orbitals. The orbitals can be described in a shorthand notation using *quantum numbers*.

6.6 REPRESENTATIONS OF ORBITALS
We consider the three-dimensional shapes of orbitals and how they can be represented by graphs of electron density.

6.7 MANY-ELECTRON ATOMS
We recognize that the energy levels for an atom with one electron are altered when the atom contains multiple electrons. Each electron has a quantum-mechanical property called *spin*. The *Pauli exclusion principle* states that no two electrons in an atom can have the same four quantum numbers (three for the orbital and one for the spin). Therefore, an orbital can hold a maximum of two electrons.

6.8 ELECTRON CONFIGURATIONS
We learn that knowing orbital energies as well as some fundamental characteristics of electrons described by *Hund's rule* allows us to determine how electrons are distributed in an atom (*electron configurations*).

6.9 ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE
We observe that the electron configuration of an atom is related to the location of the element in the periodic table.

ELECTRONIC STRUCTURE OF ATOMS

WHAT HAPPENS WHEN SOMEONE switches on a neon light? Electrons in the neon atoms are excited to a higher energy by electricity. An electron can remain in a higher-energy state for only a very short time, and it emits light when it returns to a lower energy. The resulting glow is explained by one of the most revolutionary discoveries of the twentieth century—the *quantum theory,* which explains much of the behavior of electrons in atoms.

In this chapter we explore the quantum theory and its importance in chemistry. We begin by looking at the nature of light and how our description of light was changed by the quantum theory. We will explore some of the tools used in *quantum mechanics,* the "new" physics that had to be developed to describe atoms correctly. We will then use the quantum theory to describe the arrangements of electrons in atoms— what we call the **electronic structure** of atoms. The electronic structure of an atom refers to the number of electrons in the atom as well as their distribution around the nucleus and their energies. We will see that the quantum description of the electronic structure of atoms helps us to understand the arrangement of the elements in the periodic table—why, for example, helium and neon are both unreactive gases, whereas sodium and potassium are both soft, reactive metals.
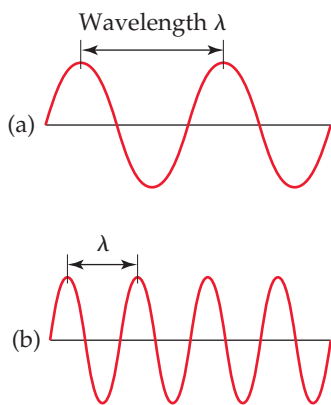
▲ **FIGURE 6.1   Water waves.** The movement of a boat through the water forms waves that move away from the boat.
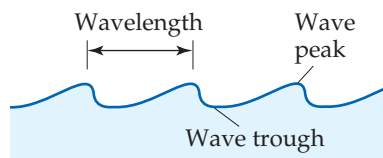
▲ **FIGURE 6.2   Water waves.** The *wavelength* is the distance between two adjacent peaks or two adjacent troughs.

GO FIGURE

If wave (a) has a wavelength of 1.0 m and a frequency of 3.0×10^8 cycles/s, what are the wavelength and frequency of wave (b)?

▲ **FIGURE 6.3   Electromagnetic waves.** Like water waves, electromagnetic radiation can be characterized by a wavelength. Notice that the shorter the wavelength, λ, the higher the frequency, ν. The wavelength in (b) is half as long as that in (a), and the frequency of the wave in (b) is therefore twice as great as the frequency in (a).

6.1 | THE WAVE NATURE OF LIGHT

Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances. To understand electronic structure, therefore, we must first learn about light. The light we see with our eyes, *visible light,* is one type of **electromagnetic radiation**. Because electromagnetic radiation carries energy through space, it is also known as *radiant energy.*

There are many types of electromagnetic radiation in addition to visible light. These different types—radio waves that carry music to our radios, infrared radiation (heat) from a glowing fireplace, X-rays—may seem very different from one another, but they all share certain fundamental characteristics.

All types of electromagnetic radiation move through a vacuum at 3.00×10^8 m/s, the *speed of light.* All have wavelike characteristics similar to those of waves that move through water. Water waves are the result of energy imparted to the water, perhaps by the dropping of a stone or the movement of a boat on the water surface (◀ **FIGURE 6.1**). This energy is expressed as the up-and-down movements of the water.

A cross section of a water wave (◀ **FIGURE 6.2**) shows that it is *periodic,* which means that the pattern of peaks and troughs repeats itself at regular intervals. The distance between two adjacent peaks (or between two adjacent troughs) is called the **wavelength**. The number of complete wavelengths, or *cycles,* that pass a given point each second is the **frequency** of the wave.

Just as with water waves, we can assign a frequency and wavelength to electromagnetic waves, as illustrated in ◀ **FIGURE 6.3**. These and all other wave characteristics of electromagnetic radiation are due to the periodic oscillations in the intensities of the electric and magnetic fields associated with the radiation.

The speed of water waves can vary depending on how they are created—for example, the waves produced by a speedboat travel faster than those produced by a rowboat. In contrast, all electromagnetic radiation moves at the same speed, 3.00×10^8 m/s, the speed of light. As a result, the wavelength and frequency of electromagnetic radiation are always related in a straightforward way. If the wavelength is long, fewer cycles of the wave pass a given point per second, and so the frequency is low. Conversely, for a wave to have a high frequency, it must have a short wavelength. This inverse relationship between the frequency and wavelength of electromagnetic radiation is expressed by the equation

$$c = \lambda \nu \qquad [6.1]$$

where c is the speed of light, λ (lambda) is wavelength, and ν (nu) is frequency.

Why do different types of electromagnetic radiation have different properties? Their differences are due to their different wavelengths. ▶ **FIGURE 6.4** shows the various types of electromagnetic radiation arranged in order of increasing wavelength, a display called the *electromagnetic spectrum.* Notice that the wavelengths span an enormous range. The wavelengths of gamma rays are comparable to the diameters of atomic nuclei, whereas the wavelengths of radio waves can be longer than a football field. Notice also that visible light, which corresponds to wavelengths of about 400 to 750 nm (4×10^{-7} m to 7×10^{-7} m), is an extremely small portion of the electromagnetic spectrum. The unit of length chosen to express wavelength depends on the type of radiation, as shown in ▼ **TABLE 6.1**.

TABLE 6.1 • Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	Television, radio
Kilometer	km	1000	Radio

⚠ **GO FIGURE**

How do the wavelength and frequency of an X-ray compare with those of the red light from a neon sign?

Wavelength (m)

Gamma rays | X-rays | Ultra-violet | Visible | Infrared | Microwaves | Radio frequency
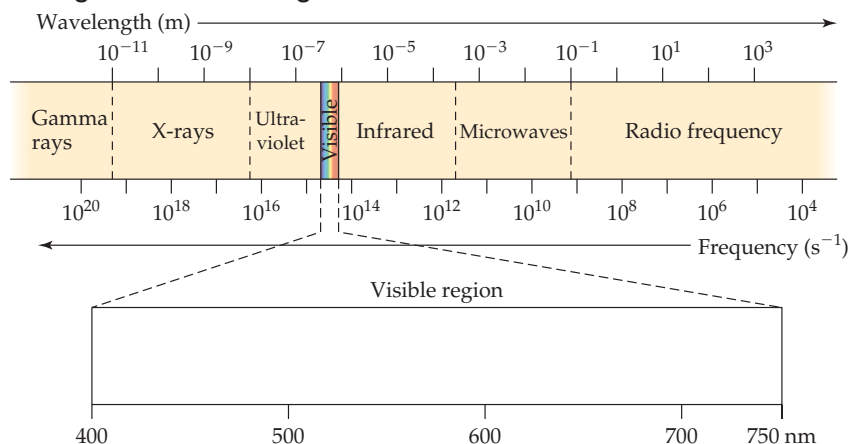
◀ **FIGURE 6.4   The electromagnetic spectrum.** Wavelengths in the spectrum range from very short gamma rays to very long radio waves.

Frequency is expressed in cycles per second, a unit also called a *hertz* (Hz). Because it is understood that cycles are involved, the units of frequency are normally given simply as "per second," which is denoted by s^{-1} or /s. For example, a frequency of 820 kilohertz (kHz), a typical frequency for an AM radio station, could be written as 820 kHz, 820,000 Hz, 820,000 s^{-1}, or 820,000/s.

SAMPLE EXERCISE 6.1   Concepts of Wavelength and Frequency

Two electromagnetic waves are represented in the margin. **(a)** Which wave has the higher frequency? **(b)** If one wave represents visible light and the other represents infrared radiation, which wave is which?

SOLUTION

(a) The lower wave has a longer wavelength (greater distance between peaks). The longer the wavelength, the lower the frequency ($\nu = c/\lambda$). Thus, the lower wave has the lower frequency, and the upper wave has the higher frequency.

(b) The electromagnetic spectrum (Figure 6.4) indicates that infrared radiation has a longer wavelength than visible light. Thus, the lower wave would be the infrared radiation.

PRACTICE EXERCISE

If one of the waves in the margin represents blue light and the other red light, which is which?

Answer: The expanded visible-light portion of Figure 6.4 tells you that red light has a longer wavelength than blue light. The lower wave has the longer wavelength (lower frequency) and would be the red light.
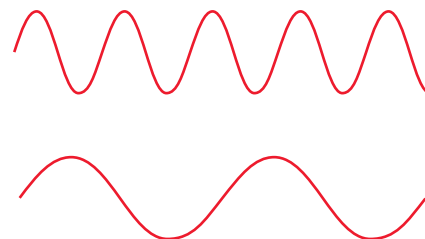
A CLOSER LOOK

THE SPEED OF LIGHT

How do we know that light has a finite speed and does not move infinitely fast?

During the late 1600s, the Danish astronomer Ole Rømer (1644–1710) measured the orbits of several of Jupiter's moons. These moons move much faster than our own—they have orbits of 1–7 days and are eclipsed by Jupiter's shadow at every revolution. Over many months, Rømer measured discrepancies of up to 10 minutes in the times of these orbits. He reasoned that the discrepancies occurred because Jupiter was farther from Earth at different times of the year. Thus, light from the Sun, which reflected off Jupiter and ultimately to his telescope, had farther to travel at different times of the year, implying that light travels at a finite speed. Rømer's data led to the first estimate of the speed of light, 3.5×10^8 m/s.

Since Rømer's time, increasingly sophisticated techniques have been used to measure the speed of light. For example, in 1927, A. A. Michelson (1852–1931) set up a rotating mirror at the top of Mount Wilson in California. The mirror bounced light to the top of Mount San Antonio, 22 miles away, where another mirror bounced the light back to Mount Wilson. Michelson was able to change the speed of the rotating mirror and measure small displacements in the position of the reflected spot. The value for the speed of light (in air) based on this experiment was $2.9980 \pm 0.0002 \times 10^8$ m/s. The main source of error was the distance between the mirrors, which was measured within a fifth of an inch in 22 miles.

By 1975, the measured value was even more precise, $2.99792458 \pm 0.00000004 \times 10^8$ m/s (in vacuum), the error being mostly due to the uncertainty in the length of the meter. In 1983, the meter was redefined based on the distance that light travels in vacuum in one second. As a result, the value for the speed of light became a fixed, exact quantity, $c = 2.99792458 \times 10^8$ m/s.

SAMPLE EXERCISE 6.2 | **Calculating Frequency from Wavelength**

The yellow light given off by a sodium vapor lamp used for public lighting has a wavelength of 589 nm. What is the frequency of this radiation?

SOLUTION

Analyze We are given the wavelength, λ, of the radiation and asked to calculate its frequency, ν.

Plan The relationship between the wavelength and the frequency is given by Equation 6.1. We can solve for ν and use the values of λ and c to obtain a numerical answer. (The speed of light, c, is a fundamental constant whose value is 3.00×10^8 m/s.)

Solve Solving Equation 6.1 for frequency gives $\nu = c/\lambda$. When we insert the values for c and λ, we note that the units of length in these two quantities are different. We can convert the wavelength from nanometers to meters, so the units cancel:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^8 \text{ m/s}}{589 \text{ nm}}\right)\left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 5.09 \times 10^{14} \text{ s}^{-1}$$

Check The high frequency is reasonable because of the short wavelength. The units are proper because frequency has units of "per second," or s^{-1}.

PRACTICE EXERCISE

(a) A laser used in eye surgery to fuse detached retinas produces radiation with a wavelength of 640.0 nm. Calculate the frequency of this radiation. (b) An FM radio station broadcasts electromagnetic radiation at a frequency of 103.4 MHz (megahertz; 1 MHz = 10^6 s^{-1}). Calculate the wavelength of this radiation. The speed of light is 2.998×10^8 m/s to four significant digits.

Answers: (a) $4.688 \times 10^{14} \text{ s}^{-1}$, (b) 2.899 m

▲ **GIVE IT SOME THOUGHT**

Our bodies are penetrated by X-rays but not by visible light. Is this because X-rays travel faster than visible light?

▲ **GO FIGURE**

Which area in the photograph corresponds to the highest temperature?

▲ **FIGURE 6.5** **Color and temperature.** The color and intensity of the light emitted by a hot object, such as this pour of molten steel, depend on the temperature of the object.

6.2 | QUANTIZED ENERGY AND PHOTONS

Although the wave model of light explains many aspects of its behavior, this model cannot explain several phenomena. Three of these are particularly pertinent to our understanding of how electromagnetic radiation and atoms interact: (1) the emission of light from hot objects (referred to as *blackbody radiation* because the objects studied appear black before heating), (2) the emission of electrons from metal surfaces on which light shines (the *photoelectric effect*), and (3) the emission of light from electronically excited gas atoms (*emission spectra*). We examine the first two phenomena here and the third in Section 6.3.

Hot Objects and the Quantization of Energy

When solids are heated, they emit radiation, as seen in the red glow of an electric stove burner or the bright white light of a tungsten lightbulb. The wavelength distribution of the radiation depends on temperature; a red-hot object, for instance, is cooler than a yellowish or white-hot one (◀ **FIGURE 6.5**). During the late 1800s, a number of physicists studied this phenomenon, trying to understand the relationship between the temperature and the intensity and wavelength of the emitted radiation. The prevailing laws of physics could not account for the observations.

In 1900 a German physicist named Max Planck (1858–1947) solved the problem by assuming that energy can be either released or absorbed by atoms only in discrete "chunks" of some minimum size. Planck gave the name **quantum** (meaning "fixed amount") to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation. He proposed that the energy, E, of a single quantum equals a constant times the frequency of the radiation:

$$E = h\nu \qquad\qquad [6.2]$$

Potential energy of person walking up steps increases in stepwise, quantized manner

Potential energy of person walking up ramp increases in uniform, continuous manner

◀ **FIGURE 6.6   Quantized versus continuous change in energy.**

The constant h is called **Planck's constant** and has a value of 6.626×10^{-34} joule-second (J-s).

According to Planck's theory, matter can emit and absorb energy only in whole-number multiples of $h\nu$, such as $h\nu$, $2h\nu$, $3h\nu$, and so forth. If the quantity of energy emitted by an atom is $3h\nu$, for example, we say that three quanta of energy have been emitted (*quanta* being the plural of *quantum*). Because the energy can be released only in specific amounts, we say that the allowed energies are *quantized*—their values are restricted to certain quantities. Planck's revolutionary proposal that energy is quantized was proved correct, and he was awarded the 1918 Nobel Prize in Physics for his work on the quantum theory.

If the notion of quantized energies seems strange, it might be helpful to draw an analogy by comparing a ramp and a staircase (▲ **FIGURE 6.6**). As you walk up a ramp, your potential energy increases in a uniform, continuous manner. When you climb a staircase, you can step only *on* individual stairs, not *between* them, so that your potential energy is restricted to certain values and is therefore quantized.

If Planck's quantum theory is correct, why are its effects not obvious in our daily lives? Why do energy changes seem continuous rather than quantized, or "jagged"? Notice that Planck's constant is an extremely small number. Thus, a quantum of energy, $h\nu$, is an extremely small amount. Planck's rules regarding the gain or loss of energy are always the same, whether we are concerned with objects on the scale of our ordinary experience or with microscopic objects. With everyday objects, however, the gain or loss of a single quantum of energy is so small that it goes completely unnoticed. In contrast, when dealing with matter at the atomic level, the impact of quantized energies is far more significant.
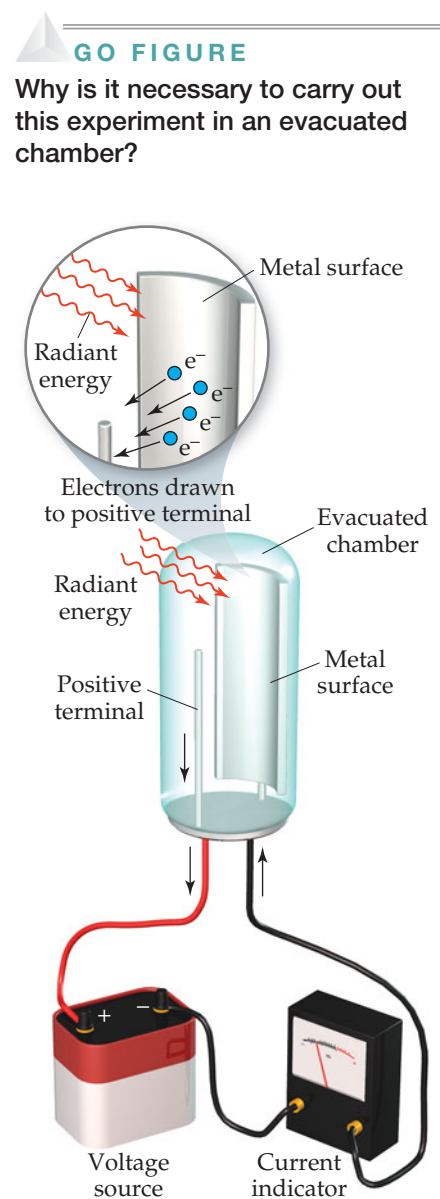
▲ **GIVE IT SOME THOUGHT**

Calculate the energy (to one significant figure) of one quantum of electromagnetic radiation whose frequency is 5×10^{-3} s^{-1}. Can this radiation produce a burst of energy $E = 5 \times 10^{-36}$ J? Why or why not?

The Photoelectric Effect and Photons

A few years after Planck presented his quantum theory, scientists began to see its applicability to many experimental observations. In 1905, Albert Einstein (1879–1955) used Planck's theory to explain the **photoelectric effect** (▶ **FIGURE 6.7**). Light shining on a clean metal surface causes the surface to emit electrons. A minimum frequency of light, different for different metals, is required for the emission of electrons. For example, light with a frequency of 4.60×10^{14} s^{-1} or greater causes cesium metal to emit electrons, but light of lower frequency has no effect.

To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface behaves like a stream of tiny energy packets. Each packet, which is like a "particle" of energy, is called a **photon**. Extending Planck's quantum theory,

▲ **GO FIGURE**

Why is it necessary to carry out this experiment in an evacuated chamber?

Metal surface

Radiant energy

Electrons drawn to positive terminal

Radiant energy

Positive terminal

Evacuated chamber

Metal surface

Voltage source

Current indicator

▲ **FIGURE 6.7   The photoelectric effect.**

Einstein deduced that each photon must have an energy equal to Planck's constant times the frequency of the light:

$$\text{Energy of photon} = E = h\nu \qquad [6.3]$$

Thus, radiant energy itself is quantized.

Under the right conditions, photons striking a metal surface can transfer their energy to electrons in the metal. A certain amount of energy—called the *work function*—is required for the electrons to overcome the attractive forces holding them in the metal. If the photons striking the metal have less energy than the work function, the electrons do not acquire sufficient energy to escape from the metal, even if the light beam is intense. If the photons have energy greater than the work function of the particular metal, however, electrons are emitted. The intensity (brightness) of the light is related to the number of photons striking the surface per unit time but not to the energy of each photon. Einstein won the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

To better understand what a photon is, imagine you have a light source that produces radiation of a single wavelength. Further suppose that you could switch the light on and off faster and faster to provide ever-smaller bursts of energy. Einstein's photon theory tells us that you would eventually come to the smallest energy burst, given by $E = h\nu$. This smallest burst consists of a single photon of light.

SAMPLE EXERCISE 6.3   **Energy of a Photon**

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

SOLUTION

Analyze Our task is to calculate the energy, E, of a photon, given $\lambda = 589$ nm.

Plan We can use Equation 6.1 to convert the wavelength to frequency: $\nu = c/\lambda$

We can then use Equation 6.3 to calculate energy: $E = h\nu$

Solve The frequency, ν, is calculated from the given wavelength, as shown in Sample Exercise 6.2: $\nu = c/\lambda = 5.09 \times 10^{14}\ \text{s}^{-1}$

The value of Planck's constant, h, is given both in the text and in the table of physical constants on the inside back cover of the text, and so we can easily calculate E:

$$E = (6.626 \times 10^{-34}\ \text{J-s})(5.09 \times 10^{14}\ \text{s}^{-1}) = 3.37 \times 10^{-19}\ \text{J}$$

Comment If one photon of radiant energy supplies 3.37×10^{-19} J, then one mole of these photons will supply

$$(6.02 \times 10^{23}\ \text{photons/mol})(3.37 \times 10^{-19}\ \text{J/photon})$$
$$= 2.03 \times 10^{5}\ \text{J/mol}$$

PRACTICE EXERCISE

(a) A laser emits light that has a frequency of $4.69 \times 10^{14}\ \text{s}^{-1}$. What is the energy of one photon of this radiation? (b) If the laser emits a pulse containing 5.0×10^{17} photons of this radiation, what is the total energy of that pulse? (c) If the laser emits 1.3×10^{-2} J of energy during a pulse, how many photons are emitted?

