Module 1 : Atomic Structure

Lecture 5 : Wave Functions and Charge Densities.

Objectives

In this Lecture you will learn the following

- Qualitative features of the radial part of the hydrogen atom solutions (orbitals) graphically.
- Polar plots for the angular part of the atomic orbitals.
- Contour diagrams of atomic orbitals.
- Probability densities for various states.

5.1 Introduction

In lecture 4 we have seen the functional forms of the orbitals of the hydrogen atom. The radial and angular parts of the orbitals are the solutions to the radial and angular parts of the Schrödinger equation. In the present lecture, we will plot/sketch these orbitals to get a qualitative picture of the "*shapes*" and "*sizes*" of these orbitals.

Orbitals are the functions of the coordinates of one electron. These functions extend over the entire three dimensional space. The values of these functions (orbitals) are significant mainly in the small region of space (say, a volume of 5 x 5 x 5^7) around the nucleus. This does not mean that orbitals do not exist outside this volume.

Plots of the radial part of the orbitals of H-atom

In figure 5.1 we have shown the radial parts of hydrogenic orbitals. These are commonly written as R_{nl} (r). The distance from the nucleus is r, and n and *l* refer to the principal and angular momentum quantum numbers, respectively. When n = 1 and *l* = 0, it is the 1s orbital. This is an exponential function and it decays monotonically to zero from r = 0 to ∞ . The square of the radial part is also shown in an adjacent figure. If the 1s orbital decays with r as e^{-r} , the square decays faster as e^{-2r} .

The radial part of 2s (n = 2, *l* = 0) is shown in fig 5.1 . This function is the product of a linear function (2- ρ) and an exponential $e^{-\rho/2}$.

Here ρ = 2 Zr / n a_0 . Here, a_0 is the Bohr radius, = 0.529 $\mathring{A}$. In the previous lecture we used the symbol σ in place of ρ . Both these represent a scaled distance r in units of na_0 / 2Z . We have deliberatively used alternative symbols so that the emphasis is on forms of the functions and not symbols. For $\rho < 2$, the function is positive, the function = 0 when ρ = 2 and for $\rho > 2$, the function is negative and it asymptotically goes to zero . ρ = 2 corresponds to the node (value of the wavefunction or the orbital = 0).

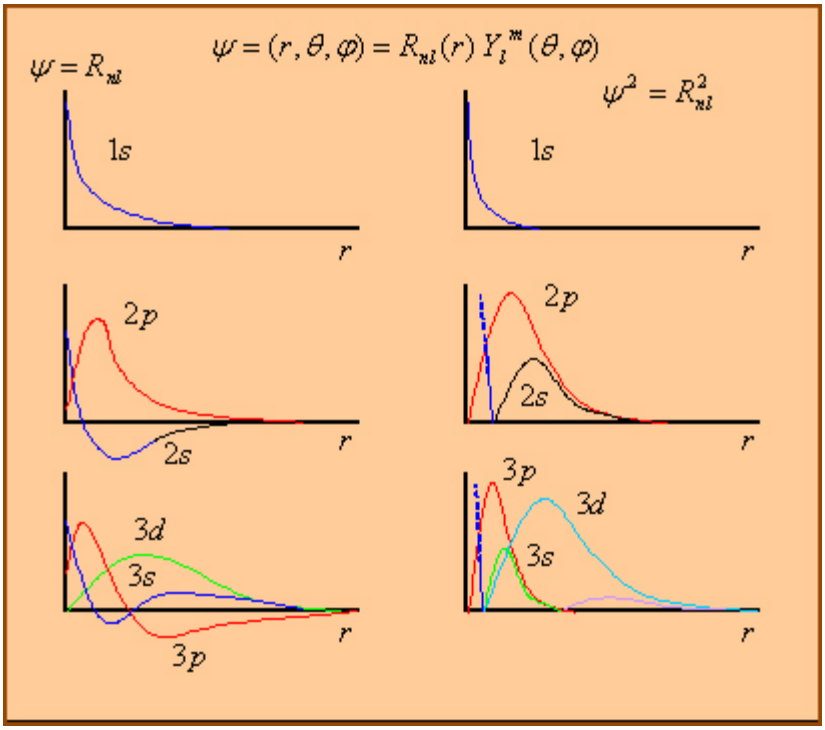

Figure 5.1 The radial parts of the orbitals for n = 1, 2, 3 and *l* = 0, 1 and 2. The squares of the orbitals are shown to the right.

