

8.2: The Wavefunctions

The solutions to the hydrogen atom Schrödinger equation are functions that are products of a **spherical harmonic function** and a **radial function**.

$$\psi_{n,l,m_l}(r, \theta, \varphi) = R_{n,l}(r)Y_l^{m_l}(\theta, \varphi) \quad (8.2.1)$$

The wavefunctions for the hydrogen atom depend upon the three variables r , θ , and φ and the three quantum numbers n , l , and m_l . The variables give the position of the electron relative to the proton in spherical coordinates. The absolute square of the wavefunction, $|\psi(r, \theta, \varphi)|^2$, evaluated at r , θ , and φ gives the probability density of finding the electron inside a differential volume $d\tau$, centered at the position specified by r , θ , and φ .

Exercise 8.2.1

What is the value of the integral

$$\int_{\text{all space}} |\psi(r, \theta, \varphi)|^2 d\tau ?$$

The quantum numbers have names: n is called the **principal quantum number**, l is called the **angular momentum quantum number**, and m_l is called the magnetic quantum number because (as we will see in [Section 8.4](#)) the energy in a magnetic field depends upon m_l . Often l is called the **azimuthal quantum number** because it is a consequence of the θ -equation, which involves the azimuthal angle Θ , referring to the angle to the zenith.

These quantum numbers have specific values that are dictated by the physical constraints or boundary conditions imposed upon the Schrödinger equation: n must be an integer greater than 0, l can have the values 0 to $n-1$, and m_l can have $2l + 1$ values ranging from $-l$ to $+l$ in unit or integer steps. The values of the quantum number l usually are coded by a letter: s means 0, p means 1, d means 2, f means 3; the next codes continue alphabetically (e.g., g means $l = 4$). The quantum numbers specify the quantization of physical quantities. The discrete energies of different states of the hydrogen atom are given by n , the magnitude of the angular momentum is given by l , and one component of the angular momentum (usually chosen by chemists to be the z-component) is given by m_l . The total number of orbitals with a particular value of n is n^2 .

Exercise 8.2.2

Consider several values for n , and show that the number of orbitals for each n is n^2 .

Exercise 8.2.3

Construct a table summarizing the allowed values for the quantum numbers n , l , and m_l for energy levels 1 through 7 of hydrogen.

Exercise 8.2.4

The notation 3d specifies the quantum numbers for an electron in the hydrogen atom. What are the values for n and l ? What are the values for the energy and angular momentum? What are the possible values for the magnetic quantum number? What are the possible orientations for the angular momentum vector?

The hydrogen atom wavefunctions, $\psi(r, \theta, \varphi)$, are called **atomic orbitals**. An atomic orbital is a function that describes one electron in an atom. The wavefunction with $n = 1$, $l = 0$, and $m_l = 0$ is called the 1s orbital, and an electron that is described by this function is said to be “in” the 1s orbital, i.e. have a 1s orbital state. The constraints on n , l , and m_l that are imposed during the solution of the hydrogen atom Schrödinger equation explain why there is a single 1s orbital, why there are three 2p orbitals, five 3d orbitals, etc. We will see when we consider multi-electron atoms in [Chapter 9](#) that these constraints explain the features of the Periodic Table. In other words, the Periodic Table is a manifestation of the Schrödinger model and the physical constraints imposed to obtain the solutions to the Schrödinger equation for the hydrogen atom.

Visualizing the variation of an electronic wavefunction with r , θ , and φ is important because the absolute square of the wavefunction depicts the charge distribution (electron probability density) in an atom or molecule. The charge distribution is central to chemistry because it is related to chemical reactivity. For example, an electron deficient part of one molecule is attracted to an electron rich region of another molecule, and such interactions play a major role in chemical interactions ranging from substitution and addition reactions to protein folding and the interaction of substrates with enzymes.