Answers: (a) 3.11×10^{-19} J, (b) 0.16 J, (c) 4.2×10^{16} photons

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The idea that the energy of light depends on its frequency helps us understand the diverse effects of different kinds of electromagnetic radiation. For example, because of the high frequency (short wavelength) of X-rays (Figure 6.4), X-ray photons cause tissue damage and even cancer. Thus, signs are normally posted around X-ray equipment warning us of high-energy radiation.

Although Einstein's theory of light as a stream of photons rather than a wave explains the photoelectric effect and a great many other observations, it also poses a dilemma. Is light a wave, or is it particle-like? The only way to resolve this dilemma is to adopt what might seem to be a bizarre position: We must consider that light possesses both wave-like and particle-like characteristics and, depending on the situation, will behave more like waves or more like particles. We will soon see that this dual nature of light is also a characteristic trait of matter.

▲ GIVE IT SOME THOUGHT

Which has more energy, a photon of infrared light or a photon of ultraviolet light?

6.3 | LINE SPECTRA AND THE BOHR MODEL

The work of Planck and Einstein paved the way for understanding how electrons are arranged in atoms. In 1913, the Danish physicist Niels Bohr (▶ FIGURE 6.8) offered a theoretical explanation of *line spectra,* another phenomenon that had puzzled scientists during the nineteenth century.
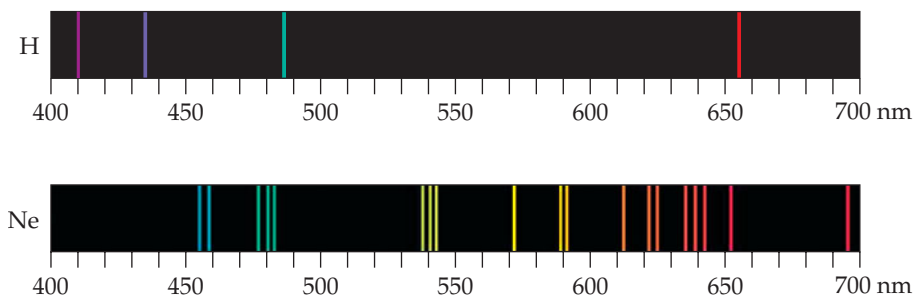
Line Spectra

A particular source of radiant energy may emit a single wavelength, as in the light from a laser. Radiation composed of a single wavelength is *monochromatic*. However, most common radiation sources, including lightbulbs and stars, produce radiation containing many different wavelengths and is *polychromatic*. A **spectrum** is produced when radiation from such sources is separated into its component wavelengths, as shown in ▶ FIGURE 6.9. The resulting spectrum consists of a continuous range of colors—violet merges into indigo, indigo into blue, and so forth, with no blank spots. This rainbow of colors, containing light of all wavelengths, is called a **continuous spectrum**. The most familiar example of a continuous spectrum is the rainbow produced when raindrops or mist acts as a prism for sunlight.

Not all radiation sources produce a continuous spectrum. When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colors of light (▶ FIGURE 6.10). The light emitted by neon gas is the familiar red-orange glow of many "neon" lights, whereas sodium vapor emits the yellow light characteristic of some modern streetlights. When light coming from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectra (▼ FIGURE 6.11). Each colored line in such spectra represents light of one wavelength. A spectrum containing radiation of only specific wavelengths is called a **line spectrum**.

When scientists first detected the line spectrum of hydrogen in the mid-1800s, they were fascinated by its simplicity. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red) were observed (Figure 6.11). In 1885, a Swiss schoolteacher named Johann Balmer showed that the wavelengths of these four lines fit an intriguingly simple formula that relates the wavelengths to integers. Later, additional lines were found in the ultraviolet and infrared regions of hydrogen's line spectrum. Soon Balmer's equation was extended to a more general one, called the *Rydberg equation,* which allows us to calculate the wavelengths of all the spectral lines of hydrogen:

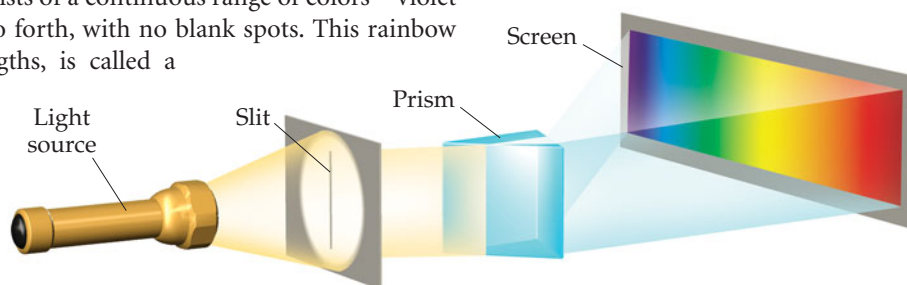$$\frac{1}{\lambda} = (R_H)\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad [6.4]$$

In this formula λ is the wavelength of a spectral line, R_H is the *Rydberg constant* ($1.096776 \times 10^7 \text{ m}^{-1}$), and n_1 and n_2 are positive integers, with n_2 being larger


▲ **FIGURE 6.8 Quantum giants.** Niels Bohr (right) with Albert Einstein. Bohr (1885–1962) made major contributions to the quantum theory and was awarded the Nobel Prize in Physics in 1922.

▲ **FIGURE 6.9 Creating a spectrum.** A continuous visible spectrum is produced when a narrow beam of white light is passed through a prism. The white light could be sunlight or light from an incandescent lamp.

Hydrogen (H)   Neon (Ne)
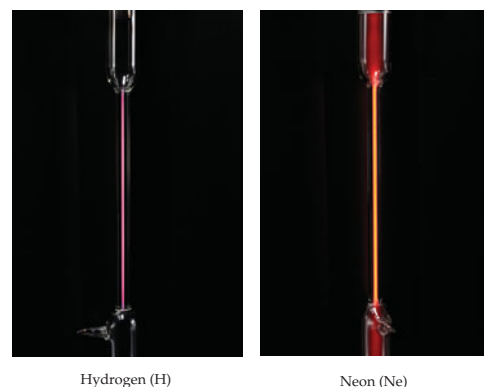
▲ **FIGURE 6.10 Atomic emission of hydrogen and neon.** Different gases emit light of different characteristic colors when an electric current is passed through them.

▲ **FIGURE 6.11 Line spectra of hydrogen and neon.**

than n_1. How could the remarkable simplicity of this equation be explained? It took nearly 30 more years to answer this question.

Bohr's Model

To explain the line spectrum of hydrogen, Bohr assumed that electrons in hydrogen atoms move in circular orbits around the nucleus, but this assumption posed a problem. According to classical physics, a charged particle (such as an electron) moving in a circular path should continuously lose energy. As an electron loses energy, therefore, it should spiral into the positively charged nucleus. This behavior, however, does not happen—hydrogen atoms are stable. So how can we explain this apparent violation of the laws of physics? Bohr approached this problem in much the same way that Planck had approached the problem of the nature of the radiation emitted by hot objects: He assumed that the prevailing laws of physics were inadequate to describe all aspects of atoms. Furthermore, he adopted Planck's idea that energies are quantized.
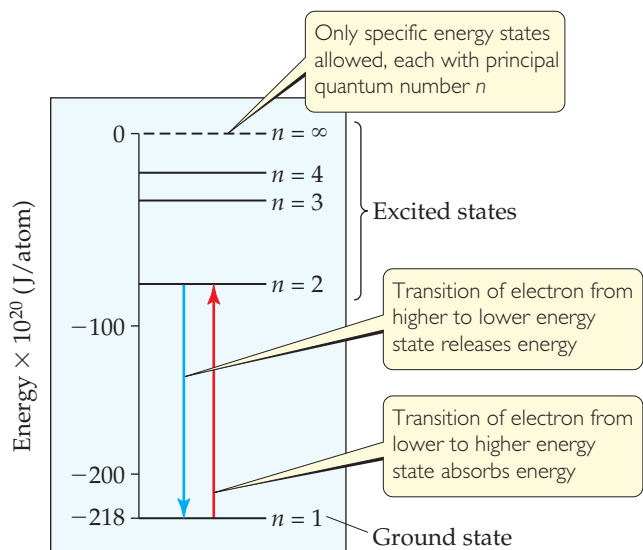
Bohr based his model on three postulates:

1. Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.
2. An electron in a permitted orbit is in an "allowed" energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.
3. Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $E = h\nu$.

⚠ GIVE IT SOME THOUGHT

Before reading further about Bohr's model, speculate as to how it explains the fact that hydrogen gas emits a line spectrum (Figure 6.11) rather than a continuous spectrum.

The Energy States of the Hydrogen Atom

Starting with his three postulates and using classical equations for motion and for interacting electrical charges, Bohr calculated the energies corresponding to the allowed orbits for the electron in the hydrogen atom. Ultimately, the calculated energies fit the formula

$$E = (-hcR_H)\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{n^2}\right) \qquad [6.5]$$

where h, c, and R_H are Planck's constant, the speed of light, and the Rydberg constant, respectively. The integer n, which can have whole-number values of 1, 2, 3, . . .∞, is called the *principal quantum number*. Each orbit corresponds to a different value of n, and the radius of the orbit gets larger as n increases. Thus, the first allowed orbit (the one closest to the nucleus) has $n = 1$, the next allowed orbit (the one second closest to the nucleus) has $n = 2$, and so forth. The electron in the hydrogen atom can be in any allowed orbit, and Equation 6.5 tells us the energy the electron has in each allowed orbit.

Note that the energies of the electron given by Equation 6.5 are negative for all values of n. The lower (more negative) the energy is, the more stable the atom is. The energy is lowest (most negative) for $n = 1$. As n gets larger, the energy becomes less negative and therefore increases. We can liken the situation to a ladder in which the rungs are numbered from the bottom. The higher one climbs (the greater the value of n), the higher the energy. The lowest-energy state ($n = 1$, analogous to the bottom rung) is called the **ground state** of the atom. When the electron is in a higher-energy state ($n = 2$ or higher), the atom is said to be in an **excited state**. ◀ FIGURE 6.12 shows the energy of the electron in a hydrogen atom for several values of n.

▲ GO FIGURE

If the transition of an electron from the $n = 3$ state to the $n = 2$ state results in emission of visible light, is the transition from the $n = 2$ state to the $n = 1$ state more likely to result in the emission of infrared or ultraviolet radiation?

▲ FIGURE 6.12 Energy states in the hydrogen atom. Only states for $n = 1$ through $n = 4$ and $n = \infty$ are shown. Energy is released or absorbed when an electron moves from one energy state to another.

What happens to the orbit radius and the energy as n becomes infinitely large? The radius increases as n^2, so when $n = \infty$ the electron is completely separated from the nucleus, and the energy of the electron is zero:

$$E = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{\infty^2}\right) = 0$$

The state in which the electron is removed from the nucleus is called the reference, or zero-energy, state of the hydrogen atom.

In his third postulate, Bohr assumed that the electron can "jump" from one allowed orbit to another by either absorbing or emitting photons whose radiant energy corresponds exactly to the energy difference between the two orbits. The electron must absorb energy in order to move to a higher-energy state (higher value of n). Conversely, radiant energy is emitted when the electron jumps to a lower-energy state (lower value of n).

If the electron jumps from an initial state of energy E_i to a final state of energy E_f, the change in energy is

$$\Delta E = E_f - E_i = E_{\text{photon}} = h\nu \qquad [6.6]$$

Bohr's model of the hydrogen atom states, therefore, that only the specific frequencies of light that satisfy Equation 6.6 can be absorbed or emitted by the atom.

Substituting the energy expression in Equation 6.5 into Equation 6.6 and recalling that $\nu = c/\lambda$, we have

$$\Delta E = h\nu = \frac{hc}{\lambda} = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad [6.7]$$

where n_i and n_f are the principal quantum numbers of the initial and final states of the atom, respectively. If n_f is smaller than n_i, the electron moves closer to the nucleus and ΔE is a negative number, indicating that the atom releases energy. For example, if the electron moves from $n_i = 3$ to $n_f = 1$, we have

$$\Delta E = (-2.18 \times 10^{-18} \text{ J})\left(\frac{1}{1^2} - \frac{1}{3^2}\right) = (-2.18 \times 10^{-18} \text{ J})\left(\frac{8}{9}\right) = -1.94 \times 10^{-18} \text{ J}$$

Knowing the energy of the emitted photon, we can calculate either its frequency or its wavelength. For the wavelength, we have

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J-s})(3.00 \times 10^8 \text{ m/s})}{1.94 \times 10^{-18} \text{ J}} = 1.02 \times 10^{-7} \text{ m}$$

We have not included the negative sign of the energy in this calculation because wavelength and frequency are always reported as positive quantities. The direction of energy flow is indicated by saying that a photon of wavelength 1.02×10^{-7} m has been *emitted*.

If we solve Equation 6.7 for $1/\lambda$ and replace $(-2.18 \times 10^{-18} \text{ J})$ by its equivalent, hcR_H from Equation 6.5, we find that Equation 6.7 derived from Bohr's theory corresponds to the Rydberg equation, Equation 6.4, which was obtained using experimental data:

$$\frac{1}{\lambda} = \frac{-hcR_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

Thus, the existence of discrete spectral lines can be attributed to the quantized jumps of electrons between energy levels.

▲ GIVE IT SOME THOUGHT

As the electron in a hydrogen atom jumps from the $n = 3$ orbit to the $n = 7$ orbit, does it absorb energy or emit energy?

SAMPLE EXERCISE 6.4 **Electronic Transitions in the Hydrogen Atom**

Using Figure 6.12, predict which of these electronic transitions produces the spectral line having the longest wavelength: $n = 2$ to $n = 1$, $n = 3$ to $n = 2$, or $n = 4$ to $n = 3$.

SOLUTION

The wavelength increases as frequency decreases ($\lambda = c/\nu$). Hence, the longest wavelength will be associated with the lowest frequency. According to Planck's equation, $E = h\nu$, the lowest frequency is associated with the lowest energy. In Figure 6.12 the energy levels (horizontal lines) that are closest together represents the smallest energy change. Thus, the $n = 4$ to $n = 3$ transition produces the longest wavelength (lowest frequency) line.

PRACTICE EXERCISE

Indicate whether each of the following electronic transitions emits energy or requires the absorption of energy: **(a)** $n = 3$ to $n = 1$; **(b)** $n = 2$ to $n = 4$.

Answers: **(a)** emits energy, **(b)** requires absorption of energy

Limitations of the Bohr Model

Although the Bohr model explains the line spectrum of the hydrogen atom, it cannot explain the spectra of other atoms, except in a crude way. Bohr also avoided the problem of why the negatively charged electron would not just fall into the positively charged nucleus by simply assuming it would not happen. Furthermore, there is a problem with describing an electron merely as a small particle circling the nucleus. As we will see in Section 6.4, the electron exhibits wavelike properties, a fact that any acceptable model of electronic structure must accommodate. As it turns out, the Bohr model was only an important step along the way toward the development of a more comprehensive model. What is most significant about Bohr's model is that it introduces two important ideas that are also incorporated into our current model:

1. *Electrons exist only in certain discrete energy levels, which are described by quantum numbers.*

2. *Energy is involved in the transition of an electron from one level to another.*

We will now start to develop the successor to the Bohr model, which requires that we take a closer look at the behavior of matter.

6.4 | THE WAVE BEHAVIOR OF MATTER

In the years following the development of Bohr's model for the hydrogen atom, the dual nature of radiant energy became a familiar concept. Depending on the experimental circumstances, radiation appears to have either a wave-like or a particle-like (photon) character. Louis de Broglie (1892–1987), who was working on his Ph.D. thesis in physics at the Sorbonne in Paris, boldly extended this idea. If radiant energy could, under appropriate conditions, behave as though it were a stream of particles (photons), could matter, under appropriate conditions, possibly show the properties of a wave?

De Broglie suggested that an electron moving about the nucleus of an atom behaves like a wave and therefore has a wavelength. He proposed that the wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity, v:

$$\lambda = \frac{h}{mv} \qquad [6.8]$$

(where h is Planck's constant). The quantity mv for any object is called its **momentum**. De Broglie used the term **matter waves** to describe the wave characteristics of material particles.

Because de Broglie's hypothesis is applicable to all matter, any object of mass m and velocity v would give rise to a characteristic matter wave. However, Equation 6.8 indicates that the wavelength associated with an object of ordinary size, such as a golf ball, is so tiny as to be completely unobservable. This is not so for an electron because its mass is so small, as we see in Sample Exercise 6.5.

SAMPLE EXERCISE 6.5   **Matter Waves**

What is the wavelength of an electron moving with a speed of 5.97×10^6 m/s? The mass of the electron is 9.11×10^{-31} kg.

SOLUTION

Analyze We are given the mass, *m,* and velocity, *v,* of the electron, and we must calculate its de Broglie wavelength, λ.

Plan The wavelength of a moving particle is given by Equation 6.8, so λ is calculated by inserting the known quantities *h, m,* and *v.* In doing so, however, we must pay attention to units.

Solve Using the value of Planck's constant, $h = 6.626 \times 10^{-34}$ J-s

we have the following: $\lambda = \dfrac{h}{mv}$

$$= \frac{(6.626 \times 10^{-34} \text{ J-s})}{(9.11 \times 10^{-31} \text{ kg})(5.97 \times 10^6 \text{ m/s})}\left(\frac{1 \text{ kg-m}^2/\text{s}^2}{1 \text{ J}}\right)$$

$$= 1.22 \times 10^{-10} \text{ m} = 0.122 \text{ nm} = 1.22 \text{ Å}$$

Comment By comparing this value with the wavelengths of electromagnetic radiation shown in Figure 6.4, we see that the wavelength of this electron is about the same as that of X-rays.

PRACTICE EXERCISE

Calculate the velocity of a neutron whose de Broglie wavelength is 500 pm. The mass of a neutron is given in the table inside the back cover of the text.

Answer: 7.92×10^2 m/s

A few years after de Broglie published his theory, the wave properties of the electron were demonstrated experimentally. When X-rays pass through a crystal, an interference pattern results that is characteristic of the wavelike properties of electromagnetic radiation. This phenomenon is called X-ray *diffraction.* As electrons pass through a crystal, they are similarly diffracted. Thus, a stream of moving electrons exhibits the same kinds of wave behavior as X-rays and all other types of electromagnetic radiation.

The technique of electron diffraction has been highly developed. In the electron microscope, for instance, the wave characteristics of electrons are used to obtain images at the atomic scale. This microscope is an important tool for studying surface phenomena at very high magnifications (▶ **FIGURE 6.13**). Electron microscopes can magnify objects by 3,000,000 times ($\times$), far more than can be done with visible light ($1000\times$), because the wavelength of the electrons is so much smaller than the wavelengths of visible light.
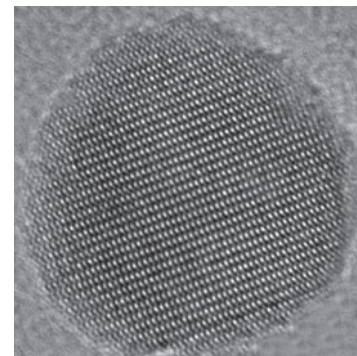

▲ **FIGURE 6.13** **Electrons as waves.** The white dots in this transmission electron micrograph indicate the tops of columns of atoms.

⚠ **GIVE IT SOME THOUGHT**

A baseball pitcher throws a fastball that moves at 95 miles per hour. Does that moving baseball generate matter waves? If so, can we observe them?
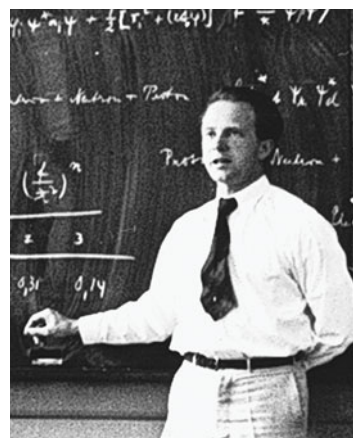
The Uncertainty Principle

The discovery of the wave properties of matter raised some new and interesting questions. Consider, for example, a ball rolling down a ramp. Using the equations of classical physics, we can calculate, with great accuracy, the ball's position, direction of motion, and speed at any instant. Can we do the same for an electron, which exhibits wave properties? A wave extends in space and its location is not precisely defined. We might therefore anticipate that it is impossible to determine exactly where an electron is located at a specific instant.

The German physicist Werner Heisenberg (▶ **FIGURE 6.14**) proposed that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and

◀ **FIGURE 6.14** **Werner Heisenberg (1901–1976).** During his postdoctoral assistantship with Niels Bohr, Heisenberg formulated his famous uncertainty principle. At 32 he was one of the youngest scientists to receive a Nobel Prize.

the momentum of an object at a given instant. The limitation becomes important only when we deal with matter at the subatomic level (that is, with masses as small as that of an electron). Heisenberg's principle is called the **uncertainty principle**. When applied to the electrons in an atom, this principle states that it is impossible for us to know simultaneously both the exact momentum of the electron and its exact location in space.

