

$J_-|2\rangle = \sqrt{2}\hbar|3\rangle$ ... (21)

$J_-|3\rangle = 0$ ... (22)

Thus for example, $\langle 1|J_x|2\rangle = \frac{1}{2}\langle 1|J_+ + J_-|2\rangle = \frac{1}{\sqrt{2}}\hbar$

Simiarly, other matrix elements can be calculated. The final result is

Matrix representing J_x, $J_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0&1&0\\1&0&1\\0&1&0\end{pmatrix}$ ... (23)

Matrix representing J_y, $J_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0&-i&0\\i&0&-i\\0&i&0\end{pmatrix}$ ... (24)

Finally, $|1\rangle = |1, 1\rangle = \begin{pmatrix}1\\0\\0\end{pmatrix}$ ... (25)

$|2\rangle = |1, 0\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix}$ ... (26)

And $|3\rangle = |1, -1\rangle = \begin{pmatrix}0\\0\\1\end{pmatrix}$ ... (27)

The Pauli wavefunction and the Pauli equation: The electron is endowed with two internal degrees of freedom corresponding to values of $\pm\frac{1}{2}\hbar$ for the component of its intrinsic angular momentum along a specified axis (say the z-axis). Accordingly, we need two wavefuntions to describe the state of an electron at each point in space. Writing them in matrix form, we have

$$\psi_P = \begin{pmatrix} \psi+(x,y,z) \\ \psi-(x,y,z) \end{pmatrix} \qquad \ldots(28)$$

Such signle column matrices are known as spinors and the wavefunction is known as the Pauli wavefunction (hence the subscript P on ψ). Writing.

$$\psi_P = \psi+\chi_+ + \psi-\chi_- = \psi+\begin{pmatrix}1\\0\end{pmatrix}+\psi-\begin{pmatrix}0\\1\end{pmatrix} \qquad \ldots(29)$$

We say that any spinor can be written as a linear combination of the basic spinors.

$$\chi_+ = \begin{pmatrix}1\\0\end{pmatrix} = |\hat{z}\uparrow\rangle \quad \text{and} \quad \chi_- = \begin{pmatrix}0\\1\end{pmatrix} = |\hat{z}\downarrow\rangle \qquad \ldots(30)$$

Thus, $\int|\psi_+|^2\,d\tau$ and $\int|\psi_-|^2\,d\tau$

would represent the probabilities of obtaining the $|\hat{z}\uparrow\rangle$ and $|\hat{z}\downarrow\rangle$ states respectively and we must have

$$\int|\psi_+|^2\,d\tau + \int|\psi_-|^2\,d\tau = 1 \qquad \ldots(31)$$

Since the electron requires information regarding its spin as well as position coordinates, the Pauli wavefunction satisfies the equation

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_+\\\psi_-\end{pmatrix} = H\begin{pmatrix}\psi_+\\\psi_-\end{pmatrix} \qquad \ldots(32)$$

where H represents the Hamiltonian. For the hydrogen atom, in the absence of any interaction other than the Coulomb interaction, H, will be of the form

$$H\psi_P = \left[-\frac{\hbar^2}{2m}\nabla^2.I + V(r).I\right]\psi_P \qquad \ldots(33)$$

where I is the 2×2 unit matrix. Thus ψ_+ and ψ_- satisfy the same equation and the spin up and spin down states have the same energy. On the other hand, if we take into account the spin-orbit interaction, H, will be the form,

$$H\psi_P = \left[-\frac{\hbar^2}{2m}\nabla^2.I + V(r).I + H'\right]\psi_P \qquad \ldots(34)$$

Where, $H' = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}L.s = \frac{Ze^2}{2m^2c^2}\frac{i}{r^3}\frac{1}{2}\hbar\left[L_x\sigma_x + L_y\sigma_y + L_z\sigma_z\right] = \frac{Ze^2}{2m^2c^2}\frac{1}{r^3}\frac{1}{2}\hbar\begin{pmatrix}L_z & L_x - iL_y\\ L_x + iL_y & -L_z\end{pmatrix}$

which is known as the Pauli operator for H'. Obviously, now the equations for ψ_+ and ψ_- will be coupled and one has to use perturbation theory to consider the effecf of H'.

Problem-1: For an eigenstate of J^2 and J_z, show that

$$\langle J_x \rangle = \langle J_y \rangle = 0$$

And $$\langle J_x^2 \rangle = \langle J_y^2 \rangle = \frac{1}{2}\hbar^2\left[j(j+1) - m^2 \right]$$

From the above results develop a classical model for the angular momentum.

Soln. $$\langle j, m | J_x | j, m \rangle = \frac{1}{2}\langle j, m | J_+ | j, m \rangle + \frac{1}{2}\langle j, m | j_- | j, m \rangle = 0$$

$$\langle j, m | j_x^2 | j, m \rangle = \frac{1}{2}\left[\langle j, m | J_+ J_+ | j, m \rangle + \langle j, m | J_+ J_- | j, m \rangle + \langle j, m | J_- J_+ | j, m \rangle + \langle j, m | j_- j_- | j, m \rangle \right]$$

$$= \frac{1}{2}[0 + \{(j+m)(j-m+1)\}^{1/2}\langle j, m | j_+ | j, m-1 \rangle + \{(j-m)(j+m+1)\}^{1/2}\langle j, m | j_- | j, m+1 \rangle + 0]$$

$$= \frac{1}{2}\hbar^2\left[j(j+1) - m^2 \right] \qquad \ldots (1)$$

etc. Obviously,

$$\langle j, m | J_z^2 | j, m \rangle = m^2\hbar^2$$

And $$\langle j, m | J^2 | j, m \rangle = j(j+1)\hbar^2$$

From the above equations we can develop a classical model for angular momentum. The total angular momentum vector OP (whose length is assumed to be $\left(\sqrt{j(j+1)}\hbar\right)$ is assumed to precess about the z-axis (see figure below). As it precesses, the z-component of OP (= OQ) remains constant, which we assume to be equal to $m\hbar$. The x-and y-components of OP change with time and their average value is zero. Now,

$$PQ^2 = j(j+1)\hbar^2 - m^2\hbar^2$$

represents $\langle J_x^2 \rangle + \langle J_y^2 \rangle$ consists with equation (1). Thus for the state $|j, m\rangle$ we may assume the total angular momentum vector precessing about the z-axis.

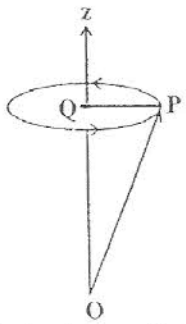


Fig: A classical model for the angular momentum vector.

