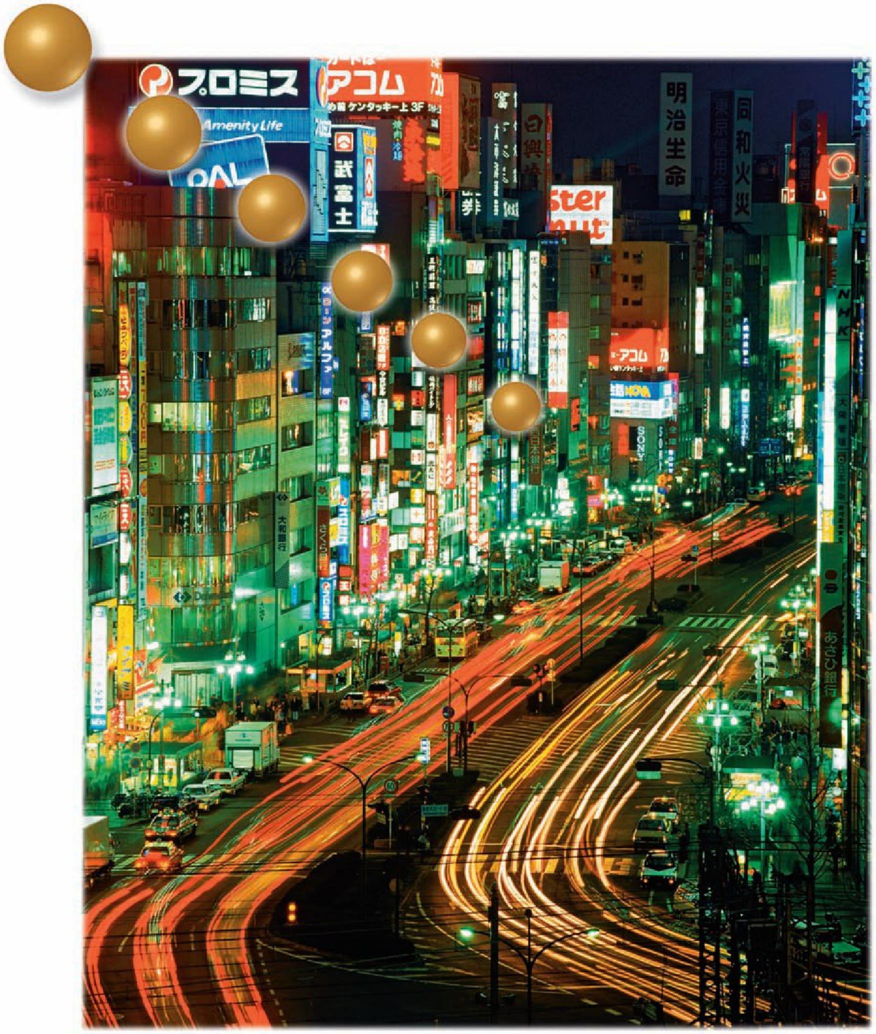
CHAPTER 6

ELECTRONIC STRUCTURE OF ATOMS



THE GLASS TUBES OF NEON LIGHTS contain various gases that can be excited by electricity. Light is produced when electrically excited atoms return to their lowest-energy states.

WHAT'S AHEAD

6.1 The Wave Nature of Light
We will learn that light (radiant energy, or *electromagnetic radiation*) has wavelike properties and so is characterized by *wavelength, frequency*, and *speed*.

6.2 Quantized Energy and Photons
We will recognize that many different types of experiments indicate that electromagnetic radiation also has particle-like properties and can be described in terms of *photons,* "particles" of light.

6.3 Line Spectra and the Bohr Model
We will explore the fact that atoms give off characteristic colors of light (*line spectra*), when appropriately stimulated. Line spectra provide clues about how electrons are arranged in atoms. Experiments show that electrons exist only at certain energy levels around a nucleus and that energy is involved in moving an electron from one level to another. The Bohr model of the atom pictures the atom as a miniature solar system, with the nucleus of an atom as the "Sun" about which electrons, like planets, orbit.

6.4 The Wave Behavior of Matter
We recognize that matter also has wavelike properties that are manifested at the atomic scale. Because of the fundamental particle-wave duality of matter, it is impossible to determine simultaneously the exact position and the exact motion of an electron in an atom (*Heisenberg's Uncertainty Principle*).

6.5 Quantum Mechanics and Atomic Orbitals
We will discover that classical mechanics treats matter as particles, while quantum mechanics treats matter as waves. We will see that we can describe how an electron exists in atoms by thinking about the electron as a standing wave surrounding the nucleus. The *wave functions* that mathematically describe the electron's position and energy in an atom are called *atomic orbitals*. The orbitals can be described in a shorthand notation using *quantum numbers*.

6.6 Representations of Orbitals
We will see how to draw pictures of orbitals and interpret graphs of electron density.

6.7 Many-Electron Atoms
We will recognize that the energy levels for one electron in an atom are altered when multiple electrons are in an atom. The electron itself 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.

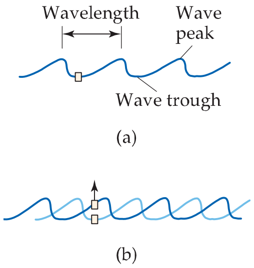
6.8 Electron Configurations
We will realize that knowing the energies of orbitals as well as some fundamental characteristics of electrons described by *Hund's rule* allows us to determine how electrons are distributed among various orbitals in an atom (*electron configurations)*.

6.9 Electron Configurations and the Periodic Table
We will observe that the electron configuration of an atom is related to the location of the element in the periodic table.

WHAT HAPPENS WHEN someone switches on a neon light? The electrons in the neon atoms, which are excited to a higher energy by electricity, emit light when they drop back down to a lower energy. The pleasing glow that results is explained by one of the most revolutionary discoveries of the twentieth century, namely, the *quantum theory*. This theory explains much of the behavior of electrons in atoms. We will see that the behavior of electrons in an atom is quite unlike anything we see in our macroscopic world.

In this chapter we will explore the quantum theory and its importance in chemistry. We will begin by looking more closely 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 an atom as well as the distribution of the electrons around the nucleus and their energies. We will see that the quantum description of the electronic structure of atoms helps us to understand the elegant 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. In the chapters that follow, we will see how the concepts of quantum theory are used to explain trends in the periodic table and the formation of bonds between atoms.

▲ **Figure 6.1 Water waves.** The movement of the boat through the water forms waves. The regular variation of the peaks and troughs enables us to sense the motion, or *propagation*, of the waves.



▲ **Figure 6.2 Characteristics of water waves.** (a) The distance between corresponding points on each wave is called the *wavelength*. In this drawing, the two corresponding points are two peaks, but they could be any other two corresponding points, such as two adjacent troughs. (b) The number of times per second that the cork bobs up and down is called the *frequency* of the wave.

6.1 THE WAVE NATURE OF LIGHT

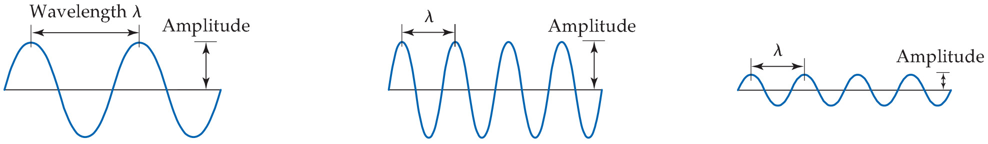
Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances. To understand electronic structure, therefore, we must first learn more about light. The light that we can see with our eyes, *visible light*, is an example 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 forms—such as the radio waves that carry music to our radios, the infrared radiation (heat) from a glowing fireplace, and the X-rays used by a dentist—may seem very different from one another, but they all share certain fundamental characteristics.

All types of electromagnetic radiation move through a vacuum at a speed of 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. We can measure the frequency of a water wave by counting the number of times per second that a cork bobbing on the water moves through a complete cycle of upward and downward motion.

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

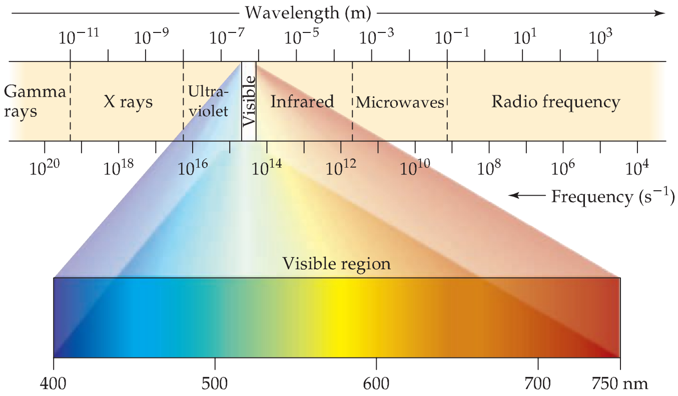
▼ **Figure 6.3 Characteristics of electromagnetic waves.** Radiant energy has wave characteristics; it consists of electromagnetic waves. Notice that the shorter the wavelength, λ, the higher the frequency, ν. The wavelength in (b) is half as long as that in (a), and the frequency of the wave in (b) is therefore twice as great as the frequency in (a). The *amplitude* of the wave relates to the intensity of the radiation, which is the maximum extent of the oscillation of the wave. In these diagrams amplitude is measured as the vertical distance from the midline of the wave to its peak. The waves in (a) and (b) have the same amplitude. The wave in (c) has the same frequency as that in (b), but its amplitude is lower.



(a) Two complete cycles of wavelength λ

(b) Wavelength half of that in (a); frequency twice as great as in (a)

(c) Same frequency as (b), smaller amplitude characteristics of electromagnetic radiation are due to the periodic oscillations in the intensities of the electric and magnetic fields associated with the radiation.



▲ **Figure 6.4 The electromagnetic spectrum.** Wavelengths in the spectrum range from very short gamma rays to very long radio waves. Notice that the color of visible light can be expressed quantitatively by wavelength.

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, namely 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, there will be fewer cycles of the wave passing a point per second, and the frequency will be low. Conversely, for a wave to have a high frequency, the wave must have a short wavelength—that is, the distance between the peaks of the waves is small. This inverse relationship between the frequency and the wavelength of electromagnetic radiation can be expressed by the equation

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

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

Why do different forms of electromagnetic radiation have different properties? Their differences are due to their different wavelengths, which are expressed in units of length. 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 similar 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 700 nm (4×10^{-7} m to 7×10^{-7} m), is an extremely small portion of the electromagnetic spectrum. We can see visible light because of the chemical reactions it triggers in our eyes. The unit of length normally chosen to express wavelength depends on the type of radiation, as shown in Table 6.1▼.

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.

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	TV, radio
Kilometer	km	1000	Radio

A Closer Look

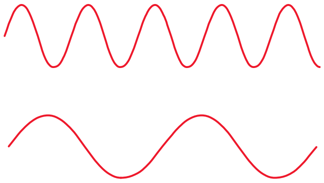
THE SPEED OF LIGHT

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

During the late 1600s, the Danish astonomer 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 one possible explanation for the discrepancies was that Jupiter was farther from Earth at different times of the year. Thus, the light from the Sun, which reflected off Jupiter and ultimately to his telescope, had farther to travel at different times of the year. Rømer's data led to an estimate of 3.5×10^8 m/s for the speed of light. In 1704, Isaac Newton (1643–1727) used estimates of the distance from the Sun to Earth and the time it takes for the light to travel that distance to calculate the speed of light as $2.4 - 2.7 \times 10^8$ m/s.

