

## 6.5: Atomic Orbitals and Their Energies

### Learning Objectives

- To apply the results of quantum mechanics to chemistry

The paradox described by Heisenberg's uncertainty principle and 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. In doing so, Schrödinger's theory today is described as quantum mechanics. A theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules. It successfully describes the energies and spatial distributions of electrons in atoms and molecules.

### 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 *wave functions* that are the solutions of Schrödinger's equations. The Schrödinger equation is similar in form to equations for the propagation of waves, which is why originally quantum mechanics was called wave mechanics, but there are significant differences between quantum wave functions and those that describe real waves. Therefore, at this point it would be best to lean only lightly on the standing wave analogy.

### Wave Functions

A wavefunction ( $\Psi$ ) A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy.  $\Psi$  is the uppercase Greek letter psi, is a mathematical expression that can be used to calculate any property of an atom. In general, wavefunctions depend on both time and position. For atoms, solutions to the Schrödinger equation correspond to arrangements of the electrons, which, if left alone, remain unchanged and are thus only functions of position. To indicate time independence we use lower case  $\psi$

Wavefunctions for each atom have some properties that are exact, for example each wavefunction describes an electron in quantum state with a specific energy. Each of these exact properties is associated with an integer. The energy of an electron in an atom is associated with the integer  $n$ , which turns out to be the same  $n$  that Bohr found in his model. These integers are called quantum numbers and different wavefunctions have different sets of quantum numbers. The important point about quantum numbers is that they are countable integers, not continuous variables like the number of points on a line. In the case of atoms, each electron has four quantum numbers which determine its wavefunction.

For other properties, there is a mathematical procedure by which the wavefunctions can be used to calculate average values and probabilities for anything, for example the probability of finding the electron at any point in space. Driven by the Heisenberg Uncertainty Principle, the calculation of probabilities is the best we can do for properties not associated directly with quantum numbers.

The properties of wave functions derived from quantum mechanics are summarized here. Although there are no equations there are a number of advanced concepts. Even if your math is not strong, try to understand the key concepts.:

- **A time independent wavefunction uses three variables to describe the position of an electron.** Three coordinates specify the position in space (as with the Cartesian coordinates  $x$ ,  $y$ , and  $z$ , or **spherical coordinates**  $r$ ,  $\theta$ ,  $\phi$ ). Figure 2.21 shows both Cartesian and spherical coordinates. For the motion of an electron about the massive nucleus, spherical coordinates can be more natural than Cartesian.

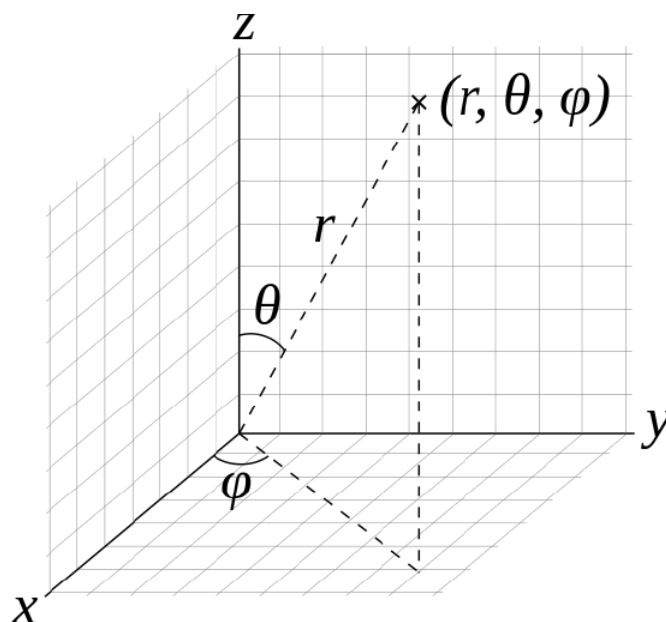


Figure 2.5.1 Cartesian (x, y, z) and spherical coordinates (r, θ, φ)

- **Wave functions have both real and imaginary parts. They are complex functions**, which is a mathematical term indicating that they contain  $\sqrt{-1}$ , represented as  $i$ . Imaginary and complex numbers have no physical significance.