Problem-2: Write the angular momentum matrices in a representation in which J^2 and J_z are diagonal. Assume $j = 1/2$.

Soln. $J_x = \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, J_y = \frac{1}{2}\hbar\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}, J_z = \frac{1}{2}\hbar\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$

Problem-3: Show that the Pauli spin matrices satisfy the following relation

$$\sigma_i\sigma_j = \delta_{ij} + i\varepsilon_{ijk}\sigma_k$$

where ε_{ijk}, which is known as the totally antisymmetric unit tensor, is defined by

$$\varepsilon_{123} = \varepsilon_{231} = \varepsilon_{312} = 1 \qquad \text{(cyclic indices)}$$

$$\varepsilon_{321} = \varepsilon_{213} = \varepsilon_{132} = -1 \qquad \text{(anticyclic indices)}$$

with all other components equal to zero.

Soln. The following properties of the Pauli matrices are easily established.

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1 \qquad \ldots(1)$$

$$\sigma_x\sigma_y = i\sigma_z, \text{ etc} \qquad \ldots(2)$$

$$\sigma_x\sigma_y + \sigma_y\sigma_x = 0, \text{ etc} \qquad \ldots(3)$$

from which equation $\sigma_i\sigma_j = \delta_{ij} + i\varepsilon_{ijk}\sigma_k$ immediately follows.

Problem-4: Using equation $\sigma_i\sigma_j = \delta_{ij} + i\varepsilon_{ijk}\sigma_k$ show

$$(\sigma.A)(\sigma.B) = A.B + i\sigma.(A\times B)$$

where A and B are arbitrary vectors. Thus

$$(\sigma.\hat{n})^2 = 1$$

where $\hat{n}$ is an arbitrary unit vector.

Soln. $(\sigma.A)(\sigma.B) = \sum_{i,j}\sigma_i A_i\sigma_j B_j = (A.B) + i\sigma.(A\times B)$

as can be verified by expanding the RHS and using equation (1), (2) and (3) of solution of problem-3.

Problem-5: Write the angular momentum matrices corresponding to $j = 3/2$ in a representation in which J^2 and J_z are diagonal.

Soln. $J_x = \frac{1}{2}\hbar\begin{pmatrix}0 & \sqrt{3} & 0 & 0\\ \sqrt{3} & 0 & 2 & 0\\ 0 & 2 & 0 & \sqrt{3}\\ 0 & 0 & \sqrt{3} & 0\end{pmatrix} \Rightarrow J_y = \frac{1}{2}\hbar\begin{pmatrix}0 & -i\sqrt{3} & 0 & 0\\ i\sqrt{3} & 0 & -2i & 0\\ 0 & 2i & 0 & -i\sqrt{3}\\ 0 & 0 & i\sqrt{3} & 0\end{pmatrix}$

$$\Rightarrow \quad J_z = \hbar \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix} \quad \Rightarrow \quad J^2 = \frac{15}{4}\hbar^2 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Problem on Pauli Spin:

Q. Prove that: $[\sigma_y, \sigma_z] = 2i\sigma_x$

$$[\sigma_y, \sigma_z] = \sigma_y\sigma_z - \sigma_z\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0\times1+(-i)\times0 & 0\times0+(-i)\times(-1) \\ i\times1+0\times0 & i\times0+0\times(-1) \end{pmatrix} - \begin{pmatrix} 1\times0+0\times i & 1\times(-i)+0\times0 \\ 0\times0+(-1)\times i & 0\times(-i)+(-1)\times0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} - \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} = \begin{pmatrix} 0 & 2i \\ 2i & 0 \end{pmatrix} = 2\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} = 2i\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = 2ir_x$$

$\therefore \quad [\sigma_y, \sigma_z] = 2ir_x$ (Proved.)

de–Broglie Concept

Some Empirical relations of calculation of λ:

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}} = \frac{h}{\sqrt{2mkT}}$$

From statistical thermodynamics

$$\Lambda = (\lambda) = \frac{h}{\sqrt{2\pi mkT}}$$

This formula is used when particle is confined in a box → i.e. volume consideration is given (wave length is calculated using translational partition functions)

$$\lambda = \frac{h}{\sqrt{2\pi mkT}}$$

When free particle is considered.

According to statistical thermodynamic

$q_{translational} \rightarrow$ unitless

$$\frac{(2\pi mkT)^{3/2}}{h^3} \cdot V$$

$\frac{1}{\lambda^3} = \frac{1}{m^3}$

Q. If electron is accelerated through a potential difference of V volt, $\lambda = \frac{12.28}{\sqrt{V}}$ Å

Soln. $\lambda = \frac{h}{\sqrt{2meV}} = \frac{6.62\times10^{-34}}{\sqrt{2\times9.8\times10^{-31}\times1.6\times10^{-19}}\sqrt{V}}$ Å $= \frac{6.62\times10^{-34}}{5.4\times10^{-25}\sqrt{V}}$ Å

$= \frac{12.27}{\sqrt{V}}$ Å

Q. Electrons are accelerated through 344 volts and are reflected from a crystal. The first reflection maximum occurs when angle is 60°. Determine the spacing of cyrstal.

Soln. **Bragg's equation :** $n\lambda = 2d\sin\theta$ (first reflection, $n = 1$)

$$\lambda = \frac{6.62\times10^{-34}}{\sqrt{2\times9.1\times10^{-31}\times1.6\times10^{-19}\times344}} = \frac{12.28}{\sqrt{344}}$$ Å

$$2d\sin\theta = \frac{12.28}{\sqrt{344}}\times10^{-10}$$

$$\Rightarrow \quad d = \frac{12.28\times10^{-10}}{18.85\times2\times\sin60^\circ}$$

$$= 0.38\times10^{-10}$$

Q. The interatomic distance for a Ni crystal was found to be 0.91 Å. When the electron with a kinetic energy 54 V is scattered the maximum at $\theta = 65^\circ$, show that this experiment verify de–Broglie equation. $(\sin 65^\circ = 0.91)$

Soln. $n = 1$

$\lambda = 2d\sin\theta = 2\times0.91\times0.91 = 1.6$ Å

From, de Broglie's equation, $\lambda = \frac{h}{\sqrt{2mE}} = \frac{12.28}{\sqrt{54}}$ Å $= 1.6$ Å

