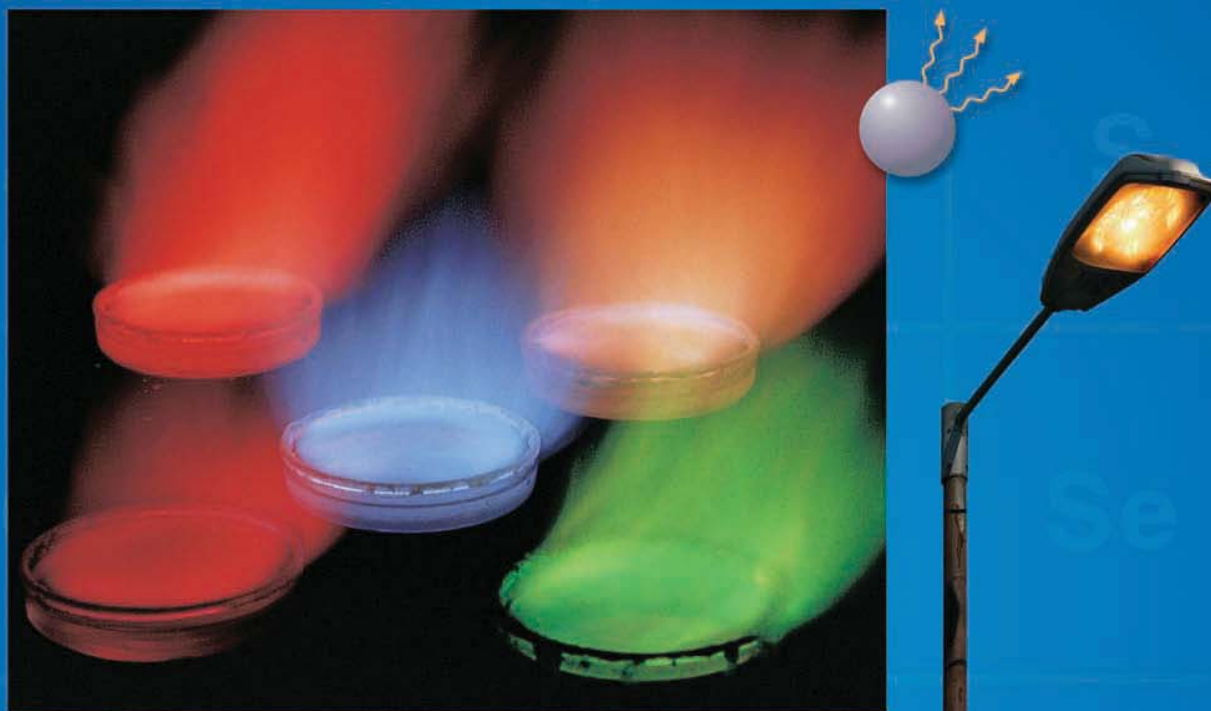


7

Quantum Theory of the Atom



Colored flames from several metal compounds; the visible light is emitted from the metal atoms. The yellow emission from sodium atoms is used in sodium street lamps.

Contents and Concepts

Light Waves, Photons, and the Bohr Theory

- 7.1 The Wave Nature of Light
- 7.2 Quantum Effects and Photons
- 7.3 The Bohr Theory of the Hydrogen Atom

To understand the formation of chemical bonds, you need to know something about the electronic structure of atoms. Because light gives us information about this structure, we begin by discussing the nature of light. Then we look at the Bohr theory of the simplest atom, hydrogen.

Quantum Mechanics and Quantum Numbers

- 7.4 Quantum Mechanics
- 7.5 Quantum Numbers and Atomic Orbitals

The Bohr theory firmly establishes the concept of energy levels but fails to account for the details of atomic structure. Here we discuss some basic notions of quantum mechanics, which is the theory currently applied to extremely small particles, such as electrons in atoms.

According to Rutherford's model (Section 2.2), an atom consists of a nucleus many times smaller than the atom itself, with electrons occupying the remaining space. How are the electrons distributed in this space? Or, we might ask, what are the electrons doing in the atom?

The answer was to come from an unexpected area: the study of colored flames. When metal compounds burn in a flame, they emit bright colors (Figure 7.1). The spectacular colors of fireworks are due to the burning of metal compounds. Lithium and strontium compounds give a deep red color; barium compounds, a green color; and copper compounds, a bluish green color.

Although the red flames of lithium and strontium appear similar, the light from each can be resolved (separated) by means of a prism into distinctly different colors. This resolution easily distinguishes the two elements. A prism disperses the colors of white light just as small raindrops spread the colors of sunlight into a rainbow or spectrum. But the light from a flame, when passed through a prism, reveals something other than a rainbow. Instead of the continuous range of color from red to yellow to violet, the spectrum from a strontium flame, for example, shows a cluster of red lines and blue lines against a black background. The spectrum of lithium is different, showing a red line, a yellow line, and two blue lines against a black background. (See Figure 7.2.)

Each element, in fact, has a characteristic line spectrum because of the emission of light from atoms in the hot gas. The spectra can be used to identify elements. How is it that each atom emits particular colors of light? What does a line spectrum tell us about the structure of an atom? If you know something about the structures of atoms, can you explain the formation of ions and molecules? We will answer these questions in this and the next few chapters.

■ See pages 286–287 for the Media Summary.

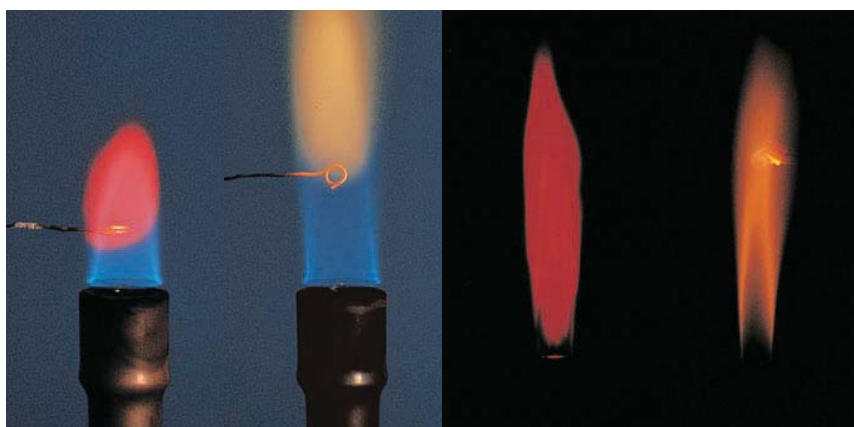


FIGURE 7.1 ▲

Flame tests of Groups IA and IIA elements

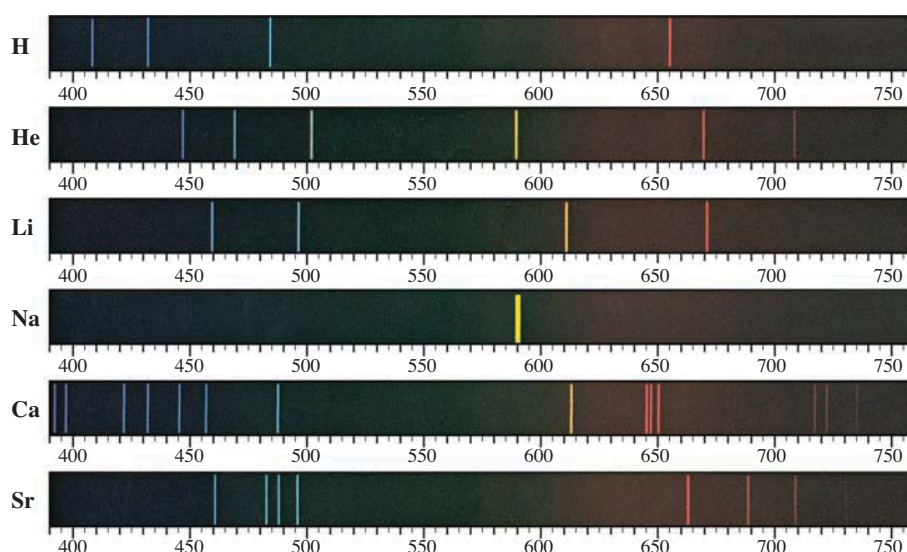
A wire loop containing a sample of a metal compound is placed in a flame. *Left to right:* flames of lithium (red), sodium (yellow), strontium (red), and calcium (orange).

Light Waves, Photons, and the Bohr Theory

In Chapter 2 we looked at the *basic structure* of atoms and we introduced the concept of a chemical bond. To understand the formation of a chemical bond between atoms, however, you need to know something about the *electronic structure* of atoms. The present theory of the electronic structure of atoms started with an explanation of the colored light produced in hot gases and flames. Before we can discuss this, we need to describe the nature of light.

FIGURE 7.2**Emission (line) spectra of some elements**

The lines correspond to visible light emitted by atoms. (Wavelengths of lines are given in nanometers.)



7.1 The Wave Nature of Light

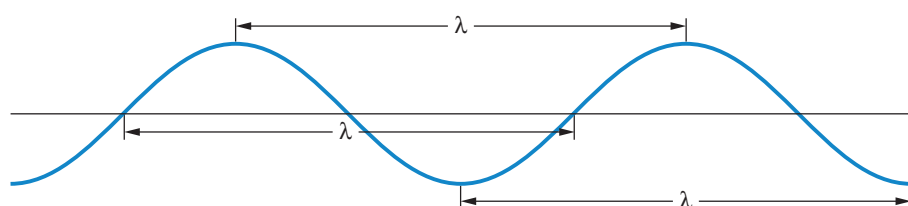
If you drop a stone into one end of a quiet pond, the impact of the stone with the water starts an up-and-down motion of the water surface. This up-and-down motion travels outward from where the stone hit; it is a familiar example of a wave. A *wave* is a continuously repeating change or oscillation in matter or in a physical field. Light is also a wave. It consists of oscillations in electric and magnetic fields that can travel through space. Visible light, x rays, and radio waves are all forms of *electromagnetic radiation*.

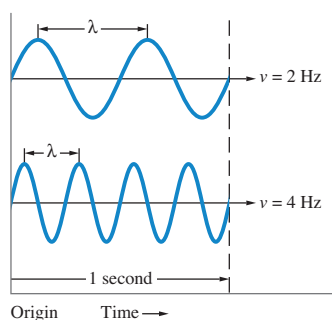
You characterize a wave by its wavelength and frequency. The **wavelength**, denoted by the Greek letter λ (lambda), is *the distance between any two adjacent identical points of a wave*. Thus, the wavelength is the distance between two adjacent peaks or troughs of a wave. Figure 7.3 shows a cross section of a water wave at a given moment, with the wavelength (λ) identified. Radio waves have wavelengths from approximately 100 mm to several hundred meters. Visible light has much shorter wavelengths, about 10^{-6} m. Wavelengths of visible light are often given in nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$). For example, light of wavelength $5.55 \times 10^{-7} \text{ m}$, the greenish yellow light to which the human eye is most sensitive, equals 555 nm.