The square of the function is shown in the adjoining figure. This function is positive throughout . The next function is R_{21} (r) which is the radial part of the 2p orbital. This function has the form $\rho e^{-\rho/2}$. The function rises from 0, reaches a maximum value and then asymptotically goes to zero as $\rho \rightarrow \infty$. This function goes to zero more slowly than $e^{-\rho/2}$ because of the multiplying factor ρ^2. Using the arguments given so far in this section, adjoining plots of $R_{n/}$ (r) and $R^2_{n/}$ (r) can be rationalized .

The 3s function has a quadratic function multiplying an exponential. The function crosses zero twice. The two crossing points are the roots of the quadratic equation $6 - 6\rho + \rho^2$. For higher values n, there will be polynomials of higher order multiplying the exponential part and the function will cross the ρ axis as many times as the zeros of the polynomial multiplying the exponential. The sketches of a few other radial parts are also shown in fig 5.1.

5.2 Polar plots of the Angular Part of Atomic Orbitals.

A very nice way of visualizing the angular parts of orbitals is through a polar plot. In a polar plot a circle of unit radius is drawn and from the center of the circle, several radii are drawn at various angles. The line vertically upwards is the θ = 0 line. The horizontal line towards the right is the $\theta = 90^0 = \pi/2$ line. To plot the Θ part of the orbital, the value of the normalized part of the orbital is marked on the radius corresponding to the particular value of θ . For example, the polar plot of $\cos\theta$ is shown in fig 5.2 . For θ = 0, $\cos\theta$ = 1 and the value of the function, 1, is at the tip of the radius at θ = 0, touching the circumference of the circle. For $\theta = \pi/4$, $\cos\theta = 1/\sqrt{2}$ and the value of 0.707 is marked . For $\theta = 90^0$, the value of zero is marked. For $\theta > \pi/2$, $\cos\theta$ is negative and only the magnitudes of $\cos\theta$ are marked on the radii. When all these points are joined we get a figure close to the shape of the number 8 as shown in Fig. 5.2