Heisenberg mathematically related the uncertainty in position, Δx, and the uncertainty in momentum, $\Delta(mv)$, to a quantity involving Planck's constant:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi} \qquad [6.9]$$

A brief calculation illustrates the dramatic implications of the uncertainty principle. The electron has a mass of 9.11×10^{-31} kg and moves at an average speed of about 5×10^6 m/s in a hydrogen atom. Let's assume that we know the speed to an uncertainty of 1% [that is, an uncertainty of $(0.01)(5 \times 10^6$ m/s$) = 5 \times 10^4$ m/s] and that this is the only important source of uncertainty in the momentum, so that $\Delta(mv) = m\,\Delta v$. We can use Equation 6.9 to calculate the uncertainty in the position of the electron:

$$\Delta x \geq \frac{h}{4\pi m \Delta v} = \left(\frac{6.626 \times 10^{-34}\ \text{J-s}}{4\pi(9.11 \times 10^{-31}\ \text{kg})(5 \times 10^4\ \text{m/s})}\right) = 1 \times 10^{-9}\ \text{m}$$

Because the diameter of a hydrogen atom is about 1×10^{-10} m, the uncertainty in the position of the electron in the atom is an order of magnitude greater than the size of the atom. Thus, we have essentially no idea where the electron is located in the atom. On the other hand, if we were to repeat the calculation with an object of ordinary mass, such as a tennis ball, the uncertainty would be so small that it would be inconsequential. In that case, m is large and Δx is out of the realm of measurement and therefore of no practical consequence.

De Broglie's hypothesis and Heisenberg's uncertainty principle set the stage for a new and more broadly applicable theory of atomic structure. In this approach, any attempt to define precisely the instantaneous location and momentum of the electron is abandoned. The wave nature of the electron is recognized, and its behavior is described in terms appropriate to waves. The result is a model that precisely describes the energy of the electron while describing its location not precisely but rather in terms of probabilities.

A CLOSER LOOK

MEASUREMENT AND THE UNCERTAINTY PRINCIPLE

Whenever any measurement is made, some uncertainty exists. Our experience with objects of ordinary dimensions, such as balls or trains or laboratory equipment, indicates that using more precise instruments can decrease the uncertainty of a measurement. In fact, we might expect that the uncertainty in a measurement can be made indefinitely small. However, the uncertainty principle states that there is an actual limit to the accuracy of measurements. This limit is not a restriction on how well instruments can be made; rather, it is inherent in nature. This limit has no practical consequences when dealing with ordinary-sized objects, but its implications are enormous when dealing with subatomic particles, such as electrons.

To measure an object, we must disturb it, at least a little, with our measuring device. Imagine using a flashlight to locate a large rubber ball in a dark room. You see the ball when the light from the flashlight bounces off the ball and strikes your eyes. When a beam of photons strikes an object of this size, it does not alter its position or momentum to any practical extent. Imagine, however, that you wish to locate an electron by similarly bouncing light off it into some detector. Objects can be located to an accuracy no greater than the wavelength of the radiation used. Thus, if we want an accurate position measurement for an electron, we must use a short wavelength. This means that photons of high energy must be employed. The more energy the photons have, the more momentum they impart to the electron when they strike it, which changes the electron's motion in an unpredictable way. The attempt to measure accurately the electron's position introduces considerable uncertainty in its momentum; the act of measuring the electron's position at one moment makes our knowledge of its future position inaccurate.

Suppose, then, that we use photons of longer wavelength. Because these photons have lower energy, the momentum of the electron is not so appreciably changed during measurement, but its position will be correspondingly less accurately known. This is the essence of the uncertainty principle: *There is an uncertainty in simultaneously knowing either the position or the momentum of the electron that cannot be reduced beyond a certain minimum level.* The more accurately one is known, the less accurately the other is known. Although we can never know the exact position and momentum of the electron, we can talk about the probability of its being at certain locations in space. In Section 6.5 we introduce a model of the atom that provides the probability of finding electrons of specific energies at certain positions in atoms.

RELATED EXERCISES: 6.47 and 6.48

What is the principal reason we must consider the uncertainty principle when discussing electrons and other subatomic particles but not when discussing our macroscopic world?

6.5 | QUANTUM MECHANICS AND ATOMIC ORBITALS

In 1926 the Austrian physicist Erwin Schrödinger (1887–1961) proposed an equation, now known as Schrödinger's wave equation, that incorporates both the wave-like behavior of the electron and its particle-like behavior. His work opened a new approach to dealing with subatomic particles, an approach known as *quantum mechanics* or *wave mechanics.* The application of Schrödinger's equation requires advanced calculus, and so we will not be concerned with its details. We will, however, qualitatively consider the results Schrödinger obtained because they give us a powerful new way to view electronic structure. Let's begin by examining the electronic structure of the simplest atom, hydrogen.

Schrödinger treated the electron in a hydrogen atom like the wave on a plucked guitar string (▼ **FIGURE 6.15**). Because such waves do not travel in space, they are called *standing waves.* Just as the plucked guitar string produces a standing wave that has a fundamental frequency and higher overtones (harmonics), the electron exhibits a lowest-energy standing wave and higher-energy ones. Furthermore, just as the overtones of the guitar string have *nodes,* points where the amplitude of the wave is zero, so do the waves characteristic of the electron.

Solving Schrödinger's equation for the hydrogen atom leads to a series of mathematical functions called **wave functions** that describe the electron in an atom. These wave functions are usually represented by the symbol ψ (lowercase Greek letter *psi*). Although the wave function has no direct physical meaning, the square of the wave function, ψ^2, provides information about the electron's location when it is in an allowed energy state.

For the hydrogen atom, the allowed energies are the same as those predicted by the Bohr model. However, the Bohr model assumes that the electron is in a circular orbit of some particular radius about the nucleus. In the quantum mechanical model, the electron's location cannot be described so simply.

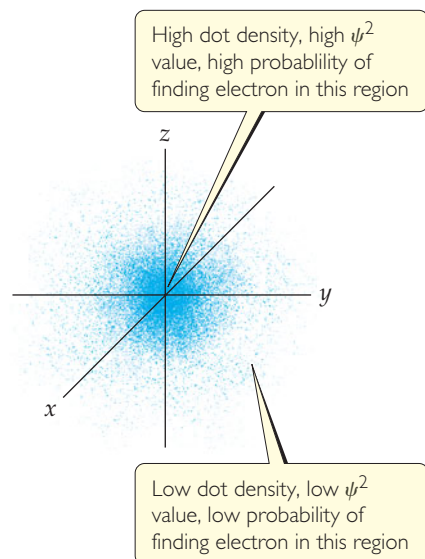According to the uncertainty principle, if we know the momentum of the electron with high accuracy, our simultaneous knowledge of its location is very uncertain. Thus, we cannot hope to specify the exact location of an individual electron around the

$n = 1$ — Fundamental

1 node

$n = 2$ — First overtone

2 nodes

$n = 3$ — Second overtone
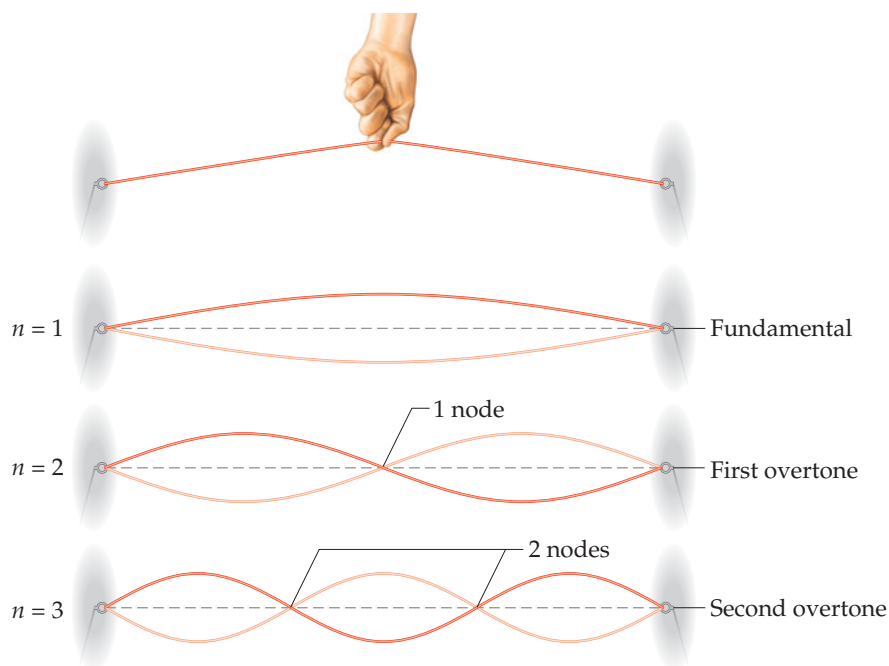
◀ **FIGURE 6.15   Standing waves in a vibrating string.**

Where in the figure is the region of highest electron density?

High dot density, high ψ^2 value, high probablility of finding electron in this region

Low dot density, low ψ^2 value, low probability of finding electron in this region

▲ **FIGURE 6.16** **Electron-density distribution.** This rendering represents the probability, ψ^2, of finding the electron in a hydrogen atom in its ground state. The origin of the coordinate system is at the nucleus.

nucleus. Rather, we must be content with a kind of statistical knowledge. We therefore speak of the *probability* that the electron will be in a certain region of space at a given instant. As it turns out, the square of the wave function, ψ^2, at a given point in space represents the probability that the electron will be found at that location. For this reason, ψ^2 is called either the **probability density** or the **electron density**.

One way of representing the probability of finding the electron in various regions of an atom is shown in ◀ **FIGURE 6.16**, where the density of the dots represents the probability of finding the electron. The regions with a high density of dots correspond to relatively large values for ψ^2 and are therefore regions where there is a high probability of finding the electron. Based on this representation, we often describe atoms as consisting of a nucleus surrounded by an electron cloud.

Orbitals and Quantum Numbers

The solution to Schrödinger's equation for the hydrogen atom yields a set of wave functions called **orbitals**. Each orbital has a characteristic shape and energy. For example, the lowest-energy orbital in the hydrogen atom has the spherical shape illustrated in Figure 6.16 and an energy of -2.18×10^{-18} J. Note that an *orbital* (quantum mechanical model, which describes electrons in terms of probabilities, visualized as "electron clouds") is not the same as an *orbit* (Bohr model, which visualizes the electron moving in a physical orbit, like a planet around a star). The quantum mechanical model does not refer to orbits because the motion of the electron in an atom cannot be precisely determined (Heisenberg uncertainty principle).

The Bohr model introduced a single quantum number, *n*, to describe an orbit. The quantum mechanical model uses three quantum numbers, *n, l,* and m_l, which result naturally from the mathematics used, to describe an orbital.

1. The *principal quantum number, n,* can have positive integral values 1, 2, 3, ... As *n* increases, the orbital becomes larger, and the electron spends more time farther from the nucleus. An increase in *n* also means that the electron has a higher energy and is therefore less tightly bound to the nucleus. For the hydrogen atom, $E_n = -(2.18 \times 10^{-18}$ J$)(1/n^2)$, as in the Bohr model.

2. The second quantum number—the *angular momentum quantum number, l*—can have integral values from 0 to $(n - 1)$ for each value of *n*. This quantum number defines the shape of the orbital. The value of *l* for a particular orbital is generally designated by the letters *s, p, d,* and *f, * corresponding to *l* values of 0, 1, 2, and 3:

Value of l	0	1	2	3
Letter used	s	p	d	f

3. The *magnetic quantum number, m_l,* can have integral values between $-l$ and *l,* including zero. This quantum number describes the orientation of the orbital in space, as we discuss in Section 6.6.

Notice that because the value of *n* can be any positive integer, an infinite number of orbitals for the hydrogen atom are possible. At any given instant, however, the electron in a hydrogen atom is described by only one of these orbitals—we say that the electron *occupies* a certain orbital. The remaining orbitals are *unoccupied* for that particular state of the hydrogen atom.

▲ **GIVE IT SOME THOUGHT**

What is the difference between an *orbit* in the Bohr model of the hydrogen atom and an *orbital* in the quantum mechanical model?

The collection of orbitals with the same value of *n* is called an **electron shell**. All the orbitals that have *n* = 3, for example, are said to be in the third shell. The set of

*The letters come from the words *sharp, principal, diffuse,* and *fundamental,* which were used to describe certain features of spectra before quantum mechanics was developed.

TABLE 6.2 • **Relationship among Values of *n*, *l*, and m_l through *n* = 4**

n	Possible Values of *l*	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	
	1	2p	1, 0, −1	3	4
3	0	3s	0	1	
	1	3p	1, 0, −1	3	
	2	3d	2, 1, 0, −1, −2	5	9
4	0	4s	0	1	
	1	4p	1, 0, −1	3	
	2	4d	2, 1, 0, −1, −2	5	
	3	4f	3, 2, 1, 0, −1, −2, −3	7	16

orbitals that have the same *n* and *l* values is called a **subshell**. Each subshell is designated by a number (the value of *n*) and a letter (*s, p, d,* or *f,* corresponding to the value of *l*). For example, the orbitals that have *n* = 3 and *l* = 2 are called 3*d* orbitals and are in the 3*d* subshell.

▲ **TABLE 6.2** summarizes the possible values of *l* and m_l for values of *n* through *n* = 4. The restrictions on possible values give rise to the following very important observations:

1. The shell with principal quantum number *n* consists of exactly *n* subshells. Each subshell corresponds to a different allowed value of *l* from 0 to (*n* − 1). Thus, the first shell (*n* = 1) consists of only one subshell, the 1*s* (*l* = 0); the second shell (*n* = 2) consists of two subshells, the 2*s* (*l* = 0) and 2*p* (*l* = 1); the third shell consists of three subshells, 3*s*, 3*p*, and 3*d*, and so forth.

2. Each subshell consists of a specific number of orbitals. Each orbital corresponds to a different allowed value of m_l. For a given value of *l*, there are (2*l* + 1) allowed values of m_l, ranging from −*l* to +*l*. Thus, each *s* (*l* = 0) subshell consists of one orbital; each *p* (*l* = 1) subshell consists of three orbitals; each *d* (*l* = 2) subshell consists of five orbitals, and so forth.

3. The total number of orbitals in a shell is n^2, where *n* is the principal quantum number of the shell. The resulting number of orbitals for the shells—1, 4, 9, 16—are related to a pattern seen in the periodic table: We see that the number of elements in the rows of the periodic table—2, 8, 18, and 32—equals twice these numbers. We will discuss this relationship further in Section 6.9.
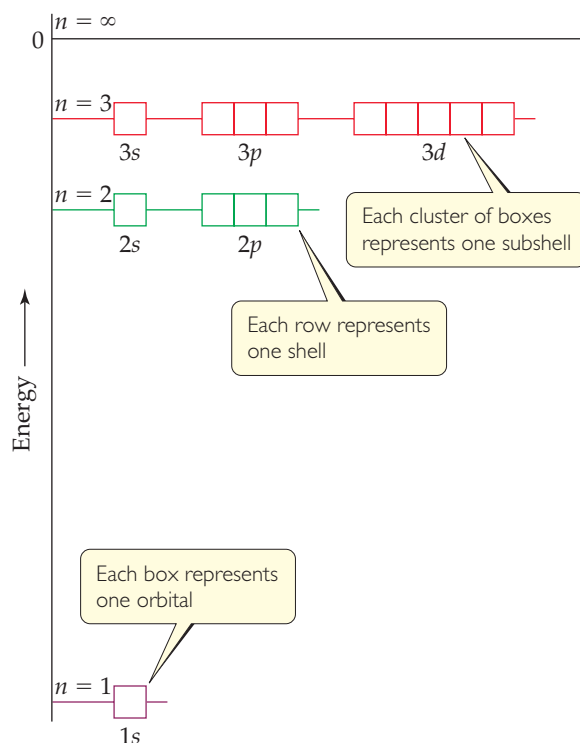
▶ **FIGURE 6.17** shows the relative energies of the hydrogen atom orbitals through *n* = 3. Each box represents an orbital, and orbitals of the same subshell, such as the three 2*p* orbitals, are grouped together. When the electron occupies the lowest-energy orbital (1*s*), the hydrogen atom is said to be in its *ground state*. When the electron occupies any other orbital, the atom is in an *excited state*. (The electron can be excited to a higher-energy orbital by absorption of a photon of appropriate energy.) At ordinary temperatures, essentially all hydrogen atoms are in the ground state.

▲ **GIVE IT SOME THOUGHT**

Notice in Figure 6.17 that the energy difference between the *n* = 1 and *n* = 2 levels is much greater than the energy difference between the *n* = 2 and *n* = 3 levels. How does Equation 6.5 explain this trend?

▲ **GO FIGURE**

If the fourth shell (the *n* = 4 energy level) were shown, how many sub-shells would it contain? How would they be labeled?

Each cluster of boxes represents one subshell

Each row represents one shell

Each box represents one orbital

n = 1 shell has one orbital
n = 2 shell has two subshells composed of four orbitals
n = 3 shell has three subshells composed of nine orbitals

▲ **FIGURE 6.17   Energy levels in the hydrogen atom.**

SAMPLE EXERCISE 6.6 | **Subshells of the Hydrogen Atom**

(a) Without referring to Table 6.2, predict the number of subshells in the fourth shell, that is, for $n = 4$. (b) Give the label for each of these subshells. (c) How many orbitals are in each of these subshells?

Analyze and Plan We are given the value of the principal quantum number, n. We need to determine the allowed values of l and m_l for this given value of n and then count the number of orbitals in each subshell.

SOLUTION

There are four subshells in the fourth shell, corresponding to the four possible values of l (0, 1, 2, and 3).

These subshells are labeled 4s, 4p, 4d, and 4f. The number given in the designation of a subshell is the principal quantum number, n; the letter designates the value of the angular momentum quantum number, l: for $l = 0$, s; for $l = 1$, p; for $l = 2$, d; for $l = 3$, f.

There is one 4s orbital (when $l = 0$, there is only one possible value of m_l: 0). There are three 4p orbitals (when $l = 1$, there are three possible values of m_l: 1, 0, −1). There are five 4d orbitals (when $l = 2$, there are five allowed values of m_l: 2, 1, 0, −1, −2). There are seven 4f orbitals (when $l = 3$, there are seven permitted values of m_l: 3, 2, 1, 0, −1, −2, −3).

PRACTICE EXERCISE

(a) What is the designation for the subshell with $n = 5$ and $l = 1$? (b) How many orbitals are in this subshell? (c) Indicate the values of m_l for each of these orbitals.

Answers: (a) 5p; **(b)** 3; **(c)** 1, 0, −1

6.6 | REPRESENTATIONS OF ORBITALS

So far we have emphasized orbital energies, but the wave function also provides information about an electron's probable location in space. Let's examine the ways in which we can picture orbitals because their shapes help us visualize how the electron density is distributed around the nucleus.

The s Orbitals

We have already seen one representation of the lowest-energy orbital of the hydrogen atom, the 1s (Figure 6.16). The first thing we notice about the electron density for the 1s orbital is that it is *spherically symmetric*—in other words, the electron density at a given distance from the nucleus is the same regardless of the direction in which we proceed from the nucleus. All of the other s orbitals (2s, 3s, 4s, and so forth) are also spherically symmetric and centered on the nucleus.

Recall that the l quantum number for the s orbitals is 0; therefore, the m_l quantum number must be 0. Thus, for each value of n, there is only one s orbital.

So how do s orbitals differ as the value of n changes? One way to address this question is to look at the **radial probability function**, also called the *radial probability density,* which is defined as the probability that we will find the electron at a specific distance from the nucleus.
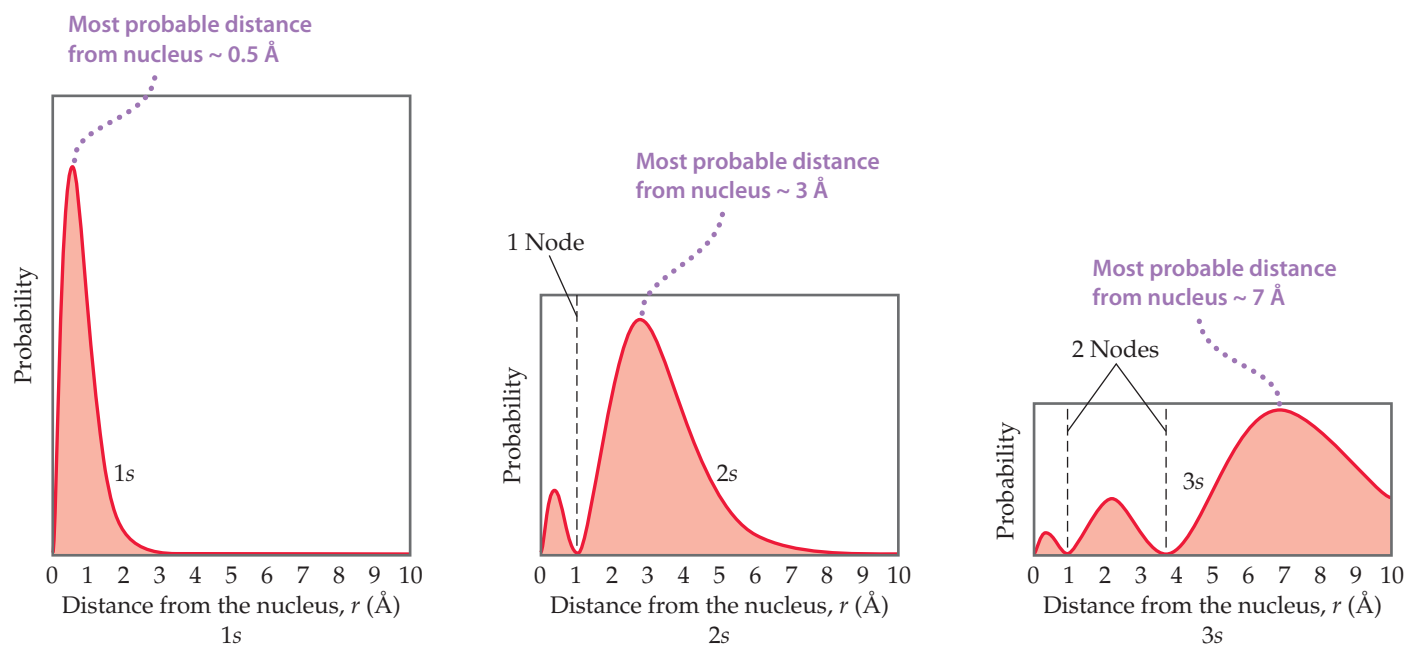
▶ **FIGURE 6.18** shows the radial probability density for the 1s, 2s, and 3s orbitals of hydrogen as a function of r, the distance from the nucleus. Three features of these graphs are noteworthy: the number of peaks, the number of points at which the probability function goes to zero (called **nodes**), and how spread out the distribution is, which gives a sense of the size of the orbital.