#### Imaginary Numbers

If you need an introduction to imaginary number, here is one. To see it you will have to be attached to the INTERNET



- The **probability of finding an electron** at a point is given by the product of the wave function  $\psi$  and its complex conjugate  $\psi^*$  in which all terms that contain  $i$  are replaced by  $-i$ . This product is called the modulus square and for wave functions it always must be a real positive number or zero. Negative, imaginary or complex probabilities of finding an electron at a point would be meaningless. This interpretation was discovered by Max Born, for which he won the Nobel prize. 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 quantum numbers specifying the wavefunction and the three coordinates specifying the position in space we are interested in. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, shown for the ground state of the hydrogen atom in [Figure 2.5.2](#)

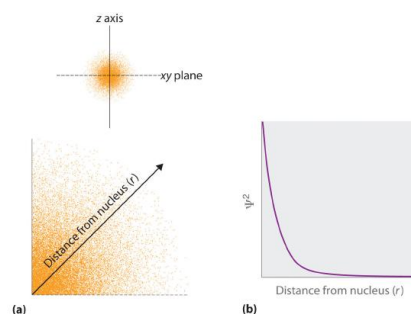


Figure 2.5.2 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space (a) The density of the dots shows electron probability. (b) In this plot of  $\Psi^2$  versus  $r$  for the ground state of the hydrogen atom, the electron probability density is greatest 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.

- **The total probability of finding the electron anywhere must be 100%.** It has to be somewhere. On the other hand, since there is a lot more space far away from a nucleus than near it, the probability of finding the electron at any one point as one moves away from the nucleus must eventually go to zero.
- **The relative phases of wave function for electrons in different atoms** determines bonding. This will be important in our discussion of chemical bonding in [Chapter 5](#). As discussed in the previous section, wavefunctions like waves, can positively reinforce each other or destructively interfere. When they reinforce they are said to be in phase, and when they interfere they are said to be out of phase. The phases are indicated as positive, +, or negative, -. Do not confuse the sign of the phase with a positive or negative electrical charge.
- **Each wavefunction has a unique sets of quantum numbers** A unique set of numbers that specifies a wave function (a solution to the Schrödinger equation), which provides important information about the energy and spatial distribution of an electron.. The spacial patterns of the three-dimensional wave functions are complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a water world, which turn out to be solutions of the Schrödinger equation for a spherically symmetric atom.
- **Each wave function 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 emerges from the wave equation.

## Quantum Numbers

Schrödinger's approach requires three quantum numbers ( $n$ ,  $l$ , and  $m_l$ ) to specify a wave function for each electron. The quantum numbers provide information about the spatial distribution of an electron. Although  $n$  can be any positive integer (NOT zero), only certain values of  $l$  and  $m_l$  are allowed for a given value of  $n$ . This is a consequence of the mathematical details of the Schrödinger equation

## The Principal Quantum Number

The principal quantum number ( $n$ ) One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus:

**Equation 2.5.1**  $n = 1, 2, 3, 4, \dots$

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 wave functions that have the same value of  $n$  are said to constitute a principal shell All the wave functions that have the same value of because those electrons have similar average distances from the nucleus. 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 ( $l$ ). One of three quantum numbers that describes the shape of the region of space occupied by an electron. 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  $n - 1$ :

**Equation 2.5.2**  $l = 0, 1, 2, \dots, n - 1$

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 wave functions that have the same values of both  $n$  and  $l$  form a subshell. A group of wave functions that have the same values of  $n$  and  $l$  and  $m_l$  is called an orbital. 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 ( $m_l$ ). One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field. 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:

**Equation 2.5.3**  $m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l$

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 wave function with an allowed combination of  $n$ ,  $l$ , and  $m_l$  values describes an atomic orbital. A wave function with an allowed combination of  $n$ ,  $l$  and  $m_l$  quantum numbers, 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.

### Example 2.5.1

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:**

**A** Given  $n = 4$ , calculate the allowed values of  $l$ . From these allowed values, count the number of subshells.

**B** 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  $n^2$ :

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise

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
<b>Designation</b>	<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 corresponding spectroscopic characteristics of lines involving them: 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 2.5.1):

- Each principal shell has  $n$  subshells. For  $n = 1$ , only a single subshell is possible (1*s*); for  $n = 2$ , there are two subshells (2*s* and 2*p*); for  $n = 3$ , there are three subshells (3*s*, 3*p*, and 3*d*); 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 2*d* subshell would require both  $n = 2$  and  $l = 2$ , which is not an allowed value of  $l$  for  $n = 2$ , a 2*d* 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.

