

## 2.10 Quantum Mechanics and The Atom

### Skills to Develop

- To apply the results of quantum mechanics to chemistry.

The wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

### Erwin Schrödinger (1887–1961)

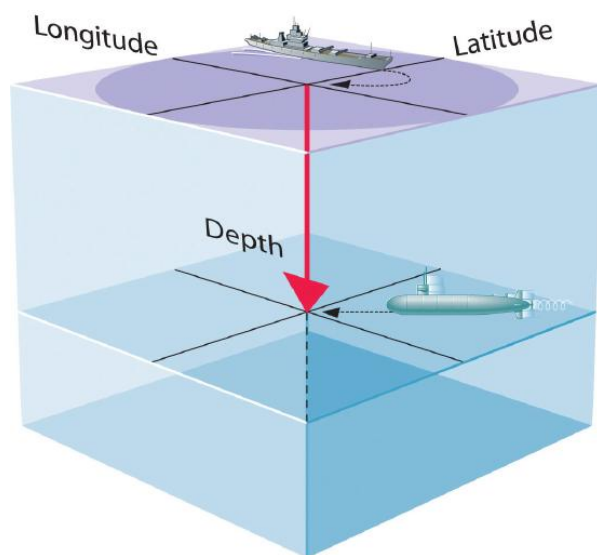
Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

### Wavefunctions

A wavefunction ( $\Psi$ ) is a mathematical function that relates the location of an electron at a given point in space (identified by  $x$ ,  $y$ , and  $z$  coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy  $E$ . The properties of wavefunctions derived from quantum mechanics are summarized here:

- A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates  $x$ ,  $y$ , and  $z$ ), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 6.5.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

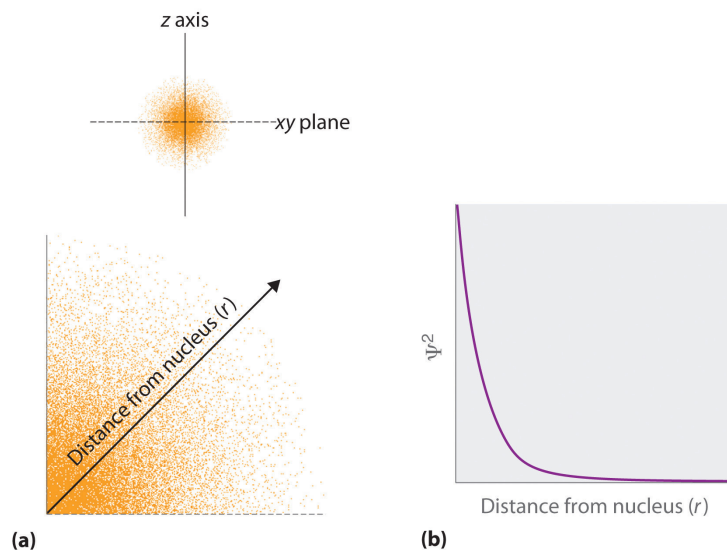


**Figure 1:** The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction ( $\Psi^2$ ) is proportional to the probability of finding an electron at a given point. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot

precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 2.

- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.



**Figure 2:** Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of  $\Psi^2$  versus  $r$  for the ground state of the hydrogen atom, the electron probability density is greatest at  $r = 0$  (the nucleus) and falls off with increasing  $r$ . Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of  $r$  is very small but not zero.

## Quantum Numbers

Schrödinger's approach uses three quantum numbers ( $n$ ,  $l$ , and  $m_l$ ) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although  $n$  can be any positive integer, only certain values of  $l$  and  $m_l$  are allowed for a given value of  $n$ .

### The Principal Quantum Number

The **principal quantum number** ( $n$ ) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \dots \quad (1)$$

As  $n$  increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of  $n$  are easier to remove from an atom. All wavefunctions that have the same value of  $n$  are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number  $n$  corresponds to the  $n$  used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

### The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number** ( $l$ ). The value of  $l$  describes the *shape* of the region of space occupied by the electron. The allowed values of  $l$  depend on the value of  $n$  and can range from 0 to  $n - 1$ :

$$l = 0, 1, 2, \dots, n - 1 \quad (2)$$

For example, if  $n = 1$ ,  $l$  can be only 0; if  $n = 2$ ,  $l$  can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both  $n$  and  $l$  form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

### The Magnetic Quantum Number

The third quantum number is the magnetic quantum number ( $m_l$ ). The value of  $m_l$  describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of  $m_l$  depend on the value of  $l$ :  $m_l$  can range from  $-l$  to  $l$  in integral steps:

$$m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l \quad (3)$$

For example, if  $l = 0$ ,  $m_l$  can be only 0; if  $l = 1$ ,  $m_l$  can be  $-1$ , 0, or  $+1$ ; and if  $l = 2$ ,  $m_l$  can be  $-2$ ,  $-1$ , 0,  $+1$ , or  $+2$ .