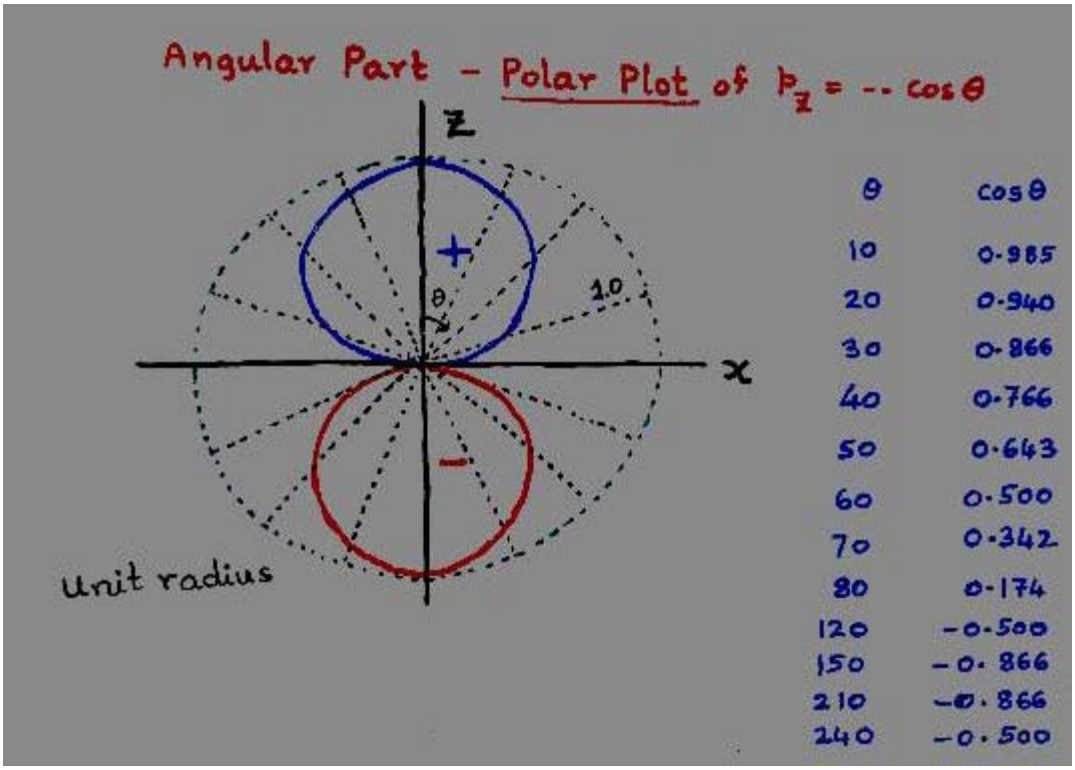

Figure 5.2 Polar plot of the $2p_z$ orbital. On a circle of unit radius, radii are drawn for various values of θ, the values of cos θ are marked on the radii and the points are joined.

The upper part is positive (value of cos θ >1) and the lower part is negative (cos θ <1) . This is the shape of the p_z orbital. In the figure, the values of cos θ are given for a few values of θ. Using the same procedure as indicated here, you can plot the polar plot of $3d_z^2$ orbital whose form is ½ (3 $\cos^2\theta$ - 1). The p_z orbital has a planar node corresponding to θ = 0 or the xy plane .

The polar plots help in clearly identifying the nodal surfaces. We can extend the idea of this polar plot to include the ϕ part of the orbital . But this would be a 3-dimensional plot and much harder to plot but not very difficult to visualize. It should be emphasized that these plots are qualitative. To get the quantitative numerical value of the orbitals, we need to substitute the value of r, θ and ϕ into the functional form of the orbital.

5.3 Density Distribution of Atomic Orbitals.

An accurate way of visualizing the orbitals is through a plot of the charge densities, which are given by e | Ψ | ^{2} or the probability densities, | Ψ | ^{2} . The plots of | Ψ | ^{2} in 3 dimensions are shown in fig 5.3. The regions where | Ψ | ^{2} is large are shown by dense dots and the regions where the density is small are shown by orbitals thin or sparse dots. The densities for 1s, 2s, 3s, $2p_x$, $2p_y$, $2p_z$, $3d_{xy}$, $3d_{x^2-y^2}$, $3d_{yz}$, $3d_{zx}$ and $3d_{z^2}$ are shown in figs 5.3 (a) to 5.3 (k). The spherical nodes of 2s and 3s can be easily identified. The planar nodes of 2p and four of the 3d orbitals can easily be identified. For the $3d_{z^2}$ orbital, the nodes are conical in shape and the angles of the two conical surfaces from the vertical z- axis are given by the two roots of the function (1/2) (3 $\cos^2\theta$ – 1). Another useful way of visualizing the orbitals is through boundary surfaces.

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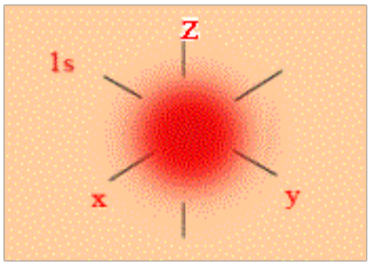

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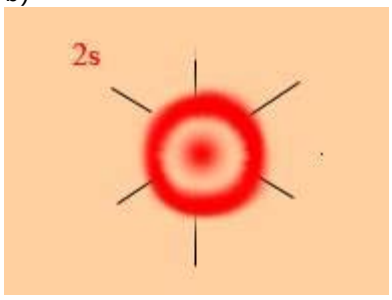

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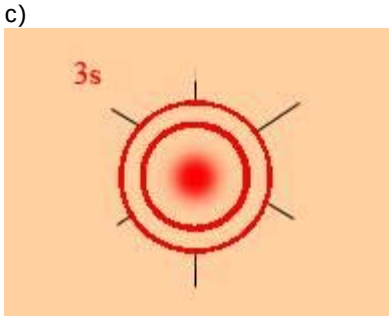