Q. Calculate the thermal de–Broglie λ of neutron at 27°C.

Soln. $\lambda = \dfrac{h}{\sqrt{2mkT}}$ (mass of neutron = 1.6×10^{-27})

$$= \frac{6.62\times10^{-34}}{\sqrt{2\times1.6\times10^{-27}\times1\times1.38\times10^{-23}\times300}} = \frac{6.62\times10^{-34}}{3.64\times10^{-24}} = 1.8\times10^{-10}\ \text{m}$$

$$= 1.8\ \text{Å} \qquad (\because\ 10^{-10}\text{m} = 1\text{Å})$$

Problem on de-Broglie:

Q. The de–Broglie wavelength for a He-atom travelling at 1000 m/s at room temperature.

Soln. $\lambda = \dfrac{h}{mv} = \dfrac{6.62\times10^{-34}}{4\times1.6\times10^{-27}\times1000} = 1.03\times10^{-10}\ \text{m}$

Q. What voltage must be applied to an electron microscope to produce electrons of wavelength of 0.50 Å.

Soln. $\lambda^2 = \dfrac{h^2}{\left(\sqrt{2meV}\right)^2}$;

$$V = \frac{h^2}{2\,m\,e\lambda^2} = \frac{\left(6.62\times10^{-34}\right)^2}{2\times9.1\times10^{-31}\times1.6\times10^{-19}\times\left(0.5\times10^{-10}\right)^2} = \frac{43.82\times10^{-68}}{7.28\times10^{-70}} = 6.02\times10^{2} = 602\ \text{V}$$

VALANCE BOND THEORY

Valance Bond Theory was the first quantum mechanical theory of chemical bond proposed by **Heitlier** and **London** in 1927, Slater and Pauling in 1930. It is collectively known as HLSP or HSPL. The theory propose that:

Covalent bond is formed by the shared pair of electron, i.e. Lewis concept. The theory makes the perfect pairing of approximation in which it is assumed that structures with electron paired in all possible way dominated the wave function of the molecule.

Let the 2 electron of H_2 designated by (1) and (2) and the 2 nuclei a and b. The wave function of the molecule: $\psi_{AB} = C_1\psi_1 + C_2\psi_2$

$\psi_1 = \phi_a(1)\phi_b(2)$

$\psi_2 = \phi_a(2)\phi_b(1)$

ϕ are the atomic orbitals; ψ_1 is the wave function corresponding to situation, where electron (1) on the atomic orbital ϕ_a centered on the nucleus (a) and electron (2) is on the atomic orbital ϕ_b centered on nucleus B. Heilter and London remove C_1 and C_2 by putting a common value of N as normalisation function.

Bonding M.O.$=\psi_+ = N_+\left[\phi_a(1)\phi_b(2)+\phi_b(1)\phi_a(2)\right]$

Antibonding M.O. $= N_-\left[\phi_a(1)\neq\phi_b(2)-\phi_b(1)\phi_a(2)\right]$

Let us normalise ψ_+ we get, the value of

$$N_+ : \int_0^\infty \psi_+\psi_+ d\tau = 1$$

$$\Rightarrow \quad \int N_+\left[\phi_a(1)\phi_b(2)+\phi_b(1)\phi_a(2)\right] N_+\left[\phi_a(1)\phi_b(2)+\phi_b(1)\phi_a(2)\right]d\tau = 1$$

$$\Rightarrow \quad N_+^2\left[\int\phi_a(1)\phi_a(1)d\tau\int\phi_b(2)\phi_b(2)d\tau + \int\phi_a(1)\phi_a(2)d\tau\int\phi_b(1)\phi_b(2)d\tau\right]$$

$$+\int\phi_a(1)\phi_a(2)d\tau\int\phi_b(1)\phi_b(2)d\tau + \int\phi_b(1)\phi_b(1)d\tau\int\phi_a(2)\phi_a(2)d\tau = 1$$

$$\Rightarrow \quad N_+^2\left[1+2s^2+1\right]=1 \qquad \left(S = \int\phi_a(1)\phi_a(2)d\tau = \int\phi_b(1)\phi_b(2)d\tau\right)$$

$$\Rightarrow \quad \boxed{N_+ = \frac{1}{\sqrt{2(1+s^2)}}}$$

Similarly, we get normalisation constant N_-

$$\boxed{N_- = \frac{1}{\sqrt{2(1-s^2)}}}$$

$\therefore$ Normalised wave functions:

$$\psi_+ = \frac{1}{\sqrt{2(1+s^2)}}\left[\phi_a(1)\phi_b(2)+\phi_a(2)\phi_b(1)\right]$$

$$\psi_- = \frac{1}{\sqrt{2(1-s^2)}}\left[\phi_a(1)\phi_b(2)-\phi_b(1)\phi_a(2)\right]$$

Q. Write down the valence bond wave function for HF molecule (assuming that it is formed from 1s orbital of H and $2p_z$ orbital of F) in the following three cases.

(i) HF is purely covalent. (ii) HF is purely ionic. (iii) HF is 80% covalent and 20% ionic.

Soln. $a \equiv (H) — (F) \equiv b$

(i) $\psi_{covalent} = \phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2)$ (ii) $\psi_{ionic} = \phi_b(1)\phi_b(2)$

(iii) $\psi = C_1\psi_{covalent} + C_2\psi_{ionic}$ $\quad \left| \underset{0.8}{C_1^2} + \underset{0.2}{C_2^2} = 0 \right.$

$$\left.\begin{array}{lll} C_1^2 = 0.8 & \therefore & C_1 = 0.89 \\ C_2^2 = 0.2 & \therefore & C_2 = 0.45 \end{array}\right\}$$

$\therefore$ $\boxed{\psi = 0.89\psi_{covalent} + 0.45\psi_{ionic}}$

$= 0.89[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] + 0.45[\phi_b(1)\phi_b(2)]$

Total probability $= \left[(0.89)^2 + (0.45)^2\right] \times 100$ (if inspection is 100)

Probability of finding electron in covalent wave function

$$C_1^2 \times 100 = 80\%$$

In ionic ψ, Probability $= C_2^2 \times 100 = 20\%$

Operator are not fixed for an eigen value equation and a function is not always eigen function, both are interdependent.

Q. Show that e^{ikx} is an eigen function of momentum operator. What is the eigen value?

Soln. $p_x = -i\hbar\frac{\partial}{\partial x}, \quad -i\hbar\frac{\partial}{\partial x}\left(e^{ikx}\right)$

$= -i\,\hbar.ike^{-ikx} = -i^2\hbar\,ke^{ikx} = \hbar\,ke^{ikx}$

$\therefore$ $\boxed{i\hbar\frac{\partial}{\partial x}\left(e^{ikx}\right) = \hbar k\left(e^{ikx}\right)}$

$\therefore$ e^{ikx} is an Eigen function

Eigen value $= \hbar k$.

