



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

PROBLEM 1 Determine the form of function R for the values of $n = 2$ and $l = 0$.

Substituting the given values of n and l in Eq. (29), we get

$$R_{2,0} = - \left\{ \left(\frac{2Z}{2a_0} \right)^3 \frac{(2 - 0 - 1)!}{2 \times 2 [(2 + 0)!]^3} \right\}^{1/2} \rho^0 e^{-\rho/2} L_2^1$$

where L_2^1 as given by Eq. (24) is

$$L_2^1 = \frac{d}{d\rho} L_2$$

where L_2 as given by Eq. (25) is

$$L_2 = e^\rho \frac{d^2}{d\rho^2} (\rho^2 e^{-\rho})$$

Now working in the reverse direction, we have

$$\begin{aligned} L_2 &= e^\rho \frac{d}{d\rho} \left\{ \frac{d}{d\rho} (\rho^2 e^{-\rho}) \right\} \\ &= e^\rho \frac{d}{d\rho} (2\rho e^{-\rho} - \rho^2 e^{-\rho}) \\ &= e^\rho (2 e^{-\rho} - 2\rho e^{-\rho} - 2\rho e^{-\rho} + \rho^2 e^{-\rho}) \\ &= (2 - 4\rho + \rho^2) \end{aligned}$$

$$L_2^1 = \frac{d}{d\rho} L_2 = \frac{d}{d\rho} (2 - 4\rho + \rho^2) = -4 + 2\rho,$$

Finally, since $\rho = \left(\frac{2Z}{n a_0} \right) r = \left(\frac{Z r}{a_0} \right)$, we have

$$\begin{aligned} R_{2,0} &= - \left\{ \left(\frac{Z}{a_0} \right)^3 \frac{1}{4 \times 8} \right\}^{1/2} e^{-\rho/2} (-4 + 2\rho) \\ &= \left(\frac{Z}{2a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \end{aligned}$$

Following the method given in Problem 1 , other functions with different values of n and l can be determined. Table 1 includes some such functions.



Quantization of Electronic Energies: The Hydrogen atom problem

Table 1 A FEW NORMALIZED $R_{n,l}$ FUNCTIONS

n	l	$R_{n,l}$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} \exp(-Zr/a_0)$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) \exp(-Zr/2a_0)$
2	1	$\frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) \exp(-Zr/2a_0)$
3	0	$\frac{2}{3}\left(\frac{Z}{3a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2}\right) \exp(-Zr/3a_0)$
3	1	$\frac{2\sqrt{2}}{9}\left(\frac{Z}{3a_0}\right)^{3/2} \left(\frac{2Zr}{a_0} - \frac{Z^2 r^2}{3a_0^2}\right) \exp(-Zr/3a_0)$
3	2	$\frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2} \left(\frac{Z^2 r^2}{a_0^2}\right) \exp(-Zr/3a_0)$

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

Energy of the Electron :

The allowed values of energy of the electron can be obtained from Eq. 22 and Eq.23. From Eq.23, we get

$$\alpha = \frac{4\pi^2\mu Z e'^2}{nh^2}, \quad (\text{since } \lambda = n)$$

Substituting this in Eq.22, we get

$$\left(\frac{4\pi^2\mu Z e'^2}{nh^2}\right)^2 = -\frac{8\pi^2\mu E}{h^2}$$

Cancelling the common terms, we get

$$E = -\frac{1}{n^2} \left(\frac{2\pi^2\mu Z^2 e'^4}{h^2}\right) \dots\dots\dots(35)$$

Eq.35 is identical with that derived earlier from the Bohr's theory. Thus, the energy of the electron depends on the value of the principal quantum number n and is independent of the values of l and m . Since the quantum number n appears only in the function $R(r)$, we conclude



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

that the energy depends only on the distance of the electron from the nucleus and not on its angular dependence.

A Summary of the Quantum Mechanical Treatment of the Hydrogen –like systems

1. To describe the mechanical state of the hydrogen –like system, 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. If the function ψ is 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. The latter one is of interest to us as it would give us the wave functions of the electron and the associated energies.