For the 1s orbital, we see that the probability rises rapidly as we move away from the nucleus, maximizing at about 0.5 Å. Thus, when the electron occupies the 1s orbital, it is *most likely* to be found this distance from the nucleus.* Notice also that in the 1s orbital the probability of finding the electron at a distance greater than about 3 Å from the nucleus is essentially zero.

---

*In the quantum mechanical model, the most probable distance at which to find the electron in the 1s orbital is actually 0.529 Å, the same as the radius of the orbit predicted by Bohr for $n = 1$. The distance 0.529 Å is often called the Bohr radius.

⚠ **GO FIGURE**

How many maxima would you expect to find in the radial probability function for the 4s orbital of the hydrogen atom? How many nodes would you expect in this function?

Most probable distance
from nucleus ~ 0.5 Å

Most probable distance
from nucleus ~ 3 Å

1 Node

Most probable distance
from nucleus ~ 7 Å

2 Nodes

Probability

1s

Distance from the nucleus, r (Å)
1s

Probability

2s

Distance from the nucleus, r (Å)
2s

Probability

3s

Distance from the nucleus, r (Å)
3s

▲ **FIGURE 6.18   Radial probability distributions for the 1s, 2s, and 3s orbitals of hydrogen.** These graphs of the radial probability function plot probability of finding the electron as a function of distance from the nucleus. As n increases, the most likely distance at which to find the electron (the highest peak) moves farther from the nucleus.

Comparing the radial probability distributions for the 1s, 2s, and 3s orbitals reveals three trends:

1. *The number of peaks increases with increasing* n, *with the outermost peak being larger than inner ones.*

2. *The number of nodes increases with increasing* n.

3. *The electron density becomes more spread out with increasing* n.

One widely used method of representing orbital *shape* is to draw a boundary surface that encloses some substantial portion, say 90%, of the electron density for the orbital. This type of drawing is called a *contour representation,* and the contour representations for the s orbitals are spheres (▼ **FIGURE 6.19**). All the orbitals have the same shape, but they differ in size, becoming larger as n increases, reflecting the fact that the electron density becomes more spread out as n increases. Although the details of how

1s

2s

3s

(a)   (b)
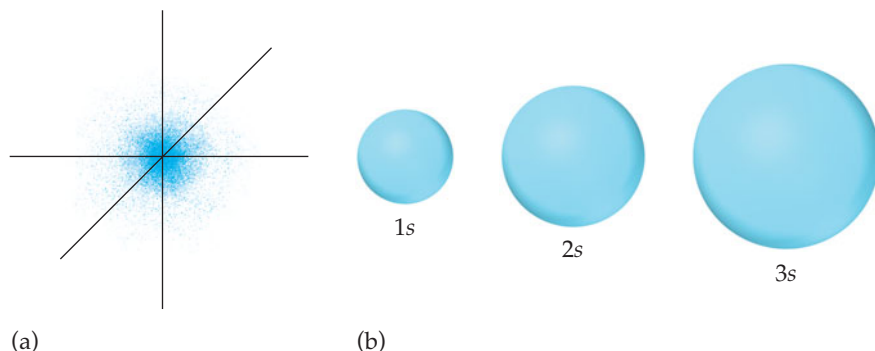
◀ **FIGURE 6.19   Comparison of the 1s, 2s, and 3s orbitals.** (a) Electron-density distribution of a 1s orbital. (b) Contour representations of the 1s, 2s, and 3s orbitals. Each sphere is centered on the atom's nucleus and encloses the volume in which there is a 90% probability of finding the electron.
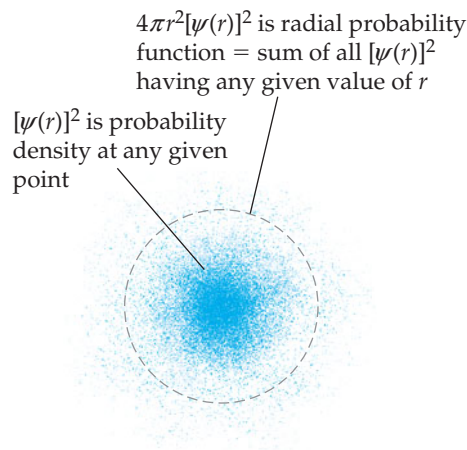
A CLOSER LOOK

PROBABILITY DENSITY AND RADIAL PROBABILITY FUNCTIONS

According to quantum mechanics, we must describe the position of the electron in the hydrogen atom in terms of probabilities. The information about the probability is contained in the wave functions, ψ, obtained from Schrödinger's equation. The square of the wave function, ψ^2, called either the probability density or the electron density, as noted earlier, gives the probability that the electron is at any *point* in space. Because s orbitals are spherically symmetric, the value of ψ for an s electron depends only on its distance from the nucleus, r. Thus, the probability density can be written as $[\psi(r)]^2$, where $\psi(r)$ is the value of ψ at r. This function $[\psi(r)]^2$ gives the probability density for any point located a distance r from the nucleus.

The radial probability function, which we used in Figure 6.18, differs from the probability density. The radial probability function equals the *total* probability of finding the electron at all the points at any distance r from the nucleus. In other words, to calculate this function, we need to "add up" the probability densities $[\psi(r)]^2$ over all points located a distance r from the nucleus. ▶ FIGURE 6.20 compares the probability density at a point ($[\psi(r)]^2$) with the radial probability function.

Let's examine the difference between probability density and radial probability function more closely. ▶ FIGURE 6.21 shows plots of $[\psi(r)]^2$ as a function of r for the 1s, 2s, and 3s orbitals of the

$4\pi r^2[\psi(r)]^2$ is radial probability function = sum of all $[\psi(r)]^2$ having any given value of r

$[\psi(r)]^2$ is probability density at any given point

▲ **FIGURE 6.20 Comparing probability density** $[\psi(r)]^2$ **and radial probability function** $4\pi r^2[\psi(r)]^2$.

electron density varies within a given contour representation are lost in these representations, this is not a serious disadvantage. For qualitative discussions, the most important features of orbitals are shape and relative size, which are adequately displayed by contour representations.

The p Orbitals

The distribution of electron density for a 2p orbital is shown in ▶ FIGURE 6.22(a). The electron density is not distributed spherically as in an s orbital. Instead, the density is concentrated in two regions on either side of the nucleus, separated by a node at the nucleus. We say that this dumbbell-shaped orbital has two *lobes*. Recall that we are making no statement of how the electron is moving within the orbital. Figure 6.22(a) portrays only the *averaged* distribution of the electron density in a 2p orbital.

Beginning with the $n = 2$ shell, each shell has three p orbitals. Recall that the l quantum number for p orbitals is 1. Therefore, the magnetic quantum number m_l can have three possible values: -1, 0, and $+1$. Thus, there are three 2p orbitals, three 3p orbitals, and so forth, corresponding to the three possible values of m_l. Each set of p orbitals has the dumbbell shapes shown in Figure 6.22(a) for the 2p orbitals. For each value of n, the three p orbitals have the same size and shape but differ from one another in spatial orientation. We usually represent p orbitals by drawing the shape and orientation of their wave functions, as shown in Figure 6.22(b). It is convenient to label these as the p_x, p_y, and p_z orbitals. The letter subscript indicates the Cartesian axis along which the orbital is oriented.* Like s orbitals, p orbitals increase in size as we move from 2p to 3p to 4p, and so forth.

*We cannot make a simple correspondence between the subscripts (x, y, and z) and the allowed m_l values (1, 0, and -1). To explain why this is so is beyond the scope of an introductory text.

hydrogen atom. You will notice that these plots look distinctly differ-
ent from the radial probability functions shown in Figure 6.18.

As shown in Figure 6.20, the collection of points a distance r
from the nucleus is the surface of a sphere of radius r. The probabil-
ity density at each point on that spherical surface is $[\psi(r)]^2$. To add
up all the individual probability densities requires calculus and so is
beyond the scope of this text. However, the result of that calculation
tells us that the radial probability function is the probability density,
$[\psi(r)]^2$, multiplied by the surface area of the sphere, $4\pi r^2$:

$$\text{Radial probability function} = 4\pi r^2 [\psi(r)]^2$$

Thus, the plots of radial probability function in Figure 6.18 are
equal to the plots of $[\psi(r)]^2$ in Figure 6.21 multiplied by $4\pi r^2$. The
fact that $4\pi r^2$ increases rapidly as we move away from the nucleus
makes the two sets of plots look very different from each other. For
example, the plot of $[\psi(r)]^2$ for the 3s orbital in Figure 6.21 shows
that the function generally gets smaller the farther we go from the
nucleus. But when we multiply by $4\pi r^2$, we see peaks that get larger
and larger as we move away from the nucleus (Figure 6.18).

The radial probability functions in Figure 6.18 provide us with
the more useful information because they tell us the probability of
finding the electron at *all* points a distance r from the nucleus, not
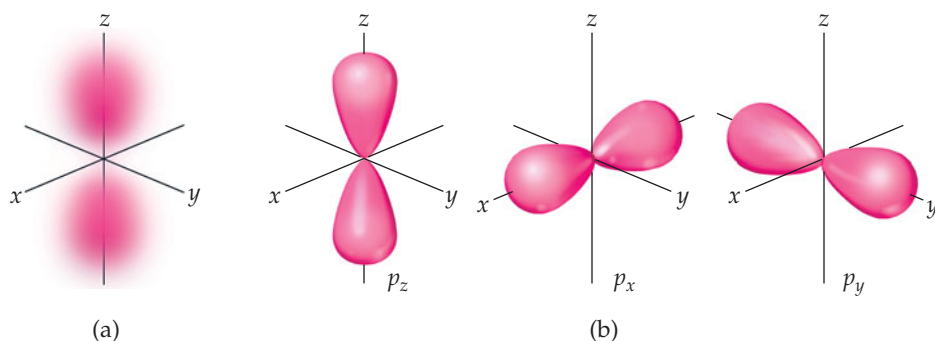just one particular point.

RELATED EXERCISES: 6.50, 6.59, 6.60, and 6.91
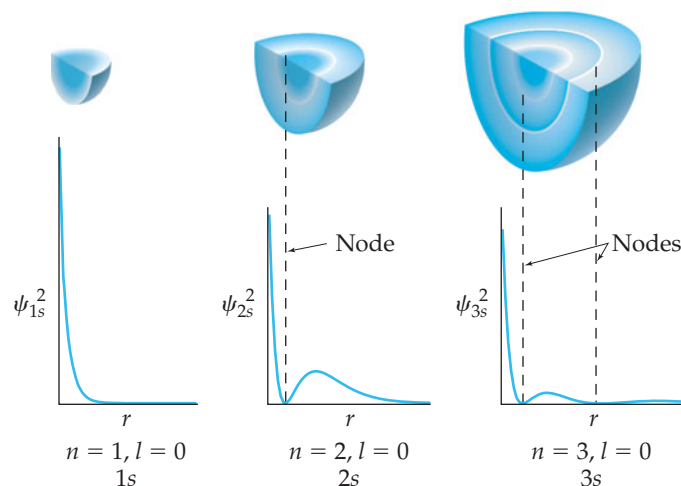
▲ **FIGURE 6.21** **Probability density $[\psi(r)]^2$ in the 1s, 2s, and 3s orbitals of hydrogen.**
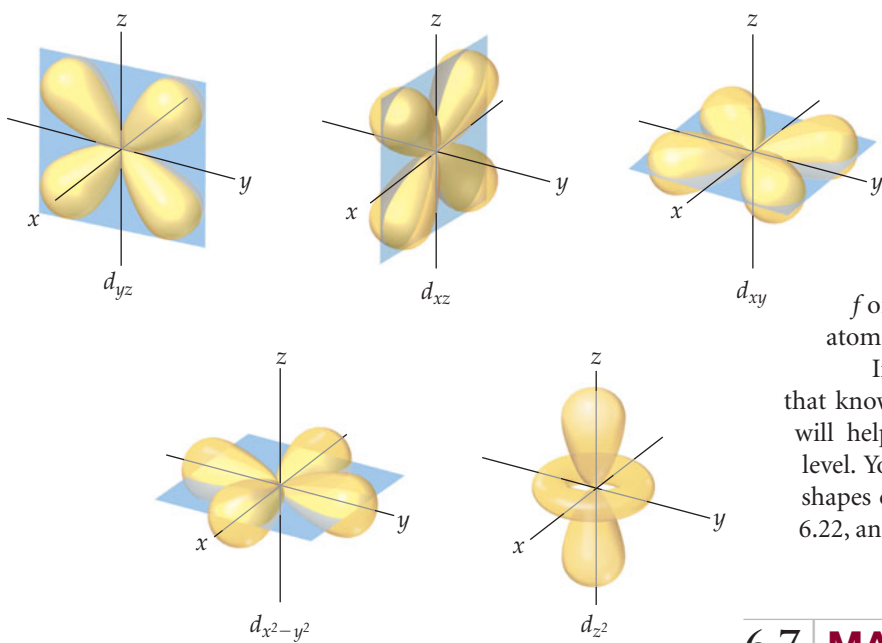

GO FIGURE

(a) Note on the left that the color is deep pink in the interior of each lobe but fades to pale pink at the edges. What does this change in color represent? (b) What label is applied to the 2p orbital aligned along the x axis?

◀ **FIGURE 6.22** **The p orbitals.**
(a) Electron-density distribution of a 2p orbital.
(b) Contour representations of the three p orbitals. The subscript on the orbital label indicates the axis along which the orbital lies.

The *d* and *f* Orbitals

When n is 3 or greater, we encounter the *d* orbitals (for which $l = 2$). There are five 3d
orbitals, five 4d orbitals, and so forth because in each shell there are five possible values
for the m_l quantum number: $-2, -1, 0, 1,$ and 2. The different *d* orbitals in a given shell
have different shapes and orientations in space, as shown in ▶ **FIGURE 6.23**. Four of the
d-orbital contour representations have a "four-leaf clover" shape, and each lies primarily
in a plane. The d_{xy}, d_{xz}, and d_{yz} lie in the *xy*, *xz,* and *yz* planes, respectively, with the lobes
oriented *between* the axes. The lobes of the $d_{x^2-y^2}$ orbital also lie in the *xy* plane, but the
lobes lie *along* the *x* and *y* axes. The d_{z^2} orbital looks very different from the other four:
It has two lobes along the *z* axis and a "doughnut" in the *xy* plane. Even though the d_{z^2}
orbital looks different from the other *d* orbitals, it has the same energy as the other four

▲ FIGURE 6.23 Contour representations of the five *d* orbitals.

d orbitals. The representations in Figure 6.23 are commonly used for all *d* orbitals, regardless of principal quantum number.

When *n* is 4 or greater, there are seven equivalent *f* orbitals (for which *l* = 3). The shapes of the *f* orbitals are even more complicated than those of the *d* orbitals and are not presented here. As you will see in the next section, however, you must be aware of *f* orbitals as we consider the electronic structure of atoms in the lower part of the periodic table.

In many instances later in the text you will find that knowing the number and shapes of atomic orbitals will help you understand chemistry at the molecular level. You will therefore find it useful to memorize the shapes of the *s, p,* and *d* orbitals shown in Figures 6.19, 6.22, and 6.23.

6.7 | MANY-ELECTRON ATOMS

One of our goals in this chapter has been to determine the electronic structures of atoms. So far, we have seen that quantum mechanics leads to an elegant description of the hydrogen atom. This atom, however, has only one electron. How does our description change when we consider an atom with two or more electrons (a *many-electron* atom)? To describe such an atom, we must consider the nature of orbitals and their relative energies as well as how the electrons populate the available orbitals.

Orbitals and Their Energies

We can describe the electronic structure of a many-electron atom in terms of orbitals like those of the hydrogen atom. Thus, we continue to designate orbitals as l*s,* 2*p_x*, and so forth. Further, these orbitals have the same general shapes as the corresponding hydrogen orbitals.

Although the shapes of the orbitals of a many-electron atom are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen the energy of an orbital depends only on its principal quantum number, *n* (Figure 6.17). For instance, the 3*s,* 3*p,* and 3*d* subshells all have the same energy. In a many-electron atom, however, the electron–electron repulsions cause the various subshells in a given shell to be at different energies, as shown in ◀ **FIGURE 6.24**.

To explain this fact, we must consider the forces between the electrons and how these forces are affected by the shapes of the orbitals. We will, however, forgo this analysis until Chapter 7.

The important idea is this: *In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l.* For example, notice in Figure 6.24 that the *n* = 3 orbitals increase in energy in the order 3*s* < 3*p* < 3*d*. Notice also that all orbitals of a given subshell (such as the five 3*d* orbitals) have the same energy as one another. Orbitals with the same energy are said to be **degenerate**.

Figure 6.24 is a *qualitative* energy-level diagram; the exact energies of the orbitals and their spacings differ from one atom to another.

GO FIGURE

Not all of the orbitals in the *n* = 4 shell are shown in this figure. Which subshells are missing?

Orbitals in a subshell are degenerate (have same energy)

Energies of subshells follow order *ns* < *np* < *nd* < *nf*
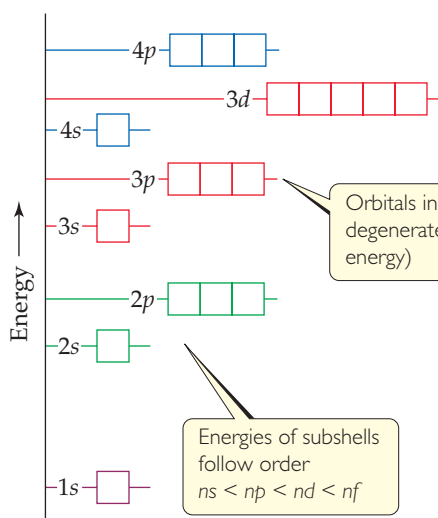
▲ FIGURE 6.24 General energy ordering of orbitals for a many-electron atom.

△ GIVE IT SOME THOUGHT

a. How may orbitals have the principal quantum number *n* = 3?
b. In a many-electron atom, what are the relative energies of these orbitals?

Electron Spin and the Pauli Exclusion Principle

We have now seen that we can use hydrogen-like orbitals to describe many-electron atoms. What, however, determines which orbitals the electrons occupy? That is, how do the electrons of a many-electron atom populate the available orbitals? To answer this question, we must consider an additional property of the electron.

When scientists studied the line spectra of many-electron atoms in great detail, they noticed a very puzzling feature: Lines that were originally thought to be single were actually closely spaced pairs. This meant, in essence, that there were twice as many energy levels as there were "supposed" to be. In 1925 the Dutch physicists George Uhlenbeck and Samuel Goudsmit proposed a solution to this dilemma. They postulated that electrons have an intrinsic property, called **electron spin**, that causes each electron to behave as if it were a tiny sphere spinning on its own axis.

By now it probably does not surprise you to learn that electron spin is quantized. This observation led to the assignment of a new quantum number for the electron, in addition to n, l, and m_l, which we have already discussed. This new quantum number, the **spin magnetic quantum number**, is denoted m_s (the subscript s stands for *spin*). Two possible values are allowed for m_s, $+\frac{1}{2}$ or $-\frac{1}{2}$, which was first interpreted as indicating the two opposite directions in which the electron can spin. A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields (▶ **FIGURE 6.25**).* These two opposite magnetic fields lead to the splitting of spectral lines into closely spaced pairs.

Electron spin is crucial for understanding the electronic structures of atoms. In 1925 the Austrian-born physicist Wolfgang Pauli (1900–1958) discovered the principle that governs the arrangements of electrons in many-electron atoms. The **Pauli exclusion principle** states that *no two electrons in an atom can have the same set of four quantum numbers* n, l, m_l, *and* m_s. For a given orbital, the values of n, l, and m_l are fixed. Thus, if we
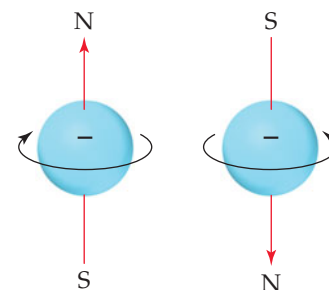
▲ **FIGURE 6.25   Electron spin.** The electron behaves as if it were spinning about an axis, thereby generating a magnetic field whose direction depends on the direction of spin. The two directions for the magnetic field correspond to the two possible values for the spin quantum number, m_s.

A CLOSER LOOK

EXPERIMENTAL EVIDENCE FOR ELECTRON SPIN

Even before electron spin had been proposed, there was experimental evidence that electrons had an additional property that needed explanation. In 1921, Otto Stern and Walter Gerlach succeeded in separating a beam of electrically neutral atoms into two groups by passing them through a nonhomogeneous magnetic field (▶ **FIGURE 6.26**).