### Note the Pattern

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

**Table 2.5.1 Allowed values of  $n$ ,  $l$ , and  $m_l$  through  $n = 4$**

$n$	$l$	Subshell Designation	$m_l$	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1 <i>s</i>	0	1	1
2	0	2 <i>s</i>	0	1	4
	1	2 <i>p</i>	-1, 0, 1	3	
3	0	3 <i>s</i>	0	1	9
	1	3 <i>p</i>	-1, 0, 1	3	
	2	3 <i>d</i>	-2, -1, 0, 1, 2	5	
4	0	4 <i>s</i>	0	1	16
	1	4 <i>p</i>	-1, 0, 1	3	
	2	4 <i>d</i>	-2, -1, 0, 1, 2	5	
	3	4 <i>f</i>	-3, -2, -1, 0, 1, 2, 3	7	

### Videos

- [Quantum numbers](#) - ChemDo

### Examples

- [Quantum Numbers and Electron Configurations](#) - Purdue - tutorial
- [Quantum Chemistry](#) - Ohio State
- [Quantum Chemistry Quizzes](#) - mhe education
- [AP Chemistry Chapter 7 Review](#) - Science Geek
- [Quantum Theory of the Atom Practice Quiz](#) - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

## Orbital Shapes

An orbital is the quantum mechanical generalization 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 having an electron.

One way of representing electron probability distributions was illustrated in Figure 2.5.1 for the 1s orbital of hydrogen. The probability of finding an electron in a region of space with volume  $V$  (such as a cubic picometer) is the product of the volume with  $\psi\psi^*$  (we can write this as  $|\psi|^2$ ). From our consideration of the properties of the wavefunction, we know that adding up the probability from every such small volume over all space will sum to unity, or a 100% probability that the electron is somewhere. 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 tiny but *not* exactly zero.

In contrast to the probability density, 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 (part (a) in Figure 2.5.2), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at  $r = 0$  (part (b) in Figure 2.5.3), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 2.5.3

By contrast, the surface area of each spherical shell is equal to  $4\pi r^2$ , which increases rapidly with increasing  $r$  (part (c) in Figure 2.5.3). Because the surface area of the spherical shells increases at first more rapidly with increasing  $r$  than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 2.5.3). As 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 because the surface area of the shell is zero (part (d) in Figure 2.5.2).

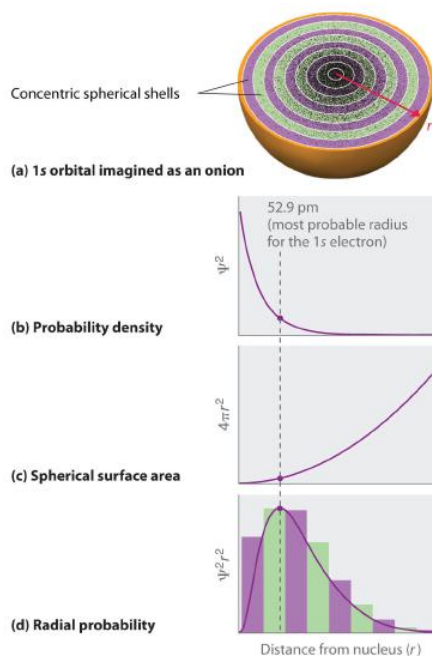


Figure 2.5.3 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density  $\Psi^2$  versus  $r$  shows that the electron probability 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 2.5.4 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 (part (c) in Figure 2.5.4). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