The **frequency** of a wave is *the number of wavelengths of that wave that pass a fixed point in one unit of time* (usually one second). For example, imagine you are anchored in a small boat on a pond when a stone is dropped into the water. Waves travel outward from this point and move past your boat. The number of wavelengths

FIGURE 7.3**Water wave (ripple)**

The wavelength (λ) is the distance between any two adjacent identical points of a wave, such as two adjacent peaks or two adjacent troughs.



**FIGURE 7.4** ▲**Relation between wavelength and frequency**

Both waves are traveling at the same speed. The top wave has a wavelength twice that of the bottom wave. The bottom wave, however, has twice the frequency of the top wave.

To understand how fast the speed of light is, it might help to realize that it takes only 2.5 s for radar waves (which travel at the speed of light) to leave Earth, bounce off the moon, and return—a total distance of 478,000 miles.

that pass you in one second is the frequency of that wave. Frequency is denoted by the Greek letter ν (nu, pronounced “new”). The unit of frequency is /s, or s^{-1} , also called the *hertz* (Hz).

The wavelength and frequency of a wave are related to each other. Figure 7.4 shows two waves, each traveling from left to right at the same speed; that is, each wave moves the same total length in 1s. The top wave, however, has a wavelength twice that of the bottom wave. In 1s, two complete wavelengths of the top wave move left to right from the origin. It has a frequency of 2/s, or 2 Hz. In the same time, four complete wavelengths of the bottom wave move left to right from the origin. It has a frequency of 4/s, or 4 Hz. Note that for two waves traveling with a given speed, wavelength and frequency are inversely related: the greater the wavelength, the lower the frequency, and vice versa. In general, with a wave of frequency ν and wavelength λ , there are ν wavelengths, each of length λ , that pass a fixed point every second. The product $\nu\lambda$ is the total length of the wave that has passed the point in 1s. This length of wave per second is the speed of the wave. For light of speed c ,

$$c = \nu\lambda$$

The speed of light waves in a vacuum is a constant and is independent of wavelength or frequency. This speed is 3.00×10^8 m/s, which is the value for c that we use in the following examples. <

Example 7.1**Obtaining the Wavelength of Light from Its Frequency**

What is the wavelength of the yellow sodium emission, which has a frequency of 5.09×10^{14} /s?

Problem Strategy Note that frequency and wavelength are related (their product equals the speed of light). Write this as an equation, and then rearrange it to give the wavelength on the left and the frequency and speed of light on the right.

Solution The frequency and wavelength are related by the formula $c = \nu\lambda$. You rearrange this formula to give

$$\lambda = \frac{c}{\nu}$$

in which c is the speed of light (3.00×10^8 m/s). Substituting yields

$$\lambda = \frac{3.00 \times 10^8 \text{ m/s}}{5.09 \times 10^{14}/\text{s}} = 5.89 \times 10^{-7} \text{ m, or } \mathbf{589 \text{ nm}}$$

Answer Check Make sure you use the same units for c and ν (we used SI units in the solution). Check that the units cancel on the right to give the units of wavelength. As a check on your arithmetic, note that the wavelength for the answer should be in the visible range (400 nm to 800 nm).

Exercise 7.1

The frequency of the strong red line in the spectrum of potassium is 3.91×10^{14} /s. What is the wavelength of this light in nanometers?

■ See Problems 7.35 and 7.36.

Example 7.2**Obtaining the Frequency of Light from Its Wavelength**

What is the frequency of violet light with a wavelength of 408 nm?

Problem Strategy Rearrange the equation relating frequency and wavelength so that the frequency is on the left and the wavelength and speed of light are on the right.

Solution You rearrange the equation relating frequency and wavelength to give

$$\nu = \frac{c}{\lambda}$$

Substituting for λ ($408 \text{ nm} = 408 \times 10^{-9} \text{ m}$) gives

$$\nu = \frac{3.00 \times 10^8 \text{ m/s}}{408 \times 10^{-9} \text{ m}} = 7.35 \times 10^{14} \text{ /s}$$

Answer Check Use the same units for wavelength and speed of light; then check that the units cancel after substituting to give the units of frequency. We have used SI units here.

Exercise 7.2

The element cesium was discovered in 1860 by Robert Bunsen and Gustav Kirchhoff, who found two bright blue lines in the spectrum of a substance isolated from a mineral water. One of the spectral lines of cesium has a wavelength of 456 nm. What is its frequency? >

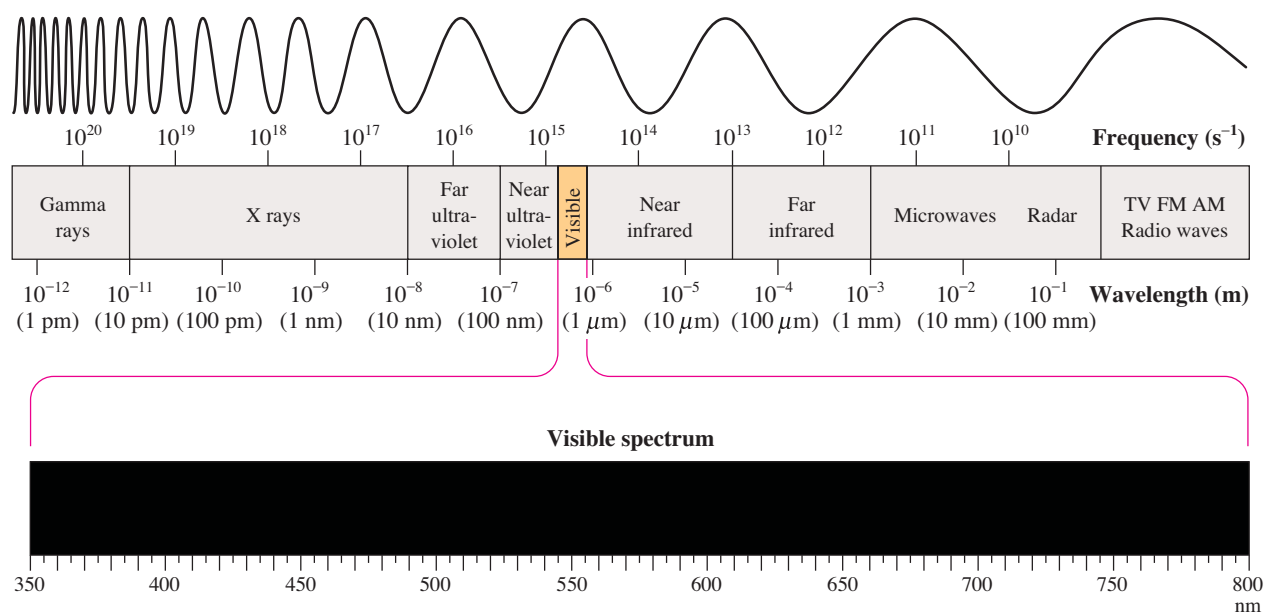
In 1854, Kirchhoff found that each element has a unique spectrum. Later, Bunsen and Kirchhoff developed the prism spectroscope and used it to confirm their discovery of two new elements, cesium (in 1860) and rubidium (in 1861).

■ See Problems 7.37 and 7.38.

FIGURE 7.5**The electromagnetic spectrum**

Divisions between regions are not defined precisely.

The range of frequencies or wavelengths of electromagnetic radiation is called the **electromagnetic spectrum**, shown in Figure 7.5. Visible light extends from the violet end of the spectrum, which has a wavelength of about 400 nm, to the red end, with a wavelength of less than 800 nm. Beyond these extremes, electromagnetic radiation is not visible to the human eye. Infrared radiation has wavelengths greater than 800 nm (greater than the wavelength of red light), and ultraviolet radiation has wavelengths less than 400 nm (less than the wavelength of violet light).



Concept Check 7.1

Laser light of a specific frequency falls on a crystal that converts this light into one with double the original frequency. How is the wavelength of this frequency-doubled light related to the wavelength of the original laser light? Suppose the original laser light was red. In which region of the spectrum would the frequency-doubled light be? (If this is in the visible region, what color is the light?)

7.2 Quantum Effects and Photons

Isaac Newton, who studied the properties of light in the seventeenth century, believed that light consisted of a beam of particles. In 1801, however, British physicist Thomas Young showed that light, like waves, could be diffracted. *Diffraction* is a property of waves in which the waves spread out when they encounter an obstruction or small hole about the size of the wavelength. You can observe diffraction by viewing a light source through a hole—for example, a streetlight through a mesh curtain. The image of the streetlight is blurred by diffraction.

By the early part of the twentieth century, the wave theory of light appeared to be well entrenched. But in 1905 the German physicist Albert Einstein (1879–1955; emigrated to the United States in 1933) discovered that he could explain a phenomenon known as the *photoelectric effect* by postulating that light had both wave and particle properties. Einstein based this idea on the work of the German physicist Max Planck (1858–1947).

Planck's Quantization of Energy

In 1900 Max Planck found a theoretical formula that exactly describes the intensity of light of various frequencies emitted by a hot solid at different temperatures. < Earlier, others had shown experimentally that the light of maximum intensity from a hot solid varies in a definite way with temperature. A solid glows red at 750°C, then white as the temperature increases to 1200°C. At the lower temperature, chiefly red light is emitted. As the temperature increases, more yellow and blue light become mixed with the red, giving white light. <

According to Planck, the atoms of the solid oscillate, or vibrate, with a definite frequency ν , depending on the solid. But in order to reproduce the results of experiments on glowing solids, he found it necessary to accept a strange idea. An atom could have only certain energies of vibration, E , those allowed by the formula

$$E = nh\nu, \quad n = 1, 2, 3, \dots$$

where h is a constant, now called **Planck's constant**, a physical constant relating energy and frequency, having the value $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$. The value of n must be 1 or 2 or some other whole number. Thus, the only energies a vibrating atom can have are $h\nu$, $2h\nu$, $3h\nu$, and so forth.

The numbers symbolized by n are called *quantum numbers*. The vibrational energies of the atoms are said to be *quantized*; that is, the possible energies are limited to certain values.

The quantization of energy seems contradicted by everyday experience. Consider the potential energy of an object, such as a tennis ball. Its potential energy depends on its height above the surface of the earth: the greater the upward height, the greater the potential energy. (Recall the discussion of potential energy in Section 6.1.) We have no problem in placing the tennis ball at any height, so it can have any energy. Imagine, however, that you could only place the tennis ball on the steps of a stairway. In that case, you could only put the tennis ball on one of the steps, so the potential energy of the tennis ball could have only certain values; its energy would be quantized. Of course, this restriction of the tennis ball is artificial;

Max Planck was professor of physics at the University of Berlin when he did this research. He received the Nobel Prize in physics for it in 1918.

