

$$\begin{aligned}
 \text{Q 1. } \Delta E &= E_2 - E_1 \\
 &= \frac{h^2}{8ml^2} (n_2^2 - n_1^2) = \frac{h^2}{8ml^2} (4 - 1) = \frac{3h^2}{8ml^2} \\
 &= \frac{3(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times (10^{-9})^2} \\
 &= 1.8072 \times 10^{-19} \text{ J.}
 \end{aligned}$$

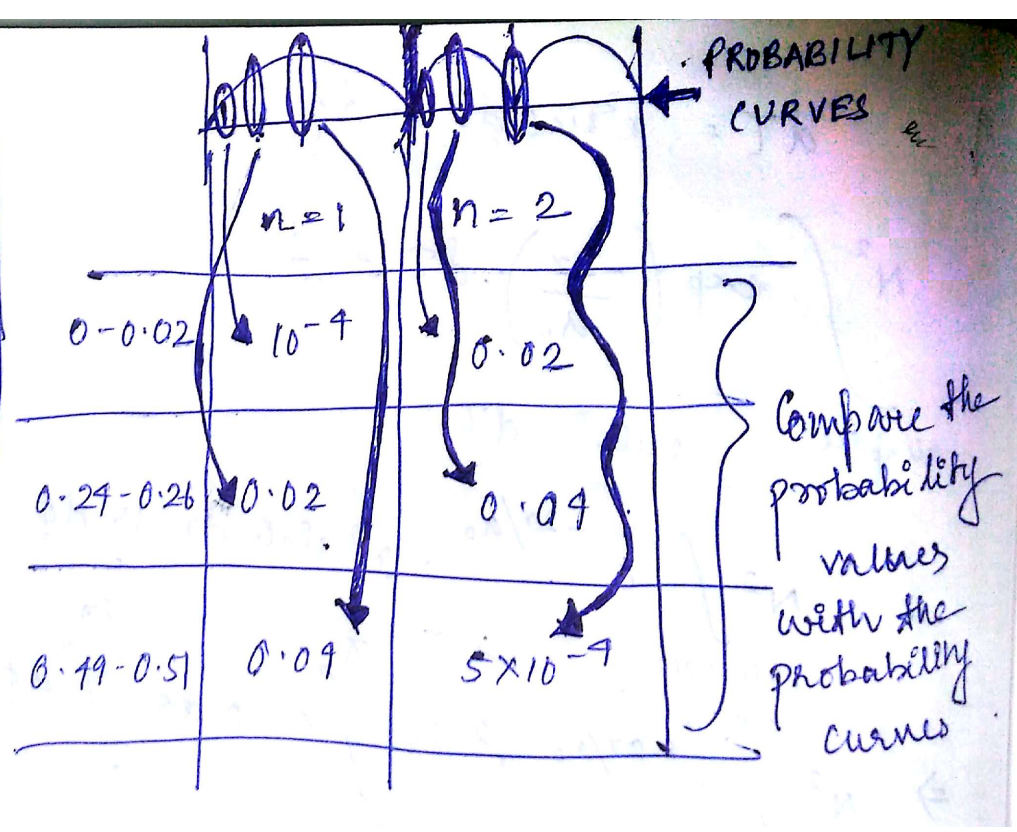
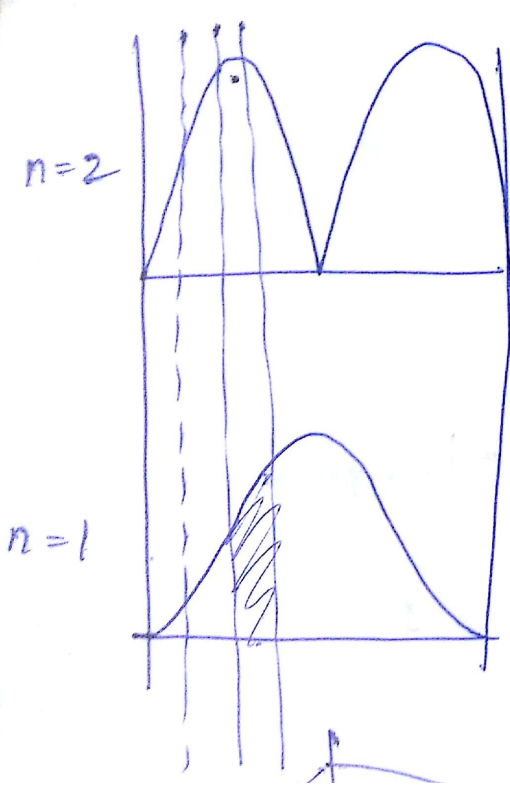
$$\text{or } h\nu = 1.8072 \times 10^{-19} \text{ J.}$$