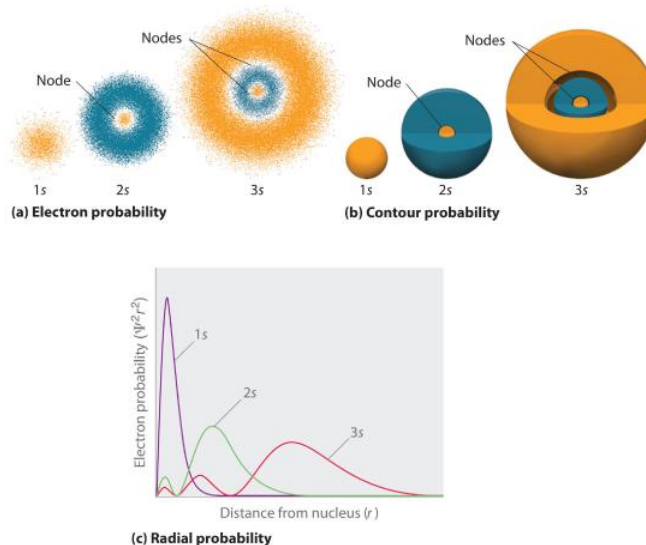


Figure 2.5.4 Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the 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

Three things happen to s orbitals as  $n$  increases (Figure 2.5.4):

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. Electron distributions that are represented as standing waves, as was shown for the hydrogen 1s, 2s, and 3s orbitals in part (b) in Figure 2.5.4. 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. This makes sense because bonding is an interaction of electrons from two atoms which will be most sensitive to forces at the edges of the orbitals.

## p Orbitals

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.

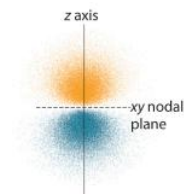


Figure 2.5.4 , the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen  $2p$  orbitals is shown in Figure 2.5.5 . 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 2.5.6 , 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.

In the next section when we consider the electron configuration of multielectron atoms, the geometric shapes provide an important clue about which orbitals will be occupied by different electrons. Because electrons in different  $p$  orbitals are geometrically distant from each other, there is less repulsion between them than would be found if two electrons were in the same  $p$  orbital. Thus, when the  $p$  orbitals are filled, it will be energetically favorable to place one electron into each  $p$  orbital, rather than two into one orbital.

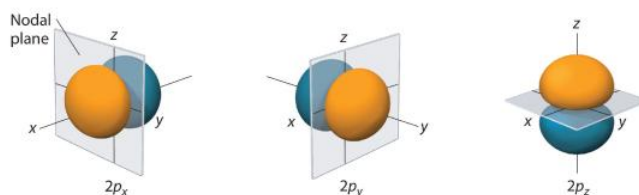


Figure 2.5.6 The Three Equivalent  $2p$  Orbitals of the Hydrogen Atom The surfaces shown enclose 90% of the total electron probability for the  $2p_x$ ,  $2p_y$ , and  $2p_z$  orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that 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 2.5.6

## $d$ Orbitals

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  $+2$ .



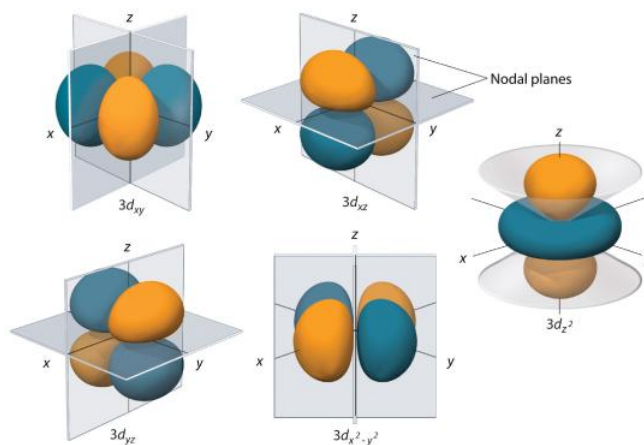


Figure 2.5.7 The Five Equivalent 3d Orbitals of the Hydrogen Atom The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four 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 2.5.7](#), 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 2.5.7](#), the phase of the wave function is positive for the two lobes of the  $3d_{z^2}$  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 2.5.7](#).

## f Orbitals

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. Equivalent illustrations of [the shapes of the f orbitals](#) are available

## 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  $\text{He}^+$ ). This is the simplest case.

The relative energies of the atomic orbitals with  $n \leq 4$  for a hydrogen atom are plotted in [Figure 2.5.8](#) 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. 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. As we have just seen, however, quantum mechanics also 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. [Figure 2.5.8](#) 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.