Visualizing wavefunctions and charge distributions is challenging because it requires examining the behavior of a function of three variables in three-dimensional space. This visualization is made easier by considering the radial and angular parts separately, but plotting the radial and angular parts separately does not reveal the shape of an orbital very well. The shape can be revealed better in a probability density plot. To make such a three-dimensional plot, divide space up into small volume elements, calculate $\psi^*\psi$ at the center of each volume element, and then shade, stipple or color that volume element in proportion to the magnitude of $\psi^*\psi$. Do not confuse such plots with polar plots, which look similar.

Probability densities also can be represented by contour maps, as shown in Figure 8.2.1.

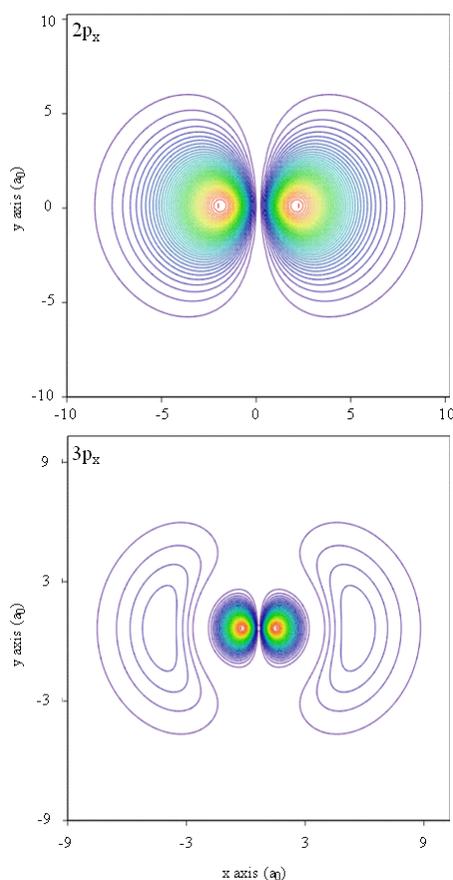


Figure 8.2.1: Contour plots in the x - y plane for the $2p_x$ and $3p_x$ orbitals of the hydrogen atom. The plots map lines of constant values of $R(r)^2$; red lines follow paths of high $R(r)^2$, blue for low $R(r)^2$. The angular function used to create the figure was a linear combination of two Spherical Harmonic functions (see Problem 10 at the end of this chapter.)

Another representational technique, virtual reality modeling, holds a great deal of promise for representation of electron densities. Imagine, for instance, being able to experience electron density as a force or resistance on a wand that you move through three-dimensional space. Devices such as these, called haptic devices, already exist and are being used to represent scientific information. Similarly, wouldn't it be interesting to "fly" through an atomic orbital and experience changes in electron density as color changes or cloudiness changes? Specially designed rooms with 3D screens and "smart" glasses that provide feedback about the direction of the viewer's gaze are currently being developed to allow us to experience such sensations.

Methods for separately examining the radial portions of atomic orbitals provide useful information about the distribution of charge density within the orbitals. Graphs of the radial functions, $R(r)$, for the 1s, 2s, and 2p orbitals plotted in Figure 8.2.2