Q. If $e^{\alpha x^2}$ a eigen function, if it is so, then what is the eigen value for operator $\frac{d}{dx}$?

Soln. $\frac{d}{dx}\left(e^{\alpha x^2}\right) \quad \Rightarrow e^{\alpha x^2}\frac{d}{dx}\left(\alpha x^2\right) = e^{\alpha x^2}\,2\alpha x = \underbrace{2\alpha x.e^{\alpha x^2}}_{\text{function}}$

$\therefore$ $e^{\alpha x^2}$ is not a eigen function with $\frac{d}{dx}$ operator.

Schrodinger Wave Equation

Schrodinger equation in a eigen value equation, i.e. the wave function is an eigen function and the energy is an eigen value of the Hamiltonian operator.

This suggests a coresponce between the Hamiltonian operator and the energy and this is the fundamental approach to the formation of quatnum mechanism.

To prove Schrodinger equation quantum mechanically. An eigen value equation:

$\hat{H}\psi = E\psi \qquad (E \rightarrow \text{constant value of energy})$

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + v$$

$$\therefore \quad \left(-\frac{\hbar^2}{2m}\cdot\frac{\partial^2}{\partial x^2} + V\right)\psi = E\psi \qquad \Rightarrow \quad -\frac{\hbar^2}{2m}\cdot\frac{\partial^2\psi}{\partial x^2} + V\psi = E\psi$$

$$\Rightarrow \quad \boxed{\frac{-\hbar^2}{2m}\cdot\frac{\partial^2\psi}{\partial x^2} = (E-V)\psi}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{2m}{\hbar^2}(E-V)\psi$$

$$\therefore \quad \boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0} \qquad \therefore \quad \frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

where, $|B\rangle = \alpha|A\rangle$

(The combination $\alpha\langle B|$ is meaningless.). Indeed because of the associative law we need not put any brackets and simply write.

$$\langle P|\alpha\beta\gamma|A\rangle$$

It is interesting to note that the combination $|B\rangle\langle A|$ can be considered as a linear operator because

$$\{|B\rangle\langle A|\}|P\rangle = |B\rangle\{\langle A|P\rangle\} = c|B\rangle$$

because $\langle A|P\rangle (= c)$ is just a complex number.

The adjoint of the operator α is denoted by $\bar{\alpha}$ and is defined as

$$\langle A|\bar{\alpha}|B\rangle = \overline{\langle B|\alpha|A\rangle} \qquad \ldots (21)$$

where $\overline{\langle B|\alpha\dagger A\rangle}$ is the complex conjugate of the number $\langle B|\alpha|A\rangle$. Now

$$\langle A|\bar{\bar{\alpha}}|B\rangle = \langle A|\bar{\beta}|B\rangle \qquad (\bar{\beta} = \alpha)$$

$$= \overline{\langle B|\beta|A\rangle} = \overline{\langle B|\bar{\alpha}|A\rangle} = \overline{\overline{\langle A|\alpha|B\rangle}} = \langle A|\alpha|B\rangle \qquad \ldots (22)$$

because the complex conjugate of the complex conjugate of a number is the original number itself. Since equation(22) holds for arbitrary $|A\rangle$ and $|B\rangle$ we have

$$\bar{\bar{\alpha}} = \alpha \qquad \ldots (23)$$

i.e. the adjoint of the adjoint of a linear operator is the original operator itself. Further, the adjoint of the product of the two operators α and β is the product of the adjoint of the two operators in reverse order, i.e.,

$$\overline{\alpha\beta} = \bar{\beta}\bar{\alpha} \qquad \ldots (24)$$

Proof: The proof is simple. Let

$$\alpha|A\rangle = |P\rangle$$

Then $\langle A|\bar{\alpha}|B\rangle = \overline{\langle B|\alpha|A\rangle} = \overline{\langle B|P\rangle}$

$$= \langle P|B\rangle \qquad (\text{using eq.}(6))$$

Since the above equation holds for arbitrary $|B\rangle$ we have

$$\langle P| = \langle A|\bar{\alpha} = \text{conjugate of } \alpha|A\rangle \qquad \ldots (25)$$

Thus if, $|Q\rangle = \alpha\beta|A\rangle$

Then, $\langle Q| = \langle A|\overline{\alpha\beta} \qquad \ldots (26)$

But if we write, $|Q\rangle = \alpha\beta|A\rangle = \alpha|R\rangle$

where $|R\rangle = \beta|A\rangle$ (consequently $\langle R| = \langle A|\bar{\beta}$), then

$$\langle Q| = \langle R|\bar{\alpha} = \langle A|\bar{\beta}\,\bar{\alpha} \qquad \ldots (27)$$

Comparing equation (26) and (27) we get equation (24). In general

$$\overline{\alpha\beta\gamma\ldots\ldots} = \ldots\ldots\bar{\gamma}\bar{\beta}\bar{\alpha} \qquad \ldots (28)$$

An operator is said to be self-adjoint if

$$\bar{\alpha} = \alpha \qquad \ldots (29)$$

A self-adjoint operator is called a real operator or a Hermitian operator.

The eigenvalue equation: For the linear operator α, consider the equation

$$\alpha|A_n\rangle = a_n|A_n\rangle \qquad \ldots (30)$$

where a_n is an arbitrary complex number. Equation (30) represents an eigenvalue equation; $|A_n\rangle$ is said to be an eigenket of the operator α, a_n being the corresponding eigenvalues. It can be easily seen that $c|A_n|$ (where c is an arbitrary complex number) is also an eigenket belonging to the same eigenvalue a_n. Now, if there is more than one ket(and they are not linearly dependent on each other) belonging to the same eigenvalue, i.e. if

$$\alpha|A_1\rangle = a_1|A_1\rangle \qquad \ldots (31)$$

$$\alpha|A_2\rangle = a_1|A_2\rangle \qquad \ldots (32)$$

then the state is said to be a degenerate state, if there are 'g' linearly independent kets belonging to the same eigenvalue then the state is said to be g-fold degenerate. For the sake of simplicity, let us consider a two-fold degenerate state describe by equation (31) and (32). If we multiply equation (31) by c_1 and equation (32) by c_2 and add we would get

$$\alpha|P\rangle = a_1|P\rangle,$$

where $|P\rangle = c_1|A_1\rangle + c_2|A_2\rangle$

implying that the linear combination $c_1|A_1\rangle + c_2|A_2\rangle$ is also an eigenket belonging to the same eigenvalue.