Radiation emitted from the human body and warm objects is mostly infrared, which is detected by burglar alarms, military night-vision scopes, and similar equipment.

Albert Einstein obtained his Ph.D. in 1905. In the same year he published five ground breaking research papers: one on the photoelectric effect (for which he received the Nobel Prize in physics in 1921); two on special relativity; a paper on the determination of molecular size; and one on Brownian motion (which led to experiments that tested kinetic-molecular theory and ended remaining doubts about the existence of atoms and molecules).

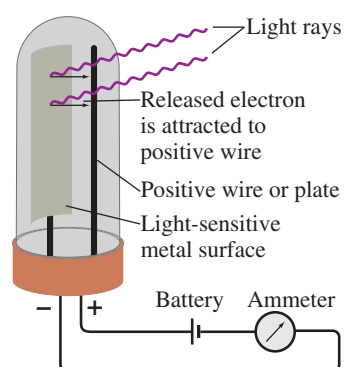


FIGURE 7.6 ▲

The photoelectric effect

Light shines on a metal surface, knocking out electrons. The metal surface is contained in an evacuated tube, which allows the ejected electrons to be accelerated to a positively charged plate. As long as light of sufficient frequency shines on the metal, free electrons are produced and a current flows through the tube. (The current is measured by an ammeter.) When the light is turned off, the current stops flowing.

in fact, a tennis ball can have a range of energies, not just particular values. As we will see, quantum effects depend on the mass of the object: the smaller the mass, the more likely you will see quantum effects. Atoms, and particularly electrons, have small enough masses to exhibit quantization of energy; tennis balls do not.

Photoelectric Effect

Planck himself was uneasy with the quantization assumption and tried unsuccessfully to eliminate it from his theory. Albert Einstein, on the other hand, boldly extended Planck's work to include the structure of light itself. Einstein reasoned that if a vibrating atom changed energy, say from $3h\nu$ to $2h\nu$, it would decrease in energy by $h\nu$, and this energy would be emitted as a bit (or quantum) of light energy. He therefore postulated that light consists of quanta (now called **photons**), or *particles of electromagnetic energy, with energy E proportional to the observed frequency of the light:*

$$E = h\nu$$

In 1905 Einstein used this photon concept to explain the photoelectric effect.

The **photoelectric effect** is *the ejection of electrons from the surface of a metal or from another material when light shines on it* (see Figure 7.6). Electrons are ejected, however, only when the frequency of light exceeds a certain *threshold value* characteristic of the particular metal. For example, although violet light will cause potassium metal to eject electrons, no amount of red light (which has a lower frequency) has any effect.

To explain this dependence of the photoelectric effect on the frequency, Einstein assumed that an electron is ejected from a metal when it is struck by a single photon. Therefore, this photon must have at least enough energy to remove the electron from the attractive forces of the metal. No matter how many photons strike the metal, if no single one has sufficient energy, an electron cannot be ejected. A photon of red light has insufficient energy to remove an electron from potassium. But a photon corresponding to the threshold frequency has just enough energy, and at higher frequencies it has more than enough energy. When the photon hits the metal, its energy $h\nu$ is taken up by the electron. The photon ceases to exist as a particle; it is said to be *absorbed*.

The wave and particle pictures of light should be regarded as complementary views of the same physical entity. This is called the *wave-particle duality* of light. The equation $E = h\nu$ displays this duality; E is the energy of a light particle or photon, and ν is the frequency of the associated wave. Neither the wave nor the particle view alone is a complete description of light.

Example 7.3

Calculating the Energy of a Photon

The red spectral line of lithium occurs at 671 nm (6.71×10^{-7} m). Calculate the energy of one photon of this light.

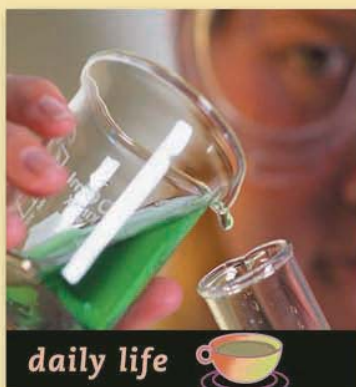
Problem Strategy Note that the energy of a photon is related to its corresponding frequency. Therefore, you will first need to obtain this frequency from the wavelength of the spectral line.

Solution The frequency of this light is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{6.71 \times 10^{-7} \text{ m}} = 4.47 \times 10^{14} \text{ /s}$$

(continued)

A Chemist Looks at . . .



Zapping Hamburger with Gamma Rays

In 1993 in Seattle, Washington, four children died and hundreds of people became sick from food poisoning when they ate undercooked hamburgers containing a danger-

ous strain of a normally harmless bacterium, *Escherichia coli*. A similar bout of food poisoning from hamburgers containing the dangerous strain of *E. coli* occurred in the summer of 1997; 17 people became ill. This time the tainted hamburger was traced to a meat processor in Nebraska, which immediately recalled 25 million pounds of ground beef. Within months, the U.S. Food and Drug Administration approved the irradiation of red meat by gamma rays to kill harmful bacteria. Gamma rays are a form of electromagnetic radiation similar to x rays, but the photons of gamma rays have higher energy.

The idea of using high-energy radiation to disinfect foods is not new (Figure 7.7). It has been known for about 50 years that high-energy radiation kills bacteria and molds in foods, prolonging their shelf life. Gamma rays kill organisms by breaking up the DNA molecules within their cells. This DNA holds the information for producing vital cell proteins.

Currently, the gamma rays used in food irradiation come from the radioactive decay of cobalt-60. It is perhaps

this association with radioactivity that has slowed the acceptance of irradiation as a food disinfectant. However, food is not made radioactive by irradiating it with gamma rays. The two major concerns about food irradiation—whether a food's nutritional value might be significantly diminished and whether decomposition products might cause cancer—appear to be without foundation. Irradiation of foods with gamma rays may soon join pasteurization as a way to protect our food supply from harmful bacteria.



FIGURE 7.7 ▲

Gamma irradiation of foods

Here, fresh produce has been irradiated to reduce spoilage and to ensure that the produce does not contain harmful bacteria. Now, meat can also be irradiated.

■ See Problems 7.91 and 7.92.

(continued)

Hence, the energy of one photon is

$$E = h\nu = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \times 4.47 \times 10^{14} / \text{s} = 2.96 \times 10^{-19} \text{ J}$$

Answer Check Be sure to use the same systems of units for the wavelength, the speed of light, and Planck's constant. Check that units cancel to give the proper units for energy in the final answer.

Exercise 7.3

The following are representative wavelengths in the infrared, ultraviolet, and x-ray regions of the electromagnetic spectrum, respectively: $1.0 \times 10^{-6} \text{ m}$, $1.0 \times 10^{-8} \text{ m}$, and $1.0 \times 10^{-10} \text{ m}$. What is the energy of a photon of each radiation? Which has the greatest amount of energy per photon? Which has the least?

■ See Problems 7.43, 7.44, 7.45, and 7.46.

7.3 The Bohr Theory of the Hydrogen Atom

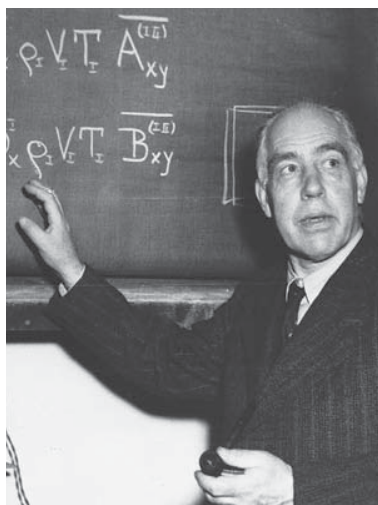


FIGURE 7.8 ▲

Niels Bohr (1885–1962)

After Bohr developed his quantum theory of the hydrogen atom, he used his ideas to explain the periodic behavior of the elements. Later, when the new quantum mechanics was discovered by Schrödinger and Heisenberg, Bohr spent much of his time developing its philosophical basis. He received the Nobel Prize in physics in 1922.

According to Rutherford's nuclear model, the atom consists of a nucleus with most of the mass of the atom and a positive charge, around which move enough electrons to make the atom electrically neutral. But this model, offered in 1911, posed a dilemma. Using the then-current theory, one could show that an electrically charged particle (such as an electron) that revolves around a center would continuously lose energy as electromagnetic radiation. As an electron in an atom lost energy, it would spiral into the nucleus (in about 10^{-10} s, according to available theory). The stability of the atom could not be explained.

A solution to this theoretical dilemma was found in 1913 by Niels Bohr (1885–1962), a Danish physicist, who at the time was working with Rutherford (see Figure 7.8). Using the work of Planck and Einstein, Bohr applied a new theory to the simplest atom, hydrogen. Before we look at Bohr's theory, we need to consider the line spectra of atoms, which we looked at briefly in the chapter opening.

Atomic Line Spectra

As described in the previous section, a heated solid emits light. A heated tungsten filament in an ordinary lightbulb is a typical example. With a prism we can spread out the light from a bulb to give a **continuous spectrum**—that is, a *spectrum containing light of all wavelengths*, like that of a rainbow (see Figure 7.9). The light emitted by a heated gas, however, yields different results. Rather than a continuous spectrum, with all colors of the rainbow, we obtain a **line spectrum**—a *spectrum showing only certain colors or specific wavelengths of light*. When the light from a hydrogen gas discharge tube (in which an electrical discharge heats hydrogen gas) is separated into its components by a prism, it gives a spectrum of lines, each line corresponding to light of a given wavelength. The light produced in the discharge tube is emitted by hydrogen atoms. Figure 7.2 shows the line spectrum of the hydrogen atom, as well as line spectra of other atoms.

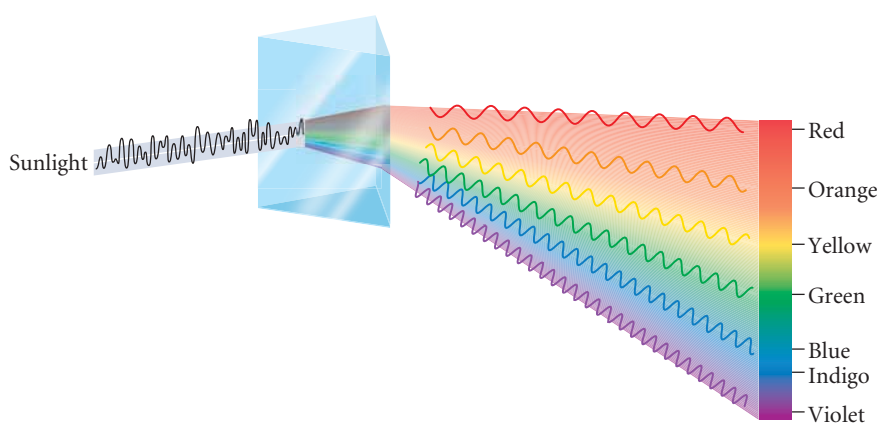
The line spectrum of the hydrogen atom is especially simple. In the visible region, it consists of only four lines (a red, a blue-green, a blue, and a violet), although others appear in the infrared and ultraviolet regions. In 1885 J. J. Balmer showed that the wavelengths λ in the visible spectrum of hydrogen could be reproduced by a simple formula:

$$\frac{1}{\lambda} = 1.097 \times 10^7/\text{m} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

FIGURE 7.9 ►

Dispersion of white light by a prism

White light, entering at the left, strikes a prism, which disperses the light into a continuous spectrum of wavelengths.



