STRUCTURE OF ATOM - III

BE
1st Sem.

Particle in Three Dimensional Box

The Schrodinger eqn for 3-dimensional for a particle in a box is,

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad \text{---(i)}$$

where ψ will depend on three independent variables x, y and z. So, to solve the above eqn we write the function as a product of three wave functions each involving only one independent variable of x, y and z respectively. Thus,

$$\psi(x, y, z) = X(x)\,Y(y)\,Z(z) \quad \text{---(ii)}$$

Substituting in eqn (i), we get

$$\nabla^2(XYZ) + \frac{8\pi^2 m}{h^2} EXYZ = 0$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(XYZ) + \frac{8\pi^2 m}{h^2} E(XYZ) = 0.$$

or $$YZ\left(\frac{\partial^2}{\partial x^2} X\right) + XZ\left(\frac{\partial^2}{\partial y^2} Y\right) + XY\left(\frac{\partial^2}{\partial z^2} Z\right) + \frac{8\pi^2 m}{h^2} EXYZ = 0 \quad \text{---(iii)}$$

Dividing by XYZ, we have

$$\frac{1}{X}\left(\frac{\partial^2}{\partial x^2} X\right) + \frac{1}{Y}\left(\frac{\partial^2}{\partial y^2} Y\right) + \frac{1}{Z}\left(\frac{\partial^2}{\partial z^2} Z\right) = -\frac{8\pi^2 m}{h^2} E = -\alpha^2 \quad \text{---(iv)}$$

The term α^2 in the above equation is a constant quantity. Hence, the sum of the three terms on the left hand side of eqn (iv) must also be a

constant quantity, if we change the value of x (or y or z) keeping the other two variables constant, even then the above constancy has to be satisfied. This is possible only when each term is independent of the other terms and each is equal to a constant quantity so that the sum of three constants is equal to α^2.

$$\frac{1}{X}\frac{\partial^2}{\partial x^2}X = -\alpha_x^2 \quad \text{---(v)}$$

$$\frac{1}{Y}\frac{\partial^2}{\partial y^2}Y = -\alpha_y^2 \quad \text{---(vi)}$$

$$\frac{1}{Z}\frac{\partial^2}{\partial z^2}Z = -\alpha_z^2 \quad \text{---(vii)}$$

where,

$$\alpha_x^2 = \frac{8\pi^2 m}{h^2}E_x \quad \text{---(viii)}$$

$$\alpha_y^2 = \frac{8\pi^2 m}{h^2}E_y \quad \text{---(ix)}$$

$$\alpha_z^2 = \frac{8\pi^2 m}{h^2}E_y \quad \text{---(x)}$$

with $\alpha^2 = \alpha_x^2 + \alpha_y^2 + \alpha_z^2$ ---(xi)

and $E = E_x + E_y + E_z$ ---(xii)

Now, we have three separate equations to be solved, each of them has a form of one-dimensional box. Thus, the normalised wave function of a three dimensional box is

$$\psi = XYZ = \left(\sqrt{\frac{2}{l_1}}\sin\frac{n_x\pi}{l_1}x\right)\left(\sqrt{\frac{2}{l_2}}\sin\frac{n_y\pi}{l_2}y\right) \times \left(\sqrt{\frac{2}{l_3}}\sin\frac{n_z\pi}{l_3}z\right)$$

or, $\psi = \sqrt{\frac{8}{l_1 l_2 l_3}} \sin\left(\frac{n_x \pi}{l_1} x\right) \sin\left(\frac{n_y \pi}{l_2} y\right) \sin\left(\frac{n_z \pi}{l_3} z\right)$

The constants α_x, α_y and α_z will be given by —(xiii)

$$\alpha_x = \frac{n_x \pi}{l_1}, \quad \alpha_y = \frac{n_y \pi}{l_2} \text{ and } \alpha_z = \frac{n_z \pi}{l_3} \quad -(xiv)$$

Then, the total energy is,

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{l_1^2} + \frac{n_y^2}{l_2^2} + \frac{n_z^2}{l_3^2}\right)$$

There are three quantum numbers one each for every degree of freedom.

l_1, l_2, l_3 are the length of each one-dimensional box.

