

2.6: The Shapes of Atomic Orbitals

The shapes of atomic orbitals are important because chemical bonds depend on the sharing of the electrons that occupy these orbitals. In one model of chemical bonding, for example, a bond consists of the overlap of atomic orbitals on adjacent atoms. The shapes of the overlapping orbitals determine the shape of the molecule.

Although we limit ourselves in this chapter to the orbitals of the hydrogen atom, we will see in [Chapter 3](#) that the orbitals of all atoms can be approximated as being hydrogen-like and therefore have very similar shapes to those of hydrogen.

The shape of an atomic orbital is determined primarily by l , the angular momentum quantum number. Recall that each value of l is assigned a letter that corresponds to particular orbitals. For example, the orbitals with $l = 0$ are called s orbitals; those with $l = 1$, p orbitals; those with $l = 2$, d orbitals, and so on. We now examine the shape of each of these orbitals.

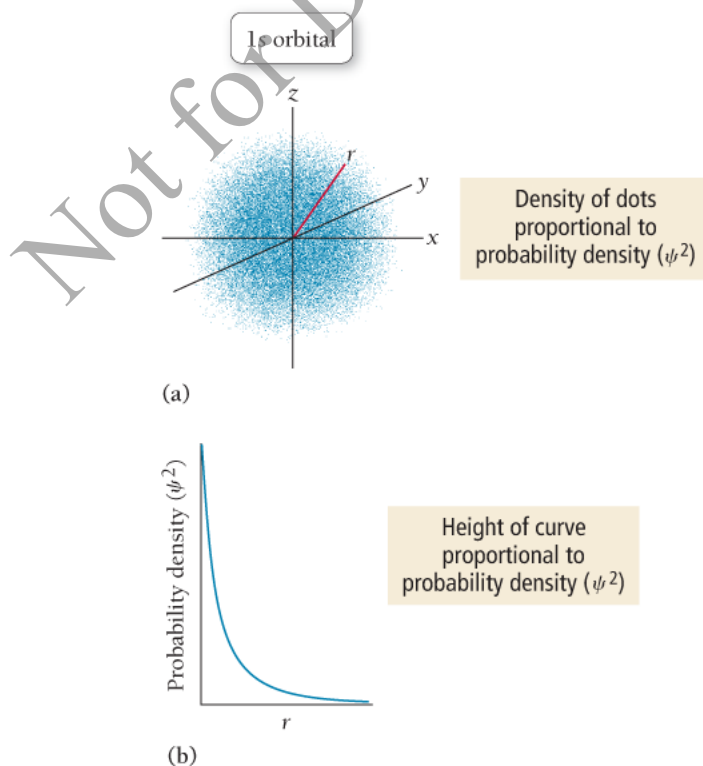
s Orbitals ($l = 0$)

The lowest energy orbital is the spherically symmetrical $1s$ orbital shown in [Figure 2.23a](#). This image is actually a three-dimensional plot of the wave function squared (ψ^2), which represents **probability density**, the probability (per unit volume) of finding the electron at a point in space.

$$\psi^2 = \text{probability density} = \frac{\text{probability}}{\text{unit volume}}$$

Figure 2.23 The $1s$ Orbital: Two Representations

In (a) the dot density is proportional to the electron probability density. In (b), the height of the curve is proportional to the electron probability density. The x -axis is r , the distance from the nucleus.



The magnitude of ψ^2 in this plot is proportional to the density of the dots shown in the image. The high dot density near the nucleus (at the very center of the plot) indicates a higher probability density for the electron there. As you move away from the nucleus, the probability density decreases. **Figure 2.23b** shows a plot of probability density (ψ^2) versus r , the distance from the nucleus. The plot represents a slice through the three-dimensional plot of ψ^2 and illustrates how the probability density decreases as r increases.