Each wavefunction with an allowed combination of  $n$ ,  $l$ , and  $m_l$  values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

#### Example1: $n=4$ Shell Structure

How many subshells and orbitals are contained within the principal shell with  $n = 4$ ?

**Given:** value of  $n$

**Asked for:** number of subshells and orbitals in the principal shell

**Strategy:**

- Given  $n = 4$ , calculate the allowed values of  $l$ . From these allowed values, count the number of subshells.
- For each allowed value of  $l$ , calculate the allowed values of  $m_l$ . The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

**Solution:**

**A** We know that  $l$  can have all integral values from 0 to  $n - 1$ . If  $n = 4$ , then  $l$  can equal 0, 1, 2, or 3. Because the shell has four values of  $l$ , it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of  $m_l$ .

**B** For  $l = 0$ ,  $m_l$  can be only 0, and thus the  $l = 0$  subshell has only one orbital. For  $l = 1$ ,  $m_l$  can be 0 or  $\pm 1$ ; thus the  $l = 1$  subshell has three orbitals. For  $l = 2$ ,  $m_l$  can be 0,  $\pm 1$ , or  $\pm 2$ , so there are five orbitals in the  $l = 2$  subshell. The last allowed value of  $l$  is  $l = 3$ , for which  $m_l$  can be 0,  $\pm 1$ ,  $\pm 2$ , or  $\pm 3$ , resulting in seven orbitals in the  $l = 3$  subshell. The total number of orbitals in the  $n = 4$  principal shell is the sum of the number of orbitals in each subshell and is equal to  $n^2 = 16$ .

#### Exercise 1: $n=3$ Shell Structure

How many subshells and orbitals are in the principal shell with  $n = 3$ ?

**Answer**

three subshells; nine orbitals

Rather than specifying all the values of  $n$  and  $l$  every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of  $l$  for a particular subshell or orbital:

$l =$	0	1	2	3
Designation	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: sharp, principle, diffuse, and fundamental.) A 1*s* orbital has  $n = 1$  and  $l = 0$ ; a 2*p* subshell has  $n = 2$  and  $l = 1$  (and has three 2*p* orbitals, corresponding to  $m_l = -1$ , 0, and  $+1$ ); a 3*d* subshell has  $n = 3$  and  $l = 2$  (and has five 3*d* orbitals, corresponding to  $m_l = -2$ ,  $-1$ , 0,  $+1$ , and  $+2$ ); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has  $n$  subshells. For  $n = 1$ , only a single subshell is possible ( $1s$ ); for  $n = 2$ , there are two subshells ( $2s$  and  $2p$ ); for  $n = 3$ , there are three subshells ( $3s$ ,  $3p$ , and  $3d$ ); and so forth. Every shell has an  $ns$  subshell, any shell with  $n \geq 2$  also has an  $np$  subshell, and any shell with  $n \geq 3$  also has an  $nd$  subshell. Because a  $2d$  subshell would require both  $n = 2$  and  $l = 2$ , which is not an allowed value of  $l$  for  $n = 2$ , a  $2d$  subshell does not exist.
- Each subshell has  $2l + 1$  orbitals. This means that all  $ns$  subshells contain a single  $s$  orbital, all  $np$  subshells contain three  $p$  orbitals, all  $nd$  subshells contain five  $d$  orbitals, and all  $nf$  subshells contain seven  $f$  orbitals.