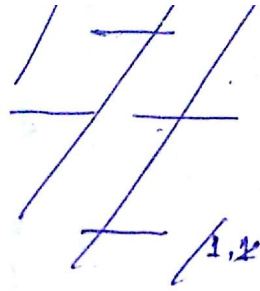
$$\nu = \frac{1.8072 \times 10^{-19}}{6.626 \times 10^{-34}} = \frac{c}{\lambda}$$

$$\text{or } \lambda = \frac{3 \times 10^8 \times 6.626 \times 10^{-34}}{1.8072 \times 10^{-19}}$$

$$= 1.0999 \times 10^{-6}$$

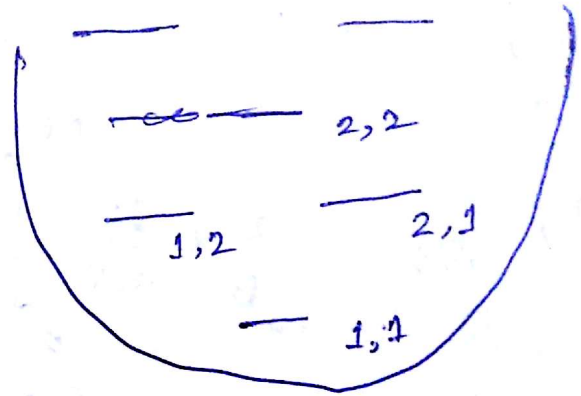
$$= 1099.9 \text{ nm}$$





$$E_{13} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2)$$

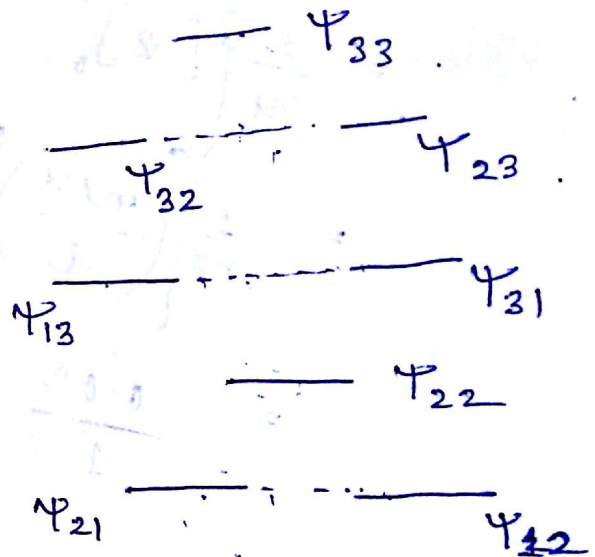
$$= \frac{h^2}{8mL^2} (1+9) = \frac{10h^2}{8mL^2} \text{ (4)}$$



$$E_{22} = \frac{h^2}{8mL^2} (4+4) = \frac{8h^2}{8mL^2} \text{ (3)}$$

$$E_{21} = \frac{h^2}{8mL^2} (4+1) = \frac{5h^2}{8mL^2} \text{ (2)}$$

$$E_{32} = \frac{h^2}{8mL^2} (9+4) = \frac{13h^2}{8mL^2} \text{ (8)}$$



6

Total no. of transitions

$$= {}^6C_2 = \frac{6!}{2! 4!} = \frac{6 \times 5 \times 4!}{4! \times 2} = 15 \text{ transitions}$$

= 15 transitions

Q. Wavefunctions of a particle in a 1-D box are orthogonal to each other.

Proof :-
$$S_{ij} = \int_0^l \psi_i^* \psi_j \cdot dx$$

$$= \int_0^l \left(\frac{2}{l}\right) \sin\left(\frac{i\pi x}{l}\right) \sin\left(\frac{j\pi x}{l}\right) \cdot dx$$

$$= \frac{1}{l} \int_0^l \left[\cos\left(\frac{(i-j)\pi x}{l}\right) - \cos\left(\frac{(i+j)\pi x}{l}\right) \right] \cdot dx$$

$$= \frac{1}{l} \left[\sin\left(\frac{(i-j)\pi x}{l}\right) - \sin\left(\frac{(i+j)\pi x}{l}\right) \right]_0^l \times \frac{l}{\pi} \left(\frac{1}{i-j} - \frac{1}{i+j} \right)$$

$$= \frac{1}{\pi} \left[\frac{1}{i-j} \sin(i-j)\pi - \frac{1}{i+j} \sin(i+j)\pi \right]$$