Here n is some whole number (integer) greater than 2. By substituting $n = 3$, for example, and calculating $1/\lambda$ and then λ , one finds $\lambda = 6.56 \times 10^{-7}$ m, or 656 nm, a wavelength corresponding to red light. The wavelengths of the other lines in the hydrogen atom visible spectrum are obtained by successively substituting $n = 4$, $n = 5$, and $n = 6$.

Bohr's Postulates

Bohr set down the following postulates to account for (1) the stability of the hydrogen atom (that the atom exists and its electron does not continuously radiate energy and spiral into the nucleus) and (2) the line spectrum of the atom.

1. Energy-level Postulate An electron can have only *specific energy values* in an atom, which are called its **energy levels**. Therefore, the atom itself can have only specific total energy values.

Bohr borrowed the idea of quantization of energy from Planck. Bohr, however, devised a rule for this quantization that could be applied to the motion of an electron in an atom. From this he derived the following formula for the energy levels of the electron in the hydrogen atom:

$$E = -\frac{R_H}{n^2} \quad n = 1, 2, 3, \dots \infty \quad (\text{for H atom})$$

where R_H is a constant (expressed in energy units) with the value 2.179×10^{-18} J. Different values of the possible energies of the electron are obtained by putting in different values of n , which can have only the integral values 1, 2, 3, and so forth (up to infinity, ∞). Here n is called the *principal quantum number*. The diagram in Figure 7.10 shows the energy levels of the electron in the H atom. <

2. Transitions Between Energy Levels An electron in an atom can change energy only by going from one energy level to another energy level. By so doing, the electron undergoes a *transition*.

By using only these two postulates, Bohr was able to explain Balmer's formula for the wavelengths in the spectrum of the hydrogen atom. According to Bohr, the emission of light from an atom occurs as follows. An electron in a higher energy level (initial energy level, E_i) undergoes a transition to a lower energy level (final energy level, E_f) (see Figure 7.10). In this process, the electron loses energy, which is emitted as a photon. Balmer's formula follows by this reasoning: The energy lost by the hydrogen atom is $\Delta E = E_f - E_i$. If we write n_i for the principal quantum number of the initial energy level, and n_f for the principal quantum number of the final energy level, then from Postulate 1,

$$E_i = -\frac{R_H}{n_i^2} \quad \text{and} \quad E_f = -\frac{R_H}{n_f^2}$$

so

$$\Delta E = \left(-\frac{R_H}{n_f^2}\right) - \left(-\frac{R_H}{n_i^2}\right) = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

For example, if the electron undergoes a transition from $n_i = 4$ to $n_f = 2$,

$$\Delta E = -2.179 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{4^2}\right) = -4.086 \times 10^{-19} \text{ J}$$

The sign of the energy change is negative. This means that energy equal to 4.086×10^{-19} J is lost by the atom in the form of a photon.

The energies have negative values because the energy of the separated nucleus and electron is taken to be zero. As the nucleus and electron come together to form a stable state of the atom, energy is released and the energy becomes less than zero, or negative.

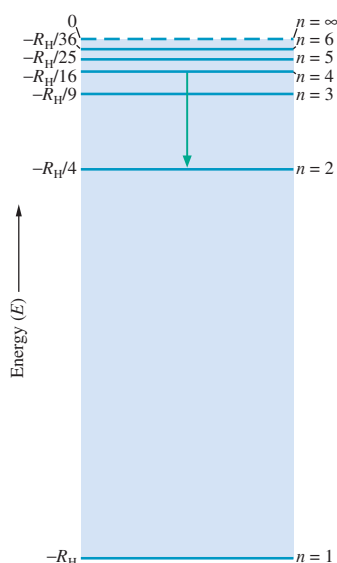
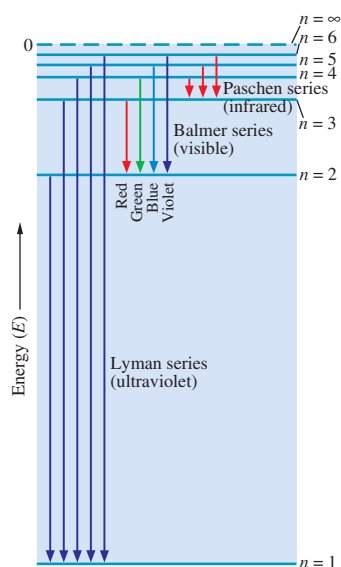


FIGURE 7.10 ▲

Energy-level diagram for the electron in the hydrogen atom

Energy is plotted on the vertical axis (in fractional multiples of R_H). The arrow represents an electron transition (discussed in Postulate 2) from level $n = 4$ to level $n = 2$. Light of wavelength 486 nm (blue-green) is emitted. (See Example 7.4 for the calculation of this wavelength.)

**FIGURE 7.11** ▲**Transitions of the electron in the hydrogen atom**

The diagram shows the Lyman, Balmer, and Paschen series of transitions that occur for $n_f = 1, 2$, and 3 , respectively.

In general, the energy of the emitted photon, $h\nu$, equals the positive energy lost by the atom ($-\Delta E$):

$$\text{Energy of emitted photon} = h\nu = -\Delta E = -(E_f - E_i)$$

That is,

$$h\nu = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Recalling that $\nu = c/\lambda$, you can rewrite this as

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

By substituting $R_H = 2.179 \times 10^{-18} \text{ J}$, $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$, and $c = 2.998 \times 10^8 \text{ m/s}$, you find that $R_H/hc = 1.097 \times 10^7/\text{m}$, which is the constant given in the Balmer formula. In Balmer's formula, the quantum number n_f is 2. This means that Balmer's formula gives wavelengths that occur when electrons in H atoms undergo transitions from energy levels $n_i > 2$ to level $n_f = 2$. If you change n_f to other integers, you obtain different series of lines (or wavelengths) for the spectrum of the H atom (see Figure 7.11).

Example 7.4**Determining the Wavelength or Frequency of a Hydrogen Atom Transition**

What is the wavelength of light emitted when the electron in a hydrogen atom undergoes a transition from energy level $n = 4$ to level $n = 2$?

Problem Strategy Remember that the wavelength or frequency of a transition depends on the difference in energies of the levels involved. For an H atom, the energy levels are $E = -R_H/n^2$. You calculate the difference in energy for the two levels to obtain the energy of the photon. Then, calculate the frequency and wavelength of the emitted light. (Although you could do this problem by “plugging into” the previously derived equation for $1/\lambda$, the method followed here requires you to remember only key formulas, shown in color in the text.)

Solution From the formula for the energy levels, you know that

$$E_i = \frac{-R_H}{4^2} = \frac{-R_H}{16} \quad \text{and} \quad E_f = \frac{-R_H}{2^2} = \frac{-R_H}{4}$$

You subtract the lower value from the higher value, to get a positive result. (The energy of the photon is positive. If your result is negative, it means you calculated $E_f - E_i$, rather than $E_i - E_f$. Simply reverse the subtraction to obtain a positive result.) Because this result equals the energy of the photon, you equate it to $h\nu$:

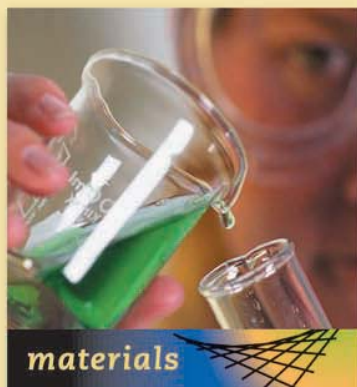
$$\left(\frac{-R_H}{16} \right) - \left(\frac{-R_H}{4} \right) = \frac{-4R_H + 16R_H}{64} = \frac{-R_H + 4R_H}{16} = \frac{3R_H}{16} = h\nu$$

The frequency of the light emitted is

$$\nu = \frac{3R_H}{16h} = \frac{3}{16} \times \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 6.17 \times 10^{14}/\text{s}$$

(continued)

A Chemist Looks at . . .



Lasers and Compact Disc Players

Lasers are sources of intense, highly directed beams of *monochromatic* light—light of very narrow wavelength range. The word *laser* is an acronym meaning light amplification by stimulated emission of radiation.

Many different kinds of lasers now exist, but the general principle of a laser can be understood by looking at the ruby laser, the first type constructed (in 1960).

Ruby is aluminum oxide containing a small concentration of chromium(III) ions, Cr^{3+} , in place of some aluminum ions. The electron transitions in a ruby laser are those of Cr^{3+} ions. Figure 7.12 shows an energy-level diagram of this ion in ruby. When you shine light of wavelength 545 nm on a ruby crystal, the light is absorbed and Cr^{3+} undergoes a transition from level 1 to level 3. Most of the ions in level 3 then undergo *radiationless transitions* to level 2. (In these transitions, the ions lose energy as heat to the crystal, rather than by emitting photons.) When an intense green light at 545 nm is flashed on a ruby crystal, Cr^{3+} ions of the ruby end up in level 2. Like all excited states, level 2 spontaneously emits photons, going to the ground state. But whereas most excited states quickly (within 10^{-8} s) emit photons, level 2 has a much longer lifetime (a fraction of a millisecond), resulting in a buildup of excited Cr^{3+} ions in this level. If these accumulated excited ions can be triggered to emit all at once, or nearly so, an intense emission of monochromatic light at 694 nm will occur.