Let's assume they used a beam of hydrogen atoms (in actuality, they used silver atoms, which contain just one unpaired electron). We would normally expect electrically neutral atoms to be unaffected by a magnetic field. However, the magnetic field arising from the electron's spin interacts with the magnet's field, deflecting the atom from its straight-line path. As shown in Figure 6.26, the magnetic field splits the beam in two, suggesting that there are two (and only two) equivalent values for the electron's magnetic field. The Stern–Gerlach experiment could be readily interpreted once it was realized that there are exactly two values for the spin of the electron. These values produce equal magnetic fields that are opposite in direction.
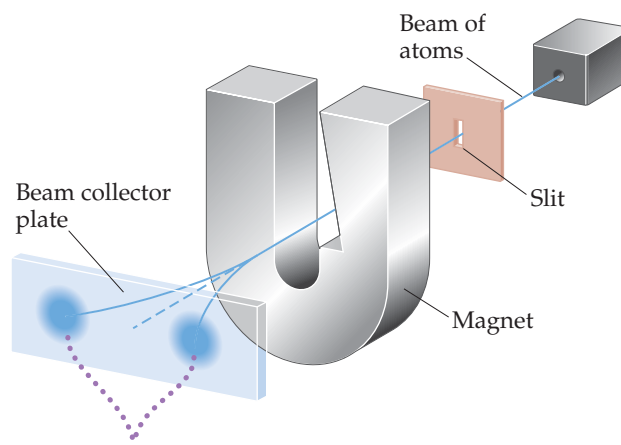
Atoms having unpaired electron with spin quantum number $m_s = +\frac{1}{2}$ deflect in one direction; those having unpaired electron with $m_s = -\frac{1}{2}$ deflect in opposite direction

▲ **FIGURE 6.26   The Stern–Gerlach experiment.**

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*As we discussed earlier, the electron has both particle-like and wave-like properties. Thus, the picture of an electron as a spinning charged sphere is, strictly speaking, just a useful pictorial representation that helps us understand the two directions of magnetic field that an electron can possess.

CHEMISTRY AND LIFE

NUCLEAR SPIN AND MAGNETIC RESONANCE IMAGING

A major challenge facing medical diagnosis is seeing inside the human body. Until recently, this was accomplished primarily by using X-rays to image human bones, muscles, and organs. However, there are several drawbacks to using X-rays for medical imaging. First, X-rays do not give well-resolved images of overlapping physiological structures. Moreover, because damaged or diseased tissue often yields the same image as healthy tissue, X-rays frequently fail to detect illness or injuries. Finally, X-rays are high-energy radiation that can cause physiological harm, even in low doses.

During the 1980s, a technique called *magnetic resonance imaging* (MRI) moved to the forefront of medical imaging technology. The foundation of MRI is a phenomenon called nuclear magnetic resonance (NMR), which was discovered in the mid-1940s. Today NMR has become one of the most important spectroscopic methods used in chemistry. It is based on the observation that, like electrons, the nuclei of many elements possess an intrinsic spin. Like electron spin, nuclear spin is quantized. For example, the nucleus of ^{1}H has two possible magnetic nuclear spin quantum numbers, $+\frac{1}{2}$ and $-\frac{1}{2}$. The hydrogen nucleus is the most common one studied by NMR.

A spinning hydrogen nucleus acts like a tiny magnet. In the absence of external effects, the two spin states have the same energy. However, when the nuclei are placed in an external magnetic field, they can align either parallel or opposed (antiparallel) to the field, depending on their spin. The parallel alignment is lower in energy than the antiparallel one by a certain amount, ΔE (▶ FIGURE 6.27). If the nuclei are irradiated with photons having energy equal to ΔE, the spin of the nuclei can be "flipped," that is, excited from the parallel to the antiparallel alignment. Detection of the flipping of nuclei between the two spin states leads to an NMR spectrum. The radiation used in an NMR experiment is in the radiofrequency range, typically 100 to 900 MHz, which is far less energetic per photon than X-rays.

Because hydrogen is a major constituent of aqueous body fluids and fatty tissue, the hydrogen nucleus is the most convenient one for study by MRI. In MRI a person's body is placed in a strong magnetic field. By irradiating the body with pulses of radiofrequency radiation and using sophisticated detection techniques, medical technicians can image tissue at specific depths in the body, giving pictures with spectacular detail (▶ FIGURE 6.28). The ability to sample at different depths allows the technicians to construct a three-dimensional picture of the body.

MRI has none of the disadvantages of X-rays. Diseased tissue appears very different from healthy tissue, resolving overlapping structures at different depths in the body is much easier, and the radio frequency radiation is not harmful to humans in the doses used. The technique has had such a profound influence on the modern practice of medicine that Paul Lauterbur, a chemist, and Peter Mansfield, a physicist, were awarded the 2003 Nobel Prize in Physiology or
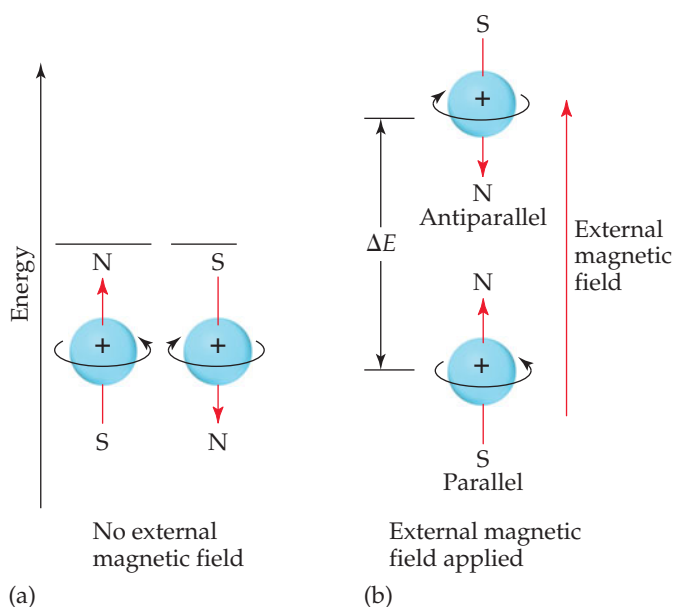
▲ FIGURE 6.27 **Nuclear spin.** Like electron spin, nuclear spin generates a small magnetic field and has two allowed values. (a) In the absence of an external magnetic field, the two spin states have the same energy. (b) When an external magnetic field is applied, the spin state in which the spin direction is parallel to the direction of the external field is lower in energy than the spin state in which the spin direction is antiparallel to the field direction. The energy difference, ΔE, is in the radio frequency portion of the electromagnetic spectrum.
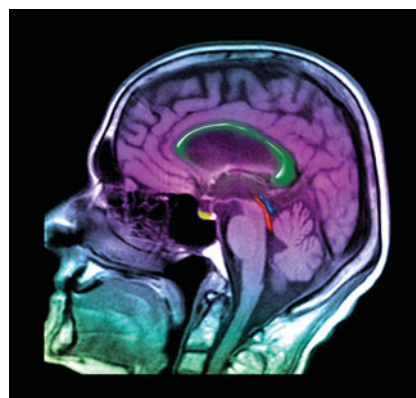
▲ FIGURE 6.28 **MRI image.** This image of a human head, obtained using magnetic resonance imaging, shows a normal brain, airways, and facial tissues.

Medicine for their discoveries concerning MRI. The major drawback of this technique is expense: The current cost of a new MRI instrument for clinical applications is over $1.5 million.

RELATED EXERCISE: 6.93

want to put more than one electron in an orbital *and* satisfy the Pauli exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two such values, we conclude that *an orbital can hold a maximum of two electrons and they must have opposite spins.* This restriction allows us to index the electrons in an atom, giving their quantum numbers and thereby defining the region in space where each electron is most likely to be found. It also provides the key to understanding the structure of the periodic table of the elements.

6.8 | ELECTRON CONFIGURATIONS

Armed with knowledge of the relative energies of orbitals and the Pauli exclusion principle, we are in a position to consider the arrangements of electrons in atoms. The way electrons are distributed among the various orbitals of an atom is called the **electron configuration** of the atom.

The most stable electron configuration—the ground state—is that in which the electrons are in the lowest possible energy states. If there were no restrictions on the possible values for the quantum numbers of the electrons, all the electrons would crowd into the l*s* orbital because it is the lowest in energy (Figure 6.24). The Pauli exclusion principle tells us, however, that there can be at most two electrons in any single orbital. Thus, *the orbitals are filled in order of increasing energy, with no more than two electrons per orbital.* For example, consider the lithium atom, which has three electrons. (Recall that the number of electrons in a neutral atom equals its atomic number.) The l*s* orbital can accommodate two of the electrons. The third one goes into the next lowest energy orbital, the 2*s*.

We can represent any electron configuration by writing the symbol for the occupied subshell and adding a superscript to indicate the number of electrons in that subshell. For example, for lithium we write $ls^2 2s^1$ (read "l*s* two, 2*s* one"). We can also show the arrangement of the electrons as

$$\text{Li} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow}$$

$$\qquad\quad 1s \qquad 2s$$
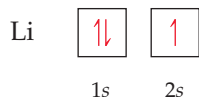
In this representation, which we call an *orbital diagram,* each orbital is denoted by a box and each electron by a half arrow. A half arrow pointing up ($\uparrow$) represents an electron with a positive spin magnetic quantum number ($m_s = +\frac{1}{2}$) and a half arrow pointing down ($\downarrow$) represents an electron with a negative spin magnetic quantum number ($m_s = -\frac{1}{2}$). This pictorial representation of electron spin, which corresponds to the directions of the magnetic fields in Figure 6.25, is quite convenient.

Electrons having opposite spins are said to be *paired* when they are in the same orbital ($\uparrow\downarrow$). An *unpaired electron* is one not accompanied by a partner of opposite spin. In the lithium atom the two electrons in the 1*s* orbital are paired and the electron in the 2*s* orbital is unpaired.

Hund's Rule

Consider now how the electron configurations of the elements change as we move from element to element across the periodic table. Hydrogen has one electron, which occupies the 1*s* orbital in its ground state:

$$\text{H} \quad \boxed{\uparrow} \quad : 1s^1$$

$$\qquad\quad 1s$$
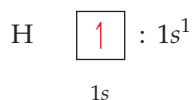
The choice of a spin-up electron here is arbitrary; we could equally well show the ground state with one spin-down electron. It is customary, however, to show unpaired electrons with their spins up.

TABLE 6.3 • **Electron Configurations of Several Lighter Elements**

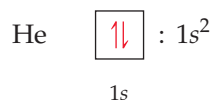| Element	Total Electrons	Orbital Diagram				Electron Configuration
		1s	2s	2p	3s	
Li	3	↑↓	↑			$1s^2 2s^1$
Be	4	↑↓	↑↓			$1s^2 2s^2$
B	5	↑↓	↑↓	↑		$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^2 2s^2 2p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

The next element, helium, has two electrons. Because two electrons with opposite spins can occupy the same orbital, both of helium's electrons are in the 1s orbital:

$$\text{He} \quad \boxed{↑↓} \ : \ 1s^2$$

1s

The two electrons present in helium complete the filling of the first shell. This arrangement represents a very stable configuration, as is evidenced by the chemical inertness of helium.

The electron configurations of lithium and several elements that follow it in the periodic table are shown in ▲ **TABLE 6.3**. For the third electron of lithium, the change in principal quantum number from $n = 1$ for the first two electrons to $n = 2$ for the third electron represents a large jump in energy and a corresponding jump in the average distance of the electron from the nucleus. In other words, it represents the start of a new shell occupied with electrons. As you can see by examining the periodic table, lithium starts a new row of the table. It is the first member of the alkali metals (group 1A).

The element that follows lithium is beryllium; its electron configuration is $1s^2 2s^2$ (Table 6.3). Boron, atomic number 5, has the electron configuration $1s^2 2s^2 2p^1$. The fifth electron must be placed in a 2p orbital because the 2s orbital is filled. Because all the three 2p orbitals are of equal energy, it does not matter which 2p orbital we place this fifth electron in.

With the next element, carbon, we encounter a new situation. We know that the sixth electron must go into a 2p orbital. However, does this new electron go into the 2p orbital that already has one electron or into one of the other two 2p orbitals? This question is answered by **Hund's rule**, which states that *for degenerate orbitals, the lowest energy is attained when the number of electrons having the same spin is maximized*. This means that electrons occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell all have the same spin magnetic quantum number. Electrons arranged in this way are said to have *parallel spins*. For a carbon atom to achieve its lowest energy, therefore, the two 2p electrons must have the same spin. For this to happen, the electrons must be in different 2p orbitals, as shown in Table 6.3. Thus, a carbon atom in its ground state has two unpaired electrons.

Similarly, for nitrogen in its ground state, Hund's rule requires that the three 2p electrons singly occupy each of the three 2p orbitals. This is the only way that all three electrons can have the same spin. For oxygen and fluorine, we place four and five

electrons, respectively, in the $2p$ orbitals. To achieve this, we pair up electrons in the $2p$ orbitals, as we will see in Sample Exercise 6.7.

Hund's rule is based in part on the fact that electrons repel one another. By occupying different orbitals, the electrons remain as far as possible from one another, thus minimizing electron–electron repulsions.


SAMPLE EXERCISE 6.7   **Orbital Diagrams and Electron Configurations**

Draw the orbital diagram for the electron configuration of oxygen, atomic number 8. How many unpaired electrons does an oxygen atom possess?

SOLUTION

Analyze and Plan Because oxygen has an atomic number of 8, each oxygen atom has 8 electrons. Figure 6.24 shows the ordering of orbitals. The electrons (represented as arrows) are placed in the orbitals (represented as boxes) beginning with the lowest-energy orbital, the $1s$. Each orbital can hold a maximum of two electrons (the Pauli exclusion principle). Because the $2p$ orbitals are degenerate, we place one electron in each of these orbitals (spin-up) before pairing any electrons (Hund's rule).

Solve Two electrons each go into the $1s$ and $2s$ orbitals with their spins paired. This leaves four electrons for the three degenerate $2p$ orbitals. Following Hund's rule, we put one electron into each $2p$ orbital until all three orbitals have one electron each. The fourth electron is then paired up with one of the three electrons already in a $2p$ orbital, so that the orbital diagram is

$$\boxed{\uparrow\downarrow}\quad\boxed{\uparrow\downarrow}\quad\boxed{\uparrow\downarrow}\;\boxed{\uparrow}\;\boxed{\uparrow}$$

$$1s\qquad 2s\qquad 2p$$
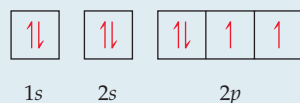
The corresponding electron configuration is written $1s^2 2s^2 2p^4$. The atom has two unpaired electrons.

PRACTICE EXERCISE

(**a**) Write the electron configuration for phosphorus, element 15. (**b**) How many unpaired electrons does a phosphorus atom possess?

Answers: (**a**) $1s^2 2s^2 2p^6 3s^2 3p^3$, (**b**) three

Condensed Electron Configurations

The filling of the $2p$ subshell is complete at neon (Table 6.3), which has a stable configuration with eight electrons (an *octet*) in the outermost occupied shell. The next element, sodium, atomic number 11, marks the beginning of a new row of the periodic table. Sodium has a single $3s$ electron beyond the stable configuration of neon. We can therefore abbreviate the electron configuration of sodium as

$$\text{Na:}\quad [\text{Ne}]3s^1$$

The symbol [Ne] represents the electron configuration of the ten electrons of neon, $1s^2 2s^2 2p^6$. Writing the electron configuration as $[\text{Ne}]3s^1$ focuses attention on the outermost electron of the atom, which is the one largely responsible for how sodium behaves chemically.

We can generalize what we have just done for the electron configuration of sodium. In writing the *condensed electron configuration* of an element, the electron configuration of the nearest noble-gas element of lower atomic number is represented by its chemical symbol in brackets. For lithium, for example, we write

$$\text{Li:}\quad [\text{He}]2s^1$$

We refer to the electrons represented by the bracketed symbol as the *noble-gas core* of the atom. More usually, these inner-shell electrons are referred to as the **core electrons**. The electrons given after the noble-gas core are called the *outer-shell electrons*. The outer-shell electrons include the electrons involved in chemical bonding, which are called the **valence electrons**. For the elements with atomic number of 30 or less, all of the outer-shell electrons are valence electrons. By comparing the condensed electron configurations of lithium and sodium, we can appreciate why these two elements are so

1A

1A
3   **Li**   [He]2s^1
11   **Na**   [Ne]3s^1
19   **K**   [Ar]4s^1
37   **Rb**   [Kr]5s^1
55   **Cs**   [Xe]6s^1
87   **Fr**   [Rn]7s^1

Alkali
metals

▲ **FIGURE 6.29**   **The outer-shell electron configurations of the alkali metals (group 1A in the periodic table).**

similar chemically. They have the same type of electron configuration in the outermost occupied shell. Indeed, all the members of the alkali metal group (1A) have a single s valence electron beyond a noble-gas configuration (◄ **FIGURE 6.29**).

Transition Metals

The noble-gas element argon ($1s^2 2s^2 2p^6 3s^2 3p^6$) marks the end of the row started by sodium. The element following argon in the periodic table is potassium (K), atomic number 19. In all its chemical properties, potassium is clearly a member of the alkali metal group. The experimental facts about the properties of potassium leave no doubt that the outermost electron of this element occupies an s orbital. But this means that the electron with the highest energy has *not* gone into a 3d orbital, which we might expect it to do. Because the 4s orbital is lower in energy than the 3d orbital (Figure 6.24), the condensed electron configuration of potassium is

$$K: \quad [Ar]4s^1$$

Following the complete filling of the 4s orbital (this occurs in the calcium atom), the next set of orbitals to be filled is the 3d. (You will find it helpful as we go along to refer often to the periodic table on the front inside cover.) Beginning with scandium and extending through zinc, electrons are added to the five 3d orbitals until they are completely filled. Thus, the fourth row of the periodic table is ten elements wider than the two previous rows. These ten elements are known as either **transition elements** or **transition metals**. Note the position of these elements in the periodic table.

In writing the electron configurations of the transition elements, we fill orbitals in accordance with Hund's rule—we add them to the 3d orbitals singly until all five orbitals have one electron each and then place additional electrons in the 3d orbitals with spin pairing until the shell is completely filled. The condensed electron configurations and the corresponding orbital diagram representations of two transition elements are as follows:

Mn: [Ar]$4s^2 3d^5$ or [Ar]

Zn: [Ar]$4s^2 3d^{10}$ or [Ar]
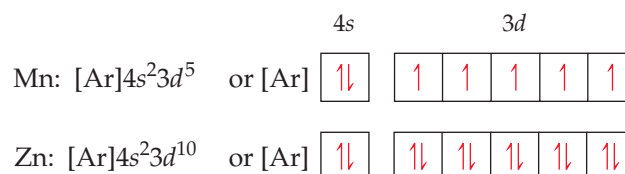
Once all the 3d orbitals have been filled with two electrons each, the 4p orbitals begin to be occupied until the completed octet of outer electrons ($4s^2 4p^6$) is reached with krypton (Kr), atomic number 36, another of the noble gases. Rubidium (Rb) marks the beginning of the fifth row. Refer again to the periodic table on the front inside cover. Notice that this row is in every respect like the preceding one, except that the value for n is greater by 1.

▲ GIVE IT SOME THOUGHT

Based on the structure of the periodic table, which becomes occupied first, the 6s orbital or the 5d orbitals?

The Lanthanides and Actinides

The sixth row of the periodic table begins with one electron in the 6s orbital of cesium (Cs) and two electrons in the 6s orbital of barium (Ba). Notice, however, that the periodic table then has a break, with elements 57–70 placed below the main portion of the table. This break point is where we begin to encounter a new set of orbitals, the 4f.

There are seven degenerate 4f orbitals, corresponding to the seven allowed values of m_l, ranging from 3 to −3. Thus, it takes 14 electrons to fill the 4f orbitals completely. The 14 elements corresponding to the filling of the 4f orbitals are known as either the **lanthanide elements** or the **rare earth elements**. These elements are set below the

other elements to avoid making the periodic table unduly wide. The properties of the lanthanide elements are all quite similar, and these elements occur together in nature. For many years it was virtually impossible to separate them from one another.

Because the energies of the 4*f* and 5*d* orbitals are very close to each other, the electron configurations of some of the lanthanides involve 5*d* electrons. For example, the elements lanthanum (La), cerium (Ce), and praseodymium (Pr) have the following electron configurations:

$$[Xe]6s^2 5d^1 \quad [Xe]6s^2 5d^1 4f^1 \quad [Xe]6s^2 4f^3$$
Lanthanum   Cerium   Praseodymium
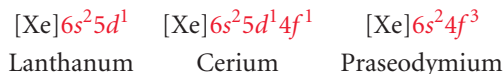
Because La has a single 5*d* electron, it is sometimes placed below yttrium (Y) as the first member of the third series of transition elements; Ce is then placed as the first member of the lanthanides. Based on their chemistry, however, La can be considered the first element in the lanthanide series. Arranged this way, there are fewer apparent exceptions to the regular filling of the 4*f* orbitals among the subsequent members of the series.

After the lanthanide series, the third transition element series is completed by the filling of the 5*d* orbitals, followed by the filling of the 6*p* orbitals. This brings us to radon (Rn), heaviest of the known noble-gas elements.

The final row of the periodic table begins by filling the 7*s* orbitals. The **actinide elements**, of which uranium (U, element 92) and plutonium (Pu, element 94) are the best known, are then built up by completing the 5*f* orbitals. The actinide elements are radioactive, and most of them are not found in nature.