In 1927, A. A. Michelson (1852–1931) performed a famous experiment to determine the speed of light. Michelson set up a rotating mirror system at the top of Mount Wilson in southern California (Figure 6.5 ▶). The mirror system bounced light from the top of Mount Wilson to the top of Mount San Antonio, 22 miles away, where another mirror system bounced the light back to Mount Wilson. If the speed of light was instantaneous, or an exact multiple of the turn speed of the rotating mirror, the reflected spot of light would appear exactly superimposed on the original spot. 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 is $2.9980 \pm 0.0002 \times 10^8$ m/s. The main source of error is the distance between the mirrors at the tops of the two mountains, which was measured within a fifth of an inch in 22 miles.

▲ **Figure 6.5 View of Mount San Antonio from the top of Mount Wilson.** The mountains are 22 miles apart.



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.

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 (which is given) and the frequency (which is the unknown) is given by Equation 6.1. We can solve this equation for ν and then 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; MHz $= 10^6 \text{ s}^{-1}$). 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)** 2.901 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?

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 and the bright white light of a tungsten lightbulb. The wavelength distribution of the radiation depends on temperature; a red-hot object is cooler than a white-hot one (Figure 6.6▶). During the late 1800s, a number of physicists were studying this phenomenon, trying to understand the relationship between the temperature and the intensity and wavelengths of the emitted radiation. The prevailing laws of physics could not account for the observations.

▲ **Figure 6.6** **Color as a function of temperature.** The color and intensity of the light emitted by a hot object depend on the temperature of the object. The temperature is highest at the center of this pour of molten steel. As a result, the light emitted from the center is most intense and of shortest wavelength.

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:

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

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 is allowed to 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 6.7◀). 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 aren't its effects more 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 size scale of our ordinary experience or with microscopic objects. With everyday macroscopic objects, however, the gain or loss of a single quantum of energy goes completely unnoticed. In contrast, when dealing with matter at the atomic level, the impact of quantized energies is far more significant.

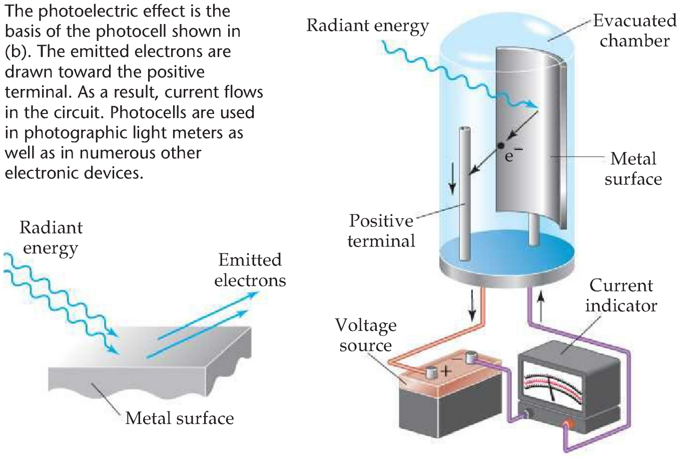
▲ Figure 6.7 **A model for quantized energy.** The potential energy of a person walking up a ramp (a) increases in a uniform, continuous manner, whereas that of a person walking up steps (b) increases in a stepwise, quantized manner.

GIVE IT SOME THOUGHT

The temperature of stars is gauged by their colors. For example, red stars have a lower temperature than blue-white stars. How is this temperature scale consistent with Planck's assumption?

The Photoelectric Effect and Photons

A few years after Planck presented his theory, scientists began to see its applicability to a great many experimental observations. They recognized that Planck's theory had within it the seeds of a revolution in the way we view the physical world. In 1905, Albert Einstein (1879–1955) used Planck's quantum theory to explain the **photoelectric effect,** which is illustrated in Figure 6.8◀. Experiments had shown that light shining on a clean metal surface causes the surface to emit electrons. Each metal has a minimum frequency of light below which no electrons are emitted. For example, light with a frequency of 4.60×10^{14} s^{-1} or greater will cause cesium metal to emit electrons, but light of lower frequency has no effect.



(a)

(b)

▼ Figure 6.8 **The photoelectric effect.** When photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal, as in (a). The photoelectric effect is the basis of the photocell shown in (b). The emitted electrons are drawn toward the positive terminal. As a result, current flows in the circuit. Photocells are used in photographic light meters as well as in numerous other electronic devices.

To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface does not behave like a wave but rather as if it were a stream of tiny energy packets. Each energy packet, called a **photon,** behaves like a tiny particle. Extending Planck's quantum theory, 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, a photon can strike a metal surface and be absorbed. When this happens, the photon can transfer its energy to an electron in the metal. A certain amount of energy—called the *work function*—is required for an electron to overcome the attractive forces that hold it in the metal. If the photons of the radiation impinging on the metal have less energy than the work function, electrons do not acquire sufficient energy to escape from the metal surface, even if the light beam is intense. If the photons of radiation have sufficient energy, electrons are emitted from the metal. If the photons have more than the minimum energy required to free electrons, the excess energy appears as the kinetic energy of the emitted electrons. Einstein won the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

To better understand what a photon is, imagine that you have a light source that produces radiation with 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 of energy consists of a single photon of light.

SAMPLE EXERCISE 6.3 | Energy of a Photon

Calculate the energy of one photon of yellow light with 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 front 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

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

This is the magnitude of enthalpies of reactions (Section 5.4), so radiation can break chemical bonds, producing what are called *photochemical reactions*.

PRACTICE EXERCISE

(a) A laser emits light with a frequency of $4.69 \times 10^{14}\ \text{s}^{-1}$. What is the energy of one photon of the radiation from this laser? **(b)** If the laser emits a pulse of energy 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 during the pulse?
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 that different kinds of electromagnetic radiation have on matter. For example, the high frequency (short wavelength) of X-rays

(Figure 6.4) causes X-ray photons to have energy high enough to 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 particles rather than a wave explains the photoelectric effect and a great many other observations, it also poses a dilemma. Is light a wave, or does it consist of particles? 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 wavelike and particle-like characteristics and, depending on the situation, will behave more like a wave or more like particles. We will soon see that this dual nature of light is also characteristic of matter.

▲ **Figure 6.9 Quantum giants.** Niels Bohr (right) with Albert Einstein. Bohr (1885–1962) made major contributions to the quantum theory. From 1911 to 1913 Bohr studied in England, working first with J. J. Thomson at Cambridge University and then with Ernest Rutherford at the University of Manchester. He published his quantum theory of the atom in 1914 and was awarded the Nobel Prize in Physics in 1922.

GIVE IT SOME THOUGHT

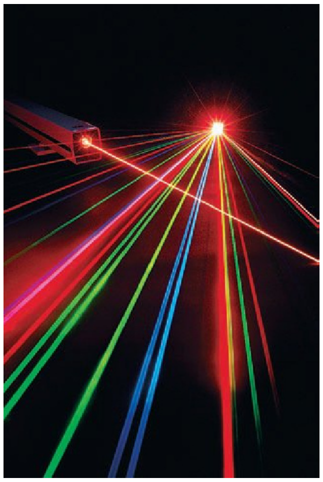
What has more energy, a photon of infrared light or a photon of ultraviolet light?

6.3 LINE SPECTRA AND THE BOHR MODEL

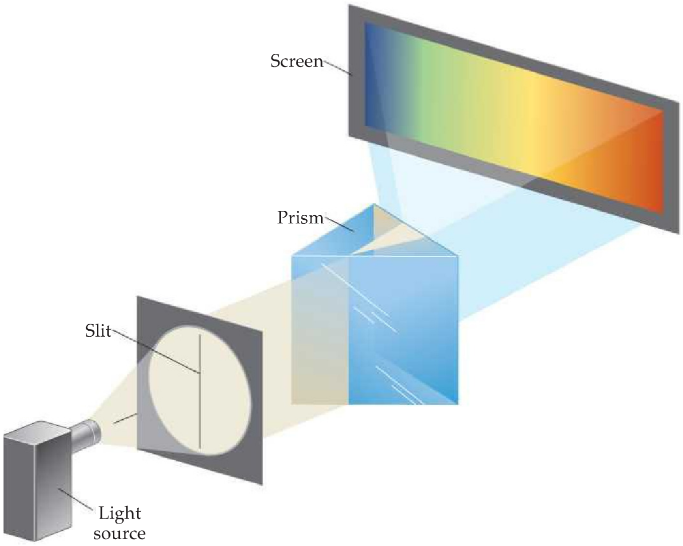
The work of Planck and Einstein paved the way for understanding how electrons are arranged in atoms. In 1913, the Danish physicist Niels Bohr (Figure 6.9▲) offered a theoretical explanation of *line spectra*, another phenomenon that had puzzled scientists during the nineteenth century. We will examine this phenomenon and then consider how Bohr used the ideas of Planck and Einstein.

Line Spectra

A particular source of radiant energy may emit a single wavelength, as in the light from a laser (Figure 6.10◀). Radiation composed of a single wavelength is said to be *monochromatic*. However, most common radiation sources, including lightbulbs and stars, produce radiation containing many different wavelengths. A **spectrum** is produced when radiation from such sources is separated into its different wavelength components. Figure 6.11▼ shows how a prism spreads light from a light source into its component wavelengths. The resulting



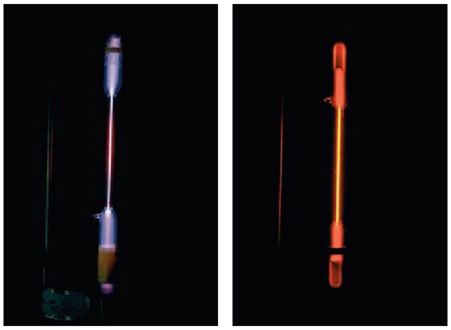
▲ **Figure 6.10 Monochromatic radiation.** Lasers produce light of a single wavelength, which we call *monochromatic light*. Different lasers produce light of different wavelengths. The photo shows beams from a variety of lasers that produce visible light of different colors. Other lasers produce light that is not visible, including infrared and ultraviolet light.



▶ **Figure 6.11 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.

spectrum consists of a continuous range of colors—violet merges into blue, blue into green, 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 6.12▶). 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, as shown in Figure 6.13▼. Each wavelength is represented by a colored line in one of these spectra. A spectrum containing radiation of only specific wavelengths is called a **line spectrum.**

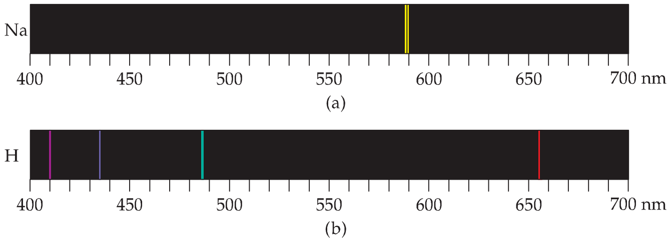


▲ **Figure 6.12** **Atomic emission.** Different gases emit light of different characteristic colors upon excitation by an electrical discharge: (a) hydrogen, (b) neon.

When scientists first detected the line spectrum of hydrogen in the mid-1800s, they were fascinated by its simplicity. At that time, only the four lines in the visible portion of the spectrum were observed, as shown in Figure 6.13. These lines correspond to wavelengths of 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red). In 1885, a Swiss schoolteacher named Johann Balmer showed that the wavelengths of these four visible lines of hydrogen fit an intriguingly simple formula that related the wavelengths of the visible line spectrum to integers. Later, additional lines were found to occur in the ultraviolet and infrared regions of the hydrogen spectrum. Soon Balmer's equation was extended to a more general one, called the *Rydberg equation*, which allowed the calculation of 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* ($1.096776 \times 10^7\ \mathrm{m}^{-1}$), and n_1 and n_2 are positive integers, with n_2 being larger than n_1. How could the remarkable simplicity of this equation be explained? It took nearly 30 more years to answer this question.