Orthogonality of eigenfunctions: When α is real, it can easily be shown that all the eigenvalues are real and for two different eigenvalues (i.e. for $a_n \neq a_m$) the corresponding eigenfunctions are necessarily orthogonal, i.e.

$$\langle A_n|A_m\rangle = 0 \qquad \text{for} \quad a_n \neq a_m \qquad \ldots (33)$$

Further, one can always normalize the kets and choose an appropriate linear combination for the kets belonging to a degenerate state such that

$$\langle A_n|A_m\rangle = \delta_{nm} \qquad \ldots (34)$$

The proof is very simple, Premultiplying equation (30) by $\langle A_n|$ we get

$$\langle A_n|\alpha|A_n\rangle = a_n\langle A_n|A_n\rangle$$

Now, $\langle A_n|A_n\rangle$ is always real and not a null ket [otherwise equation (30) has no meaning]. Further, since α is real

$$\langle A_n|\alpha|A_n\rangle = \langle A_n|\bar{\alpha}|A_n\rangle = \overline{\langle A_n|\alpha|A_n\rangle}$$

implying that $\langle A_n|\alpha|A_n\rangle$ is also real and hence a_n must be real. Futher, in order to prove equation (33) we consider:

$$\alpha|A_1\rangle = a_1|A_1\rangle \qquad \ldots (35)$$

Also, $$\alpha|A_2\rangle = a_2|A_2\rangle \qquad \ldots (36)$$

If we put $|P\rangle = \alpha|A_2\rangle$, then

$$\langle P| = \langle A_2|\bar{\alpha} = \langle A_2|\alpha$$

Also, $$\langle P| = \bar{a}_2\langle A_2| = a_2\langle A_2|$$

because a_2 is real. Thus

$$\langle A_2|\alpha = a_2\langle A_2| \qquad \ldots (37)$$

Premultiplying equation (35) by $\langle A_2|$ and postmultiplying equation (37) by $|A_1\rangle$ gives

$$\langle A_2|\alpha|A_1\rangle = a_1\langle A_2|A_1\rangle = a_2\langle A_2|A_1\rangle$$

which immediately gives the orthogonality condition given by equation (33)

Since the formalism is symmetrical with respect to bras and kets we also have the eigenvalue equation

$$\langle B_n|\alpha = \langle B_n|b_n = b_n\langle B_n|$$

where $\langle B_n|$ are the eigenbras and b_n the corresponding eigenvalues. It can be easily seen that when α is a real operator and if $|A\rangle$ is an eigenket, then $\langle A|$ is an eigenbra belonging to the same eigenvalue. Equation (37) tells us that $\langle A_2|$ is an eigenbra of the operator α belonging to the same eigenvalue a_2.

The completeness condition: We have just stated that the eigenkets of an observable form a complete set. Let $|n\rangle$, $n = 0, 1, 2, \ldots$ denote these eigenkets and let $|P\rangle$ denote an arbitrary ket. Thus

$$|P\rangle = \sum_n c_n|n\rangle$$

where Σ denote a sum over the discrete states and an integration over the continuum states. Since the eigenkets can be assumed to form an orthogonal set $(\langle m|n\rangle = \delta_{mn})$ we have

$$\langle m|P\rangle = \sum_n c_n\langle m|n\rangle = \sum_n c_n\delta_{mn} = c_m \qquad \ldots(38)$$

Thus, $$|P\rangle = \sum_n |n\rangle c_n = \left\{\sum_n |n\rangle\langle n|\right\}|P\rangle \qquad \ldots(39)$$

Since, the above equation holds for an arbitrary ket $|P\rangle$; the quantity inside the curly brackets must be a unit operator

$$\sum_n |n\rangle\langle n| = 1 \qquad \ldots(40)$$

which is usually reffered to the completeness condition. The above equation may be compared with the completeness condition of the Schrodinger wavefunctions

Examples from matrix algebra: The various axiomatic rules discuss so far can be readily understood if we consider some simple examples from the theory of matrices. Let us consider a 3×3 Hermitian matrix α given by

$$\alpha = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

We have assumed α to be a 3×3 matrix; we could have assumed it to be of an arbitrary order.

Let $$|A\rangle = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \quad \text{and} \quad |B\rangle = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$$

denote two arbitrary column vectors in the same field (i.e. having 3 rows). Now corresponding to every ket vector there is a bra vector which, in this case, is nothing but a row vector. Thus

$$\langle A| = (\bar{a}_1, \bar{a}_2, \bar{a}_3) \quad \text{and} \quad \langle B| = (\bar{b}_1, \bar{b}_2, \bar{b}_3)$$

where $\bar{a}_1, \bar{a}_2, \ldots\ldots$ are the complex conjugate of $a_1, a_2, \ldots\ldots$ The scalar product is given by

$$\langle A \mid B \rangle = (\bar{a}_1 \bar{a}_2 \bar{a}_3) \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} = \bar{a}_1 b_1 + \bar{a}_2 b_2 + \bar{a}_3 b_3$$

which is a complex number. Obviously

$$\langle A \mid B \rangle = \overline{\langle B \mid A \rangle}$$

Further, $\langle A \mid A \rangle = |a_1|^2 + |a_2|^2 + |a_3|^2 \geq 0$

The scalar product $\langle A \mid A \rangle = 0$ if and only if

$$a_1 = a_2 = a_3 = 0$$

which corresponds to a 'null vector'. Since

$$\alpha \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

implying that a linear operator operating on a null vector will always give a null vector. Further

$$|A\rangle = |B\rangle$$

if and only if

$$a_1 = b_1, \; a_2 = b_2 \text{ and } a_3 = b_3$$

Now, it can be easily shown that the eigenvalues of the operator α are $+1, -1$ and $+2$. The corresponding normalized eigenvectors are

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}, \; |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} \text{ And } |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

One can easily see that

$$\langle i \mid j \rangle = \delta_{ij}; \qquad i, j = 1, 2, 3$$

which represents the orthonormality condition. Further, they form a complete set of functions in the sense that an arbitrary vector (in the three-dimensional space) can be expressed as a linear combination of $|1\rangle, |2\rangle$ and $|3\rangle$. Thus

$$|A\rangle = \frac{a_1 + a_2}{\sqrt{2}} |1\rangle + \frac{a_1 - a_2}{\sqrt{2}} |2\rangle + a_3 |3\rangle$$

Further, $\sum_i |i\rangle\langle i| = |1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3|$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which represents the completeness condition[see equation (40)]

Simultaneous eigenkets of commuting observables:

In this section we will show that if two observables commute then one can have a complete set of simultaneous eigenkets of the two observables.