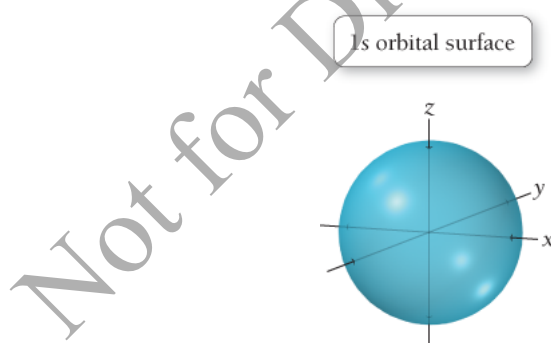
We can understand probability density with the help of a thought experiment. Imagine an electron in the 1s orbital located within the volume surrounding the nucleus. Imagine taking a photograph of the electron every second for 10 or 15 minutes. In one photograph, the electron is very close to the nucleus, in another it is farther away, and so on. Each photo has a dot showing the electron's position relative to the nucleus when the photo was taken. Remember that you can never predict where the electron will be for any one photo. However, if you took hundreds of photos and superimposed all of them, you would have a plot similar to **Figure 2.23a**—a statistical representation of how likely the electron is to be found at each point.

The thought experiment we just engaged in can result in a possible misunderstanding: that the electron is moving around (like a moth near a flame) between photographs. However, in the quantum-mechanical model, that is not the case. Recall from **Section 2.1** that the measurement affects the outcome of any quantum system. Between photographs, the location of the electron is uncertain—in a sense its location is spread out over the entire volume of the orbital. Only when the photograph is taken (that is, when a measurement of its location is made) does the location of the electron become localized to one spot. Between measurements, the electron has no single location.

An atomic orbital can also be represented by a geometrical shape that encompasses the volume where the electron is likely to be found most frequently—typically, 90% of the time. For example, the 1s orbital can be represented as the three-dimensional sphere shown in **Figure 2.24**. If we were to superimpose the dot-density representation of the 1s orbital on the shape representation, 90% of the dots would be within the sphere, meaning that when the electron is in the 1s orbital it has a 90% chance of being found within the sphere.

Figure 2.24 The 1s Orbital Surface

In this representation, the surface of the sphere encompasses the volume where the electron is found 90% of the time when the electron is in the 1s orbital.

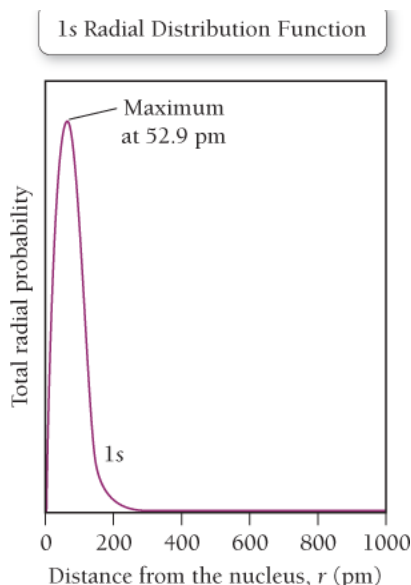


The plots we have just seen represent probability *density*. However, they are a bit misleading because they seem to imply that the electron is most likely to be found *at the nucleus*. To get a better idea of where the electron is most likely to be found, we can use a plot called the **radial distribution function**, shown in **Figure 2.25** for the 1s orbital. The radial distribution function represents the *total probability of finding the electron within a thin spherical shell at a distance r from the nucleus*.

$$\text{total radial probability (at a given } r) = \frac{\text{probability}}{\text{unit volume}} \times \text{volume of shell at } r$$

Figure 2.25 The Radial Distribution Function for the 1s Orbital

The curve shows the total probability of finding the electron within a thin shell at a distance r from the nucleus.



The radial distribution function represents, not probability density *at a point* r , but total probability *at a radius* r . In contrast to probability density, which has a maximum at the nucleus, the radial distribution function has a value of zero at the nucleus. It increases to a maximum at 52.9 pm and then decreases again with increasing r . $1 \text{ pm} = 10^{-12} \text{ m}$.