Summary of the Quantum Mechanical Treatment of Hydrogen Like Systems:

(1) To describe the mechanical state of the hydrogen like systems, we need a function ψ which depends on the six independent variables, viz, three co-ordinates of the nucleus and three for the electron.

(2) The function ψ can be written as

$$\psi = \psi_m \psi_e$$

where ψ_m depends on the coordinates of the centre of mass and ψ_e on the internal coordinates, the Schrodinger equation separates into two independent equations; one for the motion of the atom as a whole and the other involving the internal coordinates of the atom.

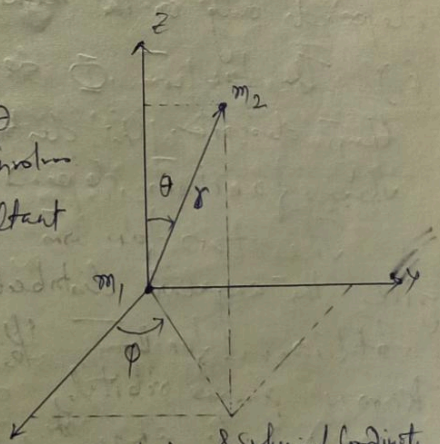
(3) The Schrodinger equation involving the internal coordinates is then transformed into the spherical polar coordinates.

(4) The Schrodinger equation splits into three equations if we write ψ_e as

$$\psi_e = R\,\Theta\,\Phi$$

The function R involves only r, Θ involves only angle θ and Φ involves only angle ϕ. The three resultant equations can be solved for the functions R, Θ and Φ by suitable transformations.

In order that these functions are finite, well behaved and consistent with the boundary conditions, certain quantum



Cartesian & Spherical Coordinates

restrictions are introduced. These restrictions appear in the form of quantum numbers.

(5)(a) The functions R depend only on r, therefore, they describe the radial distributions of the electron. These functions depend ~~upto~~ upon two quantum numbers, n and l. The permitted values of these numbers are —

Principal quantum number: $n = 1, 2, 3, 4, \ldots$

Azimuthal quantum number: $l = 0, 1, 2, \ldots, (n-1)$

We have different R functions for different values of n and l.

(b) The function Θ depend only on angle θ, therefore, they describe the distribution as a function of angle θ. These functions again depend upon two quantum numbers, viz., l and m. Though the permitted values of m are $0, \pm 1, \pm 2, \ldots, \pm l$, the Θ function depend only on the magnitude of m i.e. $|m|$.

(c) The function Φ depend only on angle φ, therefore, they describe the distribution as a function of angle φ. These functions depend only on the value of m.

The two functions Θ and Φ taken together give the angular distribution of the electron. Thus the total wave function ψ which constitutes what is known as an orbital, depends on the quantum number n, l and m, i.e., we have different ψ functions (or orbitals) for different values of n, l and m and hence different behaviours of the electron in the atom.

(P-14)

The principal quantum number describes the energy of the electron in the hydrogen-like systems and is given by the relation

(6)(a) $$E = -\frac{1}{n^2}\left(\frac{2\pi^2 \mu Z^2 e^4}{h^2}\right) = -\frac{1}{n^2}\left(\frac{Z^2 e^2}{2a_0}\right)$$

where $a_0 = \frac{h^2}{4\pi^2 \mu e^2}$

(b) The azimuthal quantum number describes the total angular momentum of the electron through the expression

$$L^2 = l(l+1)\left(\frac{h}{2\pi}\right)^2$$

It is customary to designate the values of l by letters as given below:

value of l:	0	1	2	3	4	5
designation:	s	p	d	f	g	h

The letters s, p, d and f are derived from the spectroscopic terms: sharp (s), principal (p), diffuse (d) and fundamental (f).