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 θ and ϕ involves only 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 restrictions are introduced. These restrictions appear in the form of quantum numbers.

5a. The function R depends only on r, therefore, they describe the radial distributions of the electron. These functions depend upon two quantum numbers, n and l. The permitted values of these numbers are:

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

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

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

(b) The function Θ depends only on the 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 $0, \pm 1, \pm 2, \dots, \pm l$, the Θ functions depend only on the magnitude of m, i.e., $|m|$.



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

(c) The functions 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_e which constitutes what is known as an orbital, depends on the quantum number n, l and m , i.e., we have different ψ_e functions (or orbitals) for different values of n, l and m and hence different behavior of the electron in the atom.

6a. The principal quantum number describes the energy of the electron in the hydrogen-like systems and is given by the relation

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

$$\text{where } a_0 = h^2/4\pi^2\mu e'^2$$

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

$$L^2 = l(l+1)(h/2\pi)^2$$

It is customary to design the values of l by letter as given below:

Value of l :	0	1	2	3
designation:	s	p	d	f
spectroscopic terms :	sharp	principal	diffuse	fundamental

The letter s,p,d and f are derived from the spectroscopic terms; sharp principal, diffuse and fundamental, respectively.

(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_e 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.

*** It can be noted that for all states in which $l=0$ i.e., for all s orbitals, the orbital angular momentum has a zero value (this is not possible in the Bohr's theory). The orbital motion of the electron in s orbitals without angular momentum is difficult to visualize in classical terms**



Quantization of Electronic Energies: The Hydrogen atom problem

Sl no	n	l	m	E	
i	n=1	l=0	m =0	$E = - \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$	
ii	n=2	l=0	m =0	$E = - \frac{1}{4} \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$ (Four- fold degenerate)	
			m =+1		
		l=1	m =0		
			m =-1		
iii	n=3	l=0	m =0	$E = - \frac{1}{9} \left(\frac{2\pi^2\mu Z^2 e^4}{h^2} \right)$ (Nine- fold degenerate)	
			l=1		m =0
					m =+1
		l=1	m =-1		
			l=2		m =0
					m =+1
		l=2	m =-1		
			m =+2		
m =-2					

Thus, the degeneracy of orbitals for given value of n is equal to n².

Pictorial Representations 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 function $R_{n,l}$, $\Theta_{l,|m|}$ and Φ_m describe the r , θ , ϕ dependences, respectively. 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 dependency of the wave function. A few R , Θ , Φ functions have been given in table 1, 2 and 3

Table 1 A FEW NORMALIZED $R_{n,l}$ FUNCTIONS

n	l	$R_{n,l}$
1	0	$2 \left(\frac{Z}{a_0} \right)^{3/2} \exp(-Zr/a_0)$
2	0	$\left(\frac{Z}{2a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) \exp(-Zr/2a_0)$
2	1	$\frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) \exp(-Zr/2a_0)$
3	0	$\frac{2}{3} \left(\frac{Z}{3a_0} \right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2 r^2}{9a_0^2} \right) \exp(-Zr/3a_0)$
3	1	$\frac{2\sqrt{2}}{9} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{2Zr}{a_0} - \frac{Z^2 r^2}{3a_0^2} \right) \exp(-Zr/3a_0)$
3	2	$\frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \left(\frac{Z^2 r^2}{a_0^2} \right) \exp(-Zr/3a_0)$

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

Table 2: A few normalized $\Theta_{J,m}$ functions

J	m	$\Theta_{J,m}$
0	0	$\sqrt{2}/2$
1	0	$(\sqrt{6}/2) \cos \theta$
1	± 1	$(\sqrt{3}/2) \sin \theta$
2	0	$(\sqrt{10}/4) (3 \cos^2 \theta - 1)$
2	± 1	$(\sqrt{15}/2) \sin \theta \cos \theta$
2	± 2	$(\sqrt{15}/4) \sin^2 \theta$



Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

Table 3: A few normalized Φ_m Functions

m	Φ_m
0	$1/\sqrt{2\pi}$
+ 1	$(1/\sqrt{2\pi}) \exp(i\varphi)$
- 1	$(1/\sqrt{2\pi}) \exp(-i\varphi)$
+ 2	$(1/\sqrt{2\pi}) \exp(i2\varphi)$
- 2	$(1/\sqrt{2\pi}) \exp(-i2\varphi)$

Two important features may be pointed out. These are :

1. The angular dependence depends on the quantum numbers l and m and not at all on the principal quantum number n . Thus, the angular dependence of the functions with different values of n but the same values of l and m is identical.
2. The angular part of the wave function for an s-orbital is a constant $(1/4\pi)^{1/2}$ with no θ and φ dependence for all value of n . Thus, the functions $\psi_{1s}, \psi_{2s}, \psi_{3s}, \dots$ (or simply $1s, 2s, 3s, \dots$ orbitals) depend only on r and are spherically symmetrical.

Plot of functions of s-type: since for s- orbitals

$$\psi_{n,0,0} = (1/4\pi)^{1/2} R_{n,0}$$

the plot of $\psi_{n,0,0}$ versus r will have the same form as those of R versus r . Figure 3 shows the two-dimensional plots of functions R_{1s} and R_{2s} as a function of r . In three dimension the diagram will include the plots shown in Figure 3 all around the nucleus.

The function ψ_{1s} simply shows the exponential decay with r as its form is $2(Z/a_0)^{3/2} \exp(-Zr/a_0)$. The function ψ_{2s} is not as simple. It contains a constant term $(Z/2a_0)^{3/2}$ and the term $(2 - Zr/a_0) \exp(-Zr/2a_0)$. The exponential factor of this function is just half of the corresponding exponential factor of the function, ψ_{1s} , thus the value of ψ_{2s} decreases more slowly as compare to that of ψ_{1s} . Besides this, the factor $(2 - Zr/a_0)$ introduces the new feature in the function ψ_{2s} . Depending upon the value of Zr/a_0 , the function ψ_{2s} can be positive or zero or negative, i.e, if

$Zr/a_0 < 2$, ψ_{2s} is positive; true for small values of r

$Zr/a_0 > 2$, ψ_{2s} is negative; true for large values of r

$Zr/a_0 = 2$, ψ_{2s} is zero; true for at one particular values of r

The point where the function has a zero value is known as the **nodal point**. In general, the number of nodal point points in the radial function $R_{n,l}$ is equal to $(n-l-1)$.

In chemistry the plots of probability density are more meaningful than the plots of the functions themselves. The probability density is given as $\psi^*\psi$, where ψ^* is the complex conjugate of ψ which is obtained by replacing i by $-i$. If the function does not involve i , then $\psi^*\psi$ is simply equal to ψ^2 . Figure 4 shows the probability density plots for 1s and 2s orbitals.