The shape of the radial distribution function is the result of multiplying together two functions with opposite trends in r :

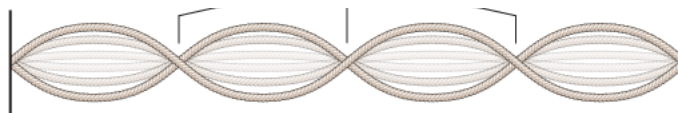
1. The probability density function (ψ^2), which is the probability per unit volume, has a maximum at the nucleus and decreases with increasing r .
2. The volume of the thin shell, which is zero at the nucleus, increases with increasing r .

At the nucleus ($r = 0$), for example, the probability *density* is at a maximum; however, the volume of a thin spherical shell is zero, so the radial distribution function is zero. As r increases, the volume of the thin spherical shell increases. We can understand this by making an analogy to an onion. A spherical shell at a distance r from the nucleus is like a layer in an onion at a distance r from its center. If the layers of the onion all have the same thickness, then the volume of any one layer—think of this as the total amount of onion in the layer—is greater as r increases. Similarly, the volume of any one spherical shell in the radial distribution function increases with increasing distance from the nucleus, resulting in a greater total probability of finding the electron within that shell. Close to the nucleus, this increase in volume with increasing r outpaces the decrease in probability density, producing a maximum at 52.9 pm. Farther out, however, the density tapers off faster than the volume increases.

The maximum in the radial distribution function, 52.9 pm, turns out to be the very same radius that Bohr had predicted for the innermost orbit of the hydrogen atom. However, there is a significant conceptual difference between the two radii. In the Bohr model, every time you probe the atom (in its lowest energy state), you would find the electron at a radius of 52.9 pm. In the quantum-mechanical model, you would generally find the electron at various radii, with 52.9 pm having the greatest probability.

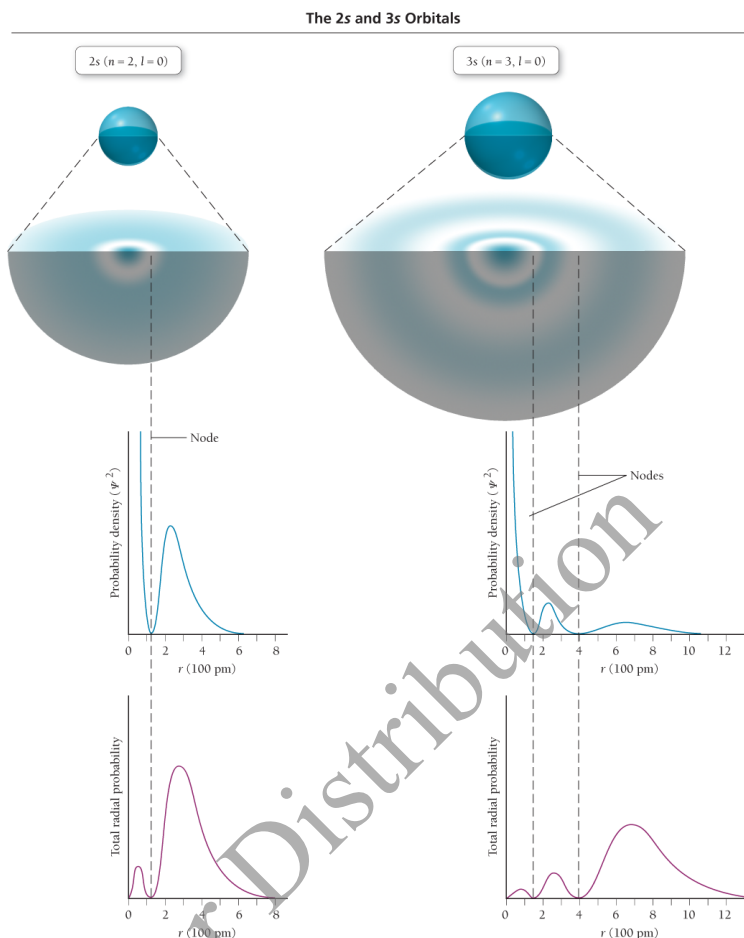
The probability densities and radial distribution functions for the 2s and 3s orbitals are shown in [Figure 2.26](#). Like the 1s orbital, these orbitals are spherically symmetric. These orbitals are larger in size than the 1s orbital, and, unlike the 1s orbital, they contain at least one **node**. A **node** is a point where the wave function (ψ), and therefore the probability density (ψ^2) and radial distribution function, all go through zero. A node in a wave function is much like a node in a standing wave on a vibrating string. We can see nodes in an orbital most clearly by looking at a slice through the orbital. Plots of probability density and the radial distribution function as a function of r both reveal the presence of nodes. The probability of finding the electron at a node is zero.