The process of *stimulated emission* is ideal for this triggering. When a photon corresponding to 694 nm encounters a Cr^{3+} ion in level 2, it stimulates the ion to undergo the transition from level 2 to level 1. The ion emits a photon corresponding to exactly the same wavelength as the original photon. In place of just one photon, there are now two photons, the original one and the one obtained by stimulated emission. The net effect is to increase the intensity of the light at this wavelength. Thus, a weak light

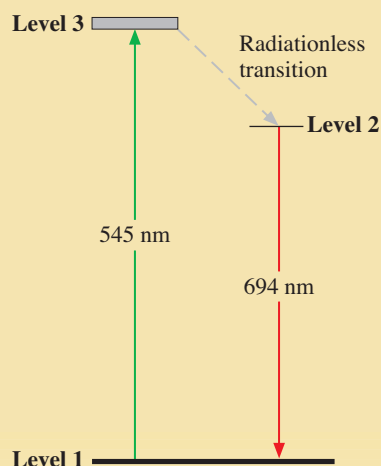


FIGURE 7.12 ▲

Energy levels of the chromium(III) ion in ruby

The energy levels have been numbered by increasing energy from 1 to 3. (Level 3 is broadened in the solid state.) When chromium(III) ions absorb the 545-nm portion of the light from a flash lamp, electrons in the ions first undergo transitions to level 3 and then radiationless transitions to level 2. (The energy is lost as heat.) Electrons accumulate in level 2 until more exist in level 2 than in level 1. Then a photon from a spontaneous emission from level 2 to level 1 can stimulate the emission from other atoms in level 2. These photons move back and forth between reflective surfaces, stimulating additional emissions and forming a laser pulse at 694 nm.

at 694 nm can be amplified by stimulated emission of the excited ruby.

Figure 7.13 shows a sketch of a ruby laser. A flash lamp emits green light (at 545 nm) that is absorbed by the ruby, building up a concentration of Cr^{3+} in level 2. A few of these excited ions spontaneously emit photons corresponding to 694 nm (red light), and these photons then stimulate other ions to emit, which in turn stimulate more ions to emit, and so forth, resulting in a pulse of laser light at 694 nm.

Laser light is *coherent*. This means that the waves forming the beam are all in phase; that is, the waves have their

maxima and minima at the same points in space and time. The property of coherence of a laser beam is used in compact disc (CD) audio players (Figure 7.14). Music is encoded on the disc in the form of pits, or indentations, on a spiral track. When the disc is played, a small laser beam scans the track and is reflected back to a detector. Light reflected from an indentation is out of phase with light from the laser and interferes with it. Because of this interference, the reflected beam is diminished in intensity and gives a diminished detector signal. Fluctuations in the signal are then converted to sound.

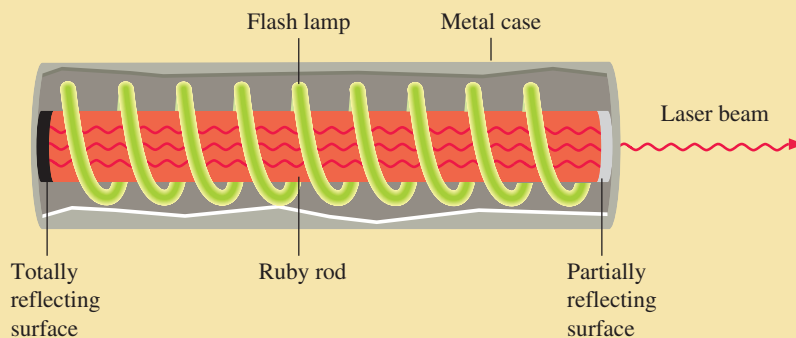


FIGURE 7.13 ▲

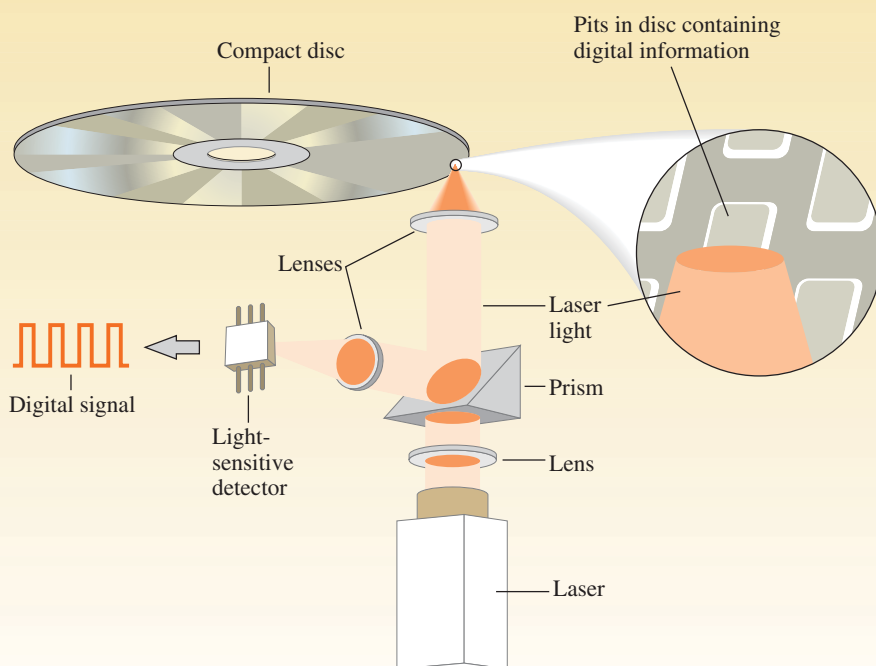
A ruby laser

A flash lamp encircles a ruby rod. Light of 545 nm (green) from the flash “pumps” electrons from level 1 to level 3, then level 2, from which stimulated emission forms a laser pulse at 694 nm (red). The stimulated emission bounces back and forth between reflective surfaces at the ends of the ruby rod, building up a coherent laser beam. One end has a partially reflective surface to allow the laser beam to exit from the ruby.

FIGURE 7.14 ►

How a compact disc player works

Music or other information is encoded in the form of pits on a compact disc. Lenses direct laser light to the disc, which reflects it back. Light reflected from a pit is out of phase with light from the laser, and these two waves interfere, reducing the intensity of the wave. As the disc moves around, light is reflected from either the main surface at full intensity (on) or from a pit at reduced intensity (off). A light-sensitive detector converts this reflected light to a digital signal (a series of on and off pulses). A converter changes this signal to one that speakers can accept.



■ See Problems 7.93 and 7.94.

(continued)

Since $\lambda = c/\nu$,

$$\lambda = \frac{3.00 \times 10^8 \text{ m/s}}{6.17 \times 10^{14} / \text{s}} = 4.86 \times 10^{-7} \text{ m, or } \mathbf{486 \text{ nm}}$$

The color is blue-green (see Figure 7.10).

Answer Check Balmer lines (lines ending with $n = 2$) are in the visible region of the spectrum. Wavelengths of visible light are in the range of 400 nm to about 800 nm. Note that the answer lies in this range.

Exercise 7.4 Calculate the wavelength of light emitted from the hydrogen atom when the electron undergoes a transition from level $n = 3$ to level $n = 1$.

■ See Problems 7.49, 7.50, 7.51, and 7.52.

According to Bohr's theory, the *emission* of light from an atom occurs when an electron undergoes a transition from an upper energy level to a lower one. To complete the explanation, we need to describe how the electron gets into the upper level prior to emission. Normally, the electron in a hydrogen atom exists in its lowest, or $n = 1$, level. To get into a higher energy level, the electron must gain energy, or be *excited*. One way this can happen is through the collision of two hydrogen atoms. During this collision, some of the kinetic energy of one atom can be gained by the electron of another atom, thereby boosting, or exciting, the electron from the $n = 1$ level to a higher energy level. The excitation of atoms and the subsequent emission of light are most likely to occur in a hot gas, where atoms have large kinetic energies.

Bohr's theory explains not only the emission but also the *absorption* of light. When an electron in the hydrogen atom undergoes a transition from $n = 3$ to $n = 2$, a photon of red light (wavelength 656 nm) is emitted. When red light of wavelength 656 nm shines on a hydrogen atom in the $n = 2$ level, a photon can be absorbed. If the photon is absorbed, the energy is gained by the electron, which undergoes a transition to the $n = 3$ level. (This is the reverse of the emission process we just discussed.) Materials that have a color, such as dyed textiles and painted walls, appear colored because of the absorption of light. For example, when white light falls on a substance that absorbs red light, the color components that are not absorbed, the yellow and blue light, are reflected. The substance appears blue-green.

Postulates 1 and 2 hold for atoms other than hydrogen, except that the energy levels cannot be obtained by a simple formula. However, if you know the wavelength of the emitted light, you can relate it to ν and then to the difference in energy levels of the atom. The energy levels of atoms have been experimentally determined in this way.

Exercise 7.5 What is the difference in energy levels of the sodium atom if emitted light has a wavelength of 589 nm?

■ See Problems 7.55 and 7.56.

Concept Check 7.2

An atom has a line spectrum consisting of a red line and a blue line. Assume that each line corresponds to a transition between two adjacent energy levels. Sketch an energy-level diagram with three energy levels that might explain this line spectrum, indicating the transitions on this diagram. Consider the transition from the highest energy level on this diagram to the lowest energy level. How would you describe the color or region of the spectrum corresponding to this transition?

Quantum Mechanics and Quantum Numbers

Bohr's theory firmly established the concept of atomic energy levels. It was unsuccessful, however, in accounting for the details of atomic structure and in predicting energy levels for atoms other than hydrogen. Further understanding of atomic structure required other theoretical developments.

7.4 Quantum Mechanics

Current ideas about atomic structure depend on the principles of *quantum mechanics*, a theory that applies to submicroscopic (that is, extremely small) particles of matter, such as electrons. The development of this theory was stimulated by the discovery of the de Broglie relation.

de Broglie Relation

According to Einstein, light has not only wave properties, which we characterize by frequency and wavelength, but also particle properties. For example, a particle of light, the photon, has a definite energy $E = h\nu$. One can also show that the photon has momentum. (The momentum of a particle is the product of its mass and speed.) This momentum, mc , is related to the wavelength of the light: $mc = h/\lambda$ or $\lambda = h/mc$. <

In 1923 the French physicist Louis de Broglie reasoned that if light (considered as a wave) exhibits particle aspects, then perhaps particles of matter show characteristics of waves under the proper circumstances. He therefore postulated that a particle of matter of mass m and speed v has an associated wavelength, by analogy with light:

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

The equation $\lambda = h/mv$ is called the **de Broglie relation**.

If matter has wave properties, why are they not commonly observed? Calculation using the de Broglie relation shows that a baseball (0.145 kg) moving at about 60 mi/hr (27 m/s) has a wavelength of about 10^{-34} m, a value so incredibly small that such waves cannot be detected. On the other hand, electrons moving at only moderate speeds have wavelengths of a few hundred picometers ($1 \text{ pm} = 10^{-12} \text{ m}$). Under the proper circumstances, the wave character of electrons should be observable.