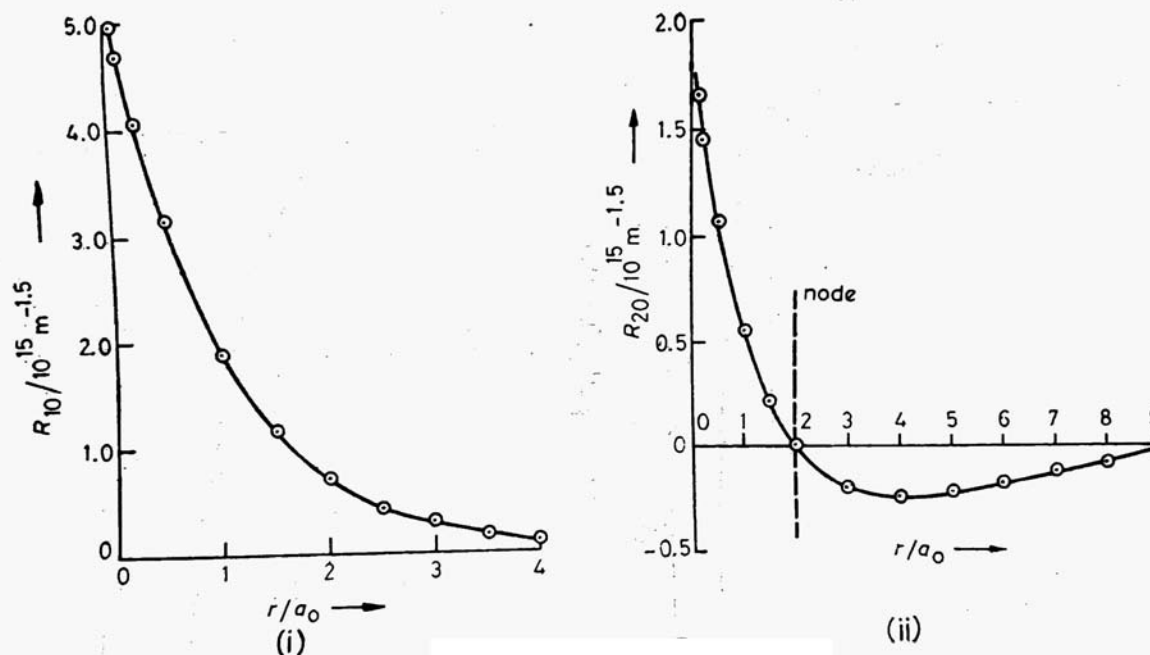


Figure 3 : Plots of functions (i) R_{1s} (ii) R_{2s}

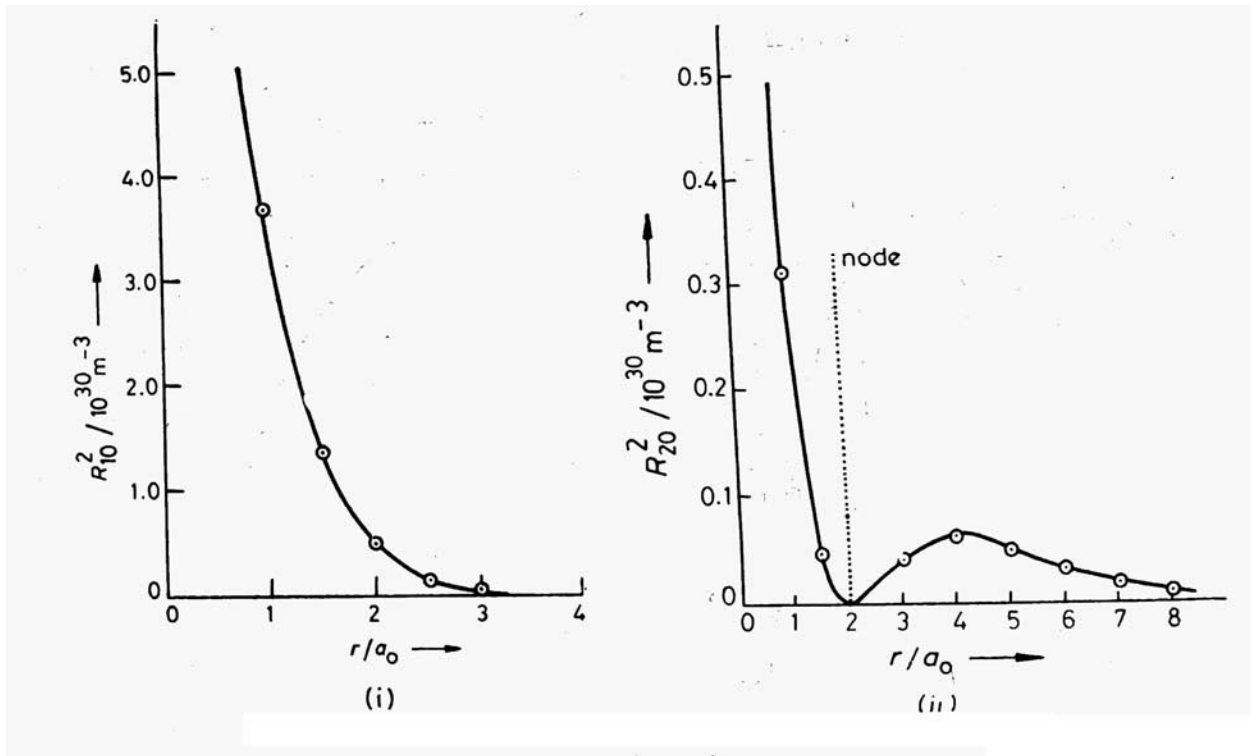


Figure 4 : Probability density distribution for the electron in 1s and 2s orbitals of the hydrogen atom

It can be seen from Figure 4 that for both 1s and 2s orbitals, 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.

Three dimensional plots of $\psi^*\psi$ versus r are shown by either dot -population picture, (or the cloud density pattern) or by the equal -probability contour (or the boundary surface) plots. In the dot -population picture , we exhibit the relative probability at a given location by the density of dots near that location, For 1s and 2s orbitals, these dot population pictures are shown in figure 5

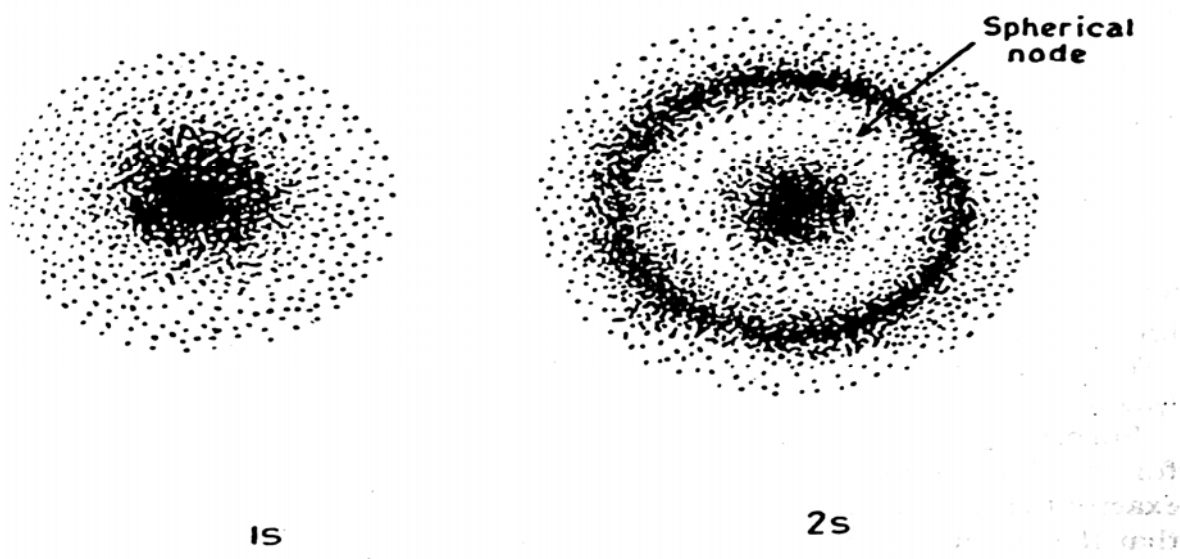


Figure 5: The dot-population pictures (or the cloud density patterns) for 1s and 2s orbitals

The dot- population pictures give the most realistic description of the electron's time average distribution.

In the equal-probability contour, we draw the contours by joining the points of identical probability. For s -orbitals, these contour are spherical in nature. If we are contended with a total of 90% probability (a fairly large probability) of finding the electron, we can draw a contour within which there exists a total of 90% probability of finding the electron. This gives us a definite shape in three dimensions and is known as the shape of the orbital. Note that if we want o account for 100% probability, we have to cover a very large distance from the nucleus, theoretically up to infinity. For 1s and 2s orbitals, the 90% probability contours are shown in figure 6.