(c) The magnetic quantum number describes the z-component of the angular momentum of the electron through the equation

$$L_z = m\left(\frac{h}{2\pi}\right)$$

(7) The energy of the electron depends only on the value of n and not at all on l and m. Thus, all ψ functions or orbitals with the same value of n, but different values of l and m are degenerate; i.e.

they have the same energy. Thus, we have

(i) $n=1 \quad l=0 \quad m=0 \quad E = -\frac{2\pi^2 \mu Z^2 e^4}{h^2}$

(ii) $n=2$

$l=0 \quad m=0$

$l=1 \quad m=0, +1, -1$ $\Big\}$ $E = -\frac{1}{4}\left(\frac{2\pi^2 \mu Z^2 e^4}{h^2}\right)$ fourfold degenerate.

(iii) $n=3$

$l=0 \quad m=0$

$l=1 \quad m=0, +1, -1$

$l=2 \quad m=0, +1, -1, +2, -2$ $\Big\}$ $E = -\frac{1}{9}\left(\frac{2\pi^2 \mu Z^2 e^4}{h^2}\right)$ ninefold degenerate.

Thus, the degeneracy of orbitals for a given value of n is equal to n^2.

Pictorial Representation of wave functions and Probability Density Distribution

The various wave functions for the hydrogen like systems are written as

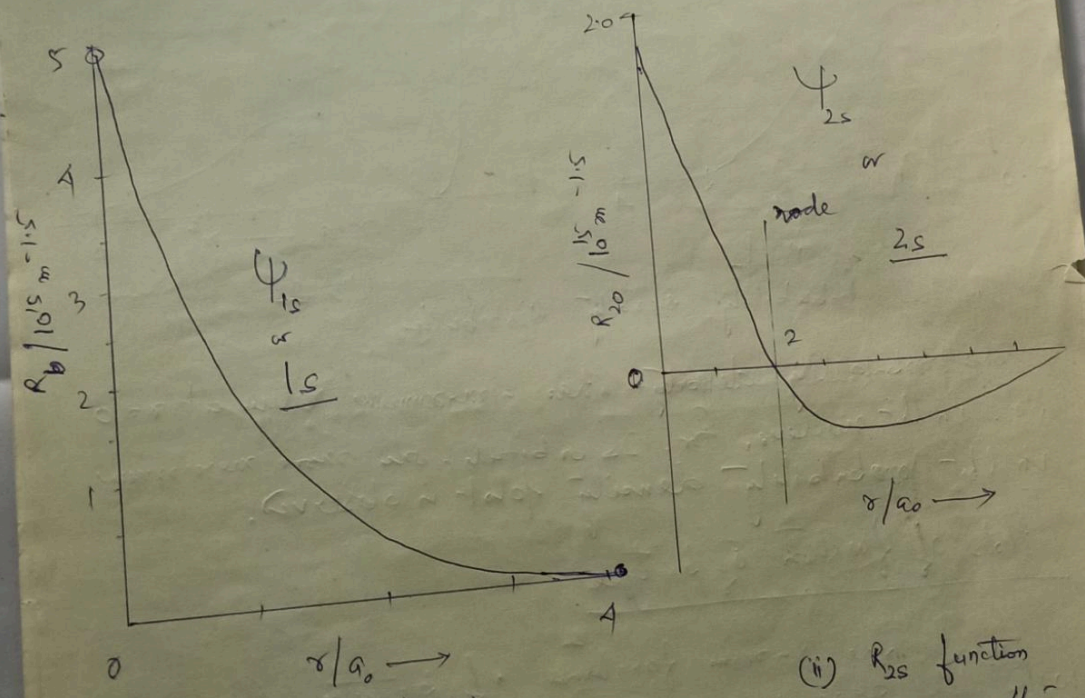
$$\psi_{n,l,m} = R_{n,l}\, \Theta_{l,|m|}\, \Phi_m$$

where the functions $R_{n,l}$, $\Theta_{l,|m|}$ and Φ_m describe the r, θ and ϕ dependences, respectively. (θ-2A)

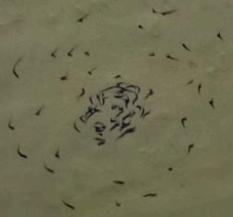
The function R depends on the two quantum numbers, n and l; Θ also depends on two quantum numbers, l and m and the function Φ depends only on one quantum number m. The two functions $\Theta_{l,|m|}$ and Φ_m taken together describe the angular dependence of the wave function.