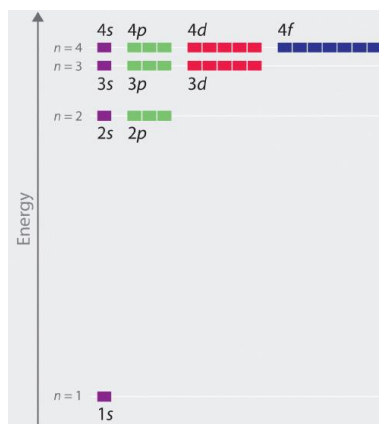


Figure 2.5.8 Orbital Energy Level Diagram for the Hydrogen Atom Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of  $n$ .

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation (Equation 2.3.3), which can be extended to other single-electron species by incorporating the nuclear charge  $Z$  (the number of protons in the nucleus):

**Equation 2.5.4** 
$$E = -\frac{Z^2}{n^2} \mathcal{R}hc$$

In general, both energy and radius decrease as the nuclear charge increases. As a result of the  $Z^2$  dependence of energy in Equation 2.24, electrons in the 1s orbital of carbon, which has a nuclear charge of +6, lie roughly 36 times lower in energy than those in the hydrogen 1s orbital, and the 1s orbital of tin, with an atomic number of 50 is roughly 2500 times lower still. The most stable and tightly bound electrons are in orbitals (those with the lowest energy) 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.

### Videos

- [Quantum Mechanics 6a- Hydrogen](#) - via science (don't bother with the first 3 minutes which are advanced math heavy, but the stunning illustrations of orbital shapes afterwards are great)
- [Electron Spin and the Pauli Principle](#) - via science.(does an excellent job explaining why electron spin is not a spinning electron)
- [Electron Orbitals](#) - Anna Tanczos - more visualizations

### Examples

- [Quantum Chemistry](#) - Ohio State
- [Quantum Chemistry Quizzes](#) - mhe education
- [AP Chemistry Chapter 7 Review](#) - Science Geek
- [Quantum Theory of the Atom Practice Quiz](#) - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

### Effective Nuclear Charges

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance  $r$  between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge ( $Z_{\text{eff}}$ ) The nuclear charge an electron actually experiences because of shielding from other electrons closer to the nucleus. that is *less* than the actual nuclear charge  $Z$ . This effect is called electron shielding. The effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron farther away.. As the distance between an electron and the nucleus approaches infinity,  $Z_{\text{eff}}$  approaches a value of 1 because all the other  $(Z - 1)$  electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At  $r \approx 0$ , the positive charge experienced by an electron is approximately the full nuclear charge, or  $Z_{\text{eff}} \approx Z$ . At intermediate values of  $r$ , the effective nuclear charge is somewhere between 1 and  $Z$ :  $1 \leq Z_{\text{eff}} \leq Z$ . Thus the actual  $Z_{\text{eff}}$  experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in  $Z_{\text{eff}}$  for different elements, as shown in Figure 2.5.9 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does  $Z_{\text{eff}} = Z$ , and only for helium are  $Z_{\text{eff}}$  and  $Z$  comparable in magnitude.

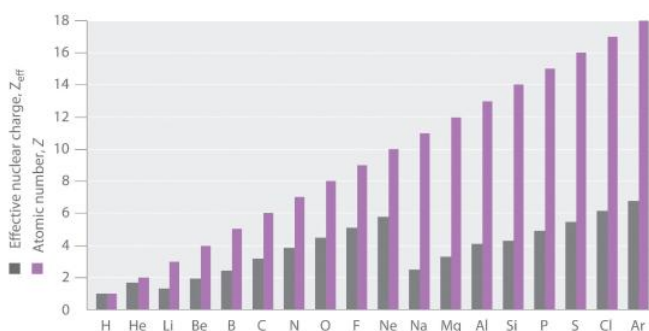


Figure 2.5.9 Relationship between the Effective Nuclear Charge  $Z_{\text{eff}}$  and the Atomic Number  $Z$  for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table Except for hydrogen,  $Z_{\text{eff}}$  is always less than  $Z$ , and  $Z_{\text{eff}}$  increases from left to right as you go across a row.