◀ **Figure 6.13** **Line spectra.** Spectra obtained from the electrical discharge from (a) Na, (b) H. Light of only a few specific wavelengths is produced, as shown by colored lines in the spectra.

Bohr's Model

Rutherford's discovery of the nuclear nature of the atom (Section 2.2) suggests that the atom can be thought of as a "microscopic solar system" in which electrons orbit the nucleus. To explain the line spectrum of hydrogen, Bohr assumed that electrons move in circular orbits around the nucleus. According to classical physics, however, an electrically charged particle (such as an electron) that moves in a circular path should continuously lose energy by emitting electromagnetic radiation. As the electron loses energy, it should spiral into the positively charged nucleus. This spiraling obviously does not happen since 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: Bohr assumed that the prevailing laws of physics were inadequate to describe all aspects of atoms. Furthermore, Bohr adopted Planck's idea that energies are quantized.

Bohr based his model on three postulates:

1. Only orbits of certain radii, corresponding to certain definite energies, are permitted for the electron in a hydrogen atom.
2. An electron in a permitted orbit has a specific energy and is in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will 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, $E = h\nu$.

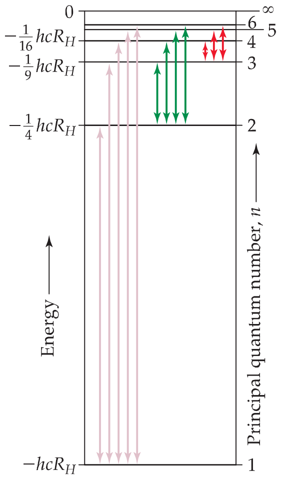
GIVE IT SOME THOUGHT

Before reading further about the details of Bohr's model, speculate as to how they explain the fact that hydrogen gas emits a line spectrum (Figure 6.13) 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 each allowed orbit for the electron in the hydrogen atom. Ultimately, the energies that Bohr calculated fit the formula

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



▲ Figure 6.14 **Energy levels in the hydrogen atom from the Bohr model.** The arrows refer to the transitions of the electron from one allowed energy state to another. The states shown are those for which $n = 1$ through $n = 6$ and the state for $n = \infty$ for which the energy, E, equals zero.

In this equation, h, c, and R_H are Planck's constant, the speed of light, and the Rydberg constant, respectively. The product of these three constants equals 2.18×10^{-18} J. The integer n, which can have whole number values of 1, 2, 3, ... to infinity (∞), 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. Equation 6.5 tells us the energy that the electron will have, depending on which orbit it is in.

The energies of the electron of a hydrogen atom given by Equation 6.5 are negative for all values of n. The lower (more negative) the energy is, the more stable the atom will be. The energy is lowest (most negative) for $n = 1$. As n gets larger, the energy becomes successively less negative and therefore increases. We can liken the situation to a ladder in which the rungs are numbered from the bottom rung on up. The higher one climbs the ladder (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 senergy (less negative) orbit—$n = 2$ or higher—the atom is said to be in an **excited state.** Figure 6.14◀ shows the energy of the electron in a hydrogen atom for several values of n.

What happens to the orbit radius and the energy as n becomes infinitely large? The radius increases as n^2, so we reach a point at which the electron is completely separated from the nucleus. When $n = \infty$, the energy is zero:

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

Thus, the state in which the electron is removed from the nucleus is the reference, or zero-energy, state of the hydrogen atom. This zero-energy state is *higher* in energy than the states with negative energies.

In his third postulate, Bohr assumed that the electron could "jump" from one allowed energy state to another by either absorbing or emitting photons whose radiant energy corresponds exactly to the energy difference between the two states. Energy must be absorbed for an electron to move to a higher energy state (one with a higher value of n). Conversely, radiant energy is emitted when the electron jumps to a lower energy state (one with a lower value of n). Thus, if the electron jumps from an initial state that has 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

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

In this equation 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 for the emitted photon, we can calculate either its frequency or its wavelength. For the wavelength, we have

$$\lambda = \frac{c}{\nu} = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \text{J-s})(3.00 \times 10^{8}\ \text{m/s})}{1.94 \times 10^{-18}\ \text{J}} = 1.03 \times 10^{-7}\ \text{m}$$

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 1.03×10^{-7} m has been *emitted*.

If we solve Equation 6.7 for $1/\lambda$, we find that this equation 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 6.14, predict which of the following 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 6.14 the shortest vertical line 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

While the Bohr model explains the line spectrum of the hydrogen atom, it cannot explain the spectra of other atoms, except in a rather 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. Therefore, there is a problem with describing an electron merely as a small particle circling about 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, and (2) energy is involved in moving 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 wavelike 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, could matter, under appropriate conditions, possibly show the properties of a wave? Suppose that the electron orbiting the nucleus of a hydrogen atom could be thought of as a wave, with a characteristic wavelength, rather than as a particle. De Broglie suggested that as the electron moves about the nucleus, it is associated with a particular wavelength. He went on to propose that the characteristic wavelength of the electron, or of any other particle, depends on its mass, m, and on its velocity, v, (where h is Planck's constant):

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

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 out of the range of any possible observation. 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

and recalling that $1\text{ J} = 1\text{ kg-m}^2/\text{s}^2$

we have the following:

$$\lambda = \frac{h}{mv}$$

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

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

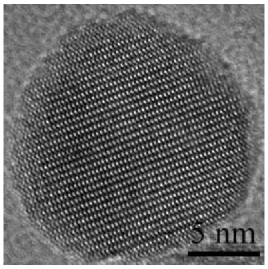
Comment: By comparing this value with the wavelengths of electromagnetic radiation shown in Figure 6.4, we see that the wavelength of this electron is about the same as that of X-rays.

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

Within a few years after de Broglie published his theory, the wave properties of the electron were demonstrated experimentally. As electrons passed through a crystal, they were diffracted by the crystal, just as X-rays are diffracted. Thus, a stream of moving electrons exhibits the same kinds of wave behavior as 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. Electron microscopes can magnify objects by 3,000,000 times (x), far more than can be done with visible light (1000x), because the wavelength of the electrons is so small compared to visible light. Figure 6.15▶ is a photograph of an electron microscope image.



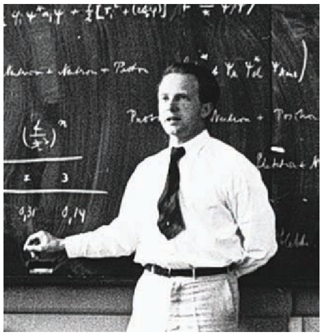
▲ Figure 6.15 **Electrons as waves.** The dots you see in this transmission electron micrograph are columns of atoms. Their regular spacing at the atomic level proves that this material is crystalline. Because this crystal is only about 15 nm in diameter, it is a nanocrystal, which has unusual properties that we will discuss in Chapter 12.

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 about classical physics. Consider, for example, a ball rolling down a ramp. Using the equations of classical physics, we can calculate the ball's position, direction of motion, and speed at any time, with great accuracy.



▲ **Figure 6.16** **Werner Heisenberg (1901–1976).** During his postdoctoral assistantship with Niels Bohr, Heisenberg formulated his famous uncertainty principle. At the age of 25, he became the chair in theoretical physics at the University of Leipzig. At 32 he was one of the youngest scientists to receive the Nobel Prize.

Can we do the same for an electron, which exhibits wave properties? A wave extends in space, and therefore 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 time.

The German physicist Werner Heisenberg (Figure 6.16 ◀) proposed that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of any object. 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 inherently impossible for us to know simultaneously both the exact momentum of the electron and its exact location in space.

Heisenberg mathematically related the uncertainty of the 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 $(0.01)(5 \times 10^6 \text{ m/s}) = 5 \times 10^4 \text{ m/s}$) and that this is the only important source of uncertainty in the momentum, so that $\Delta(mv) = m\Delta v$. We can then use Equation 6.9 to calculate the uncertainty in the position of the electron:

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

Because the diameter of a hydrogen atom is only about 1×10^{-10} m, the uncertainty is an order of magnitude greater than the size of the atom. Thus, we have essentially no idea of where the electron is located within 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 new 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 in terms of probabilities.

GIVE IT SOME THOUGHT

What is the principal reason that the uncertainty principle should be considered when discussing electrons and other subatomic particles, but is not so necessary 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 wavelike behavior and the particle-like behavior of the electron. His work opened a new way of dealing with subatomic particles, known as either *quantum mechanics* or *wave mechanics*. The application of Schrödinger's equation

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.

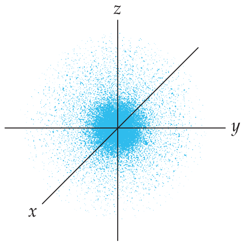
Related Exercises: 6.45 and 6.46

requires advanced calculus, and we will not be concerned with the details of his approach. We will, however, qualitatively consider the results he 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.

In the same way that a plucked guitar string vibrates as a standing wave, Schrödinger treated the electron as a standing circular wave around the nucleus. Just as the plucked guitar string produces a fundamental frequency and higher overtones (harmonics), there is a lowest-energy standing wave, and higher-energy ones, for an electron in an atom. Solving Schrödinger's equation 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 (the lowercase Greek letter *psi*). Although the wave function itself has no direct physical meaning, the square of the wave function, ψ^2, provides information about an electron's location when the electron 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 nucleus. Rather, we must be content with a kind of statistical knowledge. In the quantum mechanical model, 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 6.17▶. In this figure the density of the dots represents the probability of finding the electron. The regions with a high



▲ Figure 6.17 **Electron-density distribution.** This rendering represents the probability of where in the space surrounding the nucleus the electron is to be found in a hydrogen atom in its ground state.

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. In Section 6.6 we will say more about the ways in which we can represent electron density.

GIVE IT SOME THOUGHT

Is there a difference between stating, "The electron is located at a particular point in space" and "There is a high probability that the electron is located at a particular point in space"?

Orbitals and Quantum Numbers

The solution to Schrödinger's equation for the hydrogen atom yields a set of wave functions and corresponding energies. These wave functions are called **orbitals.** Each orbital describes a specific distribution of electron density in space, as given by the orbital's probability density. Each orbital, therefore, has a characteristic energy and shape. For example, the lowest-energy orbital in the hydrogen atom has an energy of -2.18×10^{-18} J and the shape illustrated in Figure 6.17. Note that an *orbital* (quantum mechanical model) is not the same as an *orbit* (Bohr model). The quantum mechanical model does not refer to orbits, because the motion of the electron in an atom cannot be precisely measured or tracked (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. Let's consider what information we obtain from each of these quantum numbers and how they are interrelated.

1. The *principal quantum number, n*, can have positive integral values of 1, 2, 3, and so forth. 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, $E_n = -(2.18 \times 10^{-18}\text{ J})(1/n^2)$, 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. (We will consider these shapes in Section 6.6.) 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, respectively, as summarized here:

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 will 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 is possible. The electron in a hydrogen atom is described by only one of these orbitals at any given time—we say that the electron *occupies* a certain orbital. The remaining orbitals are *unoccupied* for that particular state of the hydrogen atom. We will see that we are mainly interested in the orbitals of the hydrogen atom with small values of n.