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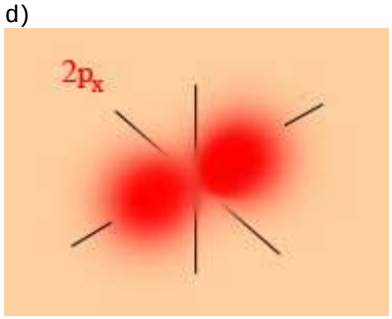

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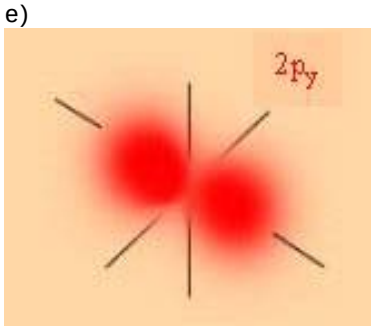

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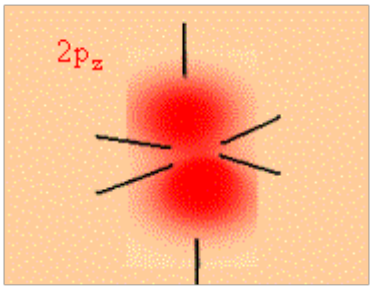

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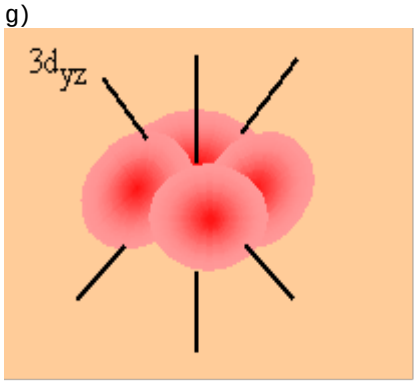

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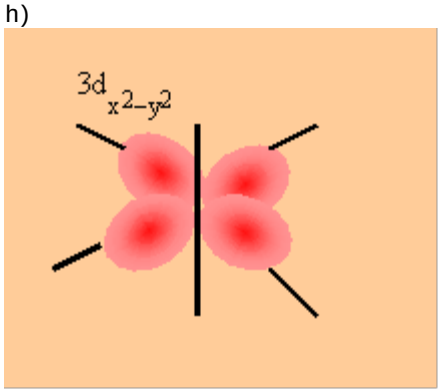

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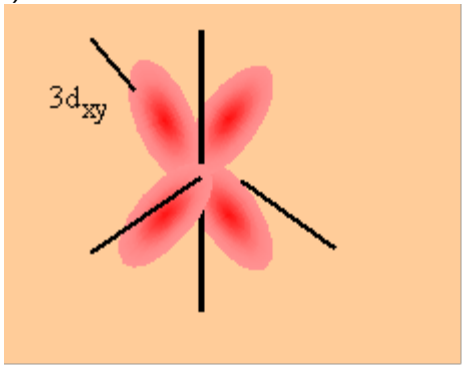

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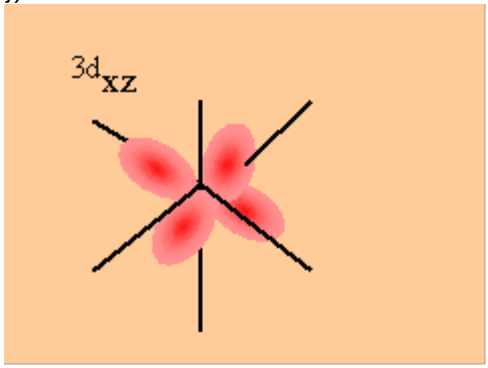