Through the probability of finding the electron in s- orbitals is maximum near to the nucleus, the total amount of the dot population (or the electronic cloud) near the nucleus is very small owing to the small volume near the nucleus. In order to visualize the total amount of the cloud within a spherical shell placed at radii r and $r+dr$ from the nucleus, we define the radial distribution function as

Radial distribution function = (volume of the spherical shell) (probability density)

$$= (4\pi r^2 dr) (\psi^2)$$

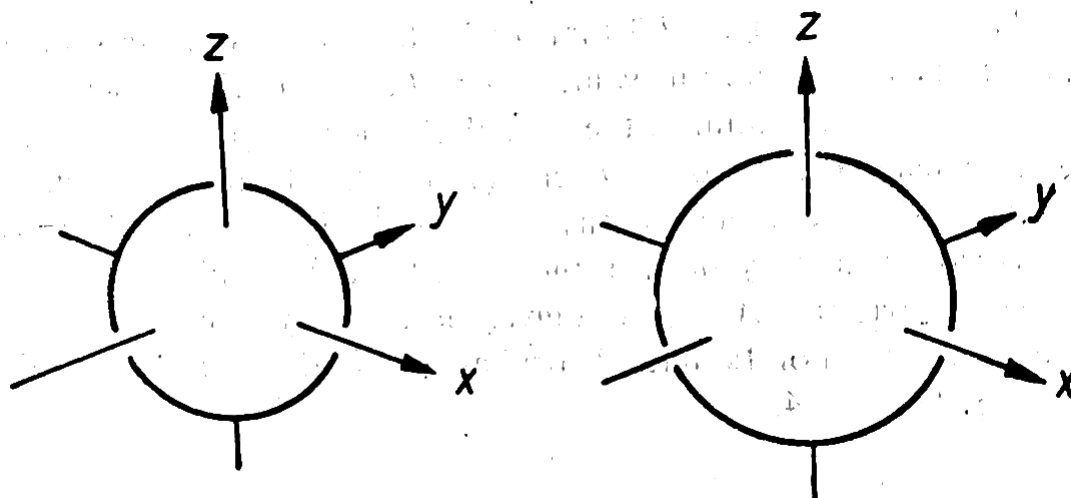


Figure 6: 90% probability contours for 1s and 2s orbitals

Thus, the radial distribution function describes the total probability of finding the electron in a spherical shell of thickness Δr and at the distance r from the nucleus. For 1s and 2s orbitals, the radial distribution versus r/a_0 plots are shown in figure 7.

Surprisingly, the r at which the maximum in the radial distribution plot for 1s orbital is observed is equal to a_0 , i.e., 52.9pm - value which is exactly the same as that calculated from the Bohr's theory. Thus, we see that the Bohr's concept of orbital is partially explained by the quantum mechanical treatment, but the very existence of the precise orbital in an atom has no place in the quantum mechanical treatment. What quantum mechanics says that the electron has some probability for its existence at all values of r , it but has a maximum value per unit radius ($dr=1$) at a distance $r= a_0$.

For the 2s orbital, there are two maxima in the radial distribution plot, one at about 0.04 nm and other at about 0.3 nm. The maximum at 0.04 nm is smaller than that at 0.3nm. In general, the number of maxima in the radial distribution plot of s orbitals is equal to the principal quantum number. Out of these maxima, the last maximum which is situated at the largest value of r has the maximum height and the others have very small heights.