**The letters s, p, d, and f 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	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

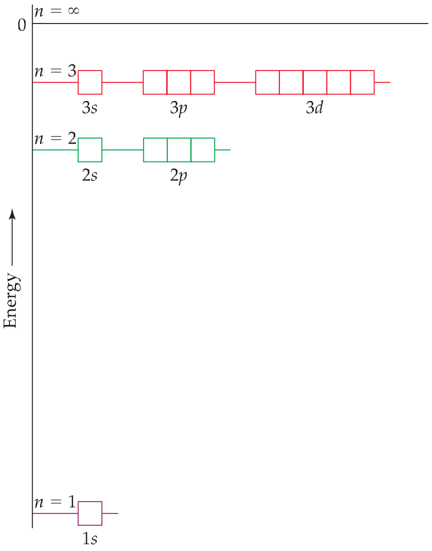
GIVE IT SOME THOUGHT

What is the difference between an *orbit* (Bohr model) and an *orbital* (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. Further, the set of 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 the quantum numbers l and m_l for values of n through $n = 4$. The restrictions on the possible values of the quantum numbers give rise to the following very important observations:

1. The shell with principal quantum number n will consist 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 $(2l + 1)$ 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—is 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 6.18 Orbital energy levels in the hydrogen atom.** Each box represents an orbital. Note that all orbitals with the same value for the principal quantum number, n, have the same energy. This is true only in one-electron systems, such as the hydrogen atom.

Figure 6.18▶ shows the relative energies of the hydrogen atom orbitals through $n = 3$. Each box represents an orbital; orbitals of the same subshell, such as the 2*p*, 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*. At ordinary temperatures, essentially all hydrogen atoms are in the ground state. The electron can be excited to a higher-energy orbital by absorption of a photon of appropriate energy.

GIVE IT SOME THOUGHT

In Figure 6.18, why is the energy difference between the $n = 1$ and $n = 2$ levels so much greater than the energy difference between the $n = 2$ and $n = 3$ levels?

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

PRACTICE EXERCISE

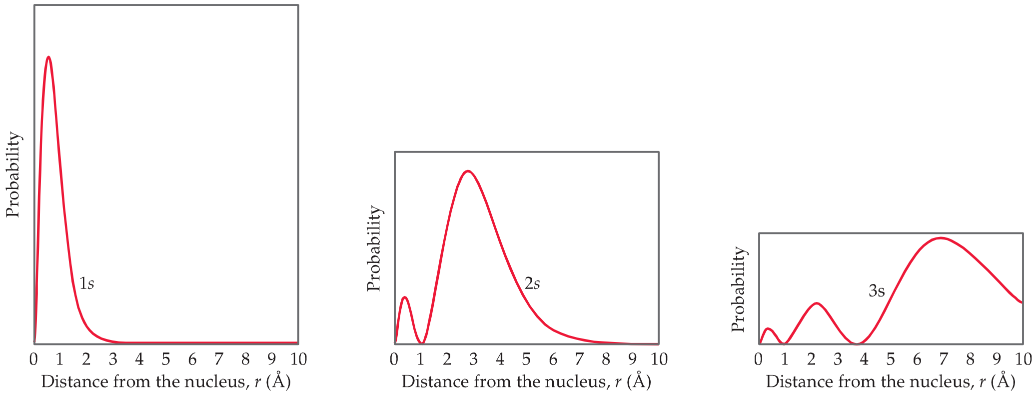
(a) What is the designation for the subshell with $n = 5$ and $l = 1$? **(b)** How many orbitals are in this subshell? **(c)** Indicate the values of m_l for each of these orbitals.
Answers: **(a)** 5*p*; **(b)** 3; **(c)** 1, 0, -1

6.6 REPRESENTATIONS OF ORBITALS

In our discussion of orbitals so far, we have emphasized their energies. But the wave function also provides information about the electron's location in space when it occupies an orbital. Let's examine the ways that we can picture the orbitals. In doing so, we will examine some important aspects of the electron-density distributions of the orbitals. First, we will look at the three-dimensional shape of the orbital—is it spherical, for example, or does it have directionality? Second, we will examine how the probability density changes as we move on a straight line farther and farther from the nucleus. Finally, we will look at the typical three-dimensional sketches that chemists use in describing the orbitals.

The *s* Orbitals

One representation of the lowest-energy orbital of the hydrogen atom, the 1*s*, is shown in Figure 6.17. This type of drawing, which shows the distribution of electron density around the nucleus, is one of the several ways we use to help us visualize orbitals. The first thing that we notice about the electron density for the 1*s* 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 (2*s*, 3*s*, 4*s*, and so forth) are spherically symmetric as well. Recall that the l quantum number



(a) (b) (c)

▲ **Figure 6.19** **Radial probability functions for the 1*s*, 2*s*, and 3*s* orbitals.** These plots show the 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 moves farther from the nucleus, similar to the Bohr model. In the 2*s* and 3*s* orbitals the radial probability function drops to zero at certain distances from the nucleus but then rises again. The points at which the probability is zero are called *nodes*.

for the s orbitals is 0; therefore the m_l quantum number must be 0. Therefore, for each value of *n*, there is only one *s* orbital.

So what is different about the *s* orbitals having different *n* quantum numbers? For example, how does the electron-density distribution of the hydrogen atom change when the electron is excited from the 1*s* orbital to the 2*s* orbital? To address questions like this, we must look at the *radial probability density*, that is, the probability that we will find the electron at a specific distance from the nucleus. In Figure 6.19▲ we have plotted the radial probability density for the 1*s* orbital as a function of *r*, the distance from the nucleus. The resulting curve is the **radial probability function** for the 1*s* orbital. (Radial probability functions are described more fully in the "A Closer Look" box in this section.) We see that the probability of finding the electron rises rapidly as we move away from the nucleus, maximizing at a distance of 0.529 Å from the nucleus, and then falls off rapidly. Thus, when the electron occupies the 1*s* orbital, it is *most likely* to be found 0.529 Å from the nucleus*. We still use the probabilistic description, consistent with the uncertainty principle. Notice also that the probability of finding the electron at a distance greater than 3 Å from the nucleus is essentially zero.

Figure 6.19(b) shows the radial probability function for the 2*s* orbital of the hydrogen atom. We can see three significant differences between this plot and that for the 1*s* orbital: (1) There are two separate maxima in the radial probability function for the 2*s* orbital, namely a small peak at about $r = 0.5$ Å and a much larger peak at about $r = 3$ Å; (2) Between these two peaks is a point at which the function goes to zero (at about $r = 1$ Å). An intermediate point at which a probability function goes to zero is called a **node.** There is a zero probability of finding the electron at a distance corresponding to a node, even though the electron might be found at shorter or longer distances; (3) The radial probability function for the 2*s* orbital is significantly broader (more spread out) than that for the 1*s* orbital. Thus, for the 2*s* orbital, there is a larger range of distances from the

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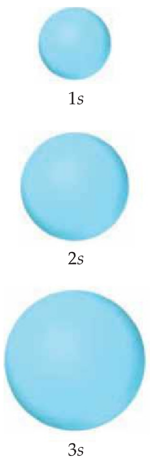
**In the quantum mechanical model, the most probable distance at which to find the electron in the 1s orbital—*0.529 Å*—is identical to the radius of the orbit predicted by Bohr for* $n = 1$*. The distance* 0.529 Å *is often called the Bohr radius.*

nucleus at which there is a high probability of finding the electron than for the 1*s* orbital. This trend continues for the 3*s* orbital, as shown in Figure 6.19(c). The radial probability function for the 3*s* orbital has three peaks of increasing size, with the largest peak maximizing even farther from the nucleus (at about $r = 7$ Å) at which it has two nodes and is even more spread out.

The radial probability functions in Figure 6.19 tell us that as *n* increases, there is also an increase in the most likely distance from the nucleus to find the electron. In other words, the size of the orbital increases with increasing *n*, just as it did in the Bohr model.

One widely used method of representing orbitals is to display a boundary surface that encloses some substantial portion, say 90%, of the total electron density for the orbital. For the *s* orbitals, these contour representations are spheres. The contour representations of the 1*s*, 2*s*, and 3*s* orbitals are shown in Figure 6.20◄. All the orbitals have the same shape, but they differ in size. Although the details of how the electron density varies within the contour representation are lost in these representations, this is not a serious disadvantage. For more qualitative discussions, the most important features of orbitals are their relative sizes and their shapes, which are adequately displayed by contour representations.



▲ Figure 6.20 **Contour representations of the 1*s*, 2*s*, and 3*s* orbitals.** The relative radii of the spheres correspond to a 90% probability of finding the electron within each sphere.

GIVE IT SOME THOUGHT

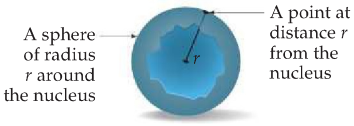
How many maxima would you expected to find in the radial probability function for the 4*s* orbital of the hydrogen atom? How many nodes would you expect in the 4*s* radial probability function?

A Closer Look PROBABILITY DENSITY AND RADIAL PROBABILITY FUNCTIONS

The quantum mechanical description of the hydrogen atom requires that we talk about the position of the electron in the atom in a somewhat unfamiliar way. In classical physics, we can exactly pinpoint the position and velocity of an orbiting object, such as a planet orbiting a star. Under quantum mechanics, however, we must describe the position of the electron in the hydrogen atom in terms of probabilities rather than an exact location—an exact answer would violate the uncertainty principle, which becomes important when considering subatomic particles. The information we need about the probability of finding the electron is contained in the wave functions, ψ, that are obtained when Schrödinger's equation is solved. Remember that there are an infinite number of wave functions (orbitals) for the hydrogen atom, but the electron can occupy only one of them at any given time. Here we will discuss briefly how we can use the orbitals to obtain radial probability functions, such as those in Figure 6.19.

In Section 6.5 we stated that the square of the wave function, ψ^2, gives the probability that the electron is at any one given point in space. Recall that this quantity is called the *probability density* for the point. For a spherically symmetric *s* orbital, the value of ψ depends only on the distance from the nucleus, *r*. Let's consider a straight line outward from the nucleus, as shown in Figure 6.21▶. The probability of finding the electron at distance *r* from the nucleus along that line is $[\psi(r)]^2$, where $\psi(r)$ is the value of ψ at distance *r*. Figure 6.23▶ shows plots of $[\psi(r)]^2$ as a function of *r* for the 1*s*, 2*s*, and 3*s* orbitals of the hydrogen atom.

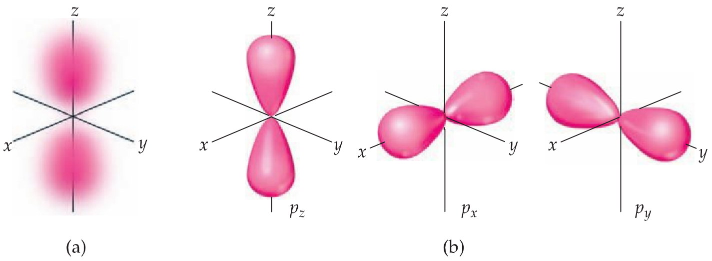
You will notice that the plots in Figure 6.23 look distinctly different from the radial probability functions plotted in Figure 6.19. These two types of plots for the *s* orbitals are very closely related, but they provide somewhat different information. The probability density, $[\psi(r)]^2$, tells us the probability of finding the electron at *a specific* point in space that is at distance *r* from the nucleus. The radial probability function, which we will denote $P(r)$, tells us the probability of finding the electron at *any* point that is distance *r* from the nucleus. In other words, to get $P(r)$ we need to "add up" the probabilities of finding the electron over all the points at distance *r* from the nucleus. The difference between these descriptions may seem rather subtle, but mathematics provides us with a precise way to connect them.