Substⁿ,

$$i=2, j=1,$$

$$S_{21} = \frac{1}{\pi} \left[\sin \pi - \frac{1}{3} \sin 3\pi \right]$$

$$\sin n\pi = 0, \text{ hence } S_{21} = 0$$

~~$i=2, j=2$~~

~~S_{22}~~

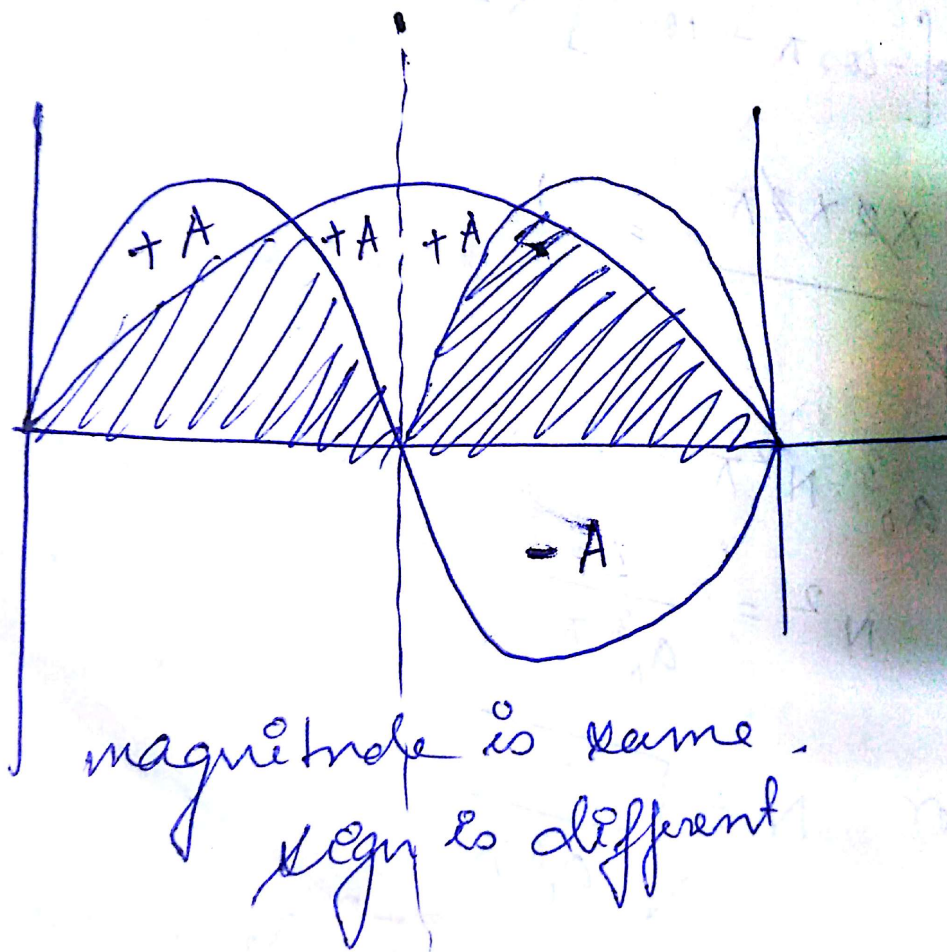
$$i=2, j=2=i$$

$$S_{ii} = \langle \psi_i | \psi_i \rangle = \int_0^l \left(\frac{2}{l}\right) \sin^2\left(\frac{i\pi x}{l}\right) \cdot dx$$

$$= \frac{1}{l} \int_0^l \left[1 - \cos\left(\frac{2i\pi x}{l}\right) \right] dx$$

$$= \frac{1}{l} \left[x - \cos\left(\frac{2i\pi x}{l}\right) + \cos 0 \right]$$

$$= \frac{1}{l} [l - \cancel{1} + \cancel{1}] = \underline{\underline{1}}$$



magnitude is same,
sign is different

6. If a hamiltonian is separable then its eigen functions of simpler are products of simpler eigen functions.

$\Psi(r_1, r_2, \dots, r_n)$ is eigen function of $H(r_1, r_2, r_3, \dots, r_n)$

$$\Psi(r_1, r_2, \dots, r_n) = \prod_{i=1}^n \Psi(r_i)$$

The above is valid when Hamiltonian is separable.

$$y \quad H = \hat{H}_1(q_1) + \hat{H}_2(q_2).$$

$$\& \quad \hat{H} \Psi(q_1, q_2) = E \Psi(q_1, q_2).$$

Assuming $\Psi = \Psi_1 \times \Psi_2$, Ψ_1 & Ψ_2 are eigen functions of H_1 and H_2 respectively.