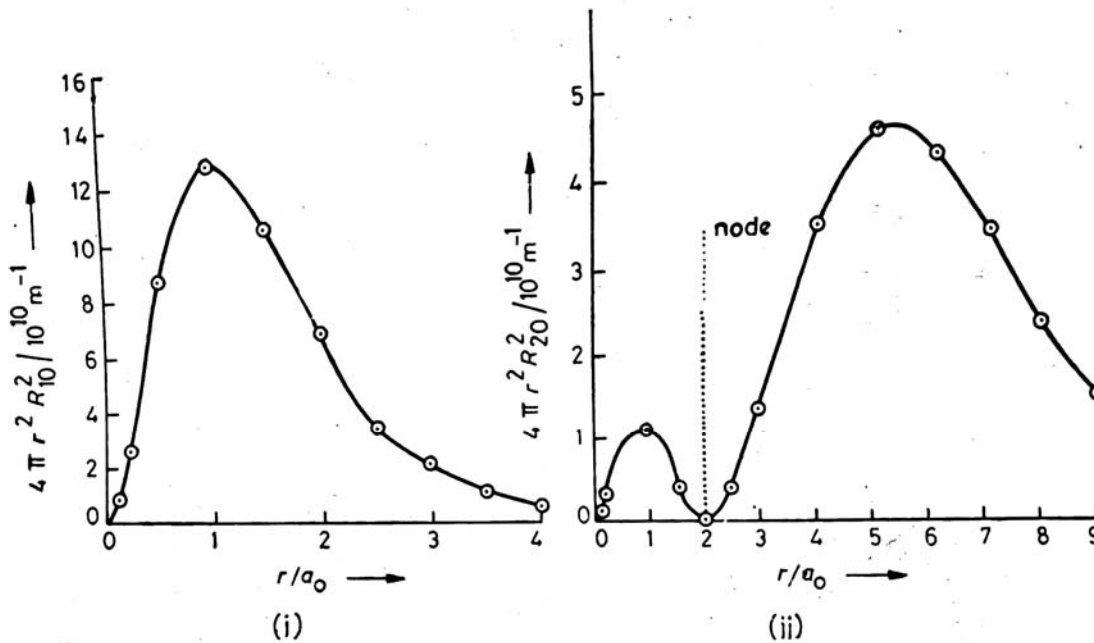
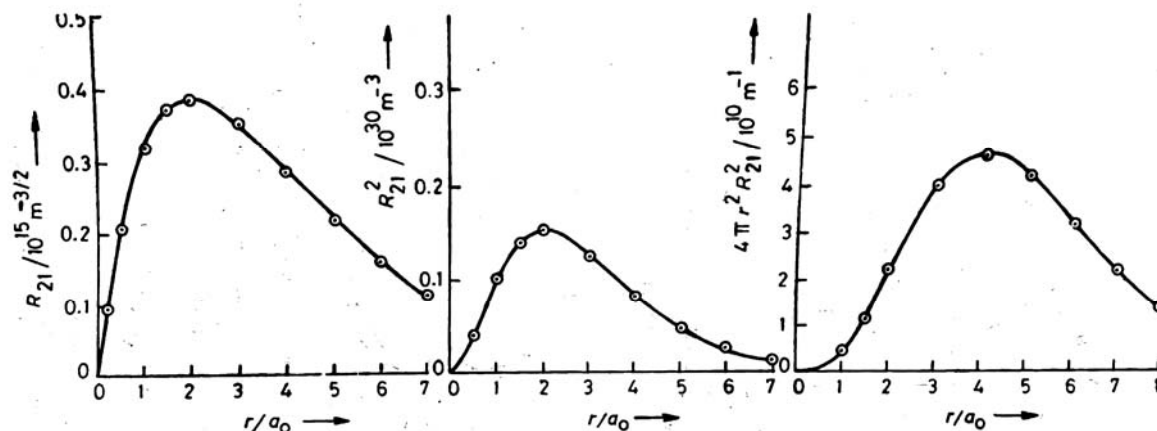


Figure 7: Radial distribution for the electron in 1s and 2s orbitals

p-type orbital :

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





Quantization of Electronic Energies: The Hydrogen atom problem

Semester IV

Figure 8 : Plots of functions $R_{2,1}$, $R^2_{2,1}$ and $4\pi r^2 R^2_{2,1}$ versus r for the electron of hydrogen

Note: 1. The 2p wave function 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.

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

Figure 8 depicts the Plots of functions $R_{2,1}$, $R^2_{2,1}$ and $4\pi r^2 R^2_{2,1}$ versus r for the electron of hydrogen.