The nodes in quantum-mechanical atomic orbitals are three-dimensional analogs of the nodes on a vibrating string.

Figure 2.26 Probability Densities and Radial Distribution Functions for the 2s and 3s Orbitals

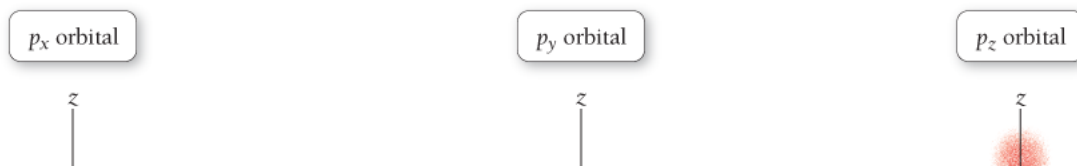


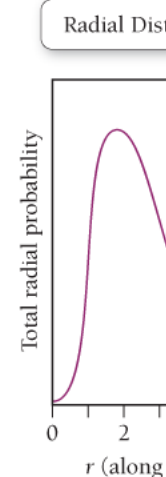
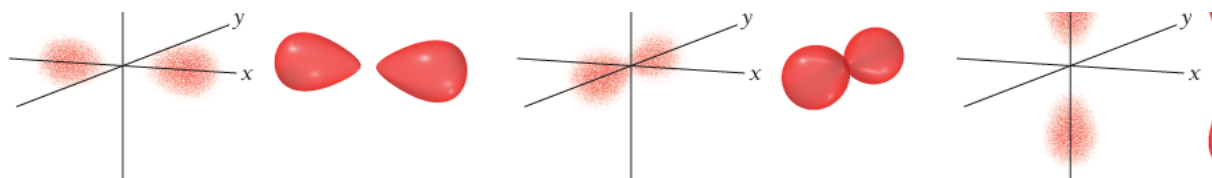
p Orbitals ($l = 1$)

Each principal level with $n = 2$ or greater contains three p orbitals ($m_l = -1, 0, +1$). The three $2p$ orbitals and their radial distribution functions are shown in Figure 2.27. The p orbitals are not spherically symmetric like the s orbitals, but have two lobes of electron density on either side of the nucleus and a node located at the nucleus. The three p orbitals differ only in their orientation and are orthogonal (mutually perpendicular) to one another. It is convenient to define an x -, y -, and z -axis system and then label each p orbital as p_x , p_y , and p_z . The $3p$, $4p$, $5p$, and higher p orbitals are all similar in shape to the $2p$ orbitals, but they contain additional nodes (like the higher s orbitals) and are progressively larger in size.

Figure 2.27 The 2p Orbitals and Their Radial Distribution Function

The radial distribution function is the same for all three $2p$ orbitals when the x -axis of the graph is taken as the axis containing the lobes of the orbital.