*Each principal shell has  $n$  subshells, and each subshell has  $2l + 1$  orbitals.*

**Table 1:** Values of  $n$ ,  $l$ , and  $m_l$  through  $n = 4$

$n$	$l$	Subshell Designation	$m_l$	Number of Orbitals in Subshell	N u m b e r o f O r b i t a l s i n S h e l l
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	-1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	-1, 0, 1	3	
	2	3d	-2, -1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	-1, 0, 1	3	
	2	4d	-2, -1, 0, 1, 2	5	
	3	4f	-3, -2, -1, 0, 1, 2, 3	7	

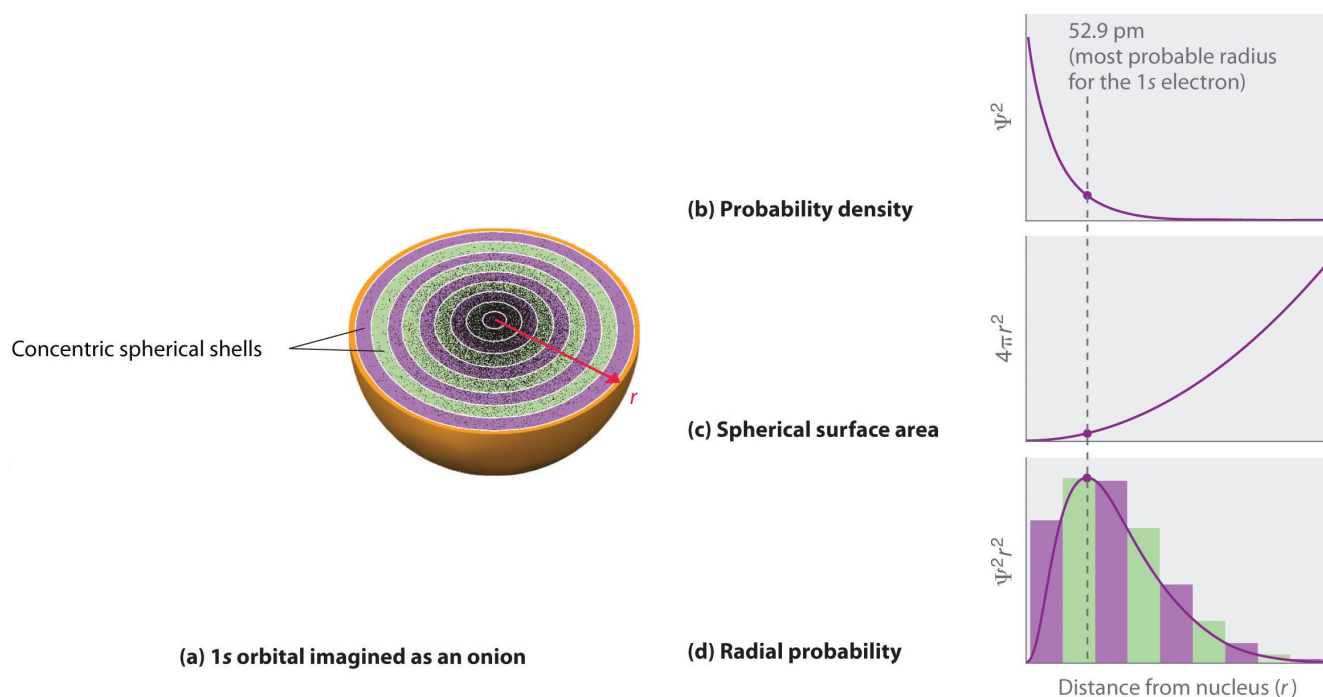
#### Skills to Develop

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of containing an electron.

One way of representing electron probability distributions was illustrated [previously](#) for the 1s orbital of hydrogen. Because  $\Psi^2$  gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of  $\Psi^2$  versus distance from the nucleus ( $r$ ) is a plot of the *probability density*. The 1s orbital is spherically symmetrical, so the probability of finding a 1s electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at  $r = 0$  (at the nucleus) and decreases steadily with increasing distance. At very large values of  $r$ , the electron probability density is very small but *not* zero.