$$\hat{H}_1 \Psi_1(q_1) = E_1 \Psi_1(q_1)$$

$$\hat{H}_2 \Psi_2(q_2) = E_2 \Psi_2(q_2).$$

$$\begin{aligned}\hat{H}\Psi(r_1, r_2) &= (\hat{H}_1 + \hat{H}_2) \Psi_1(r_1) \Psi_2(r_2) \\ &= \hat{H}_1 \Psi_1 \Psi_2 + \hat{H}_2 \Psi_1 \Psi_2 \\ &= E_1 \Psi_1 \Psi_2 + E_2 \Psi_1 \Psi_2\end{aligned}$$

(as \hat{H}_1 operates only on Ψ_1 and \hat{H}_2 only on Ψ_2)

$$\begin{aligned}&= (E_1 + E_2) \Psi_1 \Psi_2 \\ &= E \Psi\end{aligned}$$

$$\text{Now } \hat{H}\Psi = E\Psi = (E_1 + E_2) \Psi_1 \Psi_2$$

$$\text{or } E = E_1 + E_2$$

Thus, if $\hat{H} = \hat{H}_1 + \hat{H}_2$

$$\text{or rather } \hat{H}(r_1, r_2) = \hat{H}_1(r_1) + \hat{H}_2(r_2)$$

$$\text{and } \hat{H}_1 \Psi_1 = E_1 \Psi_1 \text{ \& } \hat{H}_2 \Psi_2 = E_2 \Psi_2$$

Then for the eqⁿ.

$$\hat{H}\Psi(r_1, r_2) = E\Psi(r_1, r_2)$$

Ψ can be expressed as,

$$\Psi = \Psi_1(r_1) \Psi_2(r_2)$$

$$\& E = E_1 + E_2$$

Thus if \hat{H} can be written as sum of different terms involving separate coordinates. Then eigen functions of \hat{H} are products of eigen functions of \hat{H}_1 and \hat{H}_2 and eigen value is sum.

Q7.
⇒ Why spherical coordinates are used for Hydrogen atom.

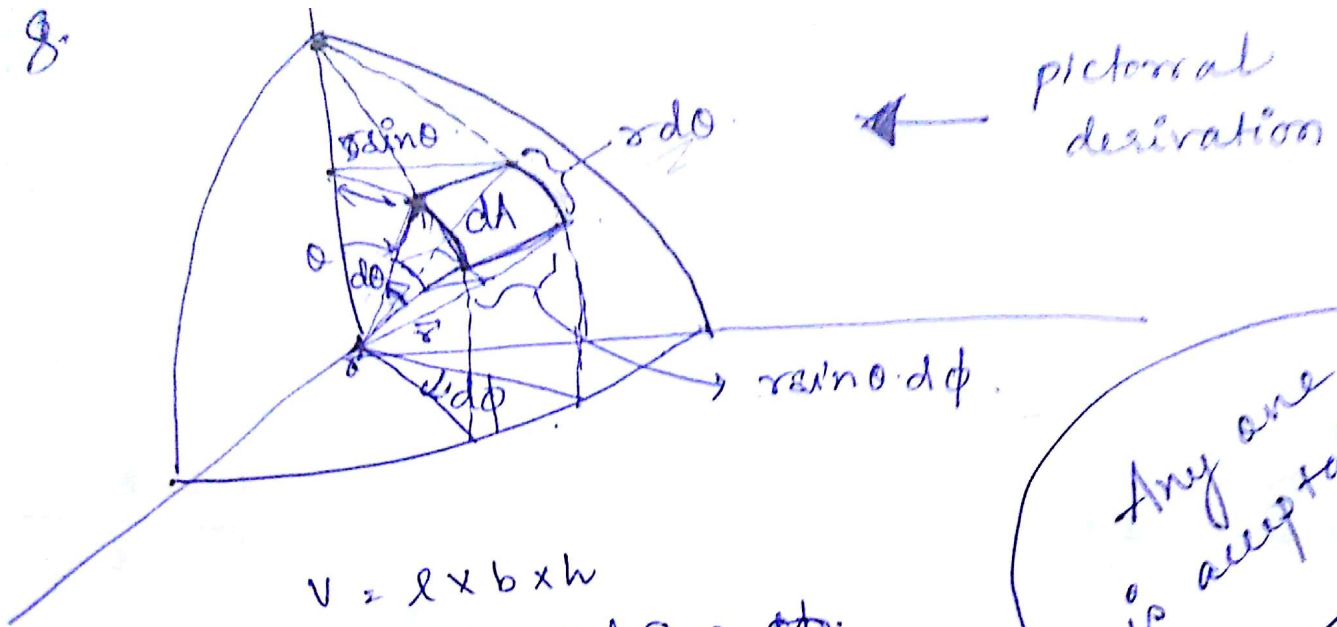
- (i) Hydrogen atom is a simple system with high degree of symmetry. The central force field (Coulombic attraction) acts along the ~~z~~ line joining the e^- to nucleus at origin. In terms of x, y, z ,