▲ Figure 6.21 **Probability at a point.** The probability density, $\psi(r)^2$ gives the probability that the electron will be found at *a specific point* at distance *r* from the nucleus. The radial probability function, $4\psi r^2 \psi(r)^2$, gives the probability that the electron will be found at *any* point distance *r* from the nucleus—in other words, at any point on the sphere of radius *r*.

The *p* Orbitals

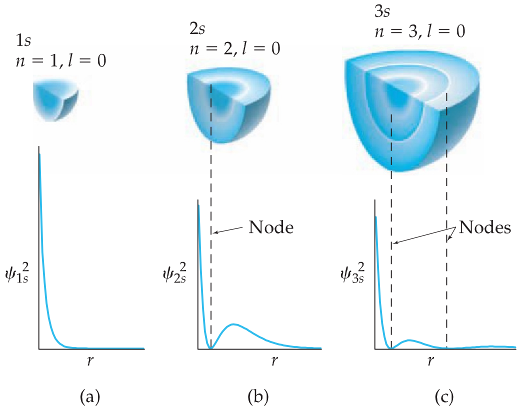
The distribution of electron density for a 2*p* orbital is shown in Figure 6.22(a) ▼. As we can see from this figure, the electron density is not distributed in a spherically symmetric fashion as in an *s* orbital. Instead, the electron density is concentrated in two regions on either side of the nucleus, 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. The only thing Figure 6.22(a) portrays is the *averaged* distribution of the electron density in a 2*p* orbital.



(a) (b)

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

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 2*p* orbitals, three 3*p* 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 2*p* 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



◀ **Figure 6.23 Probability density distribution in 1*s*, 2*s*, and 3*s* orbitals.** The lower part of the figure shows how the probability density, $\psi(r)^2$, varies as a function of distance *r* from the nucleus. The upper part of the figure shows a cutaway of the spherical electron density in each of the *s* orbitals.

As shown in Figure 6.21, the collection of points at distance *r* from the nucleus is simply a sphere of radius *r*. The probability density at every point on that sphere is $[\psi(r)]^2$. To add up all of the individual probability densities requires the use of calculus and is beyond the scope of this text (in the language of calculus "we integrate the probability density over the surface of the sphere"). The result we obtain is easy to describe, however. The radial probability function at distance *r*, $P(r)$, is simply the probability density at distance *r*, $[\psi(r)]^2$ multiplied by the surface area of the sphere, which is given by the formula $4\pi r^2$:

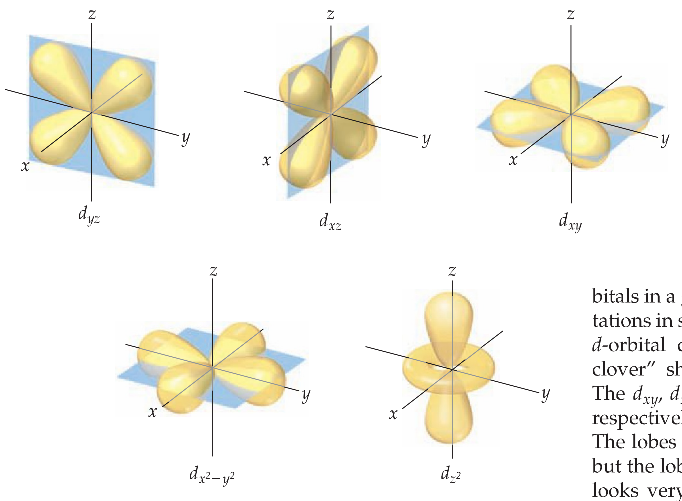
$$P(r) = 4\pi r^2[\psi(r)]^2$$

Thus, the plots of $P(r)$ in Figure 6.19 are equal to the plots of $[\psi(r)]^2$ in Figure 6.23 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. For example, the plot of $[\psi(r)]^2$ for the 3*s* orbital (Figure 6.23) 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 6.19). We will see that the radial probability functions in Figure 6.19 provide us with the more useful information because they tell us the probability for finding the electron at *all* points distance *r* from the nucleus, not just one particular point.

Related Exercises: 6.48, 6.57, 6.58, and 6.91

orbital is oriented.* Like *s* orbitals, *p* orbitals increase in size as we move from 2*p* to 3*p* to 4*p*, and so forth.

The *d* and *f* Orbitals



▲ **Figure 6.24 Contour representations of the five *d* orbitals.**

When n is 3 or greater, we encounter the *d* orbitals (for which $l = 2$). There are five 3*d* orbitals, five 4*d* 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 6.24 ◀. 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 *d* orbitals. The representations in Figure 6.24 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 orbitals shown in Figures 6.20, 6.23, and 6.24.

GIVE IT SOME THOUGHT

Note in Figure 6.22(a) 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?

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 a very elegant description of the hydrogen atom. This atom, however, has only one electron. How must our description of the electronic structure of atoms change when we consider atoms with two or more electrons (a *many-electron* atom)? To describe these atoms, 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

The quantum mechanical model would not be very useful if we could not extend what we have learned about hydrogen to other atoms. Fortunately, we can describe the electronic structure of a many-electron atom in terms of orbitals

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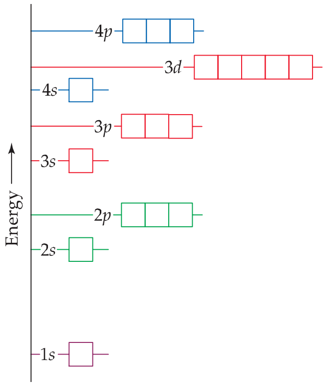
**We cannot make a simple correspondence between the subscripts (x, y, and z) and the allowed m_l values (1, 0, and −1). To explain why this is so is beyond the scope of an introductory text.*

like those of the hydrogen atom. Thus, we can continue to designate orbitals as 1*s*, $2p_x$, and so forth. Further, these orbitals have the same general shapes as the corresponding hydrogen orbitals.

Although the shapes of the orbitals for many-electron atoms 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 6.18); the 3*s*, 3*p*, and 3*d* subshells all have the same energy, for instance. In a many-electron atom, however, the electron–electron repulsions cause the different subshells to be at different energies, as shown in Figure 6.25 ▶. To understand why this is so, 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.* You can see this illustrated in Figure 6.25. Notice, for example, that the $n = 3$ orbitals (red) increase in energy in the order $3s < 3p < 3d$. Figure 6.25 is a *qualitative* energy-level diagram; the exact energies of the orbitals and their spacings differ from one atom to another. Notice that all orbitals of a given subshell (such as the five 3*d* orbitals) still have the same energy as one another, just as they do in the hydrogen atom. Orbitals with the same energy are said to be **degenerate.**



▲ **Figure 6.25 Orbital energy levels in many-electron atoms.** In a many-electron atom, the energies of the subshells in each shell follow the order $ns < np < nd < nf$. As in Figure 6.18, each box represents an orbital.

GIVE IT SOME THOUGHT

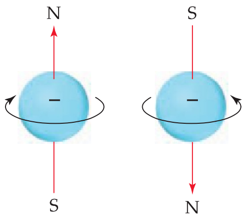
For a many-electron atom, can we predict unambiguously whether the 4*s* orbital is lower in energy or higher in energy than the 3*d* orbitals?

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 reside in? 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, as shown in Figure 6.26 ▶.* These two opposite magnetic fields lead to the splitting of spectral lines into closely spaced pairs.



▲ **Figure 6.26 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.

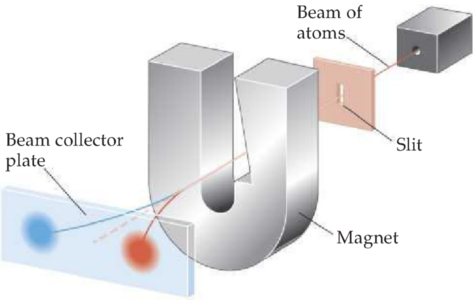
Electron spin is crucial for understanding the electronic structures of atoms. In 1925 the Austrian-born physicist Wolfgang Pauli (1900–1958) discovered the principle that governs the arrangements of electrons in many-electron atoms. The **Pauli exclusion principle** states that *no two electrons in an atom can have the same*

**As we discussed earlier, the electron has both particle-like and wavelike 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.*

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 neutral atoms into two groups by passing them through a nonhomogeneous magnetic field. Their experiment is diagrammed in Figure 6.27▶. Let's assume that they used a beam of hydrogen atoms (in actuality, they used silver atoms, which contain just one unpaired electron). We would normally expect that neutral atoms would not be affected 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 6.27, the magnetic field splits the beam in two, suggesting that there are two (and only two) equivalent values for the electron's own 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 will produce equal magnetic fields that are opposite in direction.

Related Exercise: 6.94



▲ Figure 6.27 **The Stern–Gerlach experiment.** Atoms in which the electron spin quantum number (m_s) of the unpaired electron is $+\frac{1}{2}$ are deflected in one direction, and those in which m_s is $-\frac{1}{2}$ are deflected in the other.

set of four quantum numbers n, l, m_l, and m_s. For a given orbital ($1s$, $2p_z$, and so forth), the values of n, l, and m_l are fixed. Thus, if we 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 one of the great problems in chemistry—understanding the structure of the periodic table of the elements. We will discuss these issues in the next two sections.

6.8 ELECTRON CONFIGURATIONS

Armed with knowledge of the relative energies of orbitals and the Pauli exclusion principle, we are now in a position to consider the arrangements of electrons in atoms. The way in which the electrons are distributed among the various orbitals of an atom is called the **electron configuration** of the atom. The most stable electron configuration of an atom—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 $1s$ orbital because it is the lowest in energy (Figure 6.25). 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 $1s$ orbital can accommodate two of the electrons. The third one goes into the next lowest energy orbital, the $2s$.

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 $1s^2 2s^1$ (read "1s two, 2s one"). We can also show the arrangement of the electrons as

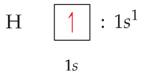
$$\text{Li}\quad \underset{1s}{\boxed{\uparrow\downarrow}}\ \underset{2s}{\boxed{\uparrow}}$$

In this kind of 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 (↿) represents an electron with a positive spin magnetic quantum number ($m_s = +\frac{1}{2}$) and a half arrow pointing down (⇂) represents an electron with a negative spin magnetic quantum number ($m_s = -\frac{1}{2}$). This pictorial representation of electron spin is quite convenient. In fact, chemists and physicists often refer to electrons as "spin-up" and "spin-down" rather than specifying the value for m_s.

Electrons having opposite spins are said to be *paired* when they are in the same orbital (↿⇂). 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.

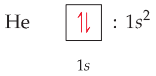
Hund's Rule

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.



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

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



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 represents a large jump in energy and a corresponding jump in the average distance of the electron from the nucleus.