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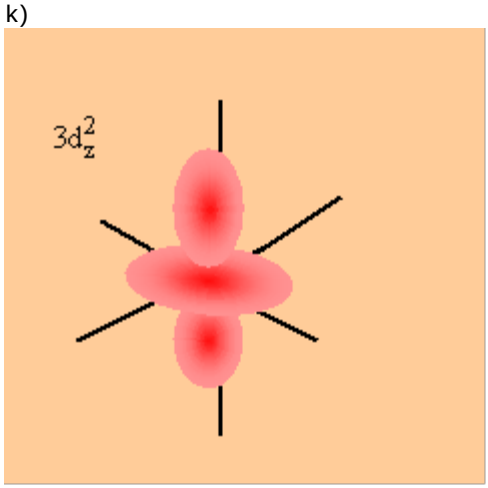
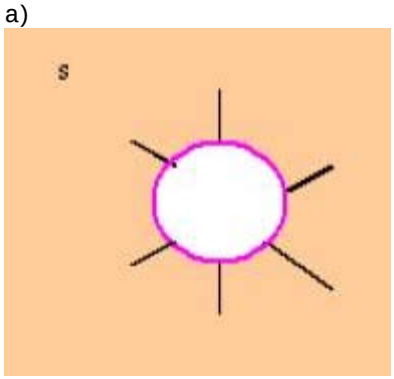


Figure 5.3 (a),….(k). The plots of the probability densities of 1s, 2s,….3d ^2_z orbitals.

A boundary surface is a surface which includes more than 95% or 99 % of the charge density of the electron inside it .The value of the percentage is of course arbitrary, but this region gives a good quantitative measure of the space inside which there is a high probability of finding the corresponding electron.

The boundary surfaces for the s, p and d orbitals are shown in fig 5.4. This does not mean that the electron can not be found outside this surface. It only means that the probability is small. If some other object approaches the atom, the electron, under the influence of the object, can easily come out of this surface or another electron can enter this surface. These influences lie at the heart of all chemical processes.

a)



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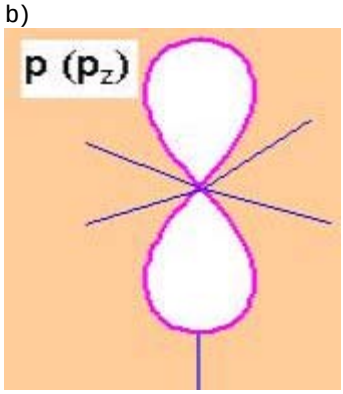

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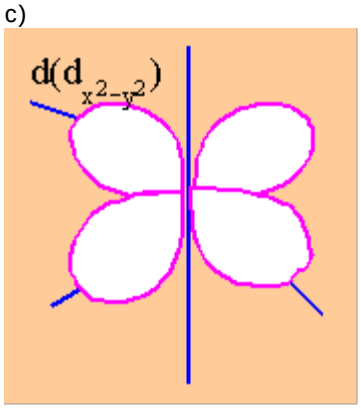

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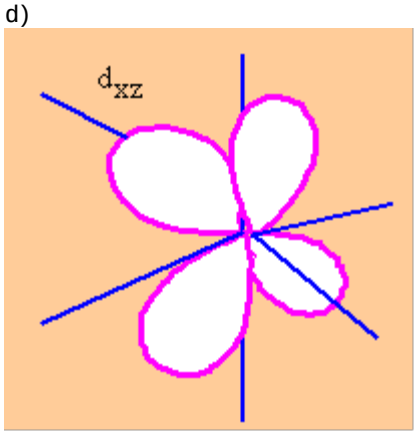

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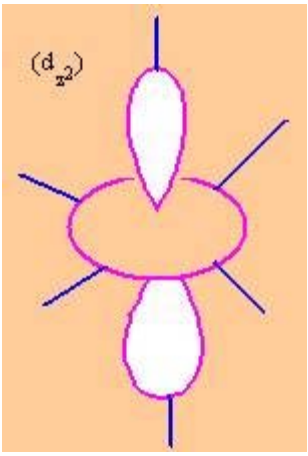

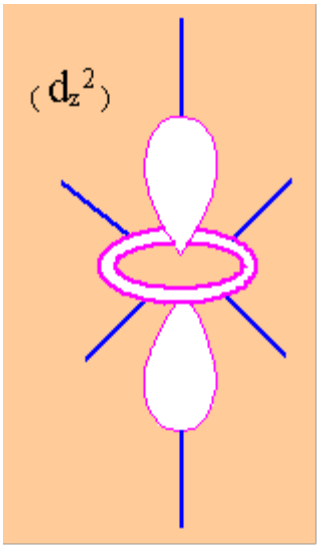

Figure 5.4 Boundary surfaces of s, p and d orbitals.