6.9 | ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

We just saw that the electron configurations of the elements correspond to their locations in the periodic table. Thus, elements in the same column of the table have related outer-shell (valence) electron configurations. As ▶ **TABLE 6.4** shows, for example, all 2A elements have an ns^2 outer configuration, and all 3A elements have an ns^2np^1 outer configuration, with the value of *n* increasing as we move down each column.

As shown in ▼ **FIGURE 6.30**, the periodic table can be divided into four blocks based on the filling order of orbitals. On the left are *two* blue columns of elements. These elements, known as the alkali metals (group 1A) and alkaline earth metals (group 2A), are those in which the valence *s* orbitals are being filled. These two columns make up the *s* block of the periodic table.

On the right is a block of *six* pink columns that comprises the *p* block, where the valence *p* orbitals are being filled. The *s* block and the *p* block elements together are the **representative elements**, sometimes called the **main-group elements**.

The orange block in Figure 6.30 has *ten* columns containing the transition metals. These are the elements in which the valence *d* orbitals are being filled and make up the *d* block.

TABLE 6.4 •
Electron Configurations of Group 2A and 3A Elements

Group 2A

Be	$[He]2s^2$
Mg	$[Ne]3s^2$
Ca	$[Ar]4s^2$
Sr	$[Kr]5s^2$
Ba	$[Xe]6s^2$
Ra	$[Rn]7s^2$

Group 3A

B	$[He]2s^2 2p^1$
Al	$[Ne]3s^2 3p^1$
Ga	$[Ar]3d^{10}4s^2 4p^1$
In	$[Kr]4d^{10}5s^2 5p^1$
Tl	$[Xe]4f^{14}5d^{10}6s^2 6p^1$

1	1s																1s
2	2s													2p			
3	3s													3p			
4	4s					3d								4p			
5	5s					4d								5p			
6	6s	4f				5d								6p			
7	7s	5f				6d								7p			

s-orbitals   *f*-orbitals   *d*-orbitals   *p*-orbitals
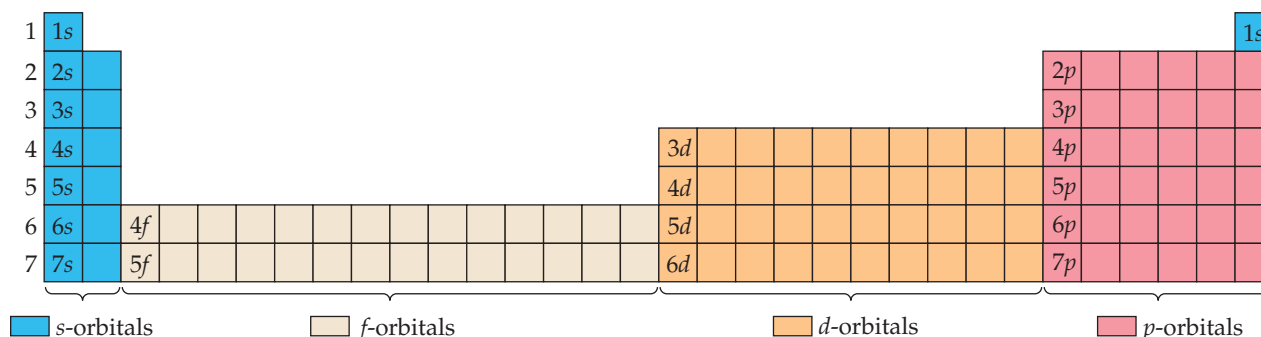
▲ **FIGURE 6.30   Regions of the periodic table.** The order in which electrons are added to orbitals is read left to right beginning in the top left corner.

The elements in the two tan rows containing *14* columns are the ones in which the valence *f* orbitals are being filled and make up the *f* block. Consequently, these elements are often referred to as the **f-block metals**. In most tables, the *f* block is positioned below the periodic table to save space:
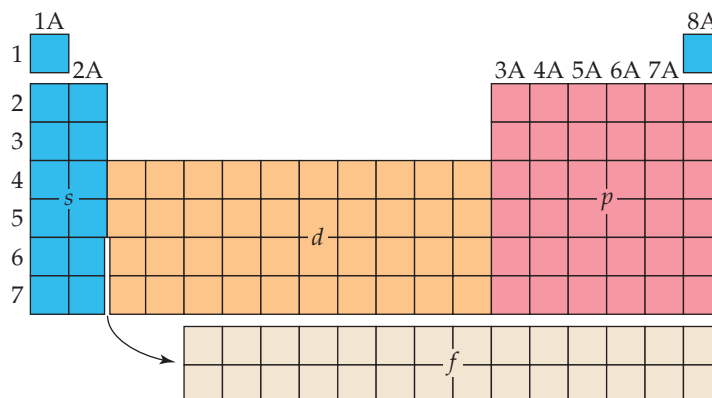
The number of columns in each block corresponds to the maximum number of electrons that can occupy each kind of subshell. Recall that 2, 6, 10, and 14 are the numbers of electrons that can fill the *s, p, d,* and *f* subshells, respectively. Thus, the *s* block has 2 columns, the *p* block has 6, the *d* block has 10, and the *f* block has 14. Recall also that l*s* is the first *s* subshell, 2*p* is the first *p* subshell, 3*d* is the first *d* subshell, and 4*f* is the first *f* subshell, as Figure 6.30 shows. Using these facts, you can write the electron configuration of an element based merely on its position in the periodic table.

Let's use the periodic table to write the electron configuration of selenium (Se, element 34). We first locate Se in the table and then move backward from it through the table, from element 34 to 33 to 32 and so forth, until we come to the noble gas that precedes Se. In this case, the noble gas is argon, Ar, element 18. Thus, the noble-gas core for Se is [Ar]. Our next step is to write symbols for the outer electrons. We do this by moving across period 4 from K, the element following Ar, to Se:
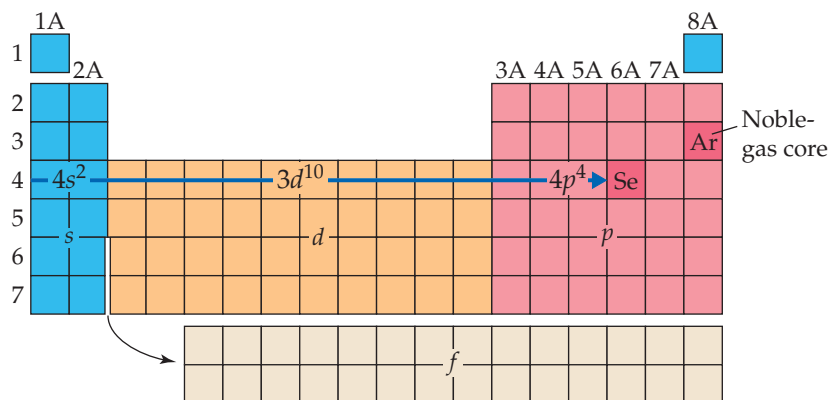

Because K is in the fourth period and the *s* block, we begin with the 4*s* electrons, meaning our first two outer electrons are written $4s^2$. We then move into the *d* block, which begins with the 3*d* electrons. (The principal quantum number in the *d* block is always one less than that of the preceding elements in the *s* block, as seen in Figure 6.30.) Traversing the *d* block adds ten electrons, $3d^{10}$. Finally we move into the *p* block, whose principal quantum number is always the same as that of the *s* block. Counting the squares as we move across the *p* block to Se tells us that we need four electrons, $4p^4$. The electron configuration for Se is therefore $[Ar]4s^23d^{10}4p^4$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Ar]3d^{10}4s^24p^3$.

As a check, we add the number of electrons in the [Ar] core, 18, to the number of electrons we added to the 4*s*, 3*d*, and 4*p* subshells. This sum should equal the atomic number of Se, 34: $18 + 2 + 10 + 4 = 34$.

SAMPLE EXERCISE 6.8   **Electron Configurations for a Group**

What is the characteristic valence electron configuration of the group 7A elements, the halogens?

SOLUTION

Analyze and Plan We first locate the halogens in the periodic table, write the electron configurations for the first two elements, and then determine the general similarity between the configurations.

Solve The first member of the halogen group is fluorine (F, element 9). Moving backward from F, we find that the noble-gas core is [He]. Moving from He to the element of next higher atomic number brings us to Li, element 3. Because Li is in the second period of the s block, we add electrons to the $2s$ subshell. Moving across this block gives $2s^2$. Continuing to move to the right, we enter the p block. Counting the squares to F gives $2p^5$. Thus, the condensed electron configuration for fluorine is

$$\text{F:} \quad [\text{He}]2s^2 2p^5$$

The electron configuration for chlorine, the second halogen, is

$$\text{Cl:} \quad [\text{Ne}]3s^2 3p^5$$

From these two examples, we see that the characteristic valence electron configuration of a halogen is $ns^2 np^5$, where n ranges from 2 in the case of fluorine to 6 in the case of astatine.

PRACTICE EXERCISE

Which family of elements is characterized by an $ns^2 np^2$ electron configuration in the outermost occupied shell?

Answer: group 4A

SAMPLE EXERCISE 6.9   **Electron Configurations from the Periodic Table**

(a) Based on its position in the periodic table, write the condensed electron configuration for bismuth, element 83. **(b)** How many unpaired electrons does a bismuth atom have?

SOLUTION

(a) Our first step is to write the noble-gas core. We do this by locating bismuth, element 83, in the periodic table. We then move backward to the nearest noble gas, which is Xe, element 54. Thus, the noble-gas core is [Xe].

Next, we trace the path in order of increasing atomic numbers from Xe to Bi. Moving from Xe to Cs, element 55, we find ourselves in period 6 of the s block. Knowing the block and the period identifies the subshell in which we begin placing outer electrons, $6s$. As we move through the s block, we add two electrons: $6s^2$.

As we move beyond the s block, from element 56 to element 57, the curved arrow below the periodic table reminds us that we are entering the f block. The first row of the f block corresponds to the $4f$ subshell. As we move across this block, we add 14 electrons: $4f^{14}$.

With element 71, we move into the third row of the d block. Because the first row of the d block is $3d$, the second row is $4d$ and the third row is $5d$. Thus, as we move through the ten elements of the d block, from element 71 to element 80, we fill the $5d$ subshell with ten electrons: $5d^{10}$.

Moving from element 80 to element 81 puts us into the p block in the $6p$ subshell. (Remember that the principal quantum number in the p block is the same as in the s block.) Moving across to Bi requires 3 electrons: $6p^3$. The path we have taken is
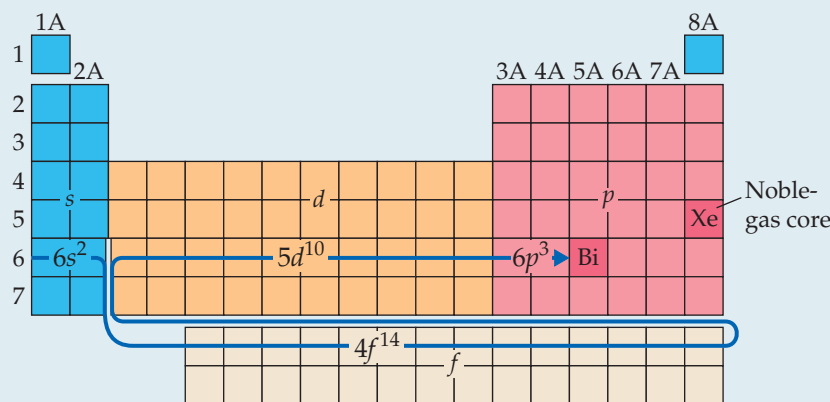
Putting the parts together, we obtain the condensed electron configuration: $[Xe]6s^2 4f^{14} 5d^{10} 6p^3$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$.

Finally, we check our result to see if the number of electrons equals the atomic number of Bi, 83: Because Xe has 54 electrons (its atomic number), we have $54 + 2 + 14 + 10 + 3 = 83$. (If we had 14 electrons too few, we would realize that we have missed the f block.)

(b) We see from the condensed electron configuration that the only partially occupied subshell is $6p$. The orbital diagram representation for this subshell is

↑	↑	↑

In accordance with Hund's rule, the three $6p$ electrons occupy the three $6p$ orbitals singly, with their spins parallel. Thus, there are three unpaired electrons in the bismuth atom.

PRACTICE EXERCISE

Use the periodic table to write the condensed electron configuration for **(a)** Co (element 27), **(b)** Te (element 52).

Answers: **(a)** $[Ar]4s^2 3d^7$ or $[Ar]3d^7 4s^2$, **(b)** $[Kr]5s^2 4d^{10} 5p^4$ or $[Kr]4d^{10} 5s^2 5p^4$

▼ **FIGURE 6.31** gives, for all the elements, the ground-state electron configurations for the valence electrons. You can use this figure to check your answers as you practice writing electron configurations. We have written these configurations with orbitals

▲ **FIGURE 6.31** Valence electron configurations of the elements.

listed in order of increasing principal quantum number. As we saw in Sample Exercise 6.9, the orbitals can also be listed in order of filling, as they would be read off the periodic table.

Figure 6.31 allow us to reexamine the concept of *valence electrons*. Notice, for example, that as we proceed from Cl ($[Ne]3s^23p^5$) to Br ($[Ar]3d^{10}4s^24p^5$) we add a complete subshell of $3d$ electrons to the electrons beyond the [Ar] core. Although the $3d$ electrons are outer-shell electrons, they are not involved in chemical bonding and are therefore not considered valence electrons. Thus, we consider only the $4s$ and $4p$ electrons of Br to be valence electrons. Similarly, if we compare the electron configurations of Ag (element 47) and Au (element 79), we see that Au has a completely full $4f^{14}$ subshell beyond its noble-gas core, but those $4f$ electrons are not involved in bonding. In general, *for representative elements we do not consider the electrons in completely filled* d *or* f *subshells to be valence electrons,* and *for transition elements we do not consider the electrons in a completely filled* f *subshell to be valence electrons.*

Anomalous Electron Configurations

The electron configurations of certain elements appear to violate the rules we have just discussed. For example, Figure 6.31 shows that the electron configuration of chromium (element 24) is $[Ar]3d^54s^1$ rather than the $[Ar]3d^44s^2$ configuration we might expect. Similarly, the configuration of copper (element 29) is $[Ar]3d^{10}4s^1$ instead of $[Ar]3d^94s^2$.

This anomalous behavior is largely a consequence of the closeness of the $3d$ and $4s$ orbital energies. It frequently occurs when there are enough electrons to form precisely half-filled sets of degenerate orbitals (as in chromium) or a completely filled d subshell (as in copper). There are a few similar cases among the heavier transition metals (those with partially filled $4d$ or $5d$ orbitals) and among the f-block metals. Although these minor departures from the expected are interesting, they are not of great chemical significance.

▲ GIVE IT SOME THOUGHT

The elements Ni, Pd, and Pt are all in the same group. By examining the electron configurations for these elements in Figure 6.31, what can you conclude about the relative energies of the nd and $(n + 1)s$ orbitals for this group?

SAMPLE INTEGRATIVE EXERCISE   **Putting Concepts Together**

Boron, atomic number 5, occurs naturally as two isotopes, ^{10}B and ^{11}B, with natural abundances of 19.9% and 80.1%, respectively. **(a)** In what ways do the two isotopes differ from each other? Does the electronic configuration of ^{10}B differ from that of ^{11}B? **(b)** Draw the orbital diagram for an atom of ^{11}B. Which electrons are the valence electrons? **(c)** Indicate three major ways in which the $1s$ electrons in boron differ from its $2s$ electrons. **(d)** Elemental boron reacts with fluorine to form BF_3, a gas. Write a balanced chemical equation for the reaction of solid boron with fluorine gas. **(e)** ΔH_f° for $BF_3(g)$ is -1135.6 kJ/mol. Calculate the standard enthalpy change in the reaction of boron with fluorine. **(f)** When BCl_3, also a gas at room temperature, comes into contact with water, the two react to form hydrochloric acid and boric acid, H_3BO_3, a very weak acid in water. Write a balanced net ionic equation for this reaction.

SOLUTION

(a) The two isotopes of boron differ in the number of neutrons in the nucleus. ∞ (Sections 2.3 and 2.4) Each of the isotopes contains five protons, but ^{10}B contains five neutrons, whereas ^{11}B contains six neutrons. The two isotopes of boron have identical electron configurations, $1s^22s^22p^1$, because each has five electrons.

(b) The complete orbital diagram is

$$1s \qquad 2s \qquad 2p$$
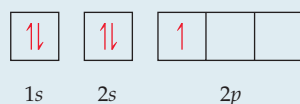
The valence electrons are the ones in the outermost occupied shell, the $2s^2$ and $2p^1$ electrons. The $1s^2$ electrons constitute the core electrons, which we represent as [He] when we write the condensed electron configuration, $[He]2s^22p^1$.

(c) The 1s and 2s orbitals are both spherical, but they differ in three important respects: First, the 1s orbital is lower in energy than the 2s orbital. Second, the average distance of the 2s electrons from the nucleus is greater than that of the 1s electrons, so the 1s orbital is smaller than the 2s. Third, the 2s orbital has one node, whereas the 1s orbital has no nodes (Figure 6.18).

(d) The balanced chemical equation is

$$2\ B(s)\ +\ 3\ F_2(g)\ \longrightarrow\ 2\ BF_3(g)$$
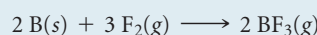
(e) $\Delta H° = 2(-1135.6) - [0 + 0] = -2271.2$ kJ. The reaction is strongly exothermic.

(f) $BCl_3(g) + 3\ H_2O(l) \longrightarrow H_3BO_3(aq) + 3\ H^+(aq) + 3\ Cl^-(aq)$. Note that because H_3BO_3 is a very weak acid, its chemical formula is written in molecular form, as discussed in Section 4.3.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 6.1   The **electronic structure** of an atom describes the energies and arrangement of electrons around the atom. Much of what is known about the electronic structure of atoms was obtained by observing the interaction of light with matter. Visible light and other forms of **electromagnetic radiation** (also known as radiant energy) move through a vacuum at the speed of light, $c = 3.00 \times 10^8$ m/s. Electromagnetic radiation has both electric and magnetic components that vary periodically in wavelike fashion. The wave characteristics of radiant energy allow it to be described in terms of **wavelength**, λ, and **frequency**, ν, which are interrelated: $c = \lambda\nu$.

SECTION 6.2   Planck proposed that the minimum amount of radiant energy that an object can gain or lose is related to the frequency of the radiation: $E = h\nu$. This smallest quantity is called a **quantum** of energy. The constant h is called **Planck's constant**: $h = 6.626 \times 10^{-34}$ J-s. In the quantum theory, energy is quantized, meaning that it can have only certain allowed values. Einstein used the quantum theory to explain the **photoelectric effect**, the emission of electrons from metal surfaces when exposed to light. He proposed that light behaves as if it consists of quantized energy packets called **photons**. Each photon carries energy, $E = h\nu$.

SECTION 6.3   Dispersion of radiation into its component wavelengths produces a **spectrum**. If the spectrum contains all wavelengths, it is called a **continuous spectrum**; if it contains only certain specific wavelengths, the spectrum is called a **line spectrum**. The radiation emitted by excited hydrogen atoms forms a line spectrum.

Bohr proposed a model of the hydrogen atom that explains its line spectrum. In this model the energy of the electron in the hydrogen atom depends on the value of a quantum number, n. The value of n must be a positive integer $(1, 2, 3, \ldots)$, and each value of n corresponds to a different specific energy, E_n. The energy of the atom increases as n increases. The lowest energy is achieved for $n = 1$; this is called the **ground state** of the hydrogen atom. Other values of n correspond to **excited states**. Light is emitted when the electron drops from a higher-energy state to a lower-energy state; light is absorbed to excite the electron from a lower energy state to a higher one. The frequency of light emitted or absorbed is such that $h\nu$ equals the difference in energy between two allowed states.

SECTION 6.4   De Broglie proposed that matter, such as electrons, should exhibit wavelike properties. This hypothesis of **matter waves** was proved experimentally by observing the diffraction of electrons. An object has a characteristic wavelength that depends on its **momentum**, mv: $\lambda = h/mv$. Discovery of the wave properties of the electron led to Heisenberg's **uncertainty principle**, which states that there is an inherent limit to the accuracy with which the position and momentum of a particle can be measured simultaneously.

SECTION 6.5   In the quantum mechanical model of the hydrogen atom, the behavior of the electron is described by mathematical functions called **wave functions**, denoted with the Greek letter ψ. Each allowed wave function has a precisely known energy, but the location of the electron cannot be determined exactly; rather, the probability of it being at a particular point in space is given by the **probability density**, ψ^2. The **electron density** distribution is a map of the probability of finding the electron at all points in space.

The allowed wave functions of the hydrogen atom are called **orbitals**. An orbital is described by a combination of an integer and a letter, corresponding to values of three quantum numbers. The *principal quantum number, n,* is indicated by the integers $1, 2, 3, \ldots$. This quantum number relates most directly to the size and energy of the orbital. The *angular momentum quantum number, l,* is indicated by the letters *s, p, d, f,* and so on, corresponding to the values of $0, 1, 2, 3, \ldots$. The l quantum number defines the shape of the orbital. For a given value of n, l can have integer values ranging from 0 to $(n - 1)$. The *magnetic quantum number, m_l,* relates to the orientation of the orbital in space. For a given value of l, m_l can have integral values ranging from $-l$ to l, including 0. Subscripts can be used to label the orientations of the orbitals. For example, the three $3p$ orbitals are designated $3p_x$, $3p_y$, and $3p_z$, with the subscripts indicating the axis along which the orbital is oriented.