Let α and β represent the operators corresponding to two observables. We assume that the two operators commute, i.e.,

$$\alpha\beta = \beta\alpha \qquad \ldots (41)$$

Let $|\alpha_1\rangle$ be an eigenket of α belonging to the eigenvalue α_1:

$$\alpha|\alpha_1\rangle = \alpha_1|\alpha_1\rangle \qquad \ldots (42)$$

Then, $\alpha\{\beta|\alpha_1\rangle\} = \beta\alpha|\alpha\rangle = \beta\alpha_1|\alpha_1\rangle$ [Using equation. (42)]

Or, $\alpha\{\beta|\alpha_1\rangle\} = \alpha_1\{\beta|\alpha_1\rangle\} \qquad \ldots (43)$

where the last step follows from the fact that α_1 is a number. Equation (43) tells us that $\beta|\alpha_1\rangle$ is also an eigenket of α belonging to the same eigenvalue α_1. If $|\alpha_1\rangle$ corresponds to a non-degenerate state, then equation (43) tells us that

$\beta|\alpha_1\rangle$ must be a multiple of $|\alpha_1\rangle$

implying $\beta|\alpha_1\rangle = \beta_1|\alpha_1\rangle \qquad \ldots (44)$

where β_1 is a number. Thus $|\alpha_1\rangle$ must be an eigenket of β. Hence, all eigenkets of α which correspond to nondegenerate states, must also be eigenkets of β and hence these will be simultaneous eigenkets.

We next consider the case when the eigenvalue α_1 correspond to a degerate state. To keep the analysis simple let the state be two-fold degenerate and let the eigenkets be $|\alpha_1\rangle$ and $|\alpha_2\rangle$; i.e.

$$\alpha|\alpha_1\rangle = \alpha_1|\alpha_1\rangle \qquad \ldots (45)$$

And $\alpha|\alpha_2\rangle = \alpha_1|\alpha_2\rangle \qquad \ldots (46)$

The kets $|\alpha_1\rangle$ and $|\alpha_2\rangle$ are assumed to be orthogonal to each other. Now, since $\beta|\alpha_1\rangle$ and $\beta|\alpha_2\rangle$ are eigenkets of α belonging to the same eigenvalue α_1, they must be expressible as a linear combination of $|\alpha_1\rangle$ and $|\alpha_2\rangle$.

$$\beta|\alpha_1\rangle = c_{11}|\alpha_1\rangle + c_{12}|\alpha_2\rangle \qquad \ldots (47)$$

And $\beta|\alpha_2\rangle = c_{21}|\alpha_1\rangle + c_{22}|\alpha_2\rangle \qquad \ldots (48)$

The kets $|\alpha_1\rangle$ and $|\alpha_2\rangle$ need not be eigenkets of β; however, we may always choose apropriate linear combinations so that they are eigenkets of β (and hence simultaneous eigenkets of α and β). Let the required linear combination be

$$d_1|\alpha_1\rangle + d_2|\alpha_2\rangle$$

Then, $\beta\left[d_1|\alpha_1\rangle + d_2|\alpha_2\rangle\right] = \beta'\left[d_1|\alpha_1\rangle + d_2|\alpha_2\rangle\right]$

If we now use equation (47) and (48), we would obtain

$$d_1\left[c_{11}|\alpha_1\rangle + c_{12}|\alpha_2\rangle\right] + d_2\left[c_{21}|\alpha_1\rangle + c_{22}|\alpha_2\rangle\right] = \beta' d_1|\alpha_1\rangle + \beta' d_2|\alpha_2\rangle$$

Since $|\alpha_1\rangle$ and $|\alpha_2\rangle$ are orthogonal to each other, we get

$$d_1(c_{11} - \beta') + d_2 c_{21} = 0$$

And $\quad d_1 c_{12} + d_2 (c_{22} - \beta') = 0$

For non-trivial solutions, we must have

$$\begin{vmatrix} c_{11} - \beta' & c_{21} \\ c_{12} & c_{22} - \beta' \end{vmatrix} = 0 \qquad \ldots (49)$$

the roots of which will give the two allowed values of β'. Once β' is known, we can obtain the ratio d_1 / d_2 which will give the simultaneous eigenket. As an example we consider the two matrices.

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

which commute with each other, i.e.

$$\sigma_x \alpha = \alpha \sigma_x$$

Now, the eigenvalues of σ_x are +1 and −1 and are nondegenerate; hence both the eigenvectors are also eigenvectors of α. Thus

$$|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad |2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

(which are eigenvectors of σ_x) represent a complete set of simultaneous eigenvectors of σ_x and α. They form a complete set in the sense that an arbitrary vector can be represented as a linear combination of $|1\rangle$ and $|2\rangle$

$$\begin{pmatrix} a \\ b \end{pmatrix} = \frac{(a+b)}{\sqrt{2}} \left[\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right] + (a-b) \left[\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \right]$$

It may be seen that

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

are eigenvectors of α but not eigenvectors of σ_x. However, $|1\rangle$ and $|2\rangle$ can be expressed as a linear combination of the above vectors.

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \text{ and } \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Once again, $\quad \sigma_z \alpha = \alpha \sigma_z$

and the eigenvectors, $\quad \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

form a complete set of simultaneous eigenvectors of σ_z and α. Similarly,

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \text{ and } \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$$

form a complete set of simultaneous eigenvectors of

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \text{ and } \alpha = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Notice that although σ_x, σ_y and σ_z do not commute with each other, they commute independently with α; and one can form simultaneous eigenkets of either σ_x and α or of σ_y and α or of σ_z and α.