The wave property of electrons was first demonstrated in 1927 by C. Davisson and L. H. Germer in the United States and by George Paget Thomson (son of J. J. Thomson) in Britain. They showed that a beam of electrons, just like x rays, can be diffracted by a crystal. The German physicist Ernst Ruska used this wave property to construct the first *electron microscope* in 1933; he shared the 1986 Nobel Prize in physics for this work. A modern instrument is shown in Figure 7.15. The *resolving power*, or ability to distinguish detail, of a microscope that uses waves depends on their wavelength. To resolve detail the size of several hundred picometers, we need a wavelength on that order. X rays have wavelengths in this range, but so far no practical means have been found for focusing them. Electrons, on the other hand, are readily focused with electric and magnetic fields. Figure 7.16 shows a photograph taken with an electron microscope, displaying the detail that is possible with this instrument.

A photon has a rest mass of zero but a relativistic mass m as a result of its motion. Einstein's equation $E = mc^2$ relates this relativistic mass to the energy of the photon, which also equals $h\nu$. Therefore, $mc^2 = h\nu$, or $mc = h\nu/c = h/\lambda$.



FIGURE 7.15 ▲

Scanning electron microscope

This microscope can resolve details down to 3 nm in a sample. The operator places the sample inside the chamber at the left and views the image on the video screens.



FIGURE 7.16 ▲

Scanning electron microscope image

This image is of a wasp's head. Color has been added by computer for contrast in discerning different parts of the image.

Example 7.5**Calculate the Wavelength of a Moving Particle**

a. Calculate the wavelength (in meters) of the wave associated with a 1.00-kg mass moving at 1.00 km/hr. b. What is the wavelength (in picometers) associated with an electron, whose mass is 9.11×10^{-31} kg, traveling at a speed of 4.19×10^6 m/s? (This speed can be attained by an electron accelerated between two charged plates differing by 50.0 volts; voltages in the kilovolt range are used in electron microscopes.)

Problem Strategy The questions ask for the wavelength associated with a moving mass, which is given by de Broglie's relation, $\lambda = h/mv$. Be careful to use consistent units in substituting into this equation. If you use SI units, then in part a you will need to convert km/hr to m/s. In part b, you will need to convert the answer in meters to picometers.

Solution a. A speed v of 1.00 km/hr equals

$$1.00 \frac{\text{km}}{\text{hr}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \times \frac{10^3 \text{ m}}{1 \text{ km}} = 0.278 \text{ m/s}$$

Substituting quantities (all expressed in SI units for consistency), you get

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{1.00 \text{ kg} \times 0.278 \text{ m/s}} = \mathbf{2.38 \times 10^{-33} \text{ m}}$$

$$\text{b. } \lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{9.11 \times 10^{-31} \text{ kg} \times 4.19 \times 10^6 \text{ m/s}} = 1.74 \times 10^{-10} \text{ m} = \mathbf{174 \text{ pm}}$$

Answer Check Make sure that you are using the correct equation for the de Broglie relation; units should cancel to give units of length (for wavelength). Check that the final units are those asked for in the problem statement.

Exercise 7.6

Calculate the wavelength (in picometers) associated with an electron traveling at a speed of 2.19×10^6 m/s.

■ See Problems 7.57 and 7.58.

Concept Check 7.3

A proton is approximately 2000 times heavier than an electron. How would the speeds of these particles compare if their corresponding wavelengths were about equal?

Wave Functions

De Broglie's relation applies quantitatively only to particles in a force-free environment. It cannot be applied directly to an electron in an atom, where the electron is subject to the attractive force of the nucleus. But in 1926 Erwin Schrödinger, guided by de Broglie's work, devised a theory that could be used to find the wave properties of electrons in atoms and molecules. *The branch of physics that mathematically describes the wave properties of submicroscopic particles is called **quantum mechanics** or **wave mechanics**.* <

Without going into the mathematics of quantum mechanics here, we will discuss some of the most important conclusions of the theory. In particular, quantum mechanics alters the way we think about the motion of particles. Our usual concept of motion comes from what we see in the everyday world. We might, for instance, visually follow a ball

Schrödinger received the Nobel Prize in physics in 1933 for his wave formulation of quantum mechanics. Werner Heisenberg won the Nobel Prize the previous year for his matrix-algebra formulation of quantum mechanics. The two formulations yield identical results.

that has been thrown. The path of the ball is given by its position and velocity (or momentum) at various times. We are therefore conditioned to think in terms of a continuous path for moving objects. In Bohr's theory, the electron was thought of as moving about, or orbiting, the nucleus in the way the earth orbits the sun. Quantum mechanics vastly changes this view of motion. We can no longer think of an electron as having a precise orbit in an atom. To describe such an orbit, we would have to know the exact position of the electron at various times and exactly how long it would take it to travel to a nearby position in the orbit. That is, at any moment we would have to know not only the precise position but also the precise momentum (mass times speed) of the electron.

In 1927 Werner Heisenberg showed from quantum mechanics that it is impossible to know simultaneously, with absolute precision, both the position and the momentum of a particle such as an electron. Heisenberg's **uncertainty principle** is a relation that states that the product of the uncertainty in position and the uncertainty in momentum of a particle can be no smaller than Planck's constant divided by 4π . Thus, letting Δx be the uncertainty in the x coordinate of the particle and letting Δp_x be the uncertainty in the momentum in the x direction, we have

$$(\Delta x)(\Delta p_x) \geq \frac{h}{4\pi}$$

There are similar relations in the y and z directions. The uncertainty principle says that the more precisely you know the position (the smaller Δx , Δy , and Δz), the less well you know the momentum of the particle (the larger Δp_x , Δp_y , and Δp_z). In other words, if you know very well where a particle is, you cannot know where it is going!

The uncertainty principle is significant only for particles of very small mass such as electrons. You can see this by noting that the momentum equals mass times velocity, so $p_x = mv_x$. The preceding relation becomes

$$(\Delta x)(\Delta v_x) \geq \frac{h}{4\pi m}$$

For dust particles and baseballs, where m is relatively large, the term on the right becomes nearly zero, and the uncertainties of position and velocity are quite small. The path of a baseball has meaning. For electrons, however, the uncertainties in position and momentum are normally quite large. We cannot describe the electron in an atom as moving in a definite orbit.

Although quantum mechanics does not allow us to describe the electron in the hydrogen atom as moving in an orbit, it does allow us to make *statistical* statements about where we would find the electron if we were to look for it. For example, we can obtain the *probability* of finding an electron at a certain point in a hydrogen atom. Although we cannot say that an electron will definitely be at a particular position at a given time, we can say that the electron is likely (or not likely) to be at this position.

Information about a particle in a given energy level (such as an electron in an atom) is contained in a mathematical expression called a *wave function*, denoted by the Greek letter psi, ψ . The wave function is obtained by solving an equation of quantum mechanics (Schrödinger's equation). Its square, ψ^2 , gives the probability of finding the particle within a region of space.

The wave function and its square, ψ^2 , have values for all locations about a nucleus. Figure 7.17 shows values of ψ^2 for the electron in the lowest energy level of the hydrogen atom along a line starting from the nucleus. Note that ψ^2 is large near the nucleus ($r = 0$), indicating that the electron is most likely to be found in this region. The value of ψ^2 decreases rapidly as the distance from the nucleus increases, but ψ^2 never goes to exactly zero, although the probability does become extremely small at large distances from the nucleus. This means that an atom does not have a definite boundary, unlike in the Bohr model of the atom.

Figure 7.18 shows another view of this electron probability. The graph plots the probability of finding the electron in different spherical shells at particular distances

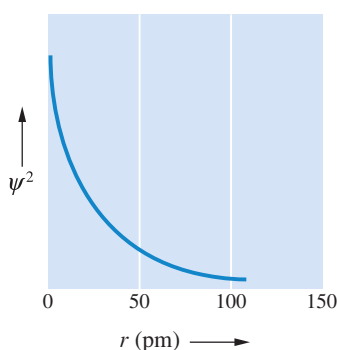


FIGURE 7.17 ▲
Plot of ψ^2 for the lowest energy level of the hydrogen atom

The square of the wave function is plotted versus the distance, r , from the nucleus.

Instrumental Methods



Scanning Tunneling Microscopy

The 1986 Nobel Prize in physics went to three physicists for their work in developing microscopes for viewing extremely small objects. Half of the prize went to Ernst Ruska for the development of the electron microscope,

described earlier. The other half was awarded to Gerd Binnig and Heinrich Rohrer, at IBM's research laboratory in Zurich, Switzerland, for their invention of the *scanning tunneling microscope* in 1981. This instrument makes possible the viewing of atoms and molecules on a solid surface (Figure 7.19).

The scanning tunneling microscope is based on the concept of quantum mechanical *tunneling*, which in turn depends on the probability interpretation of quantum mechanics. Consider a hydrogen atom, which consists of an electron about a proton (call it A), and imagine another proton (called B) some distance from the first. In classical terms, if we were to move the electron from the region of proton A to the region of proton B, energy would have to be supplied to remove the electron from the attractive field of proton A. Quantum mechanics, however, gives us a different picture. The probability of the electron in the hydrogen atom being at a location far from proton A, say near proton B, is very small but not zero. In effect, this means that the electron, which nominally belongs to proton A, may find itself near proton B without extra energy having been supplied. The electron is said to have *tunneled* from one atom to another.

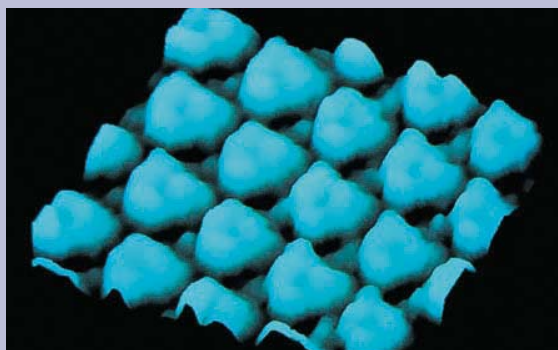


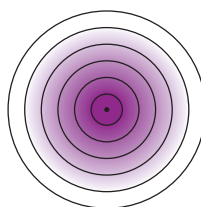
FIGURE 7.19 ▲
Scanning tunneling microscope image of benzene molecules on a metal surface

Benzene molecules, C_6H_6 , are arranged in a regular array on a rhodium metal surface.

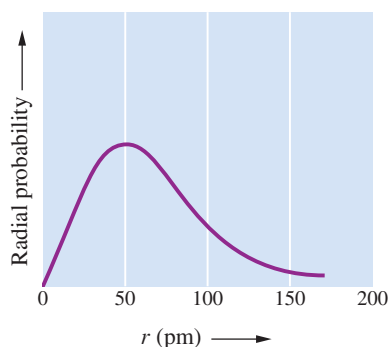
The scanning tunneling microscope consists of a tungsten metal needle with an extremely fine point (the probe) placed close to the sample to be viewed (Figure 7.20). If the probe is close enough to the sample, electrons can tunnel from the probe to the sample. The probability for this can be increased by having a small voltage applied between the probe and sample. Electrons tunneling from the probe to the sample give rise to a measurable electric current. The magnitude of the current depends on the distance between the probe and the sample (as well as on the wave function of the atom in the sample). By adjusting this distance, the current can be maintained at a fixed value. As the probe scans the sample, it moves toward or away from

FIGURE 7.18 ►
Probability of finding an electron in a spherical shell about the nucleus

(A) The diagram shows the probability density for an electron in a hydrogen atom. The region is marked off in shells about the nucleus. (B) The graph shows the probability of finding the electron within shells at various distances from the nucleus (radial probability). The curve exhibits a maximum, which means that the radial probability is greatest for a given distance from the nucleus.