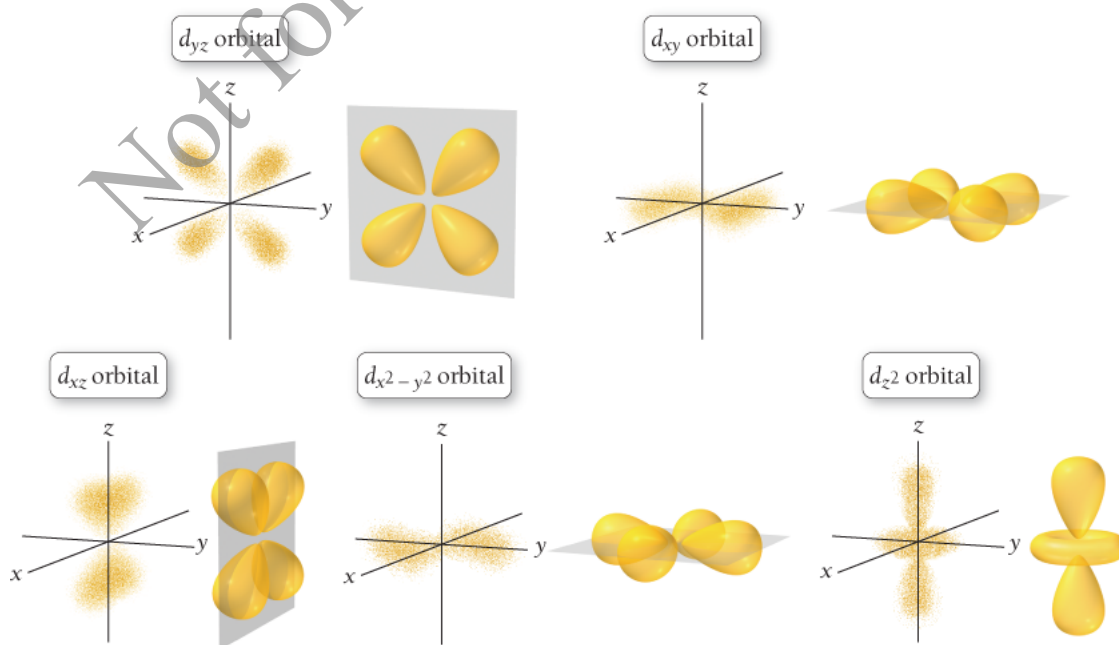




d Orbitals ($l = 2$)

Each principal level with $n = 3$ or greater contains five d orbitals ($m_l = -2, -1, 0, +1, +2$). The five $3d$ orbitals are shown in [Figure 2.28](#). Four of these orbitals have a cloverleaf shape, with four lobes of electron density around the nucleus and two perpendicular nodal planes. The d_{xy} , d_{xz} , and d_{yz} orbitals are oriented along the xy , xz , and yz planes, respectively, and their lobes are oriented *between* the corresponding axes. The four lobes of the $d_{x^2-y^2}$ orbital are oriented along the x - and y -axes. The d_{z^2} , etc., orbital is different in shape from the other four, having two lobes oriented along the z -axis and a donut-shaped ring along the xy plane. The $4d$, $5d$, $6d$, etc., orbitals are all similar in shape to the $3d$ orbitals, but they contain additional nodes and are progressively larger in size.