Problem-1: Determine the orthonormal set of the eigenvectors of the matrix

$$\begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}$$

Prove the completeness condition

Soln. The normalized eigenvectors are

$$|1\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix};\ |2\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix};\ |3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

Problem-2: Prove that

$$\overline{|P\rangle\langle Q|} = |Q\rangle\langle P|$$

Soln. Let $\alpha = |P\rangle\langle Q|$ and let $|B\rangle = \alpha|A\rangle = \left[\langle Q|A\rangle\right]|P\rangle$

Thus, $\langle B| = \overline{\langle Q|A\rangle}\langle P| = \langle A|Q\rangle\langle P|$

But $\langle B| = \langle A|\bar{\alpha}\rangle$. Therefore, $\bar{\alpha} = |Q\rangle\langle P|$

Problem: Consider the matrices

$$\alpha_1 = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{2} & 0 \\ \sqrt{2} & 0 & \sqrt{2} \\ 0 & \sqrt{2} & 0 \end{pmatrix};\ \alpha_2 = \frac{1}{2}\begin{pmatrix} 0 & -i\sqrt{2} & 0 \\ i\sqrt{2} & 0 & -i\sqrt{2} \\ 0 & i\sqrt{2} & 0 \end{pmatrix};\ \alpha_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \text{ and } \beta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Show that α_1, α_2 and α_3 commute independently with β but not with each other. Construct simultaneous set of eigenvectors of α_1 and β. Repeat the analysis for α_2 and β and for α_3 and β

Soln. Simultaneous eigenvectors of α_1 and β are

$$\frac{1}{2}\begin{pmatrix} 1 \\ \sqrt{2} \\ 1 \end{pmatrix}, \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \text{ and } \frac{1}{\sqrt{5}}\begin{pmatrix} 1 \\ -\sqrt{2} \\ 1 \end{pmatrix}$$

Simultaneous eigenvectors of α_2 and β are

$$\frac{1}{2}\begin{pmatrix} 1 \\ i\sqrt{2} \\ -1 \end{pmatrix}, \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \text{ and } \frac{1}{2}\begin{pmatrix} 1 \\ -i\sqrt{2} \\ -1 \end{pmatrix}$$

Simultaneous eigenvectors of α_3 and β are

$$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \text{ and } \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

SECOND ORDER PERTURBATION

It is the correction to the energy i.e. based on the function that is modified during Ist order perturbation energy. For the second order perturbation the energy state never be equal. The energy correction for second order is this

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{\langle \phi_m | W | \phi_n \rangle^2}{E_n^0 - E_m^0}}$$

If n = m then value become zero.

Problem: The unperturbed energy level of system are $E_0 = 0$, $E_1 = 2$ and $E_2 = 4$.
The second order correction to the energy for the ground state has been found to be when

$$V_{10} = 2; \qquad V_{20} = 4; \qquad V_{12} = 6$$

(a) -6 (b) 0 (c) $+6$ (d) -8

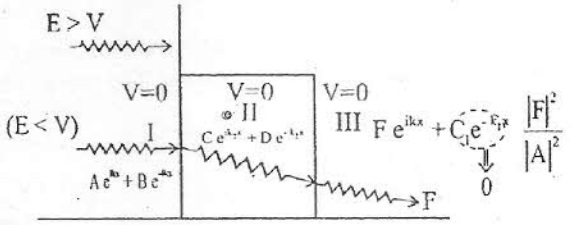
Soln. $$E_n^2 = \sum_{m \neq n} \frac{\langle \phi_m | W | \phi_n \rangle^2}{E_n - E_m}$$

$$= \frac{\langle V_{1,0} \rangle^2}{E_0 - E_1} + \frac{\langle V_{2,0} \rangle^2}{E_0 - E_2} + \frac{\langle V_{2,1} \rangle^2}{E_1 - E_2} + \frac{\langle V_{1,3} \rangle^2}{E_3 - E_1} + \frac{\langle V_{2,3} \rangle^2}{E_3 - E_2} = \frac{(2)^2}{0-2} + \frac{(4)^2}{0-4}$$

For ground state $= \frac{4}{0-2} + \frac{16}{-4} = -2 - 4 = \boxed{-6}$

Correct answer is (a).

TUNNELLING



For Ist region:

$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-0)\psi=0;$ A = amplitude of incident wave.

B = amplitude of reflected wave.

$\Rightarrow \quad k^2=\frac{8\pi^2 mE}{h^2}$ F = amplitude of transmitted wave.

$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E\psi)=0,$ G = zero

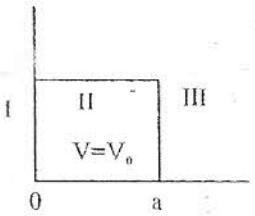
$\psi = A\sin kx + B\cos kx \quad \Rightarrow \quad \boxed{\psi = -Ae^{ikx}+Be^{-ikx}}$

For IInd region: $\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V_0)\psi=0 \quad \Rightarrow \quad \boxed{\psi = Ce^{ik_2x}+De^{-ik_2x}}$

For IIIrd region: $\boxed{\psi = Fe^{ikx}}$

Tunnelling represent the behaviour of particle in presence of potential barrier. Suppose a particle of mass 'm' and energy 'E' coming from the left approaches the potential barrier then according to classical mechanics. If $E < V_0$ (barrier height) it can not pass through the barrier.

According to Quantum Mechanics: The particle can penetrate the barrier and appear on other side and this effect is called Tunnelling.



Limit $0 \le x \le a$, $V = V_0$, outside $\left.\begin{matrix} x > a \\ x < 0 \end{matrix}\right] V = 0$

For Ist region:

$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \quad \Rightarrow \quad \frac{\partial^2\psi}{\partial x^2}+\alpha^2\psi=0$ where, $\alpha^2=\frac{8\pi^2 mE}{h^2}$

$\boxed{\psi_I = Ae^{+i\alpha x}+Be^{-i\alpha x}}$

For IInd region: $\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 m}{h^2}(E-V_0)\psi=0 \qquad \beta^2=\frac{8\pi^2 m}{h^2}(E-V_0)$

$\frac{\partial^2\psi}{\partial x^2}+\beta^2\psi=0 \qquad \boxed{\psi_{II} = Ce^{+i\beta x}+De^{-i\beta x}}$

For IIIrd region:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{8\pi^2 mE}{h^2}\psi=0 \quad \Rightarrow \quad \frac{d^2\psi}{dx^2}+\alpha^2\psi=0 \qquad \text{where } \alpha=\frac{8\pi^2 mE}{h^2}$$

$$\boxed{\psi_{III}=F e^{i\alpha x}+C_A e^{-i\alpha x}}$$ Wave is propagating in +x direction only in IIIrd region.