An **electron shell** is the set of all orbitals with the same value of n, such as $3s$, $3p$, and $3d$. In the hydrogen atom all the orbitals in an electron shell have the same energy. A **subshell** is the set of one or more orbitals with the same n and l values; for example, $3s$, $3p$, and $3d$ are each subshells of the $n = 3$ shell. There is one orbital in an s subshell, three in a p subshell, five in a d subshell, and seven in an f subshell.

SECTION 6.6   Contour representations are useful for visualizing the shapes of the orbitals. Represented this way, s orbitals appear as spheres that increase in size as n increases. The **radial probability function** tells us the probability that the electron will be found at a certain distance from the nucleus. The wave function for each p orbital has two lobes on opposite sides of the nucleus. They are oriented along the x, y, and z axes. Four of the d orbitals appear as shapes with four lobes around the nucleus; the fifth one, the d_{z^2} orbital, is represented as two lobes along the z axis and a "doughnut" in the xy plane. Regions in which the wave function is zero are called **nodes**. There is zero probability that the electron will be found at a node.

SECTION 6.7   In many-electron atoms, different subshells of the same electron shell have different energies. For a given value of n, the

energy of the subshells increases as the value of l increases: $ns<np<nd<nf$. Orbitals within the same subshell are **degenerate**, meaning they have the same energy.

Electrons have an intrinsic property called **electron spin**, which is quantized. The **spin magnetic quantum number**, m_s, can have two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, which can be envisioned as the two directions of an electron spinning about an axis. The **Pauli exclusion principle** states that no two electrons in an atom can have the same values for n, l, m_l, and m_s. This principle places a limit of two on the number of electrons that can occupy any one atomic orbital. These two electrons differ in their value of m_s.

SECTIONS 6.8 AND 6.9 The **electron configuration** of an atom describes how the electrons are distributed among the orbitals of the atom. The ground-state electron configurations are generally obtained by placing the electrons in the atomic orbitals of lowest possible energy with the restriction that each orbital can hold no more than two electrons. When electrons occupy a subshell with more than one degenerate orbital, such as the $2p$ subshell, **Hund's rule** states that the lowest energy is attained by maximizing the number of electrons with the same electron spin. For example, in the ground-state electron configuration of carbon, the two $2p$ electrons have the same spin and must occupy two different $2p$ orbitals.

Elements in any given group in the periodic table have the same type of electron arrangements in their outermost shells. For example, the electron configurations of the halogens fluorine and chlorine are $[\text{He}]2s^22p^5$ and $[\text{Ne}]3s^23p^5$, respectively. The outer-shell electrons are those that lie outside the orbitals occupied in the next lowest noble-gas element. The outer-shell electrons that are involved in chemical bonding are the **valence electrons** of an atom; for the elements with atomic number 30 or less, all the outer-shell electrons are valence electrons. The electrons that are not valence electrons are called **core electrons**.

The periodic table is partitioned into different types of elements, based on their electron configurations. Those elements in which the outermost subshell is an s or p subshell are called the **representative** (or **main-group**) **elements**. The alkali metals (group 1A), halogens (group 7A), and noble gases (group 8A) are representative elements. Those elements in which a d subshell is being filled are called the **transition elements** (or **transition metals**). The elements in which the $4f$ subshell is being filled are called the **lanthanide** (or **rare earth**) **elements**. The **actinide elements** are those in which the $5f$ subshell is being filled. The lanthanide and actinide elements are collectively referred to as the **_f_-block metals**. These elements are shown as two rows of 14 elements below the main part of the periodic table. The structure of the periodic table, summarized in Figure 6.30, allows us to write the electron configuration of an element from its position in the periodic table.

KEY SKILLS

- Calculate the wavelength of electromagnetic radiation given its frequency or its frequency given its wavelength. (Section 6.1)

- Order the common kinds of radiation in the electromagnetic spectrum according to their wavelengths or energy. (Section 6.1)

- Explain what photons are and be able to calculate their energies given either their frequency or wavelength. (Section 6.2)

- Explain how line spectra relate to the idea of quantized energy states of electrons in atoms. (Section 6.3)

- Calculate the wavelength of a moving object. (Section 6.4)

- Explain how the uncertainty principle limits how precisely we can specify the position and the momentum of subatomic particles such as electrons. (Section 6.4)

- Relate the quantum numbers to the number and type of orbitals and recognize the different orbital shapes. (Section 6.5)

- Interpret radial probability function graphs for the orbitals. (Section 6.6)

- Draw an energy-level diagram for the orbitals in a many-electron atom and describe how electrons populate the orbitals in the ground state of an atom, using the Pauli exclusion principle and Hund's rule. (Section 6.8)

- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom. (Section 6.9)

KEY EQUATIONS

- $c = \lambda\nu$ [6.1]   light as a wave: c = speed of light $(3.00 \times 10^8 \text{ m/s})$, λ = wavelength in meters, ν = frequency in s^{-1}

- $E = h\nu$ [6.2]   light as a particle (photon): E = energy of photon in joules, h = Planck's constant $(6.626 \times 10^{-34} \text{ J-s})$, ν = frequency in s^{-1} (same frequency as previous formula)

- $\lambda = h/mv$ [6.8]   matter as a wave: λ = wavelength, h = Planck's constant, m = mass of object in kg, v = speed of object in m/s

- $\Delta x \cdot \Delta(mv) \geq \dfrac{h}{4\pi}$ [6.9]   Heisenberg's uncertainty principle. The uncertainty in position (Δx) and momentum $[\Delta(mv)]$ of an object cannot be zero; the smallest value of their product is $h/4\pi$

EXERCISES

VISUALIZING CONCEPTS

6.1 Consider the water wave shown here. (**a**) How could you measure the speed of this wave? (**b**) How would you determine the wavelength of the wave? (**c**) Given the speed and wavelength of the wave, how could you determine the frequency of the wave? (**d**) Suggest an independent experiment to determine the frequency of the wave. [Section 6.1]

6.2 A popular kitchen appliance produces electromagnetic radiation with a frequency of 2450 MHz. With reference to Figure 6.4, answer the following: (**a**) Estimate the wavelength of this radiation. (**b**) Would the radiation produced by the appliance be visible to the human eye? (**c**) If the radiation is not visible, do photons of this radiation have more or less energy than photons of visible light? (**d**) Propose the identity of the kitchen appliance. [Section 6.1]

6.3 The following diagrams represent two electromagnetic waves. Which wave corresponds to the higher-energy radiation? Explain. [Section 6.2]
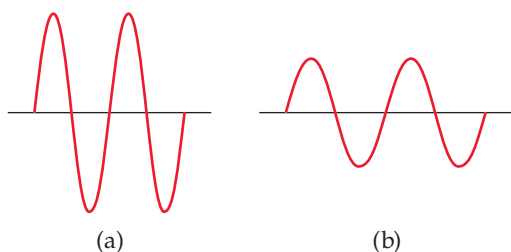
6.4 As shown in the accompanying photograph, an electric stove burner on its highest setting exhibits an orange glow. (**a**) When the burner setting is changed to low, the burner continues to produce heat but the orange glow disappears. How can this observation be explained with reference to one of the fundamental observations that led to the notion of quanta? (**b**) Suppose that the energy provided to the burner could be increased beyond the highest setting of the stove. What would we expect to observe with regard to visible light emitted by the burner? [Section 6.2]

6.5 The familiar phenomenon of a rainbow results from the diffraction of sunlight through raindrops. (**a**) Does the wavelength of light increase or decrease as we proceed outward from the innermost band of the rainbow? (**b**) Does the frequency of light increase or decrease as we proceed outward? (**c**) Suppose that instead of sunlight, the visible light from a hydrogen discharge tube (Figure 6.10) was used as the light source. What do you think the resulting "hydrogen discharge rainbow" would look like? [Section 6.3]

6.6 A certain quantum mechanical system has the energy levels shown in the diagram below. The energy levels are indexed by a single quantum number n that is an integer. (**a**) As drawn, which quantum numbers are involved in the transition that requires the most energy? (**b**) Which quantum numbers are involved in the transition that requires the least energy? (**c**) Based on the drawing, put the following in order of increasing wavelength of the light absorbed or emitted during the transition: (*i*) $n = 1$ to $n = 2$; (*ii*) $n = 3$ to $n = 2$; (*iii*) $n = 2$ to $n = 4$; (*iv*) $n = 3$ to $n = 1$. [Section 6.3]

6.7 Consider a fictitious one-dimensional system with one electron. The wave function for the electron, drawn at the top of the next page, is $\psi(x) = \sin x$ from $x = 0$ to $x = 2\pi$. (**a**) Sketch the probability density, $\psi^2(x)$, from $x = 0$ to $x = 2\pi$. (**b**) At what value or values of x will there be the greatest prob-

ability of finding the electron? **(c)** What is the probability that the electron will be found at $x = \pi$? What is such a point in a wave function called? [Section 6.5]

6.8 The contour representation of one of the orbitals for the $n = 3$ shell of a hydrogen atom is shown below. **(a)** What is the quantum number l for this orbital? **(b)** How do we label this orbital? **(c)** How would you modify this sketch to show the analogous orbital for the $n = 4$ shell? [Section 6.6]

6.9 The drawing below shows part of the orbital diagram for an element. **(a)** As drawn, the drawing is *incorrect*. Why? **(b)** How would you correct the drawing without changing the number of electrons? **(c)** To which group in the periodic table does the element belong? [Section 6.8]

6.10 State where in the periodic table these elements appear:
   (a) elements with the valence-shell electron configuration ns^2np^5
   (b) elements that have three unpaired p electrons
   (c) an element whose valence electrons are $4s^24p^1$
   (d) the d-block elements

THE WAVE NATURE OF LIGHT (section 6.1)

6.11 What are the basic SI units for **(a)** the wavelength of light, **(b)** the frequency of light, **(c)** the speed of light?

6.12 **(a)** What is the relationship between the wavelength and the frequency of radiant energy? **(b)** Ozone in the upper atmosphere absorbs energy in the 210–230-nm range of the spectrum. In what region of the electromagnetic spectrum does this radiation occur?

6.13 Label each of the following statements as true or false. For those that are false, correct the statement. **(a)** Visible light is a form of electromagnetic radiation. **(b)** Ultraviolet light has longer wavelengths than visible light. **(c)** X-rays travel faster than microwaves. **(d)** Electromagnetic radiation and sound waves travel at the same speed.

6.14 Determine which of the following statements are false and correct them. **(a)** The frequency of radiation increases as the wavelength increases. **(b)** Electromagnetic radiation travels through a vacuum at a constant speed, regardless of wavelength. **(c)** Infrared light has higher frequencies than visible light. **(d)** The glow from a fireplace, the energy within a microwave oven, and a foghorn blast are all forms of electromagnetic radiation.

6.15 Arrange the following kinds of electromagnetic radiation in order of increasing wavelength: infrared, green light, red light, radio waves, X-rays, ultraviolet light.

6.16 List the following types of electromagnetic radiation in order of increasing wavelength: **(a)** the gamma rays produced by a radioactive nuclide used in medical imaging; **(b)** radiation from an FM radio station at 93.1 MHz on the dial; **(c)** a radio signal from an AM radio station at 680 kHz on the dial; **(d)** the yellow light from sodium vapor streetlights; **(e)** the red light of a light-emitting diode, such as in a calculator display.

6.17 **(a)** What is the frequency of radiation that has a wavelength of 10 μm, about the size of a bacterium? **(b)** What is the wavelength of radiation that has a frequency of 5.50×10^{14} s^{-1}? **(c)** Would the radiations in part (a) or part (b) be visible to the human eye? **(d)** What distance does electromagnetic radiation travel in 50.0 μs?

6.18 **(a)** What is the frequency of radiation whose wavelength is 5.0×10^{-5} m? **(b)** What is the wavelength of radiation that has a frequency of 2.5×10^8 s^{-1} ? **(c)** Would the radiations in part (a) or part (b) be detected by an X-ray detector? **(d)** What distance does electromagnetic radiation travel in 10.5 fs?

6.19 An argon ion laser emits light at 532 nm. What is the frequency of this radiation? Using Figure 6.4, predict the color associated with this wavelength.

6.20 It is possible to convert radiant energy into electrical energy using photovoltaic cells. Assuming equal efficiency of conversion, would infrared or ultraviolet radiation yield more electrical energy on a per-photon basis?

QUANTIZED ENERGY AND PHOTONS (section 6.2)

6.21 If human height were quantized in one-foot increments, what would happen to the height of a child as she grows up?

6.22 Einstein's 1905 paper on the photoelectric effect was the first important application of Planck's quantum hypothesis. Describe Planck's original hypothesis, and explain how Einstein made use of it in his theory of the photoelectric effect.

6.23 (a) Calculate the energy of a photon of electromagnetic radiation whose frequency is $6.75 \times 10^{12}\,\text{s}^{-1}$. (b) Calculate the energy of a photon of radiation whose wavelength is 322 nm. (c) What wavelength of radiation has photons of energy $2.87 \times 10^{-18}\,\text{J}$?

6.24 (a) A red laser pointer emits light with a wavelength of 650 nm. What is the frequency of this light? (b) What is the energy of one of these photons? (c) The laser pointer emits light because electrons in the material are excited (by a battery) from their ground state to an upper excited state. When the electrons return to the ground state, they lose the excess energy in the form of 650 nm photons. What is the energy gap between the ground state and excited state in the laser material?

6.25 (a) Calculate and compare the energy of a photon of wavelength $3.3\,\mu\text{m}$ with that of wavelength 0.154 nm. (b) Use Figure 6.4 to identify the region of the electromagnetic spectrum to which each belongs.

6.26 An AM radio station broadcasts at 1010 kHz, and its FM partner broadcasts at 98.3 MHz. Calculate and compare the energy of the photons emitted by these two radio stations.

6.27 One type of sunburn occurs on exposure to UV light of wavelength in the vicinity of 325 nm. (a) What is the energy of a photon of this wavelength? (b) What is the energy of a mole of these photons? (c) How many photons are in a 1.00 mJ burst of this radiation? (d) These UV photons can break chemical bonds in your skin to cause sunburn—a form of radiation damage. If the 325-nm radiation provides exactly the energy to break an average chemical bond in the skin, estimate the average energy of these bonds in kJ/mol.

6.28 The energy from radiation can be used to cause the rupture of chemical bonds. A minimum energy of 941 kJ/mol is required to break the nitrogen–nitrogen bond in N_2. What is the longest wavelength of radiation that possesses the necessary energy to break the bond? What type of electromagnetic radiation is this?

6.29 A diode laser emits at a wavelength of 987 nm. (a) In what portion of the electromagnetic spectrum is this radiation found? (b) All of its output energy is absorbed in a detector that measures a total energy of 0.52 J over a period of 32 s. How many photons per second are being emitted by the laser?

6.30 A stellar object is emitting radiation at 3.55 mm. (a) What type of electromagnetic spectrum is this radiation? (b) If a detector is capturing 3.2×10^8 photons per second at this wavelength, what is the total energy of the photons detected in one hour?

6.31 Molybdenum metal must absorb radiation with a minimum frequency of $1.09 \times 10^{15}\,\text{s}^{-1}$ before it can eject an electron from its surface via the photoelectric effect. (a) What is the minimum energy needed to eject an electron? (b) What wavelength of radiation will provide a photon of this energy? (c) If molybdenum is irradiated with light of wavelength of 120 nm, what is the maximum possible kinetic energy of the emitted electrons?

6.32 Sodium metal requires a photon with a minimum energy of $4.41 \times 10^{-19}\,\text{J}$ to emit electrons. (a) What is the minimum frequency of light necessary to emit electrons from sodium via the photoelectric effect? (b) What is the wavelength of this light? (c) If sodium is irradiated with light of 405 nm, what is the maximum possible kinetic energy of the emitted electrons? (d) What is the maximum number of electrons that can be freed by a burst of light whose total energy is $1.00\,\mu\text{J}$?

BOHR'S MODEL; MATTER WAVES (sections 6.3 and 6.4)

6.33 Explain how the existence of line spectra is consistent with Bohr's theory of quantized energies for the electron in the hydrogen atom.

6.34 (a) In terms of the Bohr theory of the hydrogen atom, what process is occurring when excited hydrogen atoms emit radiant energy of certain wavelengths and only those wavelengths? (b) Does a hydrogen atom "expand" or "contract" as it moves from its ground state to an excited state?

6.35 Is energy emitted or absorbed when the following electronic transitions occur in hydrogen: (a) from $n = 4$ to $n = 2$, (b) from an orbit of radius 2.12 Å to one of radius 8.46 Å, (c) an electron adds to the H^+ ion and ends up in the $n = 3$ shell?

6.36 Indicate whether energy is emitted or absorbed when the following electronic transitions occur in hydrogen: (a) from $n = 2$ to $n = 6$, (b) from an orbit of radius 4.76 Å to one of radius 0.529 Å, (c) from the $n = 6$ to the $n = 9$ state.

6.37 (a) Using Equation 6.5, calculate the energy of an electron in the hydrogen atom when $n = 2$ and when $n = 6$. Calculate the wavelength of the radiation released when an electron moves from $n = 6$ to $n = 2$. (b) Is this line in the visible region of the electromagnetic spectrum? If so, what color is it?

6.38 (a) Calculate the energies of an electron in the hydrogen atom for $n = 1$ and for $n = \infty$. How much energy does it require to move the electron out of the atom completely (from $n = 1$ to $n = \infty$), according to Bohr? Put your answer in kJ/mol. (b) The energy for the process $H + \text{energy} \rightarrow H^+ + e^-$ is called the ionization energy of hydrogen. The experimentally determined value for the ionization energy of hydrogen is 1310 kJ/mol. How does this compare to your calculation?

6.39 The visible emission lines observed by Balmer all involved $n_f = 2$. (a) Explain why only the lines with $n_f = 2$ were observed in the visible region of the electromagnetic spectrum. (b) Calculate the wavelengths of the first three lines in the Balmer series—those for which $n_i = 3, 4,$ and 5—and identify these lines in the emission spectrum shown in Figure 6.11.

6.40 The Lyman series of emission lines of the hydrogen atom are those for which $n_f = 1$. (a) Determine the region of the electromagnetic spectrum in which the lines of the Lyman series are observed. (b) Calculate the wavelengths of the first three lines in the Lyman series—those for which $n_i = 2, 3,$ and 4.

6.41 One of the emission lines of the hydrogen atom has a wavelength of 93.8 nm. (a) In what region of the electromagnetic spectrum is this emission found? (b) Determine the initial and final values of n associated with this emission.

6.42 The hydrogen atom can absorb light of wavelength 2626 nm. **(a)** In what region of the electromagnetic spectrum is this absorption found? **(b)** Determine the initial and final values of n associated with this absorption.

6.43 Use the de Broglie relationship to determine the wavelengths of the following objects: **(a)** an 85-kg person skiing at 50 km/hr, **(b)** a 10.0-g bullet fired at 250 m/s, **(c)** a lithium atom moving at 2.5×10^5 m/s, **(d)** an ozone (O_3) molecule in the upper atmosphere moving at 550 m/s.

6.44 Among the elementary subatomic particles of physics is the muon, which decays within a few nanoseconds after formation. The muon has a rest mass 206.8 times that of an electron. Calculate the de Broglie wavelength associated with a muon traveling at a velocity of 8.85×10^5 cm/s.

6.45 Neutron diffraction is an important technique for determining the structures of molecules. Calculate the velocity of a neutron needed to achieve a wavelength of 0.955 Å. (Refer to the inside cover for the mass of the neutron).

6.46 The electron microscope has been widely used to obtain highly magnified images of biological and other types of materials. When an electron is accelerated through a particular potential field, it attains a speed of 8.95×10^6 m/s. What is the characteristic wavelength of this electron? Is the wavelength comparable to the size of atoms?

6.47 Using Heisenberg's uncertainty principle, calculate the uncertainty in the position of **(a)** a 1.50-mg mosquito moving at a speed of 1.40 m/s if the speed is known to within ±0.01 m/s; **(b)** a proton moving at a speed of $(5.00\pm0.01) \times 10^4$ m/s. (The mass of a proton is given in the table of fundamental constants in the inside cover of the text.)

6.48 Calculate the uncertainty in the position of **(a)** an electron moving at a speed of $(3.00\pm0.01) \times 10^5$ m/s, **(b)** a neutron moving at this same speed. (The masses of an electron and a neutron are given in the table of fundamental constants in the inside cover of the text.) **(c)** What are the implications of these calculations to our model of the atom?

QUANTUM MECHANICS AND ATOMIC ORBITALS (sections 6.5 and 6.6)

6.49 **(a)** Why does the Bohr model of the hydrogen atom violate the uncertainty principle? **(b)** In what way is the description of the electron using a wave function consistent with de Broglie's hypothesis? **(c)** What is meant by the term *probability density*? Given the wave function, how do we find the probability density at a certain point in space?

6.50 **(a)** According to the Bohr model, an electron in the ground state of a hydrogen atom orbits the nucleus at a specific radius of 0.53 Å. In the quantum mechanical description of the hydrogen atom, the most probable distance of the electron from the nucleus is 0.53 Å. Why are these two statements different? **(b)** Why is the use of Schrödinger's wave equation to describe the location of a particle very different from the description obtained from classical physics? **(c)** In the quantum mechanical description of an electron, what is the physical significance of the square of the wave function, ψ^2?

6.51 **(a)** For $n = 4$, what are the possible values of l? **(b)** For $l = 2$, what are the possible values of m_l? **(c)** If m_l is 2, what are the possible values for l?