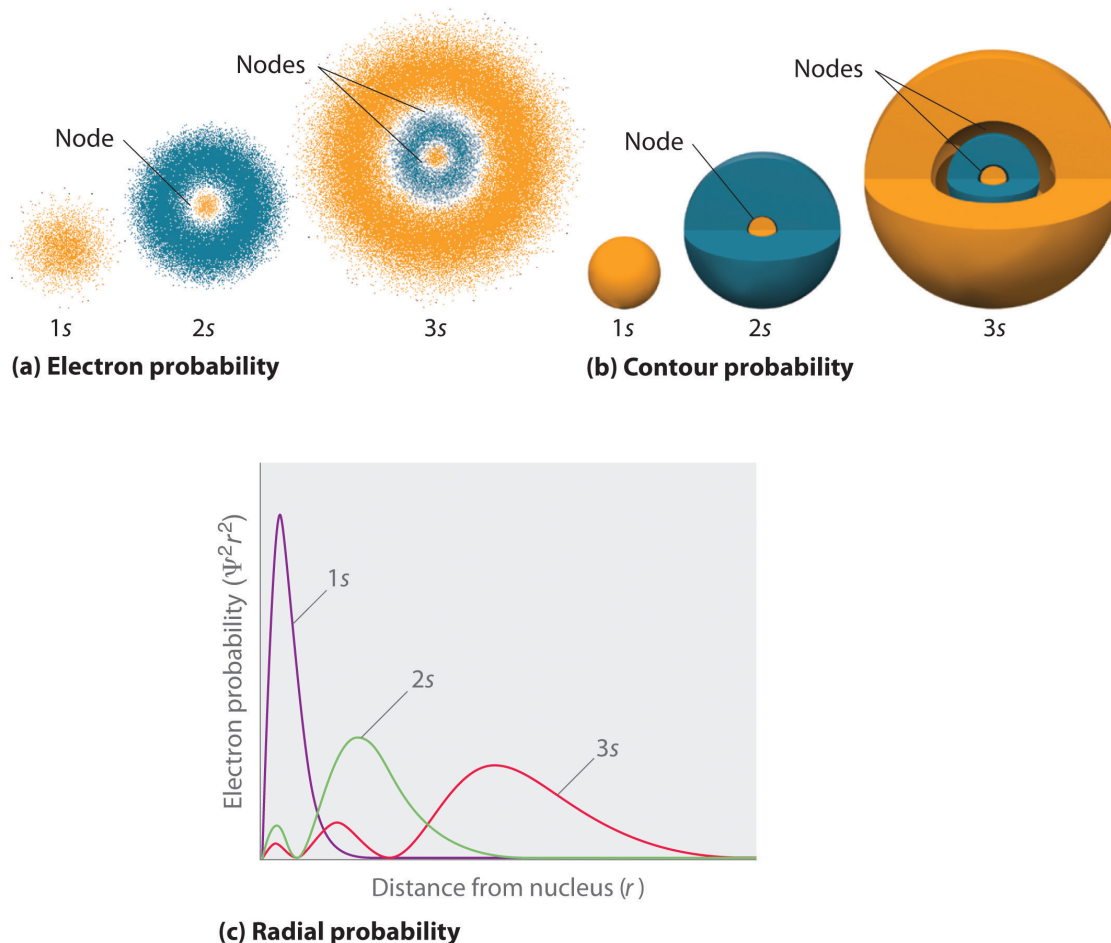
In contrast, we can calculate the *radial probability* (the probability of finding a 1s electron at a distance  $r$  from the nucleus) by adding together the probabilities of an electron being at all points on a series of  $x$  spherical shells of radius  $r_1, r_2, r_3, \dots, r_{x-1}, r_x$ . In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure 1a), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at  $r = 0$  (Figure 1b), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1. In contrast, the surface area of each spherical shell is equal to  $4\pi r^2$ , which increases very rapidly with increasing  $r$  (Figure 1c). Because the surface area of the spherical shells increases more rapidly with increasing  $r$  than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure 1d). Most important, when  $r$  is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure 1d).



**Figure 1:** Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density  $\Psi^2$  versus  $r$  shows that the electron probability density is greatest at  $r = 0$  and falls off smoothly with increasing  $r$ . The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by  $4\pi r^2$ , increases rapidly with increasing  $r$ . (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of  $r$ . Because the surface area of each shell increases more rapidly with increasing  $r$  than the electron probability density decreases, a plot of electron probability versus  $r$  (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at  $r = 0.529 \text{ \AA}$  (52.9 pm), which is exactly the radius calculated by Bohr for the  $n = 1$  orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 2 compares the electron probability densities for the hydrogen 1s, 2s, and 3s orbitals. Note that all three are spherically symmetrical. For the 2s and 3s orbitals, however (and for all other s orbitals as well), the electron probability density does not fall off smoothly with increasing  $r$ . Instead, a series of minima and maxima are observed in the radial probability plots (Figure 2c). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave *phase* in the wavefunction  $\Psi$ .



**Figure 2:** Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus ( $r$ ) in all directions (radial probability), the most probable radius increases as  $n$  increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of  $r$ .