TABLE 6.3 ■ Electron Configurations of Several Lighter Elements

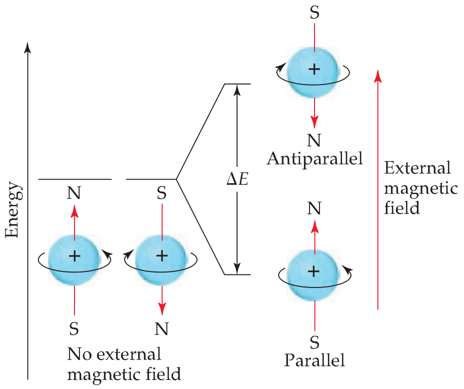
Element	Total Electrons	Orbital Diagram					Electron Configuration
		1*s*	2*s*	2*p*			3*s*	
Li	3	↿⇂	↿					$1s^22s^1$
Be	4	↿⇂	↿⇂					$1s^22s^2$
B	5	↿⇂	↿⇂	↿				$1s^22s^22p^1$
C	6	↿⇂	↿⇂	↿	↿			$1s^22s^22p^2$
N	7	↿⇂	↿⇂	↿	↿	↿		$1s^22s^22p^3$
Ne	10	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂		$1s^22s^22p^6$
Na	11	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	↿	$1s^22s^22p^63s^1$

Chemistry and Life

NUCLEAR SPIN AND MAGNETIC RESONANCE IMAGING

A major challenge facing medical diagnosis is seeing inside the human body from the outside. 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 new 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 (a proton) 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.



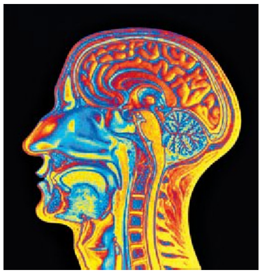
▲ **Figure 6.28** **Nuclear spin.** Like electron spin, nuclear spin generates a small magnetic field and has two allowed values. In the absence of an external magnetic field (left), the two spin states have the same energy. If an external magnetic field is applied (right), the parallel alignment of the nuclear magnetic field is lower in energy than the antiparallel alignment. The energy difference, ΔE, is in the radio frequency portion of the electromagnetic spectrum.

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 6.28◀). If the nuclei are irradiated with photons with 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, tissue can be imaged at specific depths within the body, giving pictures with spectacular detail (Figure 6.29▼). The ability to sample at different depths allows medical 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 radiofrequency 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 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 Exercises: 6.94 and 6.95



◀ **Figure 6.29** **MRI image.** This image of a human head, obtained using MRI, shows the structures of a normal brain, airways, and facial tissues.

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 $1s^22s^2$ (Table 6.3). Boron, atomic number 5, has the electron configuration $1s^22s^22p^1$. 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 is occupied.

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 with the same spin is maximized*. This means that electrons will occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell will 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 will 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.

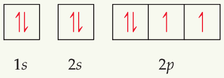
SAMPLE EXERCISE 6.7 | Orbital Diagrams and Electron Configurations

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 6.25 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 representation is



The corresponding electron configuration is written $1s^22s^22p^4$. 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)** $1s^22s^22p^63s^23p^3$, **(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 $[\mathrm{Ne}]3s^1$ helps focus attention on the outermost electrons of the atom, which are the ones largely responsible for the chemical behavior of an element.

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 example, we can write the electron configuration of lithium as

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

We refer to the electrons represented by the symbol for a noble gas 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 lighter elements (those with atomic number of 30 or less), all of the outer-shell electrons are valence electrons. As we will discuss later, many of the heavier elements have completely filled subshells that are not involved in bonding and are therefore not considered valence electrons.

By comparing the condensed electron configuration of lithium with that of sodium, we can appreciate why these two elements are so 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.

Transition Metals

The noble-gas element argon marks the end of the row started by sodium. The configuration for argon is $1s^2 2s^2 2p^6 3s^2 3p^6$. 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 3*d* orbital, which we might have expected it to do. Here the ordering of energy levels is such that the 4*s* orbital is lower in energy than the 3*d* orbital (Figure 6.25). Hence, the condensed electron configuration of potassium is

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

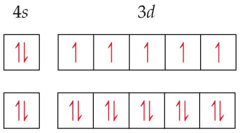
Following the complete filling of the 4*s* orbital (this occurs in the calcium atom), the next set of orbitals to be filled is the 3*d* (You will find it helpful as we go along to refer often to the periodic table on the front inside cover.) Beginning with scandium and extending through zinc, electrons are added to the five 3*d* 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 deriving the electron configurations of the transition elements, the orbitals are filled in accordance with Hund's rule—electrons are added to the 3*d* orbitals singly until all five orbitals have one electron each. Additional electrons are then placed in the 3*d* 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 similarly to the preceding one: 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, and the subsequent set of elements (elements 57–70) is placed below the main portion of the table. This place 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 $4f$ and $5d$ orbitals are very close to each other, the electron configurations of some of the lanthanides involve $5d$ electrons. For example, the elements lanthanum (La), cerium (Ce), and praseodymium (Pr) have the following electron configurations:

[Xe]$6s^2 5d^1$	[Xe]$6s^2 5d^1 4f^1$	[Xe]$6s^2 4f^3$
Lanthanum	Cerium	Praseodymium

Because La has a single $5d$ 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 $4f$ orbitals among the subsequent members of the series.

After the lanthanide series, the third transition element series is completed by the filling of the $5d$ orbitals, followed by the filling of the $6p$ 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

TABLE 6.4 ■ Electron Configurations of the Group 2A and 3A Elements

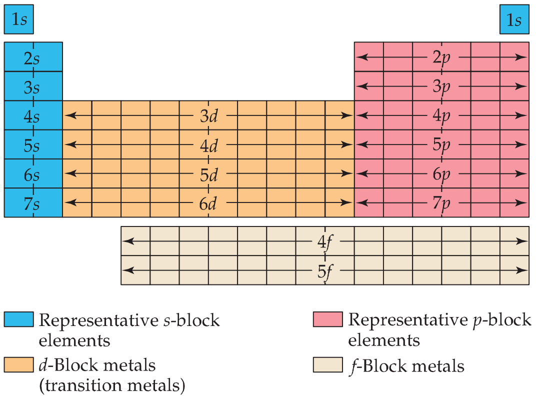
Group 2A	
Be	[He]$2s^2$
Mg	[Ne]$3s^2$
Ca	[Ar]$4s^2$
Sr	[Kr]$5s^2$
Ba	[Xe]$6s^2$
Ra	[Rn]$7s^2$
Group 3A	
B	[He]$2s^2 2p^1$
Al	[Ne]$3s^2 3p^1$
Ga	[Ar]$3d^{10}4s^2 4p^1$
In	[Kr]$4d^{10}5s^2 5p^1$
Tl	[Xe]$4f^{14}5d^{10}6s^2 6p^1$

Our rather brief survey of electron configurations of the elements has taken us through the periodic table. We have seen that the electron configurations of the elements are related to their locations in the periodic table. The periodic table is structured so that elements with the same pattern of outer-shell (valence) electron configuration are arranged in columns. For example, the electron configurations for the elements in groups 2A and 3A are given in Table 6.4◀. We see that all the 2A elements have ns^2 outer configurations, while the all the 3A elements have ns^2np^1 configurations.

Earlier, in Table 6.2, we saw that the total number of orbitals in each shell is equal to n^2: 1, 4, 9, or 16. Because each orbital can hold two electrons, each shell can accommodate up to $2n^2$ electrons: 2, 8, 18, or 32. The structure of the periodic table reflects this orbital structure. The first row has two elements, the second and third rows have eight elements, the fourth and fifth rows have 18 elements, and the sixth row has 32 elements (including the lanthanide metals). Some of the numbers repeat because we reach the end of a row of the periodic table before a shell completely fills. For example, the third row has eight elements, which corresponds to filling the 3*s* and 3*p* orbitals. The remaining orbitals of the third shell, the 3*d* orbitals, do not begin to fill until the fourth row of the periodic table (and after the 4*s* orbital is filled). Likewise, the 4*d* orbitals do not begin to fill until the fifth row of the table, and the 4*f* orbitals don't begin filling until the sixth row.

All these observations are evident in the structure of the periodic table. For this reason, we will emphasize that *the periodic table is your best guide to the order in which orbitals are filled*. You can easily write the electron configuration of an element based on its location in the periodic table. The pattern is summarized in Figure 6.30◀. Notice that the elements can be grouped by the *type* of orbital into which the electrons are placed. On the left are *two* columns of elements, depicted in blue. 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. On the right is a pink block of *six* columns. These are the elements in which the valence *p* orbitals are being filled. The *s* block and the *p* block of the periodic table together are the **representative elements,** which are sometimes called the **main-group elements.**

In the middle of Figure 6.30 is a gold block of *ten* columns containing the transition metals. These are the elements in which the valence *d* orbitals are being filled. Below the main portion of the table are two tan rows containing *14* columns. These elements are often referred to as the ***f*-block metals,** because they are the ones in which the valence *f* orbitals are being filled. Recall that the numbers 2, 6, 10, and 14 are precisely the number of electrons that can fill the *s*, *p*, *d*, and *f* subshells, respectively. Recall also that the 1*s* subshell is the first *s* subshell, the 2*p* is the first *p* subshell, the 3*d* is the first *d* subshell, and the 4*f* is the first *f* subshell.



▲ **Figure 6.30 Regions of the periodic table.** This block diagram of the periodic table shows the order in which electrons are added to orbitals as we move through the table from beginning to end.

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 them.

Solve: The first member of the halogen group is fluorine, atomic number 9. The condensed electron configuration for fluorine is

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

Similarly, that 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^2np^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^2np^2 electron configuration in the outermost occupied shell?

Answer: group 4A

SAMPLE EXERCISE 6.9 | Electron Configurations from the Periodic Table

(a) Write the electron configuration for bismuth, element number 83. **(b)** Write the condensed electron configuration for this element. **(c)** How many unpaired electrons does each atom of bismuth possess?

SOLUTION

(a) We write the electron configuration by moving across the periodic table one row at a time and writing the occupancies of the orbital corresponding to each row (refer to Figure 6.29).

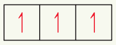
First row	$1s^2$
Second row	$2s^2 2p^6$
Third row	$3s^2 3p^6$
Fourth row	$4s^2 3d^{10} 4p^6$
Fifth row	$5s^2 4d^{10} 5p^6$
Sixth row	$6s^2 4f^{14} 5d^{10} 6p^3$
Total:	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$

Note that 3 is the lowest possible value that n may have for a d orbital and that 4 is the lowest possible value of n for an f orbital.

The total of the superscripted numbers should equal the atomic number of bismuth, 83. The electrons may be listed, as shown above in the "Total" row, in the order of increasing principal quantum number. However, it is equally correct to list the orbitals in the order in which they are read from Figure 6.30: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^3$.

(b) We write the condensed electron configuration by locating bismuth on the periodic table and then moving *backward* to the nearest noble gas, which is Xe, element 54. Thus, the noble-gas core is [Xe]. The outer electrons are then read from the periodic table as before. Moving from Xe to Cs, element 55, we find ourselves in the sixth row. Moving across this row to Bi gives us the outer electrons. Thus, the abbreviated electron configuration is $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^3$ or $[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^3$.