Figure 2.28 The $3d$ Orbitals



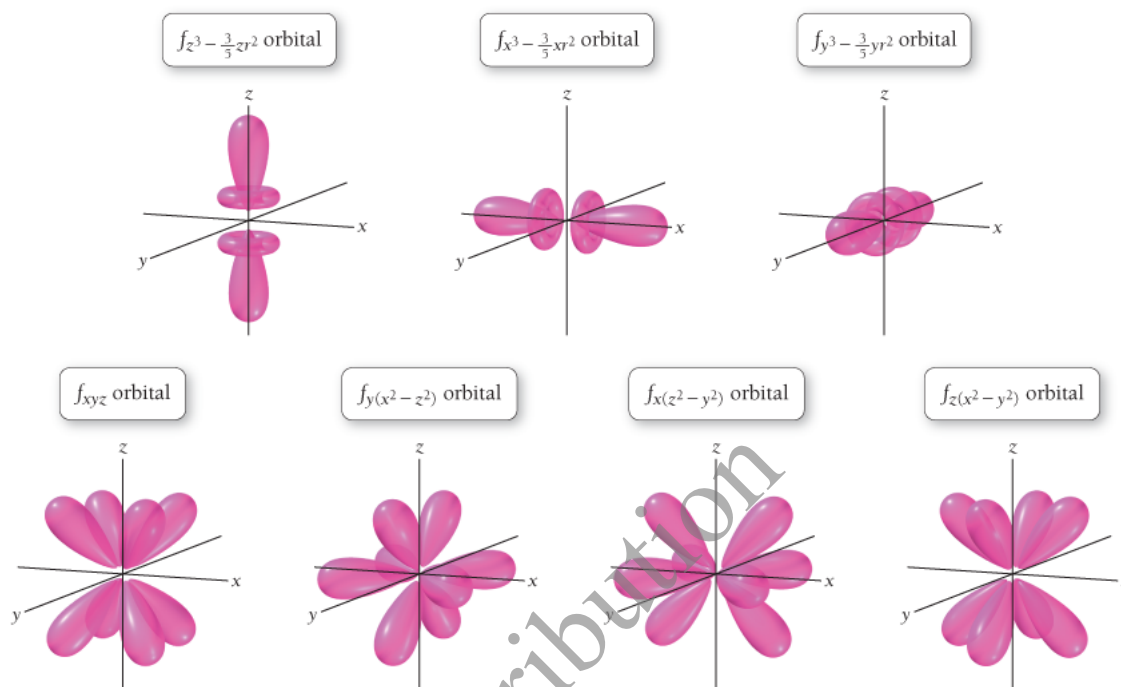
A nodal plane is a plane where the electron probability density is zero. For example, in the d_{xy}

orbitals, the nodal planes lie in the xz and yz planes.

f Orbitals ($l = 3$)

Each principal level with $n = 4$ or greater contains seven f orbitals ($m_l = -3, -2, -1, 0, +1, +2, +3$) as shown in Figure 2.29. These f orbitals have more lobes and nodes than d orbitals.

Figure 2.29 The $4f$ Orbitals



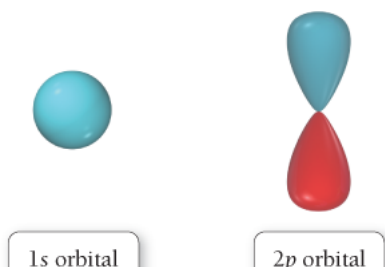
The Phase of Orbitals

The orbitals we have just shown are three-dimensional waves. We can understand an important property of these orbitals by analogy to one-dimensional waves. Consider the following one-dimensional waves:



The wave on the left has a positive amplitude over its entire length, while the wave on the right has a positive amplitude over half of its length and a negative amplitude over the other half. The sign of the amplitude of a wave—positive or negative—is known as its **phase**. In these images, blue indicates positive phase and red indicates negative phase. The phase of a wave determines how it interferes with another wave, as we saw in Section 2.2.

Just as a one-dimensional wave has a phase, so does a three-dimensional wave. We often represent the phase of a quantum-mechanical orbital with color. For example, the phase of a $1s$ and $2p$ orbital can be represented as:



In these depictions, blue represents positive phase and red represents negative phase. The $1s$ orbital is all one phase, while the $2p$ orbital exhibits two different phases. The phase of quantum-mechanical orbitals is important in bonding, as we shall see in [Chapter 6](#).

The Shape of Atoms

If some orbitals are shaped like dumbbells and three-dimensional cloverleaves, and if most of the volume of an atom is empty space diffusely occupied by electrons in these orbitals, then why do we often depict atoms as spheres? Atoms are usually drawn as spheres because most atoms contain many electrons occupying a number of different orbitals. Therefore, the shape of an atom is obtained by superimposing all of its orbitals. If we superimpose the s , p , and d orbitals, we get a spherical shape, as shown in [Figure 2.30](#).

Figure 2.30 Why Atoms Are Depicted as Spherical

Atoms are depicted as spherical because all the orbitals together make up a spherical shape.



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