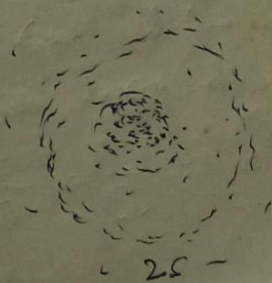
Plots of functions of s-type: s orbitals are given by

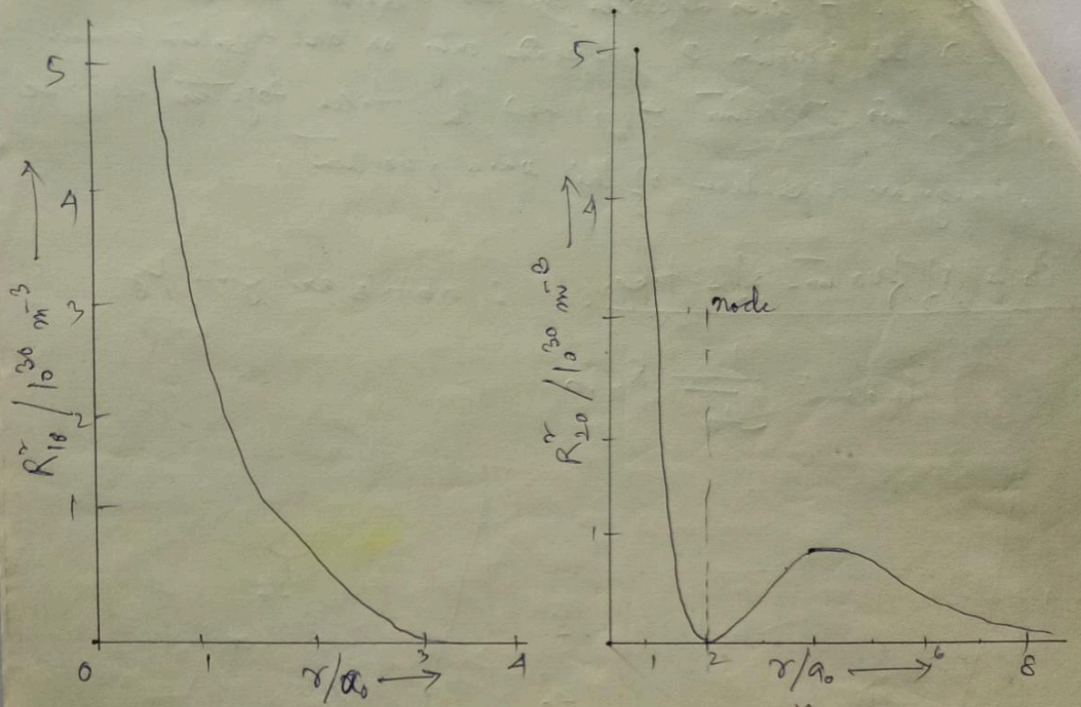
$$\psi_{n,0,0} = \frac{1}{\sqrt{4\pi}} R_{n,0}$$



The point where the function has zero value is known as the nodal point.


1s


2s



(i) 1s (ii) 2s

Probability density distribution

The probability density has a maximum value at $r=0$ i.e. in the nucleus. For, 2s orbital, one more maximum in the probability density plot is observed.