The trend that you see in Figure 2.5.9 for the first three principal shells corresponding to  $n = 1, 2$ , and  $3$ , continues in the further shells. The atomic number and thus the nuclear charge increase linearly, but the sawtooth pattern for  $Z_{\text{eff}}$  repeats itself, resetting as the quantum number  $n$  changes. Chemical bonding and reactivity involves the sharing or exchange of electrons between atoms. Those electrons which can participate are those held least strongly by the atom, the outermost electrons, which, no matter what the atomic number, and nuclear charge, are bound to their atom by roughly the same energy range because of the shielding effect.

In multielectron atoms this shifts the energies of the different orbitals for a typical multielectron atom as shown in Figure 2.5.10. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing  $l$ . An  $ns$  orbital always lies below the corresponding  $np$  orbital, which in turn lies below the  $nd$  orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 2.5.11 for example, an electron in the  $2s$  orbital penetrates inside a filled  $1s$  orbital more than an electron in a  $2p$  orbital does. Hence in an atom with a filled  $1s$  orbital, the  $Z_{\text{eff}}$  experienced by a  $2s$  electron is greater than the  $Z_{\text{eff}}$  experienced by a  $2p$  electron. Consequently, the  $2s$  electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 2.5.10.

#### Note the Pattern

Due to electron shielding,  $Z_{\text{eff}}$  increases more rapidly going across a row of the periodic table than going down a column.

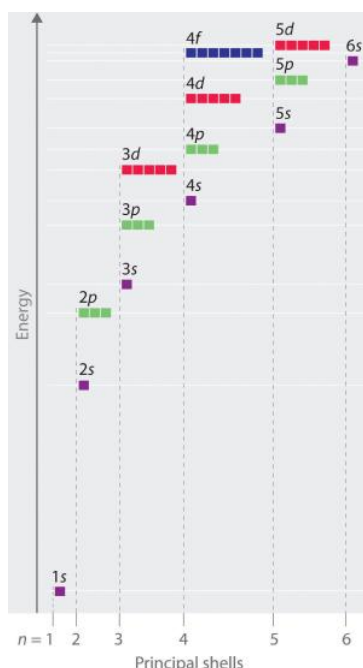


Figure 2.5.10 Orbital Energy Level Diagram for a Typical Multielectron Atom

Because of the effects of shielding and the different radial distributions of orbitals with the same value of  $n$  but different values of  $l$ , the different subshells are not degenerate in a multielectron atom. (Compare this with [Figure 2.5.8](#) For a given value of  $n$ , the  $ns$  orbital is always lower in energy than the  $np$  orbitals, which are lower in energy than the  $nd$  orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of  $n$ ; for example, the  $4s$  orbital is lower in energy than the  $3d$  orbitals for most atoms.

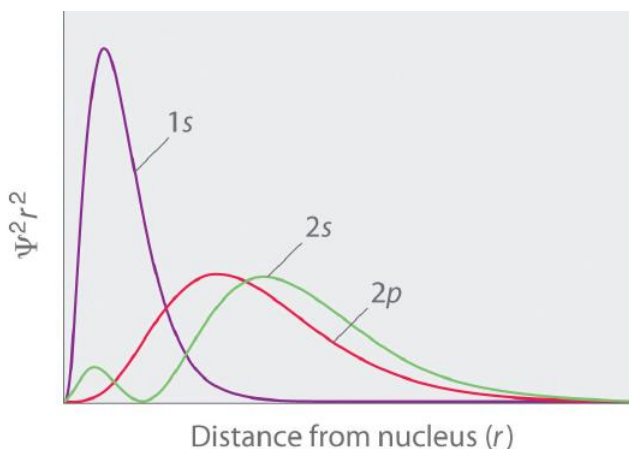


Figure 2.5.11 Orbital Penetration A comparison of the radial probability distribution of the  $2s$  and  $2p$  orbitals for various states of the hydrogen atom shows that the  $2s$  orbital penetrates inside the  $1s$  orbital more than the  $2p$  orbital does. Consequently, when an electron is in the small inner lobe of the  $2s$  orbital, it experiences a relatively large value of  $Z_{\text{eff}}$ , which causes the energy of the  $2s$  orbital to be lower than the energy of the  $2p$  orbital.

Notice in [Figure 2.5.10](#) that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the  $3d$  orbitals in most atoms is actually between the energies of the  $4s$  and the  $4p$  orbitals.