Where $C_A e^{-i\alpha x}=0$

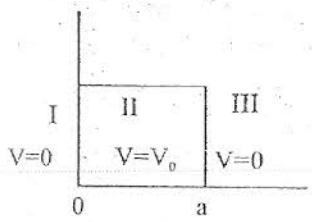
Q. The probability of Tunnelling is given by transmission coefficient $\left(T=\frac{|F|^2}{|A|^2}\right)$

$$R=\frac{|B|^2}{|A|^2}$$ limit $0\le x\le a$, $V=V_0$, Outside $\left.\begin{matrix}x>a\\ x<0\end{matrix}\right]$ $V=0$

when $\psi_I=\psi_{II}$ and $x=0$.

$$A e^{i\alpha 0}+B e^{-i\alpha 0}=C e^{i\alpha 0}+D e^{i\alpha 0}$$

$$A+B=C+D \qquad \ldots(1)$$



$\psi_I=\psi_{II}$ $\qquad$ $\psi_{II}=\psi_{III}$

$x=0$ $\qquad$ $\frac{\partial\psi_{II}}{\partial x}=\frac{\partial\psi_{III}}{\partial x}$ $\quad x=a$

$\frac{\partial\psi_I}{\partial x}=\frac{\partial\psi_{II}}{\partial x}$

when $x=0$

$$\frac{d\psi_I}{dx}=i\alpha A e^{i\alpha x}-i\alpha B e^{-i\alpha x} \quad \Rightarrow \quad \frac{d\psi_{II}}{dx}=i\beta C e^{i\beta x}-i\beta D e^{-i\beta x}$$

when $x=0$

$$\frac{d\psi_I}{dx}=i\alpha A-i\alpha B \quad \Rightarrow \quad \frac{d\psi_{II}}{dx}=i\beta C-i\beta D$$

$$\therefore \quad i\alpha A-i\alpha B=i\beta C-i\beta D \qquad \ldots(ii)$$

$\Rightarrow$ $x=a$

$$C+D=F;\ C e^{i\beta x}+D e^{-i\beta x}=F e^{i\alpha x}$$

Putting $x=a$

$$C e^{i\beta a}+D e^{-i\beta a}=F e^{-i\alpha a} \qquad \ldots(iii)$$

$$i\beta C e^{-i\beta a}-i\beta D e^{-i\beta a}=i\alpha F e^{+i\alpha a} \qquad \ldots(iv)$$

Multiply equation (i) by $i\beta$ then,

$$A+B=C+D\times i\beta$$

$$i\beta A + i\beta B = i\beta C + i\beta D$$
$$+i\alpha A - i\alpha B = i\beta C - i\beta D$$
$$i\beta A + i\beta B + i\alpha A - i\alpha B = 2i\beta C$$

$$A = \frac{F\, e^{i\alpha a}}{4i\alpha\beta}\left[(\beta+i\alpha)^2 e^{-\beta a} - (\beta - i\alpha)^2 e^{\beta a}\right]; \quad A^2 = A^* A = F^2\left[1 + \frac{(\alpha^2+\beta^2)^2}{4\alpha^2\beta^2}\left(e^{\beta a} - e^{-\beta a}\right)^2\right]$$

$$\boxed{A^2 = F^2\left[1 + \frac{(\alpha^2+\beta^2)^2}{4\alpha^2\beta^2}\sinh^2 \beta a\right]} \qquad \therefore \quad \sinh x = e^x - e^{-x}$$

Putting value of α and β

$$\boxed{T = \left[1 + \frac{V_0^2}{4E(V_0 - E)}\sinh^2 \frac{\sqrt{2m(V_0 - E)}}{\hbar} a\right]}$$

If $e^{\beta a} > e^{-\beta a}$

$$\boxed{T = \frac{16E(V_0 - E)}{V_0^2} e^{-2a} \frac{\sqrt{2m(V_0 - E)}}{\hbar}}$$ for I, II, III all region.

Q. A beam of electron collide on energy barrier of height 0.030 eV and of infinite width. Find the fraction of electron reflected and transmitted at the barrier. If the energy of impinging or colliding electron is:

(a) 0.030 (b) 0.025 eV (c) 0.040 eV

Soln. (a) In this case E = 0.030 and energy of barrier 0.030 means

$$\boxed{E = V}.$$

This shows that the reflection is 100% and transmittance zero.

(b) In this case also $\boxed{E < V}$ Reflection = 100%, transmittance = 0

$\because$ E = 0.025 eV and V = 0.030 eV

(c) Can be calculated

Here E > V i.e., E = 0.040 eV, V = 0.030 eV

means, there is reflection and transmittance both.

$$p_1 = \sqrt{2mE} = \sqrt{2\times 9.1\times 10^{-31}\times 0.040\times 1.6\times 10^{-19}}\ J$$

$$p_2 = \sqrt{2m(E-V)} = \sqrt{2\times 9.1\times 10^{-31}\times 0.010\times 1.6\times 10^{-19}}\ J$$

$$\therefore \quad T = \frac{4p_1p_2}{(p_1+p_2)^2}$$

HERMITIAN ADJOINT OF OPERATORS

$(A^\dagger) = (A^T)^*$; $\quad (A^\dagger) = (A^*)^T$

$\langle \phi_n | A | \phi_m \rangle^T = \langle \phi_m | A | \phi_n \rangle$

Here Ist ϕ_m under operator and transpose change function.

If $A^\dagger = A$, Then it is Hermitian.

If A is Hermitian $\quad A^\dagger = A$

If p_x is Hermitian $\quad p_x{}^\dagger = p_x$

$$\int \psi^* (p_x)^\dagger \psi \, dx = \int \psi^* (p_x) \psi dx \qquad \left|(p_x)^\dagger = (p_x)\right|$$

This shows px is Hermitian and $(p_x)^\dagger = p_x$

$$\int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right)^\dagger \psi dx = \int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right) \psi dx$$

Now prove it,

$$\text{L.H.S.} = \left[\int \psi^* \left(-i\hbar \frac{\partial}{\partial x}\right)^\dagger \psi dx \right] = (-i\hbar) \int \psi^* \frac{\partial}{\partial x} \psi dx$$

General Property:

1. $(A+B)^\dagger = A^\dagger + B^\dagger$ 2. $(A^\dagger)^\dagger = A$ 3. $(AB)^\dagger = B^\dagger A^\dagger$

4. $(A^\dagger)^n = (A^n)^\dagger$ 5. $ABCD|\psi\rangle^\dagger = \langle \psi | D^\dagger C^\dagger B^\dagger A^\dagger$ 6. $(a\,A)^\dagger = a^* A^\dagger$

$A^\dagger = A$ A is Hermitian.

$A^\dagger = -A$ A is antihermitian.

$$\left(\frac{d}{dx}\right)^\dagger = -\frac{d}{dx}$$