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

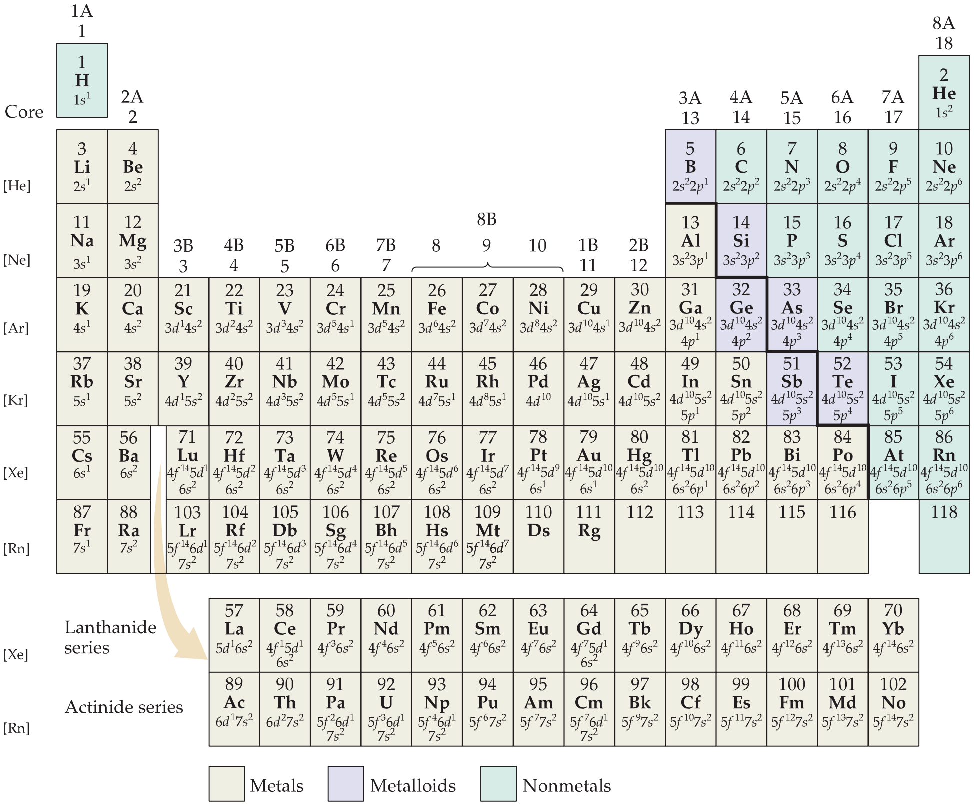


In accordance with Hund's rule, the three $6p$ electrons occupy the three $6p$ orbitals singly, with their spins parallel. Thus, there are three unpaired electrons in each atom of bismuth.

PRACTICE EXERCISE

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

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



Core	1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1 **H** $1s^1$																	2 **He** $1s^2$
[He]	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
[Ne]	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
[Ar]	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $3d^{10}4s^2$ $4p^1$	32 **Ge** $3d^{10}4s^2$ $4p^2$	33 **As** $3d^{10}4s^2$ $4p^3$	34 **Se** $3d^{10}4s^2$ $4p^4$	35 **Br** $3d^{10}4s^2$ $4p^5$	36 **Kr** $3d^{10}4s^2$ $4p^6$
[Kr]	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^35s^2$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $4d^{10}5s^2$ $5p^1$	50 **Sn** $4d^{10}5s^2$ $5p^2$	51 **Sb** $4d^{10}5s^2$ $5p^3$	52 **Te** $4d^{10}5s^2$ $5p^4$	53 **I** $4d^{10}5s^2$ $5p^5$	54 **Xe** $4d^{10}5s^2$ $5p^6$
[Xe]	55 **Cs** $6s^1$	56 **Ba** $6s^2$	71 **Lu** $4f^{14}5d^1$ $6s^2$	72 **Hf** $4f^{14}5d^2$ $6s^2$	73 **Ta** $4f^{14}5d^3$ $6s^2$	74 **W** $4f^{14}5d^4$ $6s^2$	75 **Re** $4f^{14}5d^5$ $6s^2$	76 **Os** $4f^{14}5d^6$ $6s^2$	77 **Ir** $4f^{14}5d^7$ $6s^2$	78 **Pt** $4f^{14}5d^9$ $6s^1$	79 **Au** $4f^{14}5d^{10}$ $6s^1$	80 **Hg** $4f^{14}5d^{10}$ $6s^2$	81 **Tl** $4f^{14}5d^{10}$ $6s^26p^1$	82 **Pb** $4f^{14}5d^{10}$ $6s^26p^2$	83 **Bi** $4f^{14}5d^{10}$ $6s^26p^3$	84 **Po** $4f^{14}5d^{10}$ $6s^26p^4$	85 **At** $4f^{14}5d^{10}$ $6s^26p^5$	86 **Rn** $4f^{14}5d^{10}$ $6s^26p^6$
[Rn]	87 **Fr** $7s^1$	88 **Ra** $7s^2$	103 **Lr** $5f^{14}6d^1$ $7s^2$	104 **Rf** $5f^{14}6d^2$ $7s^2$	105 **Db** $5f^{14}6d^3$ $7s^2$	106 **Sg** $5f^{14}6d^4$ $7s^2$	107 **Bh** $5f^{14}6d^5$ $7s^2$	108 **Hs** $5f^{14}6d^6$ $7s^2$	109 **Mt** $5f^{14}6d^7$ $7s^2$	110 **Ds**	111 **Rg**	112	113	114	115	116		118

[Xe]	Lanthanide series	57 **La** $5d^16s^2$	58 **Ce** $4f^15d^1$ $6s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^1$ $6s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$
[Rn]	Actinide series	89 **Ac** $6d^17s^2$	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^1$ $7s^2$	92 **U** $5f^36d^1$ $7s^2$	93 **Np** $5f^46d^1$ $7s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^1$ $7s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$

Metals Metalloids Nonmetals

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

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

The electron configurations in 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 have added a complete subshell of $3d$ electrons to the outer-shell electrons beyond the noble-gas core of Ar. 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 configuration of Ag and Au, 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 completely full* d *or* f *subshells to be among the valence electrons*, and *for transition elements we likewise do not consider a completely full* f *subshell to be among the valence electrons*.

Anomalous Electron Configurations

If you inspect Figure 6.31 closely, you will see that the electron configurations of certain elements appear to violate the rules we have just discussed. For example, the electron configuration of chromium is $[\mathrm{Ar}]3d^5 4s^1$ rather than the $[\mathrm{Ar}]3d^4 4s^2$ configuration we might have expected. Similarly, the configuration of copper is $[\mathrm{Ar}]3d^{10} 4s^1$ instead of $[\mathrm{Ar}]3d^9 4s^2$. This anomalous behavior is largely a consequence of the closeness of the 3*d* and 4*s* orbital energies. It frequently occurs when there are enough electrons to lead to precisely half-filled sets of degenerate orbitals (as in chromium) or to completely fill a *d* subshell (as in copper). There are a few similar cases among the heavier transition metals (those with partially filled 4*d* or 5*d* 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

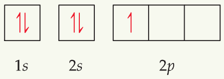
The elements Ni, Pd, and Pt are all in the same group. By examining the electron configurations for these elements in Figure 6.31, what can you conclude about the relative energies of the *nd* and $(n + 1)$ *s* orbitals for this group?

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

Boron, atomic number 5, occurs naturally as two isotopes, $^{10}\mathrm{B}$ and $^{11}\mathrm{B}$, 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 $^{10}\mathrm{B}$ differ from that of $^{11}\mathrm{B}$? **(b)** Draw the orbital diagram for an atom of $^{11}\mathrm{B}$. Which electrons are the valence electrons? **(c)** Indicate three major ways in which the 1*s* electrons in boron differ from its 2*s* 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 $-1135.6\ \mathrm{kJ\ mol^{-1}}$. 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 $^{10}\mathrm{B}$ contains five neutrons, whereas $^{11}\mathrm{B}$ contains six neutrons. The two isotopes of boron have identical electron configurations, $1s^2 2s^2 2p^1$, because each has five electrons.
(b) The complete orbital diagram is



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, $[\mathrm{He}]2s^2 2p^1$.
(c) The 1*s* and 2*s* orbitals are both spherical, but they differ in three important respects: First, the 1*s* orbital is lower in energy than the 2*s* orbital. Second, the average distance of the 2*s* electrons from the nucleus is greater than that of the 1*s* electrons, so the 1*s* orbital is smaller than the 2*s*. Third, the 2*s* orbital has one node, whereas the 1*s* orbital has no nodes (Figure 6.19).
(d) The balanced chemical equation is

$$2\ \mathrm{B}(s) + 3\ \mathrm{F_2}(g) \longrightarrow 2\ \mathrm{BF_3}(g)$$

(e) $\Delta H^\circ = 2(-1135.6) - [0 + 0] = -2271.2\ \mathrm{kJ}$. The reaction is strongly exothermic.
(f) $\mathrm{BCl_3}(g) + 3\ \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3BO_3}(aq) + 3\ \mathrm{H^+}(aq) + 3\ \mathrm{Cl^-}(aq)$. 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 REVIEW

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 by 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; the frequencies observed in the spectrum follow a simple mathematical relationship that involves small integers.

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 number n, called the quantum number. The value of n must be a positive integer (1, 2, 3, ...), 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** of the atom. Light is emitted when the electron drops from a higher energy state to a lower energy state; light must be absorbed to excite the electron from a lower energy state to a higher one. The frequency of light emitted or absorbed must be such that $h\nu$ equals the difference in energy between two allowed states of the atom.

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 for the orbital. The principal quantum number, n, is indicated by the integers 1,2,3, ... 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, ... 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. Cartesian labels 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 spatial characteristics (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 4*f* subshell is being filled are called the **lanthanide** (or **rare earth**) **elements.** The **actinide elements** are those in which the 5*f* 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

- Be able to calculate the wavelength of electromagnetic radiation given its frequency or its frequency given its wavelength.
- Be able to order the common kinds of radiation in the electromagnetic spectrum according to their wavelengths or energy.
- Understand the concept of photons, and be able to calculate their energies given either their frequency or wavelength.
- Be able to explain how line spectra of the elements relate to the idea of quantized energy states of electrons in atoms.
- Be familiar with the wavelike properties of matter.
- Understand how the uncertainty principle limits how precisely we can specify the position and the momentum of subatomic particles such as electrons.
- Know how the quantum numbers relate to the number and type of orbitals, and recognize the different orbital shapes.
- Interpret radial probability function graphs for the orbitals.
- Be able to 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.
- Be able to use the periodic table to write abbreviated electron configurations and determine the number of unpaired electrons in an atom.

KEY EQUATIONS

- $c = \lambda\nu$ [6.1] light as a wave: c = speed of light (3.00×10^8 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 (6.626×10^{-34} 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 $h/4\pi$

VISUALIZING CONCEPTS

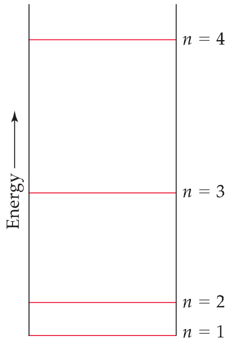
6.1 Consider the water wave shown here. **(a)** How could you measure the speed of this wave? **(b)** How would you determine the wavelength of the wave? **(c)** Given the speed and wavelength of the wave, how could you determine the frequency of the wave? **(d)** Suggest an independent experiment to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

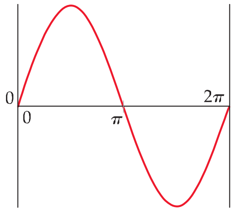
6.3 As shown in the accompanying photograph, an electric stove burner on its highest setting exhibits an orange glow. **(a)** When the burner setting is changed to low, the burner continues to produce heat but the orange glow disappears. How can this observation be explained with reference to one of 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]

6.4 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 6.12) was used as the light source. What do you think the resulting "hydrogen discharge rainbow" would look like? [Section 6.3]

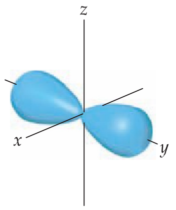
6.5 A certain quantum mechanical system has the energy levels shown in the diagram below. The energy levels are indexed by a single quantum number n that is an integer. **(a)** As drawn, which quantum numbers are involved in the transition that requires the most energy? **(b)** Which quantum numbers 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]



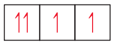
6.6 Consider a fictitious one-dimensional system with one electron. The wave function for the electron, drawn at the top of the next column, is $\psi(x) = \sin x$ from $x = 0$ to $x = 2\pi$. **(a)** Sketch the probability density, $\psi^2(x)$, from $x = 0$ to $x = 2\pi$ **(b)** At what value or values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



6.7 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]



6.8 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]



EXERCISES

The Wave Nature of Light

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

6.10 **(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?