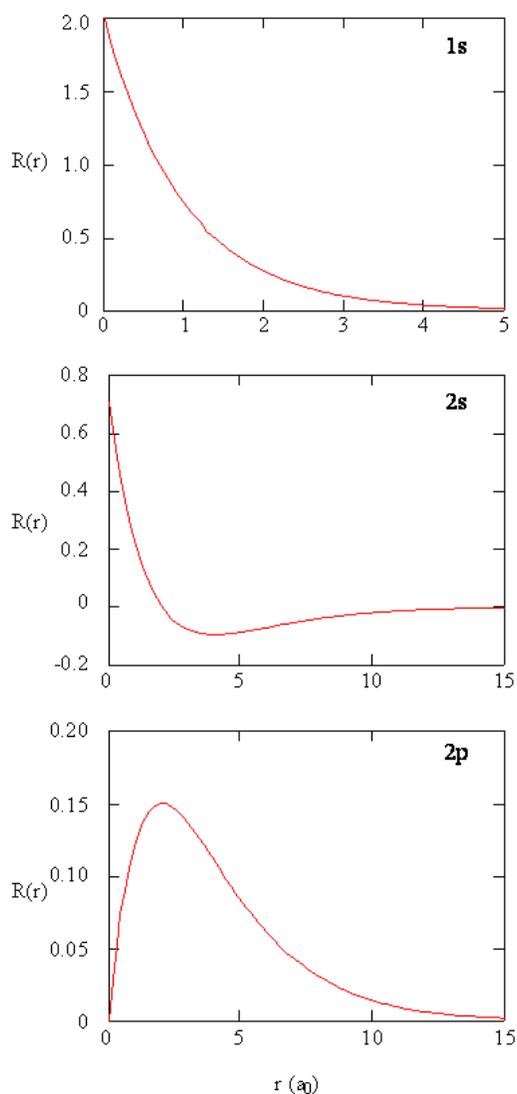


Figure 8.2.2: Radial function, $R(r)$, for the 1s, 2s, and 2p orbitals.

The 1s function in Figure 8.2.2 starts with a high positive value at the nucleus and exponentially decays to essentially zero after 5 Bohr radii. The high value at the nucleus may be surprising, but as we shall see later, the probability of finding an electron at the nucleus is vanishingly small.

Next notice how the radial function for the 2s orbital, Figure 8.2.2, goes to zero and becomes negative. This behavior reveals the presence of a radial node in the function. A radial node occurs when the radial function equals zero other than at $r = 0$ or $r = \infty$. Nodes and limiting behaviors of atomic orbital functions are both useful in identifying which orbital is being described by which wavefunction. For example, all of the s functions have non-zero wavefunction values at $r = 0$, but p, d, f and all other functions go to zero at the origin. It is useful to remember that there are $n - 1 - l$ radial nodes in a wavefunction, which means that a 1s orbital has no radial nodes, a 2s has one radial node, and so on.

Exercise 8.2.5

Examine the mathematical forms of the radial wavefunctions. What feature in the functions causes some of them to go to zero at the origin while the s functions do not go to zero at the origin?

Exercise 8.2.6

What mathematical feature of each of the radial functions controls the number of radial nodes?

Exercise 8.2.7

At what value of r does the 2s radial node occur?

Exercise 8.2.8

Make a table that provides the energy, number of radial nodes, and the number of angular nodes and total number of nodes for each function with $n = 1, 2,$ and 3 . Identify the relationship between the energy and the number of nodes. Identify the relationship between the number of radial nodes and the number of angular nodes.

The quantity $R(r) \cdot R(r)$ gives the **radial probability density**; i.e., the probability density for the electron to be at a point located the distance r from the proton. Radial probability densities for three types of atomic orbitals are plotted in Figure (\PageIndex{3}).

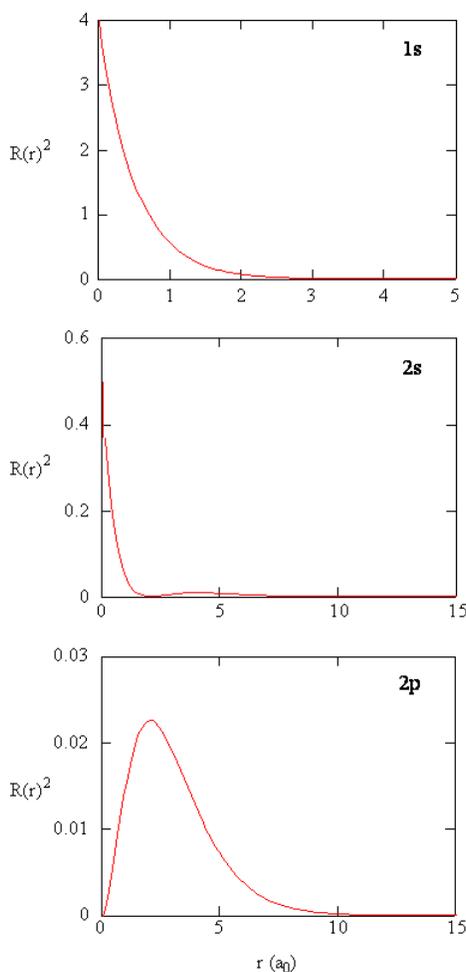


Figure 8.2.3: Radial probability densities for the 1s, 2s, and 2p orbitals.