$$r = \sqrt{x^2 + y^2 + z^2}$$

using polar coordinates eliminates the above complicated dependence on x, y, z and simplifies calculation.

- (ii) It separates the function in terms of r, θ, ϕ and each function part of each variable can be solved individually.

8.



$$V = l \times b \times h$$

$$= \cancel{dr} \cdot \cancel{r \sin \theta} \cdot \cancel{r \sin \theta} \cdot d\phi$$

$$r dr \cdot r \sin \theta \cdot d\phi \cdot dr$$

$$= r^2 \sin \theta \cdot dr \cdot d\theta \cdot d\phi$$

Jacobian
derivation

$$J(r, \theta, \phi) =$$

$$\begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix}$$

$$\begin{aligned} x &= r \sin \theta \cos \phi \\ y &= r \sin \theta \sin \phi \\ z &= r \cos \theta \end{aligned}$$

$$= \begin{vmatrix} \sin \theta \cos \phi & r \cos \theta \cos \phi & -r \sin \theta \sin \phi \\ \sin \theta \sin \phi & r \cos \theta \sin \phi & r \sin \theta \cos \phi \\ \cos \theta & -r \sin \theta & 0 \end{vmatrix} \begin{pmatrix} dr \\ d\theta \\ d\phi \end{pmatrix}$$

$$= \cancel{r} \sin^2 \theta \cos^2 \phi \cdot dr \cdot d\theta \cdot d\phi$$

$$= r \sin^2 \theta \cdot dr \cdot d\theta \cdot d\phi$$

Any one
is acceptable

$$9. \quad d\tau = r^2 \sin\theta \, d\theta \cdot dr \cdot d\phi$$

$$N^2 \int_{\text{all space}} \exp\left(\frac{-2r}{a_0}\right) \cdot d\tau = 1$$

substⁿ $d\tau$,

$$N^2 \int_{\text{all space}} e^{-2r/a_0} \cdot r^2 \sin\theta \cdot dr \cdot d\theta \cdot d\phi = 1$$

$$\Rightarrow N^2 \int_0^{+\infty} e^{-2r/a_0} \cdot r^2 \cdot dr \cdot \int_0^\pi \sin\theta \cdot d\theta \cdot \int_0^{2\pi} d\phi = 1$$

Let $\frac{2r}{a_0} = z \Rightarrow \frac{2}{a_0} \cdot dr = dz$ or $dr = \frac{a_0}{2} \cdot dz$

$$N^2 \int_0^\infty e^{-z} \cdot \left(\frac{a_0}{2} z\right)^2 \cdot \frac{a_0}{2} dz \cdot \int_0^\pi \sin\theta \cdot d\theta \cdot \int_0^{2\pi} d\phi = 1$$

$$\frac{a_0^3}{8} N^2 \int_0^\infty e^{-z} \cdot z^2 \cdot dz \cdot \int_0^\pi \sin\theta \cdot d\theta \cdot \int_0^{2\pi} d\phi = 1$$

$$\Rightarrow \frac{a_0^3 \cdot N^2}{8} \cdot 2! \cdot [\cos\theta]_0^\pi \cdot 2\pi = 1$$

$$\begin{aligned} z-1 &= 2 \\ z &= 3 \\ \Rightarrow \Gamma(3) &= 2! \end{aligned}$$

$$\Rightarrow \frac{a_0^3 \cdot N^2}{4} \times [-\cos\pi + \cos 0] \times 2\pi = 1$$

$$2) \quad \frac{a_0^3 N^2 \cdot \cancel{2} \cdot \cancel{2\pi}}{\cancel{4}} = 1$$

$$a_0^3 \cdot N^2 \cdot \pi = 1$$

$$\Rightarrow N^2 = \frac{1}{a_0^3 \cdot \pi}$$

$$\text{or } N = \sqrt{\frac{1}{a_0^3 \cdot \pi}}$$

$$1 / 1^{3/2} \cdot 0^{-1/a_0}$$