A



B

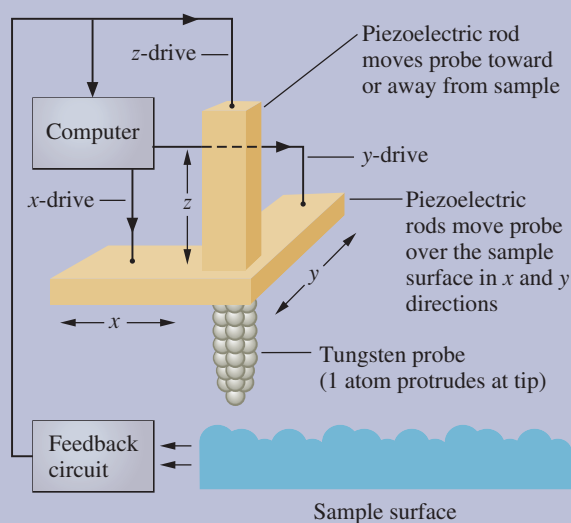


FIGURE 7.20 ▲

The scanning tunneling microscope

A tunneling current flows between the probe and the sample when there is a small voltage between them. A feedback circuit, which provides this voltage, senses the current and varies the voltage on a piezoelectric rod (z-drive) in order to keep the distance constant between the probe and sample. A computer has been programmed to provide voltages to the x-drive and the y-drive to move the probe over the surface of the sample.

the sample to maintain a fixed current; in effect, the probe follows the contours of the sample. (The probe is attached to the end of a piezoelectric rod, which undergoes very small changes in length when small voltages are applied to it.)

Researchers routinely use the scanning tunneling microscope to study the arrangement of atoms and molecules

on surfaces. Lately, scientists have also used the microscope probe to move atoms about a surface in an effort to construct miniature devices. Figure 7.21 shows 48 iron atoms that were arranged in a circle on a copper surface. Each of the iron atoms looks like a sharp mountain peak rising from a plain. Inside this “quantum corral” (as it has come to be called), you can see the wavelike distribution of electrons trapped within. Here is graphic proof of the wave-like nature of electrons!

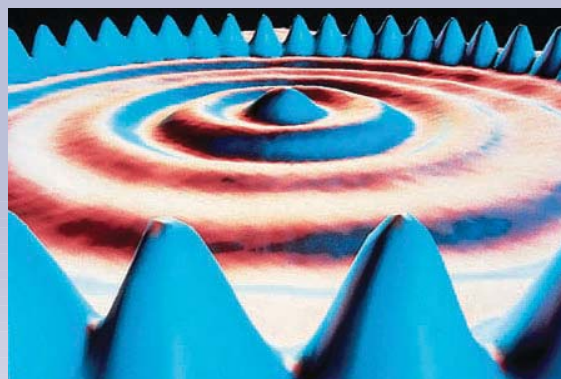


FIGURE 7.21 ▲

Quantum corral

IBM scientists used a scanning tunneling microscope probe to arrange 48 iron atoms in a circle on a copper metal surface. The iron atoms appear as the tall peaks in the diagram. Note the wave-like ripple of electrons trapped within the circle of atoms (called a *quantum corral*). [IBM Research Division, Almaden Research Center; research done by Donald M. Eigler and coworkers.]

■ See Problems 7.95 and 7.96.

from the nucleus, rather than the probability at a point. Even though the probability of finding the electron at a point near the nucleus is high, the volume of any shell there is small. Therefore, the probability of finding the electron *within a shell* is greatest at some distance from the nucleus. This distance just happens to equal the radius that Bohr calculated for an electron orbit in his model.

7.5

Quantum Numbers and Atomic Orbitals

Three different quantum numbers are needed because there are three dimensions to space.

According to quantum mechanics, each electron in an atom is described by four different quantum numbers, three of which (n , l , and m_l) specify the wave function that gives the probability of finding the electron at various points in space. < A wave function for an electron in an atom is called an **atomic orbital**. An atomic orbital is pictured

qualitatively by describing the region of space where there is high probability of finding the electrons. The atomic orbital so pictured has a definite shape. A fourth quantum number (m_s) refers to a magnetic property of electrons called *spin*. We first look at quantum numbers, then at atomic orbitals.

Quantum Numbers

The allowed values and general meaning of each of the four quantum numbers of an electron in an atom are as follows:

1. Principal Quantum Number (n) *This quantum number is the one on which the energy of an electron in an atom principally depends; it can have any positive value: 1, 2, 3, and so on.* The energy of an electron in an atom depends principally on n . The smaller n is, the lower the energy. In the case of the hydrogen atom or single-electron atomic ions, such as Li^{2+} and He^+ , n is the only quantum number determining the energy (which is given by Bohr's formula, discussed in Section 7.3). For other atoms, the energy also depends to a slight extent on the l quantum number.

The size of an orbital also depends on n . The larger the value of n is, the larger the orbital. Orbitals of the same quantum state n are said to belong to the same *shell*. Shells are sometimes designated by the following letters:

Letter	K	L	M	N . . .
n	1	2	3	4 . . .

2. Angular Momentum Quantum Number (l) (Also Called Azimuthal Quantum Number) *This quantum number distinguishes orbitals of given n having different shapes; it can have any integer value from 0 to $n - 1$.* Within each shell of quantum number n , there are n different kinds of orbitals, each with a distinctive shape denoted by an l quantum number. For example, if an electron has a principal quantum number of 3, the possible values for l are 0, 1, and 2. Thus, within the M shell ($n = 3$), there are three kinds of orbitals, each having a different shape for the region where the electron is most likely to be found. These orbital shapes will be discussed later in this section.

Although the energy of an orbital is principally determined by the n quantum number, the energy also depends somewhat on the l quantum number (except for the H atom). For a given n , the energy of an orbital increases with l .

Orbitals of the same n but different l are said to belong to different *subshells* of a given shell. The different subshells are usually denoted by letters as follows:

Letter	s	p	d	f	g . . .
l	0	1	2	3	4 . . .

To denote a subshell within a particular shell, we write the value of the n quantum number for the shell, followed by the letter designation for the subshell. For example, $2p$ denotes a subshell with quantum numbers $n = 2$ and $l = 1$. <

3. Magnetic Quantum Number (m_l) *This quantum number distinguishes orbitals of given n and l —that is, of given energy and shape but having a different orientation in space; the allowed values are the integers from $-l$ to $+l$.* For $l = 0$ (s subshell), the allowed m_l quantum number is 0 only; there is only one orbital in the s subshell. For $l = 1$ (p subshell), $m_l = -1, 0$, and $+1$; there are three different orbitals in the p subshell. The orbitals have the same shape but different orientations in space. In

The rather odd choice of letter symbols for l quantum numbers survives from old spectroscopic terminology (describing the lines in a spectrum as sharp, principal, diffuse, and fundamental).

TABLE 7.1

Permissible Values of Quantum Numbers for Atomic Orbitals

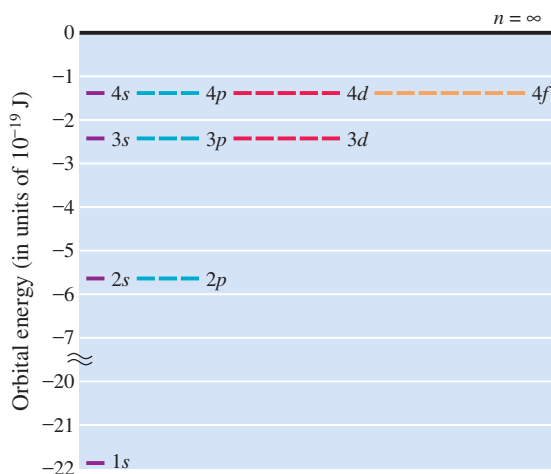
n	l	m_l^*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	-1, 0, +1	2p	3
3	0	0	3s	1
3	1	-1, 0, +1	3p	3
3	2	-2, -1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	-1, 0, +1	4p	3
4	2	-2, -1, 0, +1, +2	4d	5
4	3	-3, -2, -1, 0, +1, +2, +3	4f	7

*Any one of the m_l quantum numbers may be associated with the n and l quantum numbers on the same line.

FIGURE 7.22

Orbital energies of the hydrogen atom

The lines for each subshell indicate the number of different orbitals of that subshell. (Note break in the energy scale.)



Electron spin will be discussed further in Section 8.1.

addition, all orbitals of a given subshell have the same energy. Note that there are $2l + 1$ orbitals in each subshell of quantum number l .

4. Spin Quantum Number (m_s) This quantum number refers to the two possible orientations of the spin axis of an electron; possible values are $+\frac{1}{2}$ and $-\frac{1}{2}$. An electron acts as though it were spinning on its axis like the earth. Such an electron spin would give rise to a circulating electric charge that would generate a magnetic field. In this way, an electron behaves like a small bar magnet, with a north and a south pole. <

Table 7.1 lists the permissible quantum numbers for all orbitals through the $n = 4$ shell. These values follow from the rules just given. Energies for the orbitals are shown in Figure 7.22 for the hydrogen atom. Note that all orbitals with the same principal quantum number n have the same energy. For atoms with more than one electron, however, only orbitals in the same subshell (denoted by a given n and l) have the same energy. We will have more to say about orbital energies in Chapter 8.

Example 7.6

Applying the Rules for Quantum Numbers

State whether each of the following sets of quantum numbers is permissible for an electron in an atom. If a set is not permissible, explain why.

- $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$
- $n = 3, l = 1, m_l = -2, m_s = -\frac{1}{2}$

- $n = 2, l = 1, m_l = 0, m_s = +\frac{1}{2}$
- $n = 2, l = 0, m_l = 0, m_s = 1$

Problem Strategy Apply the rules for quantum numbers in order, first to n , then to l and m_l , and finally

(continued)

(continued)

to m_s . A set of quantum numbers is impermissible if it disobeys any rule.

Solution a. **Not permissible.** The l quantum number is equal to n ; it must be less than n .

b. **Not permissible.** The magnitude of the m_l quantum number (that is, the m_l value, ignoring its sign) must not be greater than l .

c. **Permissible.**

d. **Not permissible.** The m_s quantum number can be only $+\frac{1}{2}$ or $-\frac{1}{2}$.