## s Orbitals ( $l=0$ )

Three things happen to s orbitals as  $n$  increases (Figure 2):

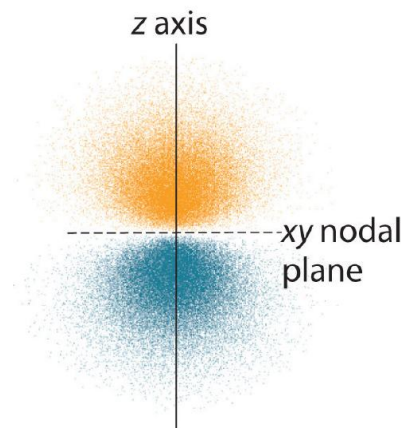
1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the s orbitals also become higher in energy as  $n$  increases because of their increased distance from the nucleus.



Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1s, 2s, and 3s orbitals in part (b) in Figure 2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2s and 3s orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

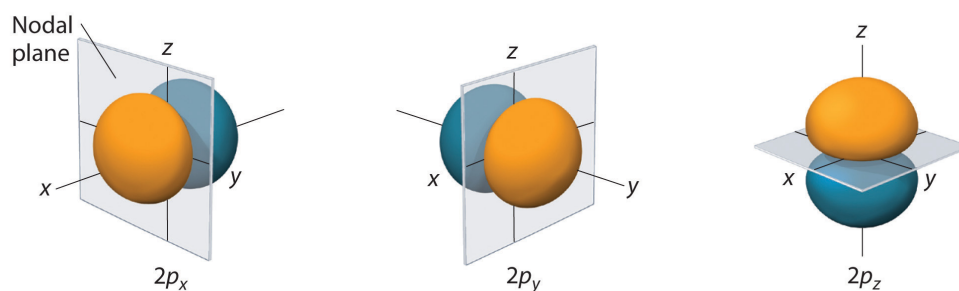
### $p$ Orbitals ( $l=1$ )

Only  $s$  orbitals are spherically symmetrical. As the value of  $l$  increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the  $2p$  subshell has  $l = 1$ , with three values of  $m_l$  ( $-1$ ,  $0$ , and  $+1$ ), there are three  $2p$  orbitals.



**Figure 3:** Electron Probability Distribution for a Hydrogen  $2p$  Orbital. The nodal plane of zero electron density separates the two lobes of the  $2p$  orbital. As in Figure 2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen  $2p$  orbitals is shown in Figure 3. Because this orbital has two lobes of electron density arranged along the  $z$  axis, with an electron density of zero in the  $xy$  plane (i.e., the  $xy$  plane is a nodal plane), it is a  $2p_z$  orbital. As shown in Figure 4, the other two  $2p$  orbitals have identical shapes, but they lie along the  $x$  axis ( $2p_x$ ) and  $y$  axis ( $2p_y$ ), respectively. Note that each  $p$  orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the  $2p$  orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

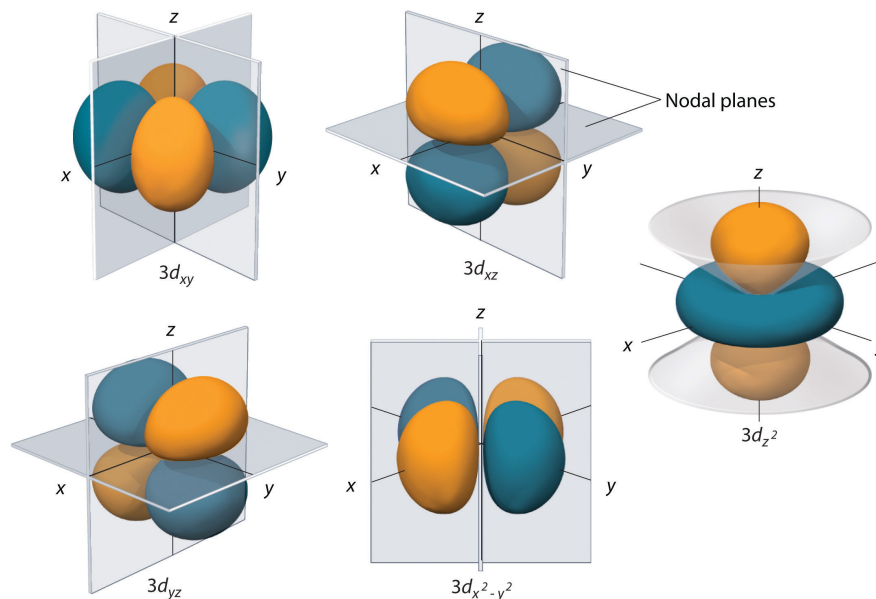


**Figure 4** The Three Equivalent  $2p$  Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each  $2p$  orbital. The phase of the wave function is positive (orange) in the region of space where  $x$ ,  $y$ , or  $z$  is positive and negative (blue) where  $x$ ,  $y$ , or  $z$  is negative. Just as with the  $s$  orbitals, the size and complexity of the  $p$  orbitals for any atom increase as the principal quantum number  $n$  increases. The shapes of the 90% probability surfaces of the  $3p$ ,  $4p$ , and higher-energy  $p$  orbitals are, however, essentially the same as those shown in Figure 4.