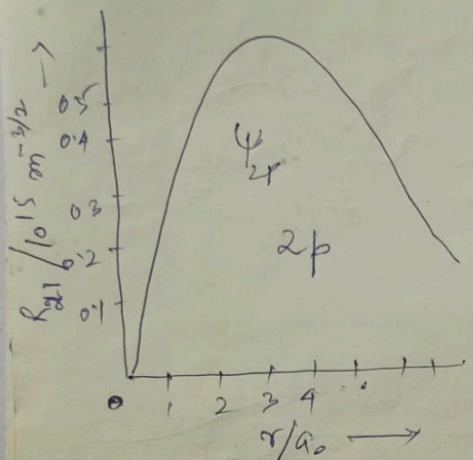
Plots of function of p-type

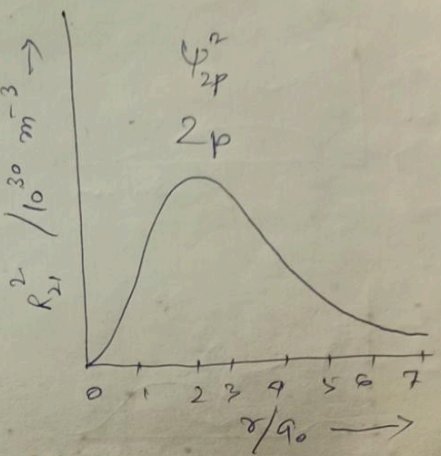
The various functions of p-type ($l=1$) with the same value of n but with different values of m will have the same radial distribution function since the latter depends only on the values of n and l and not on the value of m. For $n=2$, the radial distribution function is

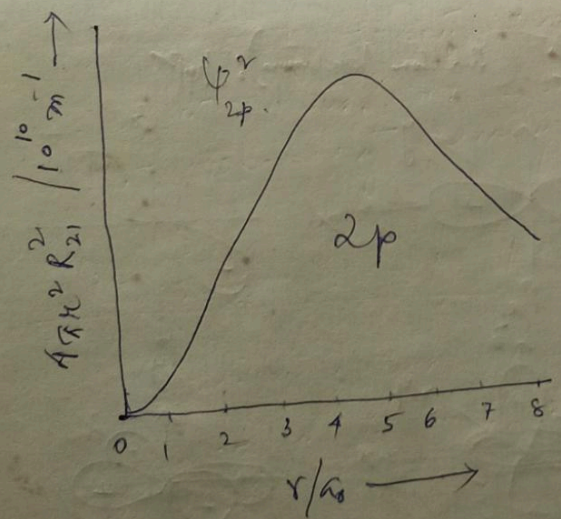
$$R_{2,1} = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \exp\left(-Zr/2a_0\right)$$

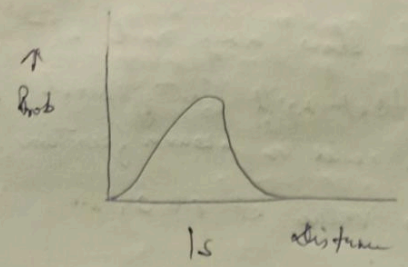
The 2p- wave functions will not show any node at finite values of r. This is consistent with the general formula $(n-l-1)$ for the number of nodes in a wave function.

(ii) The 2p- wave functions have zero value at $r=0$.

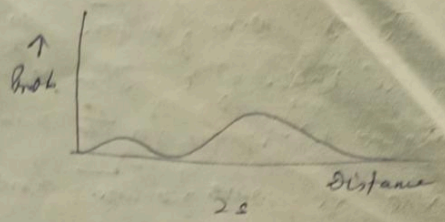




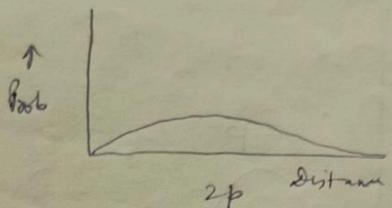




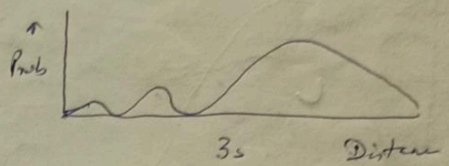
1s



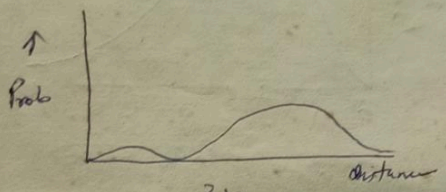
2s



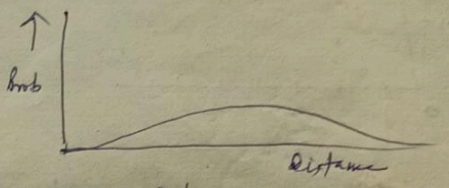
2p



3s



3p



3d

Shapes of Atomic orbitals (Ballon picture): 1s 2p