When the radial probability density for every value of r is multiplied by the area of the spherical surface represented by that particular value of r , we get the radial distribution function. The radial distribution function gives the probability density for an electron to be found anywhere on the surface of a sphere located a distance r from the proton. Since the area of a spherical surface is $4\pi r^2$, the radial distribution function is given by $4\pi r^2 R(r) \cdot R(r)$.

Radial distribution functions are shown in Figure 8.2.4. At small values of r , the radial distribution function is low because the small surface area for small radii modulates the high value of the radial probability density function near the nucleus. As we

increase r , the surface area associated with a given value of r increases, and the r^2 term causes the radial distribution function to increase even though the radial probability density is beginning to decrease. At large values of r , the exponential decay of the radial function outweighs the increase caused by the r^2 term and the radial distribution function decreases.

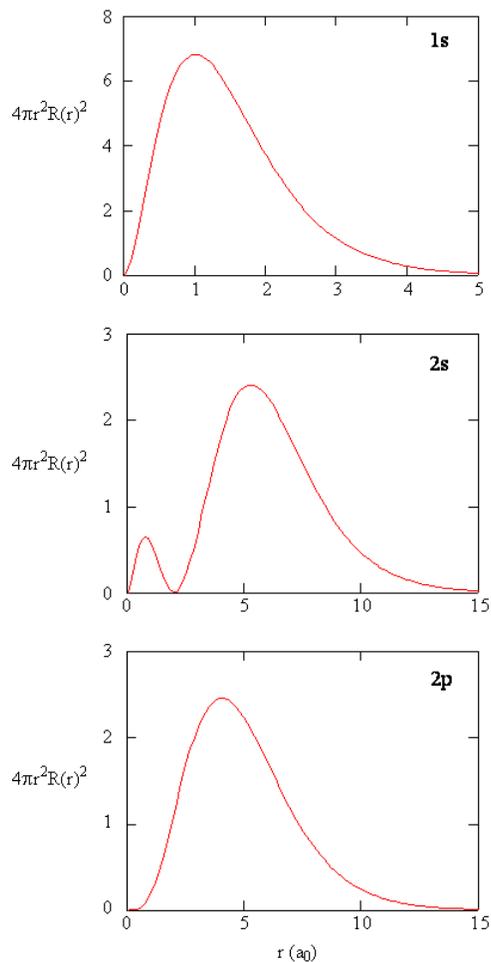


Figure 8.2.4: The radial distribution function for the 1s, 2s, and 2p orbitals.

Exercise 8.2.9

Write a quality comparison of the radial function and radial distribution function for the 2s orbital. See Figure (\PageIndex{5})

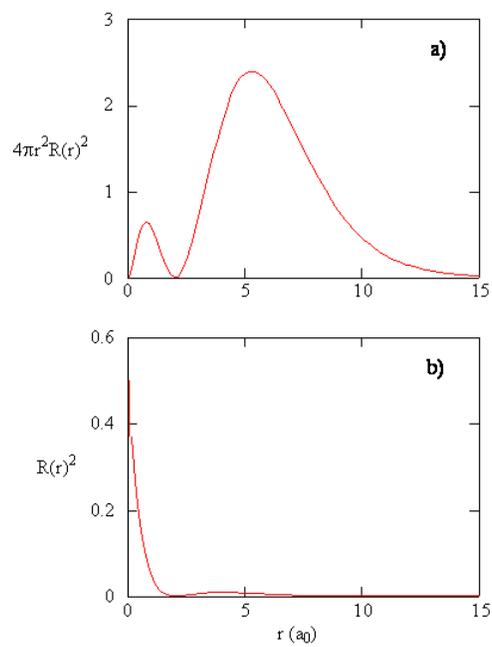


Figure 8.2.5: Comparison of a) the radial distribution function and b) the radial probability density for the 2s orbital.

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