## d Orbitals ( $l=2$ )

Subshells with  $l = 2$  have five  $d$  orbitals; the first principal shell to have a  $d$  subshell corresponds to  $n = 3$ . The five  $d$  orbitals have  $m_l$  values of  $-2, -1, 0, +1$ , and  $+2$ .



**Figure 5:** The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital,  $3d_{z^2}$ , has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen 3d orbitals, shown in Figure 5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the  $3d_{xy}$ ,  $3d_{xz}$ , and  $3d_{yz}$  orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the  $3d_{x^2-y^2}$  orbital. The fifth 3d orbital, called the  $3d_{z^2}$  orbital, has a unique shape: it looks like a  $2p_z$  orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the  $3d_{z^2}$  orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 5, the phase of the wave function is positive for the two lobes of the  $dz^2$  orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as  $n$  increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 5.

## f Orbitals ( $l=3$ )

Principal shells with  $n = 4$  can have subshells with  $l = 3$  and  $m_l$  values of  $-3, -2, -1, 0, +1, +2$ , and  $+3$ . These subshells consist of seven f orbitals. Each f orbital has three nodal surfaces, so their shapes are complex. Because f orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of  $l$  are not discussed at all.

## Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or  $\text{He}^+$ ).

The relative energies of the atomic orbitals with  $n \leq 4$  for a hydrogen atom are plotted in Figure 6; note that the orbital energies depend on *only* the principal quantum number  $n$ . Consequently, the energies of the 2s and 2p orbitals of hydrogen are the same; the energies of the 3s, 3p, and 3d orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen atom, all orbitals with the same value of  $n$  (e.g., the three 2p orbitals) are **degenerate**, meaning that they have the same energy. The orbital



energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are 4 orbitals with different electron density distributions in the  $n = 2$  principal shell (one 2s and three 2p orbitals), 9 in the  $n = 3$  principal shell, and 16 in the  $n = 4$  principal shell. The different values of  $l$  and  $m_l$  for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure 6 shows that the energy levels become closer and closer together as the value of  $n$  increases, as expected because of the  $1/n^2$  dependence of orbital energies.



**Figure 6:** Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of  $n$ .

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of [Bohr's equation](#), which can be extended to other single-electron species by incorporating the nuclear charge  $Z$  (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} R h c \quad (4)$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the  $n = 2$  orbitals. In ions with only a single electron, the energy of a given orbital depends on only  $n$ , and all subshells within a principal shell, such as the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals, are degenerate.

## Summary

There is a relationship between the locations of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave-particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions** ( $\Psi$ ) to describe the mathematical relationship between the location of electrons in atoms and molecules and their energies. Wavefunctions have four important properties:

1. the wavefunction uses three variables (Cartesian axes  $x$ ,  $y$ , and  $z$ ) to describe the position of an electron;
2. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
3. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and

4. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number**  $n$  can be any positive integer; as  $n$  increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of  $n$  constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number**  $l$  can have integral values between 0 and  $n - 1$ ; it describes the shape of the electron distribution. wavefunctions that have the same values of both  $n$  and  $l$  constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number**  $m_l$  can have  $2l + 1$  integral values, ranging from  $-l$  to  $+l$ , and describes the orientation of the electron distribution. Each wavefunction with a given set of values of  $n$ ,  $l$ , and  $m_l$  describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The four chemically important types of atomic orbital correspond to values of  $\ell = 0, 1, 2$ , and  $3$ . Orbitals with  $\ell = 0$  are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of  $n > 1$  and  $\ell = 0$  contain one or more nodes. Orbitals with  $\ell = 1$  are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with  $\ell = 2$  are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with  $\ell = 3$  are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} Rhc$$

In atoms or ions with only a single electron, all orbitals with the same value of  $n$  have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as  $n$  increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

## Contributors

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