6.52 How many possible values for l and m_l are there when **(a)** $n = 3$; **(b)** $n = 5$?

6.53 Give the numerical values of n and l corresponding to each of the following orbital designations: **(a)** 3p, **(b)** 2s , **(c)** 4f , **(d)** 5d.

6.54 Give the values for n, l, and m_l for **(a)** each orbital in the 2p subshell, **(b)** each orbital in the 5d subshell.

6.55 Which of the following represent impossible combinations of n and l: **(a)** 1p, **(b)** 4s, **(c)** 5f, **(d)** 2d?

6.56 For the table that follows, write which orbital goes with the quantum numbers. Don't worry about x, y, z subscripts. If the quantum numbers are not allowed, write "not allowed."

n	l	m_l	Orbital
2	1	-1	2p (example)
1	0	0	
3	-3	2	
3	2	-2	
2	0	-1	
0	0	0	
4	2	1	
5	3	0	

6.57 Sketch the shape and orientation of the following types of orbitals: **(a)** s, **(b)** p_z, **(c)** d_{xy}.

6.58 Sketch the shape and orientation of the following types of orbitals: **(a)** p_x, **(b)** d_{z^2}, **(c)** $d_{x^2-y^2}$.

6.59 **(a)** What are the similarities and differences between the 1s and 2s orbitals of the hydrogen atom? **(b)** In what sense does a 2p orbital have directional character? Compare the "directional" characteristics of the p_x and $d_{x^2-y^2}$ orbitals. (That is, in what direction or region of space is the electron density concentrated?) **(c)** What can you say about the average distance from the nucleus of an electron in a 2s orbital as compared with a 3s orbital? **(d)** For the hydrogen atom, list the following orbitals in order of increasing energy (that is, most stable ones first): 4f, 6s , 3d, 1s, 2p.

6.60 **(a)** With reference to Figure 6.18, what is the relationship between the number of nodes in an s orbital and the value of the principal quantum number? **(b)** Identify the number of nodes; that is, identify places where the electron density is zero, in the $2p_x$ orbital; in the 3s orbital. **(c)** What information is obtained from the radial probability functions in Figure 6.18? **(d)** For the hydrogen atom, list the following orbitals in order of increasing energy: 3s, 2s, 2p, 5s, 4d.

## MANY-ELECTRON ATOMS AND ELECTRON CONFIGURATIONS (sections 6.7–6.9)

6.61 For a given value of the principal quantum number, n, how do the energies of the s, p, d, and f subshells vary for **(a)** hydrogen, **(b)** a many-electron atom?

6.62 **(a)** The average distance from the nucleus of a 3s electron in a chlorine atom is smaller than that for a 3p electron. In light of this fact, which orbital is higher in energy? **(b)** Would you expect

it to require more or less energy to remove a 3s electron from the chlorine atom, as compared with a 2p electron? Explain.

6.63 **(a)** What experimental evidence is there for the electron having a "spin"? **(b)** Draw an energy-level diagram that shows the relative energetic positions of a 1s orbital and a 2s orbital. Put

two electrons in the 1s orbital. (**c**) Draw an arrow showing the excitation of an electron from the 1s to the 2s orbital.

6.64 (**a**) State the Pauli exclusion principle in your own words. (**b**) The Pauli exclusion principle is, in an important sense, the key to understanding the periodic table. Explain.

6.65 What is the maximum number of electrons that can occupy each of the following subshells: (**a**) 3p, (**b**) 5d, (**c**) 2s, (**d**) 4f ?

6.66 What is the maximum number of electrons in an atom that can have the following quantum numbers: (**a**) $n = 2$, $m_s = -\frac{1}{2}$, (**b**) $n = 5$, $l = 3$; (**c**) $n = 4$, $l = 3$, $m_l = -3$; (**d**) $n = 4$, $l = 0$, $m_l = 0$?

6.67 (**a**) What are "valence electrons"? (**b**) What are "core electrons"? (**c**) What does each box in an orbital diagram represent? (**d**) What quantity is represented by the half arrows in an orbital diagram?

6.68 For each element, indicate the number of valence electrons, core electrons, and unpaired electrons in the ground state: (**a**) carbon, (**b**) phosphorus, (**c**) neon.

6.69 Write the condensed electron configurations for the following atoms, using the appropriate noble-gas core abbreviations: (**a**) Cs, (**b**) Ni, (**c**) Se, (**d**) Cd, (**e**) U, (**f**) Pb.

6.70 Write the condensed electron configurations for the following atoms and indicate how many unpaired electrons each has: (**a**) Mg, (**b**) Ge, (**c**) Br, (**d**) V, (**e**) Y, (**f**) Lu.

6.71 Identify the specific element that corresponds to each of the following electron configurations and indicate the number of unpaired electrons for each: (**a**) $1s^2 2s^2$, (**b**) $1s^2 2s^2 2p^4$, (**c**) $[Ar]4s^1 3d^5$, (**d**) $[Kr]5s^2 4d^{10} 5p^4$.

6.72 Identify the group of elements that corresponds to each of the following generalized electron configurations and indicate the number of unpaired electrons for each:
(**a**) [noble gas] $ns^2 np^5$
(**b**) [noble gas] $ns^2 (n-1)d^2$
(**c**) [noble gas] $ns^2 (n-1)d^{10} np^1$
(**d**) [noble gas] $ns^2 (n-2)f^6$

6.73 What is wrong with the following electron configurations for atoms in their ground states? (**a**) $ls^2 2s^2 3s^1$, (**b**) $[Ne]2s^2 2p^3$, (**c**) $[Ne]3s^2 3d^5$.

6.74 The following electron configurations represent excited states. Identify the element, and write its ground-state condensed electron configuration. (**a**) $1s^2 2s^2 3p^2 4p^1$, (**b**) $[Ar]3d^{10} 4s^1 4p^4 5s^1$, (**c**) $[Kr]4d^6 5s^2 5p^1$.

ADDITIONAL EXERCISES

6.75 Consider the two waves shown here, which we will consider to represent two electromagnetic radiations:
(**a**) What is the wavelength of wave A? Of wave B?
(**b**) What is the frequency of wave A? Of wave B?
(**c**) Identify the regions of the electromagnetic spectrum to which waves A and B belong.
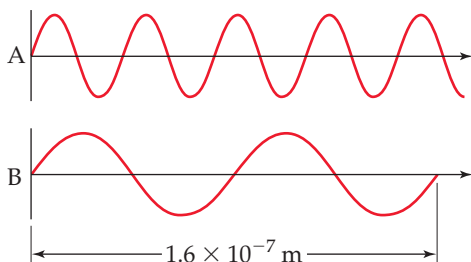
6.76 If you put 120 volts of electricity through a pickle, the pickle will smoke and start glowing orange-yellow. The light is emitted because sodium ions in the pickle become excited; their return to the ground state results in light emission. (**a**) The wavelength of this emitted light is 589 nm. Calculate its frequency. (**b**) What is the energy of 0.10 mole of these photons? (**c**) Calculate the energy gap between the excited and ground states for the sodium ion. (**d**) If you soaked the pickle for a long time in a different salt solution, such as strontium chloride, would you still observe 589-nm light emission? Why or why not?

6.77 Certain elements emit light of a specific wavelength when they are burned. Historically, chemists used such emission wavelengths to determine whether specific elements were present in a sample. Characteristic wavelengths for some of the elements are given in the following table:

| Ag	328.1 nm	Fe	372.0 nm
Au	267.6 nm	K	404.7 nm
Ba	455.4 nm	Mg	285.2 nm
Ca	422.7 nm	Na	589.6 nm
Cu	324.8 nm	Ni	341.5 nm

(**a**) Determine which elements emit radiation in the visible part of the spectrum. (**b**) Which element emits photons of highest energy? Of lowest energy? (**c**) When burned, a sample of an unknown substance is found to emit light of frequency $6.59 \times 10^{14}\ s^{-1}$. Which of these elements is probably in the sample?

6.78 In June 2004, the Cassini–Huygens spacecraft began orbiting Saturn and transmitting images to Earth. The closest distance between Saturn and Earth is 746 million miles. What is the minimum amount of time it takes for the transmitted signals to travel from the spacecraft to Earth?

6.79 The rays of the Sun that cause tanning and burning are in the ultraviolet portion of the electromagnetic spectrum. These rays are categorized by wavelength. So-called UV-A radiation has wavelengths in the range of 320–380 nm, whereas UV-B radiation has wavelengths in the range of 290–320 nm. (**a**) Calculate the frequency of light that has a wavelength of 320 nm. (**b**) Calculate the energy of a mole of 320-nm photons. (**c**) Which are more energetic, photons of UV-A radiation or photons of UV-B radiation? (**d**) The UV-B radiation from the Sun is considered a greater cause of sunburn in humans than is UV-A radiation. Is this observation consistent with your answer to part (c)?

6.80 The watt is the derived SI unit of power, the measure of energy per unit time: 1 W = 1 J-s. A semiconductor laser in a CD player has an output wavelength of 780 nm and a power level of 0.10 mW. How many photons strike the CD surface during the playing of a CD 69 minutes in length?

6.81 Carotenoids are yellow, orange, and red pigments synthesized by plants. The observed color of an object is not the color of light it absorbs but rather the complementary color, as described by a color wheel such as the one shown here. On this wheel, complementary colors are across from each other. (**a**) Based on this wheel, what color is absorbed most strongly if a plant is orange? (**b**) If a particular carotenoid absorbs photons at 455 nm, what is the energy of the photon?
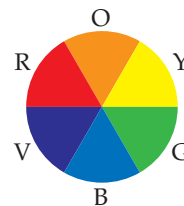
6.82 A photocell is a device used to measure the intensity of light. In a certain experiment, when light of wavelength 630 nm is directed onto the photocell, electrons are emitted at the rate of 2.6×10^{-12} C/s (coulombs per second). Assume that each photon that impinges on the photocell emits one electron. How many photons per second are striking the photocell? How much energy per second is the photocell absorbing?

6.83 In an experiment to study the photoelectric effect, a scientist measures the kinetic energy of ejected electrons as a function of the frequency of radiation hitting a metal surface. She obtains the following plot. The point labeled "ν_0" corresponds to light with a wavelength of 680 nm. (a) What is the value of ν_0 in s^{-1}? (b) What is the value of the work function of the metal in units of kJ/mol of ejected electrons? (c) What happens when the metal is irradiated with light of frequency less than ν_0? (d) Note that when the frequency of the light is greater than ν_0, the plot shows a straight line with a nonzero slope. Why is this the case? (e) Can you determine the slope of the line segment discussed in part (d)? Explain.
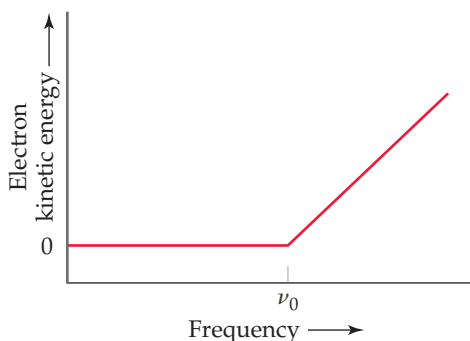
6.84 The human retina has three types of receptor cones, each sensitive to a different range of wavelengths of visible light, as shown in this figure (the colors are merely to differentiate the three curves from one another; they do not indicate the actual colors represented by each curve):
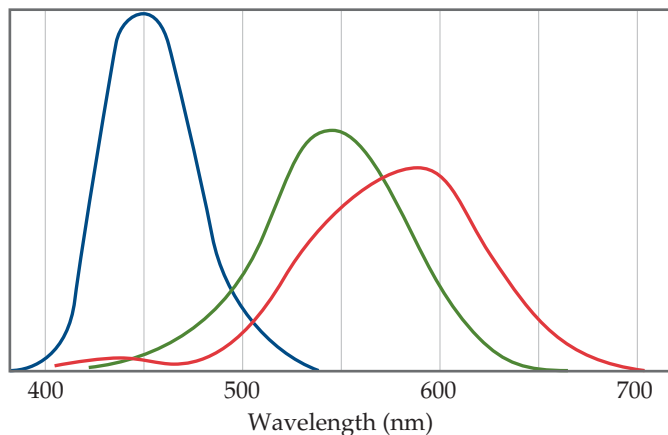
(a) Estimate the energies of photons with wavelengths at the maximum for each type of cone. (b) The color of the sky is due to scattering of solar light by the molecules of the atmosphere. Lord Rayleigh was one of the first to study scattering of this kind. He showed that the amount of scattering for very small particles such as molecules is inversely proportional to the fourth power of the wavelength. Estimate the ratio of the scattering efficiency of light at the wavelength of the maximum for the "blue" cones, as compared with that for the "green" cones. (c) Explain why the sky appears blue even though all wavelengths of solar light are scattered by the atmosphere.

6.85 The series of emission lines of the hydrogen atom for which $n_f = 3$ is called the *Paschen series*. (a) Determine the region of the electromagnetic spectrum in which the lines of the Paschen series are observed. (b) Calculate the wavelengths of the first three lines in the Paschen series—those for which $n_i = 4, 5$, and 6.

6.86 When the spectrum of light from the Sun is examined in high resolution in an experiment similar to that illustrated in Figure 6.9, dark lines are evident. These are called Fraunhofer lines, after the scientist who studied them extensively in the early nineteenth century. Altogether, about 25,000 lines have been identified in the solar spectrum between 2950 Å and 10,000 Å. The Fraunhofer lines are attributed to absorption of certain wavelengths of the Sun's "white" light by gaseous elements in the Sun's atmosphere. (a) Describe the process that causes absorption of specific wavelengths of light from the solar spectrum. (b) To determine which Fraunhofer lines belonged to a given element, say neon, what experiments could a scientist conduct here on Earth?

[6.87] Bohr's model can be used for hydrogen-like ions—ions that have only one electron, such as He^+ and Li^{2+}. (a) Why is the Bohr model applicable to He^+ ions but not to neutral He atoms? (b) The ground-state energies of H, He^+, and Li^{2+} are tabulated as follows:

Atom or ion	H	He⁺	Li²⁺
Ground-state energy	-2.18×10^{-18} J	-8.72×10^{-18} J	-1.96×10^{-17} J

By examining these numbers, propose a relationship between the ground-state energy of hydrogen-like systems and the nuclear charge, Z. (c) Use the relationship you derive in part (b) to predict the ground-state energy of the C^{5+} ion.

[6.88] An electron is accelerated through an electric potential to a kinetic energy of 18.6 keV. What is its characteristic wavelength? [*Hint*: Recall that the kinetic energy of a moving object is $E = \frac{1}{2}mv^2$, where m is the mass of the object and v is the speed of the object.]

6.89 In the television series *Star Trek,* the transporter beam is a device used to "beam down" people from the *Starship Enterprise* to another location, such as the surface of a planet. The writers of the show put a "Heisenberg compensator" into the transporter beam mechanism. Explain why such a compensator (which is entirely fictional) would be necessary to get around Heisenberg's uncertainty principle.

6.90 Which of the quantum numbers governs (a) the shape of an orbital, (b) the energy of an orbital, (c) the spin properties of the electron, (d) the spatial orientation of the orbital?

[6.91] Consider the discussion of radial probability functions in "A Closer Look" in Section 6.6. (a) What is the difference between the probability density as a function of r and the radial probability function as a function of r? (b) What is the significance of the term $4\pi r^2$ in the radial probability functions for the s orbitals? (c) Based on Figures 6.18 and 6.21, make sketches of what you think the probability density as a function of r and the radial probability function would look like for the $4s$ orbital of the hydrogen atom.

[6.92] For orbitals that are symmetric but not spherical, the contour representations (as in Figures 6.22 and 6.23) suggest where nodal planes exist (that is, where the electron density is zero). For example, the p_x orbital has a node wherever $x = 0$. This equation is satisfied by all points on the yz plane, so this plane is called a nodal plane of the p_x orbital. **(a)** Determine the nodal plane of the p_z orbital. **(b)** What are the two nodal planes of the d_{xy} orbital? **(c)** What are the two nodal planes of the $d_{x^2-y^2}$ orbital?

[6.93] The "Chemistry and Life" box in Section 6.7 described the techniques called NMR and MRI. **(a)** Instruments for obtaining MRI data are typically labeled with a frequency, such as 600 MHz. Why do you suppose this label is relevant to the experiment? **(b)** What is the value of ΔE in Figure 6.27 that would correspond to the absorption of a photon of radiation with frequency 450 MHz? **(c)** In general, the stronger the magnetic field, the greater the information obtained from an NMR or MRI experiment. Why do you suppose this is the case?

6.94 Suppose that the spin quantum number, m_s, could have *three* allowed values instead of two. How would this affect the number of elements in the first four rows of the periodic table?

6.95 Using the periodic table as a guide, write the condensed electron configuration and determine the number of unpaired electrons for the ground state of (a) Si, (b) Zn, (c) Zr, (d) Sn, (e) Ba, (f) Tl.

6.96 Scientists have speculated that element 126 might have a moderate stability, allowing it to be synthesized and characterized. Predict what the condensed electron configuration of this element might be.

INTEGRATIVE EXERCISES

6.97 Microwave ovens use microwave radiation to heat food. The energy of the microwaves is absorbed by water molecules in food and then transferred to other components of the food. **(a)** Suppose that the microwave radiation has a wavelength of 11.2 cm. How many photons are required to heat 200 mL of coffee from 23 °C to 60 °C? **(b)** Suppose the microwave's power is 900 W (1 Watt = 1 joule-second). How long would you have to heat the coffee in part (a)?

6.98 The stratospheric ozone (O_3) layer helps to protect us from harmful ultraviolet radiation. It does so by absorbing ultraviolet light and falling apart into an O_2 molecule and an oxygen atom, a process known as photodissociation.

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

Use the data in Appendix C to calculate the enthalpy change for this reaction. What is the maximum wavelength a photon can have if it is to possess sufficient energy to cause this dissociation? In what portion of the spectrum does this wavelength occur?

6.99 The discovery of hafnium, element number 72, provided a controversial episode in chemistry. G. Urbain, a French chemist, claimed in 1911 to have isolated an element number 72 from a sample of rare earth (elements 58–71) compounds. However, Niels Bohr believed that hafnium was more likely to be found along with zirconium than with the rare earths. D. Coster and G. von Hevesy, working in Bohr's laboratory in Copenhagen, showed in 1922 that element 72 was present in a sample of Norwegian zircon, an ore of zirconium. (The name hafnium comes from the Latin name for Copenhagen, *Hafnia*). **(a)** How would you use electron configuration arguments to justify Bohr's prediction? **(b)** Zirconium, hafnium's neighbor in group 4B, can be produced as a metal by reduction of solid $ZrCl_4$ with molten sodium metal. Write a balanced chemical equation for the reaction. Is this an oxidation-reduction reaction? If yes, what is reduced and what is oxidized? **(c)** Solid zirconium dioxide, ZrO_2, is reacted with chlorine gas in the presence of carbon. The products of the reaction are $ZrCl_4$ and two gases, CO_2 and CO in the ratio 1:2. Write a balanced chemical equation for the reaction. Starting with a 55.4-g sample of ZrO_2, calculate the mass of $ZrCl_4$ formed, assuming that ZrO_2 is the limiting reagent and assuming 100% yield. **(d)** Using their electron configurations, account for the fact that Zr and Hf form chlorides MCl_4 and oxides MO_2.

6.100 **(a)** Account for formation of the following series of oxides in terms of the electron configurations of the elements and the discussion of ionic compounds in Section 2.7: K_2O, CaO, Sc_2O_3, TiO_2, V_2O_5, CrO_3. **(b)** Name these oxides. **(c)** Consider the metal oxides whose enthalpies of formation (in kJ mol^{-1}) are listed here.

Oxide	$K_2O(s)$	$CaO(s)$	$TiO_2(s)$	$V_2O_5(s)$
ΔH_f°	−363.2	−635.1	−938.7	−1550.6

Calculate the enthalpy changes in the following general reaction for each case:

$$M_nO_m(s) + H_2(g) \longrightarrow nM(s) + mH_2O(g)$$

(You will need to write the balanced equation for each case and then compute ΔH°.) **(d)** Based on the data given, estimate a value of ΔH_f° for $Sc_2O_3(s)$.

6.101 The first 25 years of the twentieth century were momentous for the rapid pace of change in scientists' understanding of the nature of matter. (**a**) How did Rutherford's experiments on the scattering of α particles by a gold foil set the stage for Bohr's theory of the hydrogen atom? (**b**) In what ways is de Broglie's hypothesis, as it applies to electrons, consistent with J. J. Thomson's conclusion that the electron has mass? In what sense is it consistent with proposals preceding Thomson's work that the cathode rays are a wave phenomenon?

[**6.102**] The two most common isotopes of uranium are ^{235}U and ^{238}U. (**a**) Compare the number of protons, the number of electrons, and the number of neutrons in atoms of these two isotopes. (**b**) Using the periodic table in the front inside cover, write the electron configuration for a U atom. (**c**) Compare your answer to part (b) to the electron configuration given in Figure 6.31. How can you explain any differences between these two electron configurations? (**d**) ^{238}U undergoes radioactive decay to ^{234}Th. How many protons, electrons, and neutrons are gained or lost by the ^{238}U atom during this process? (**e**) Examine the electron configuration for Th in Figure 6.31. Are you surprised by what you find? Explain.

6.103 Imagine sunlight falling on three square areas. One is an inert black material. The second is a photovoltaic cell surface, which converts radiant energy into electricity. The third is an area on a green tree leaf. Draw diagrams that show the energy conversions in each case, using Figure 5.9 as a model. How are these three examples related to the idea of sustainable energy sources?