5.4 The radial distribution functions.

A convenient way of visualizing the electron density is through a plot of the radial distribution function. The radial distribution function is defined by

$P(r) = 4 \pi r^2 |\Psi|^2$

The value of $P(r)$ is the probability density of finding the electron in a spherical shell at a distance r, or ..... $4 \pi r^2 |\Psi|^2 dr$ gives the probability of finding the electron in a spherical shell of radius r and thickness dr. A sketch of 1s orbital is shown in Fig. 5.5.

(a) $|\Psi|^2$

Figure 5.5 1s orbital.

Figure 5.5 (a) a plot of $|\Psi|^2$, (b) $4\pi r^2 |\Psi|^2$ Notice how the maxima in (a) and (b) are at completely different locations. Can you rationalize the difference? This radial distribution function is a product of an increasing function and a decreasing function.

Finally we comment on the shapes of the nodes once again. 1s orbital has no node. 2s has a spherical node. The 2p orbitals have a planar node. The planar or the angular node of a $2p_z$ orbital is shown in Fig 5.6.

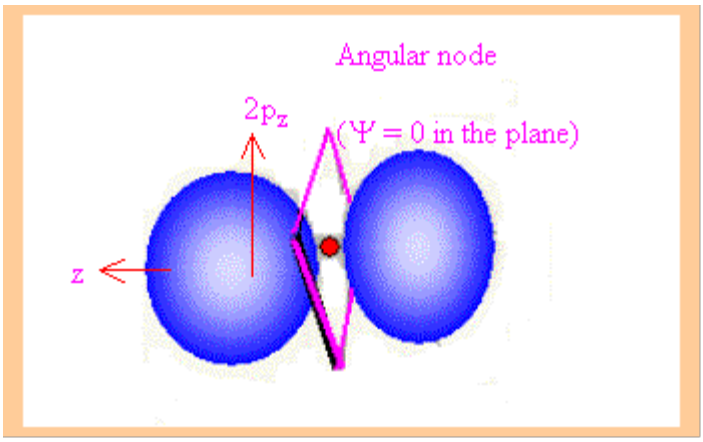

Figure 5.6 The nodal plane of a $2p_z$ orbital.

5.5 Problems

5.1) List the number of radial nodes and angular nodes in the following orbitals. a) 3p, b) 4d, c) 5s, d) 4f and e) 5f

5.2) Obatin the formulae for the angular parts of the 4f orbitals (from reference books) and for any one of them, determine the shapes and the locations of the angular nodes.

5.3) Although the p, d,f,g ---- orbitals do not have spherical symmetry, all atoms on the average are spherically symmetrical. Can you justify and rationalize this observation?

5.4) Qualitatively, sketch the radial parts of 4d and 5f orbitals. Even if the formulae ar not known, you can see the trends in 1s , 2s, 3s; 2p, 3p, 4p; 3d, 4d---- and arrive at these radial forms using inductive reasoning.

5.5) In the case of a $2p_z$ orbital, at what point in space is the probability of finding the electron greatest ? (Do not use the radial probability density, but use the probability density, $|\Psi|^2$)

5.6) For a hydrogen like atom (nuclear charge +Ze , $Z \geq 1$ and only one electron present), the 1s orbital has the form $\Psi_{1s}(r) = (z^3 / \pi a_0^3)^{1/2} \exp(-z\, r / a_0)$. Obtain the most probable distance for finding the electron from the nucleus using the radial distribution function . Compare the values of this distance for n = 1, 2, 10, 18, 36 and 90.

Recap

In this lecture you would have learnt the following

Summary

In this lecture, you have been introduced to the pictorial representation of atomic orbitals of hydrogen like atoms. Plots of radial parts of the wavefunction and their squares as well as the radial probability densities have been shown as a function of r. The theta part of the wavefunction was plotted as a polar plot. The polar plot gives a good idea of the shapes of orbitals as well as the structures of their nodes. The charge density plots and the boundary surfaces of the orbitals give an idea of the variation of the probability density in space and the region in space wherein the probability of finding an electron is very large (say 99%).