6.11 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)** The frequency of radiation increases as the wavelength increases. **(c)** Ultraviolet light has longer wavelengths than visible light. **(d)** X-rays travel faster than microwaves. **(e)** Electromagnetic radiation and sound waves travel at the same speed.

6.12 Determine which of the following statements are false, and correct them. **(a)** Electromagnetic radiation is incapable of passing through water. **(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.

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

6.14 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.

6.15 **(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 $5.50 \times 10^{14}\ \text{s}^{-1}$? **(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?

6.16 **(a)** What is the frequency of radiation whose wavelength is 10.0 Å? **(b)** What is the wavelength of radiation that has a frequency of $7.6 \times 10^{10}\ s^{-1}$? **(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 25.5 fs?

6.17 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.

6.18 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

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

6.20 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.

6.21 **(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 1 mole 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?

6.22 If you put 120 volts of electricity through a pickle, the pickle will smoke and start glowing an orange-yellow color. The light is emitted because the sodium ions in the pickle become excited; their return to the ground state results in light emission (see Figure 6.13b and Sample Exercise 6.3). **(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?

6.23 **(a)** Calculate and compare the energy of a photon of wavelength 3.3 μm with that of wavelength 0.154 nm. **(b)** Use Figure 6.4 to identify the region of the electromagnetic spectrum to which each belongs.

6.24 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.

6.25 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.

6.26 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?

6.27 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?

6.28 A stellar object is emitting radiation at 3.55 mm. **(a)** What type of electromagnetic spectrum is this radiation? **(b)** If the 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?

6.29 Molybdenum metal must absorb radiation with a minimum frequency of $1.09 \times 10^{15}\ s^{-1}$ 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?

6.30 Sodium metal requires a photon with a minimum energy of 4.41×10^{-19} 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 439 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 μJ?

Bohr's Model; Matter Waves

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

6.32 **(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?

6.33 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?

6.34 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.

6.35 **(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 $n = 2$. Is this line in the visible region of the electromagnetic spectrum? If so, what color is it? **(b)** 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. **(c)** 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?

6.36 For each of the following electronic transitions in the hydrogen atom, calculate the energy, frequency, and wavelength of the associated radiation, and determine whether the radiation is emitted or absorbed during the transition: **(a)** from $n = 4$ to $n = 1$, **(b)** from $n = 5$ to $n = 2$, **(c)** from $n = 3$ to $n = 6$. Does any of these transitions emit or absorb visible light?

6.37 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 6.13.

6.38 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.

6.39 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.

6.40 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.

6.41 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.

6.42 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.

6.43 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).

6.44 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 9.38×10^6 m/s. What is the characteristic wavelength of this electron? Is the wavelength comparable to the size of atoms?

6.45 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 $(5.00 \pm 0.01) \times 10^4$ m/s. (The mass of a proton is given in the table of fundamental constants in the inside cover of the text.)

6.46 Calculate the uncertainty in the position of **(a)** an electron moving at a speed of $(3.00 \pm 0.01) \times 10^5$ 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

6.47 **(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?

6.48 **(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?

6.49 **(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?

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

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

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

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

6.54 For the table below, 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	

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

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

6.57 **(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): $4f$, $6s$, $3d$, $1s$, $2p$.

6.58 **(a)** With reference to Figure 6.19, 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 6.19? **(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

6.59 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?

6.60 **(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.

6.61 **(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.

6.62 **(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 why.

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

6.64 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)** $n = 4$, $l = 1$, $m_l = 1$?

6.65 **(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 direction (up or down) of the half-arrows in an orbital diagram?

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

6.67 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.

6.68 Write the condensed electron configurations for the following atoms, and indicate how many unpaired electrons each has: **(a)** Ga, **(b)** Ca, **(c)** V, **(d)** I, **(e)** Y, **(f)** Pt, **(g)** Lu.

6.69 Ions also have electron configurations (Section 7.4). Cations have fewer valence electrons, and anions have more valence electrons, respectively, than their parent atoms. For example, chloride, Cl^-, has an electron configuration of $1s^22s^22p^63s^23p^6$, for a total of 18 electrons, compared to 17 for neutral chlorine, the element. Na has an electron configuration of $1s^22s^22p^63s^1$, but Na^+ has an electron configuration of $1s^22s^22p^6$. Write out the electron configurations for **(a)** F^-, **(b)** I^-, **(c)** O^{2-}, **(d)** K^+, **(e)** Mg^{2+}, **(f)** Al^{3+}.

6.70 In the transition metals (the *d*-block), the electron configuration of cations is different than what you might expect. Instead of the d electrons being lost first, *s* electrons are lost first. For example, the electron configuration of iron, Fe, is $[Ar]4s^23d^6$; but the electron configuration of Fe^{2+} is $[Ar]3d^6$; the 4s electrons are eliminated to make the cation. Write out the electron configurations of **(a)** Zn^{2+} **(b)** Pt^{2+} **(c)** Cr^{3+} **(d)** Ti^{4+}.

6.71 Identify the specific element that corresponds to each of the following electron configurations: **(a)** $1s^22s^2$, **(b)** $1s^22s^22p^4$, **(c)** $[Ar]4s^13d^5$, **(d)** $[Kr]5s^24d^{10}5p^4$, **(e)** $1s^1$.

6.72 Identify the group of elements that corresponds to each of the following generalized electron configurations:

(a) [noble gas] ns^2np^5
(b) [noble gas] $ns^2(n-1)d^2$
(c) [noble gas] $ns^2(n-1)d^{10}np^1$
(d) [noble gas] $ns^2(n-2)f^6$

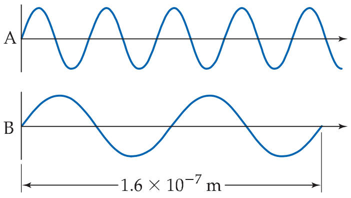
6.73 What is wrong with the following electron configurations for atoms in their ground states? **(a)** $1s^22s^23s^1$, **(b)** $[Ne]2s^22p^3$, **(c)** $[Ne]3s^23d^5$.

6.74 The following electron configurations represent excited states. Identify the element, and write its ground-state condensed electron configuration. **(a)** $1s^22s^23p^24p^1$, **(b)** $[Ar]3d^{10}4s^14p^45s^1$, **(c)** $[Kr]4d^65s^25p^1$.

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 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. Some characteristic wavelengths for some of the elements are

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?

6.77 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?

6.78 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)?

6.79 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?

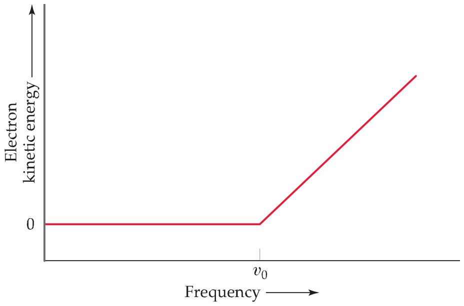
6.80 The color wheel (Figure 24.24) is a convenient way to relate what colors of light are absorbed by a sample and the visible appearance of the sample. If all visible colors are absorbed by a sample, the sample appears black. If no colors are absorbed by the sample, the sample appears white. If the sample absorbs red, then what we see is green; such *complementary colors* are across the wheel from each other. Carrots appear orange because they contain a compound called carotene. Based on the color wheel, what is the possible wavelength range for the light absorbed by carotene?

6.81 A photocell, such as the one illustrated in Figure 6.8(b), 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} Coulombs/sec. 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?

6.82 The light-sensitive substance in black-and-white photographic film is AgBr. Photons provide the energy necessary to transfer an electron from Br^- to Ag^+ to produce elemental Ag and Br and thereby darken the film. **(a)** If a minimum energy of 2.00×10^5 J/mol is needed for this process, what is the minimum energy needed from each photon? **(b)** Calculate the wavelength of the light necessary to provide photons of this energy. **(c)** Explain why this film can be handled in a darkroom under red light.

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 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.

6.85 When the spectrum of light from the Sun is examined in high resolution in an experiment similar to that illustrated in Figure 6.11, 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)** If a scientist wanted to know which Fraunhofer lines belonged to a given element, say neon, what experiments could she conduct here on Earth to provide data?

[6.86] 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^+**	**Li^{2+}**
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.

6.87 Under appropriate conditions, molybdenum emits X-rays that have a characteristic wavelength of 0.711 Å. These X-rays are used in diffraction experiments to determine the structures of molecules. **(a)** Why are X-rays, and not visible light, suitable for the determination of structure at the atomic level? **(b)** How fast would an electron have to be moving to have the same wavelength as these X-rays?

[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 ν 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 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 the "A Closer Look" box 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 6.19 and 6.22, make sketches of what you think the probability density as a function of *r* and the radial probability function would look like for the 4*s* orbital of the hydrogen atom.

6.92 The "magic numbers" in the periodic table are the atomic numbers of elements with high stability (the noble gases): 2, 10, 18, 36, 54, and 86. In terms of allowed values of orbitals and spin quantum numbers, explain why these electron arrangements correspond to special stability.

[6.93] For non-spherically symmetric orbitals, the contour representations (as in Figures 6.23 and 6.24) 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?

[6.94] As noted in Figure 6.26, the spin of an electron generates a magnetic field, with spin-up and spin-down electrons having opposite fields. In the absence of a magnetic field, a spin-up and a spin-down electron have the same energy. **(a)** Why do you think that the use of a magnet was important in the discovery of electron spin (see the "A Closer Look" box in Section 6.8)? **(b)** Imagine that the two spinning electrons in Figure 6.26 were placed between the poles of a horseshoe magnet, with the north pole of the magnet at the top of the figure. Based on what you know about magnets, would you expect the left or right electron in the figure to have the lower energy? **(c)** A phenomenon called *electron spin resonance* (ESR) is closely related to nuclear magnetic resonance. In ESR a compound with an unpaired electron is placed in a magnetic field, which causes the unpaired electron to have two different energy states analogous to Figure 6.28.

ESR uses microwave radiation to excite the unpaired electron from one state to the other. Based on your reading of the "Chemistry and Life" box in Section 6.8, does an ESR experiment require photons of greater or lesser energy than an NMR experiment?

[6.95] The "Chemistry and Life" box in Section 6.8 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 6.28 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?

6.96 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?

6.97 Using only a periodic table as a guide, write the condensed electron configurations for the following atoms: **(a)** Se, **(b)** Rh, **(c)** Si, **(d)** Hg, **(e)** Hf.

6.98 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

6.99 Microwave ovens use microwave radiation to heat food. The energy of the microwaves is absorbed by water molecules in food, 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/sec). How long would you have to heat the coffee in part (a)?

6.100 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?

6.101 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.

6.102 **(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, then compute ΔH°.) **(d)** Based on the data given, estimate a value of ΔH_f° for $Sc_2O_3(s)$.

6.103 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 that preceded Thomson's work, that the cathode rays are a wave phenomenon?

[6.104] 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.

6.105 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?