### Key Equation

#### energy of hydrogen-like orbitals

Equation 2.5.4:  $E = -\frac{Z^2}{n^2} \mathcal{R}hc$

## Summary

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 **wave functions ( $\Psi$ )** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties: (1) the wave function uses three variables (Cartesian axes  $x$ ,  $y$ , and  $z$ ) to describe the position of an electron; (2) the magnitude of the wave function is proportional to the intensity of the wave; (3) the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot; (4) describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and (5) each spatial distribution of the electron described by a wave function 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 wave functions 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. Wave functions 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 wave function 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  $l = 0, 1, 2$ , and  $3$ . Orbitals with  $l = 0$  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  $l = 0$  contain one or more nodes. Orbitals with  $l = 1$  are  $p$  orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with  $l = 2$  are  $d$  orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with  $l = 3$  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**. 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.

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge ( $Z_{\text{eff}}$ )** to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of  $l$  and the same value of  $n$  overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

## Key Takeaway

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

## Conceptual Problems

1. Why does an electron in an orbital with  $n = 1$  in a hydrogen atom have a lower energy than a free electron ( $n = \infty$ )?
2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with  $n = 2$  greater than, less than, or equal to the energy of an orbital with  $n = 4$ ? Justify your answer.
5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.

1.  $1s, 2p$
  2.  $2p, 2s$
  3.  $2s, 3s$
  4.  $3d, 4s$
6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
8. What quantum number defines each of the following?
1. the overall shape of an orbital
  2. the orientation of an electron with respect to a magnetic field
  3. the orientation of an orbital in space
  4. the average energy and distance of an electron from the nucleus
9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with $n =$			
		4	3	2	1
H	1				1
He	2				2
Ne	10			8	2
Ar	18		8	8	2
Li	3			1	2
Na	11		1	8	2
K	19	1	8	8	2
Be	4			2	2

1. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
  2. Using Bohr's model, what are the implications for the reactivity of each element?
  3. Give the actual electron configuration of each element in the table.
10. What happens to the energy of a given orbital as the nuclear charge  $Z$  of a species increases? In a multielectron atom and for a given nuclear charge, the  $Z_{\text{eff}}$  experienced by an electron depends on its value of  $l$ . Why?
11. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.
12. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?
13. Describe the relationship between electron shielding and  $Z_{\text{eff}}$  on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
14. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
1.  $2s, 3s$

2.  $3p, 4d$
3.  $2p, 1s$
4.  $3d, 4s$

### Numerical Problems

1. How many subshells are possible for  $n = 3$ ? What are they?
2. How many subshells are possible for  $n = 5$ ? What are they?
3. What value of  $l$  corresponds to a  $d$  subshell? How many orbitals are in this subshell?
4. What value of  $l$  corresponds to an  $f$  subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
  1.  $2s$
  2.  $3p$
  3.  $4d$
  4.  $6f$
6. State the number of orbitals and electrons that can occupy each subshell.
  1.  $1s$
  2.  $4p$
  3.  $5d$
  4.  $4f$
7. How many orbitals and subshells are found within the principal shell  $n = 6$ ? How do these orbital energies compare with those for  $n = 4$ ?
8. How many nodes would you expect a  $4p$  orbital to have? A  $5s$  orbital?
9. A  $p$  orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of  $n$ ? If an  $s$  orbital has two nodes, what is the value of  $n$ ?

### Answers

1. Three subshells, with  $l = 0$  ( $s$ ),  $l = 1$  ( $p$ ), and  $l = 2$  ( $d$ ).
- 2.
3. A  $d$  subshell has  $l = 2$  and contains 5 orbitals.
- 4.
5.
  1. 2 electrons; 1 orbital
  2. 6 electrons; 3 orbitals
  3. 10 electrons; 5 orbitals
  4. 14 electrons; 7 orbitals
- 6.
7. A principal shell with  $n = 6$  contains six subshells, with  $l = 0, 1, 2, 3, 4$ , and  $5$ , respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with  $n = 6$  are higher than those of the corresponding orbitals with the same value of  $l$  for  $n = 4$ .
- 8.
- 9.

### Contributors

- Anonymous

Modified by Joshua Halpern

[Imaginary Number Video](#) from IceDave33 on YouTube



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