Answer Check Check that n is a positive integer (it cannot be zero). Also, check that l is a positive integer

(but zero is allowed) and that m_l is an integer whose magnitude (its value except for sign) is equal to or less than l . The m_s quantum number can be only $+\frac{1}{2}$ or $-\frac{1}{2}$.

Exercise 7.7 Explain why each of the following sets of quantum numbers is not permissible for an orbital.

a. $n = 0, l = 1, m_l = 0, m_s = +\frac{1}{2}$

b. $n = 2, l = 3, m_l = 0, m_s = -\frac{1}{2}$

c. $n = 3, l = 2, m_l = +3, m_s = +\frac{1}{2}$

d. $n = 3, l = 2, m_l = +2, m_s = 0$

■ See Problems 7.69 and 7.70.

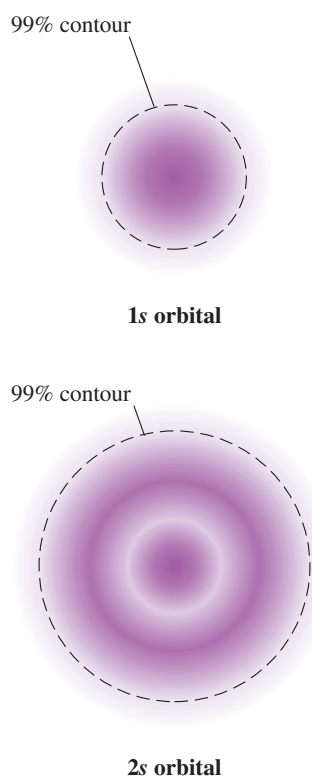


FIGURE 7.23 ▲

Cross-sectional representations of the probability distributions of s orbitals

In a $1s$ orbital, the probability distribution is largest near the nucleus. In a $2s$ orbital, it is greatest in a spherical shell about the nucleus. Note the relative “size” of the orbitals, indicated by the 99% contours.

Atomic Orbital Shapes

An s orbital has a spherical shape, though specific details of the probability distribution depend on the value of n . Figure 7.23 shows cross-sectional representations of the probability distributions of a $1s$ and a $2s$ orbital. The color shading is darker where the electron is more likely to be found. In the case of a $1s$ orbital, the electron is most likely to be found near the nucleus. The shading becomes lighter as the distance from the nucleus increases, indicating that the electron is less likely to be found there.

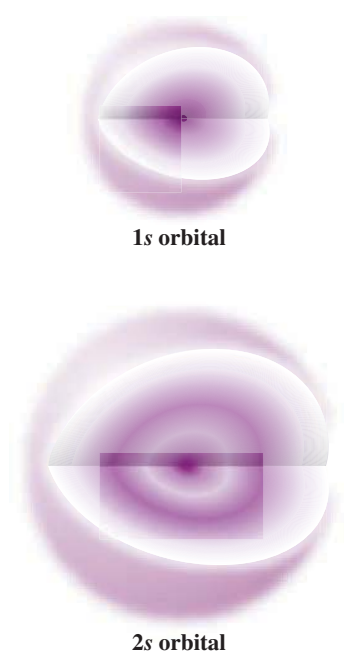
The orbital does not abruptly end at some particular distance from the nucleus. An atom, therefore, has an indefinite extension, or “size.” We can gauge the “size” of the orbital by means of the *99% contour*. The electron has a 99% probability of being found within the space of the 99% contour (the sphere indicated by the dashed line in the diagram).

A $2s$ orbital differs in detail from a $1s$ orbital. The electron in a $2s$ orbital is likely to be found in two regions, one near the nucleus and the other in a spherical shell about the nucleus. (The electron is most likely to be here.) The 99% contour shows that the $2s$ orbital is larger than the $1s$ orbital.

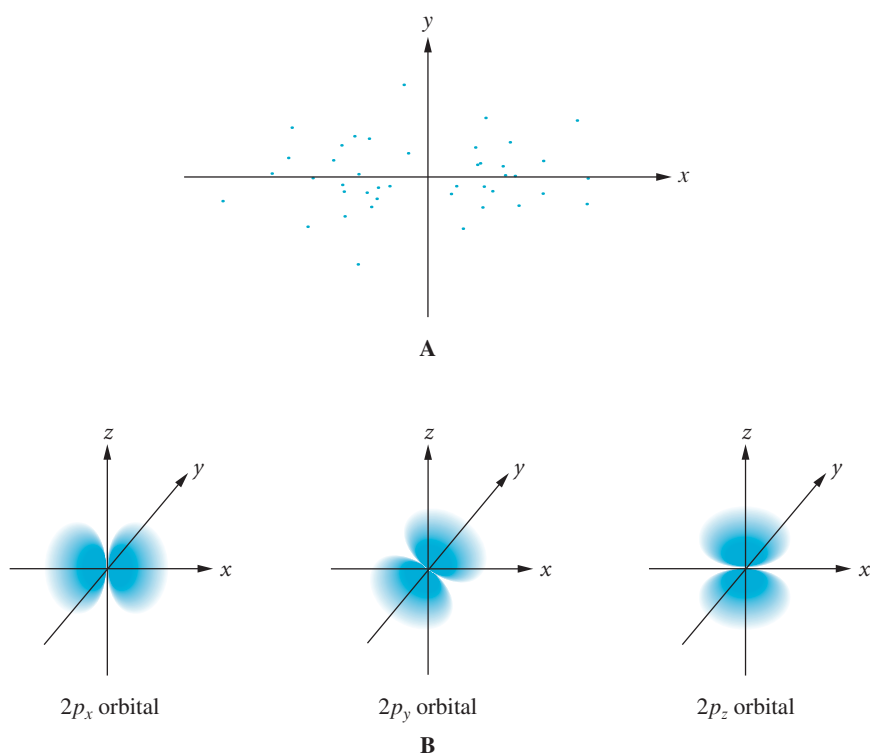
A cross-sectional diagram cannot portray the three-dimensional aspect of the $1s$ and $2s$ atomic orbitals. Figure 7.24 shows cutaway diagrams, which better illustrate this three-dimensionality.

There are three p orbitals in each p subshell. All p orbitals have the same basic shape (two lobes arranged along a straight line with the nucleus between the lobes) but differ in their orientations in space. Because the three orbitals are set at right angles to each other, we can show each one as oriented along a different coordinate axis (Figure 7.25). We denote these orbitals as $2p_x$, $2p_y$, and $2p_z$. A $2p_x$ orbital has its greatest electron probability along the x -axis, a $2p_y$ orbital along the y -axis, and a $2p_z$ orbital along the z -axis. Other p orbitals, such as $3p$, have this same general shape, with differences in detail depending on n . We will discuss s and p orbital shapes again in Chapter 10 in reference to chemical bonding.

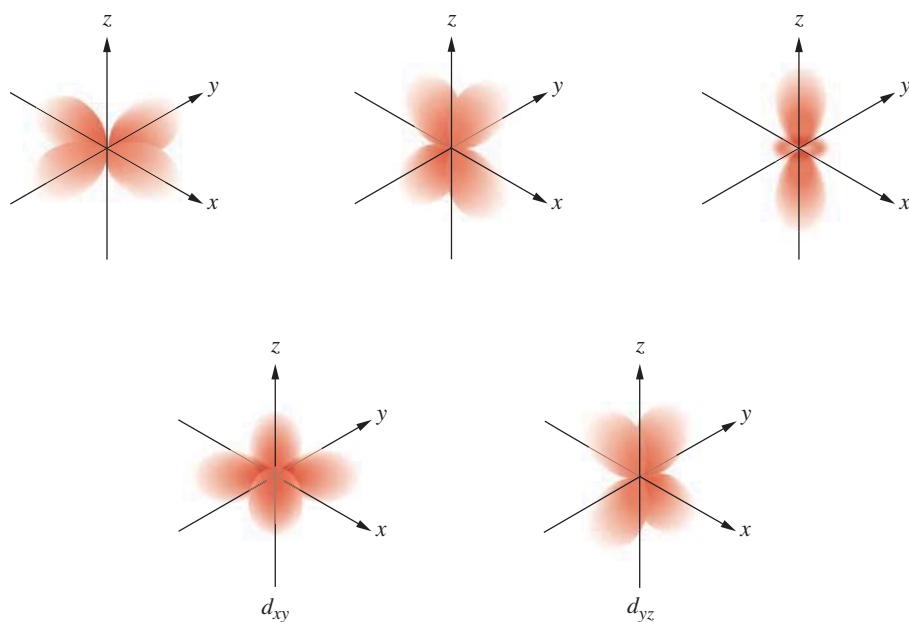
There are five d orbitals, which have more complicated shapes than do s and p orbitals. These are represented in Figure 7.26.

**FIGURE 7.24** ▲**Cutaway diagrams showing the spherical shape of s orbitals**

In both diagrams, a segment of each orbital is cut away to reveal the electron distribution of the orbital.

**FIGURE 7.25** ▲**The $2p$ orbitals**

(A) Electron distribution in the $2p_x$ orbital. Note that it consists of two lobes oriented along the x -axis.
 (B) Orientations of the three $2p$ orbitals. The drawings depict the general shape and orientation of the orbitals, but not the detailed electron distribution as in (A).

**FIGURE 7.26** ▲**The five $3d$ orbitals**

These are labeled by subscripts, as in d_{xy} , that describe their mathematical characteristics.

A Checklist for Review

Important Terms

wavelength (λ) (7.1)
 frequency (ν) (7.1)
 electromagnetic spectrum (7.1)
 Planck's constant (7.2)
 photons (7.2)
 photoelectric effect (7.2)

continuous spectrum (7.3)
 line spectrum (7.3)
 energy levels (7.3)
 de Broglie relation (7.4)
 quantum (wave) mechanics (7.4)
 uncertainty principle (7.4)

atomic orbital (7.5)
 principal quantum number (n) (7.5)
 angular momentum quantum number (l) (7.5)
 magnetic quantum number (m_l) (7.5)
 spin quantum number (m_s) (7.5)

Key Equations

$$c = \nu\lambda$$

$$E = h\nu$$

$$E = -\frac{R_H}{n^2} \quad n = 1, 2, 3, \dots \infty \quad (\text{for H atom})$$

$$\text{Energy of emitted photon} = h\nu = -(E_f - E_i)$$

$$\lambda = \frac{h}{m\nu}$$

Summary of Facts and Concepts

One way to study the electronic structure of the atom is to analyze the electromagnetic radiation that is emitted from an atom. Electromagnetic radiation is characterized by its *wavelength* λ and frequency ν , and these quantities are related to the speed of light c ($c = \nu\lambda$).

Einstein showed that light consists of particles (*photons*), each of energy $E = h\nu$, where h is Planck's constant. According to Bohr, electrons in an atom have *energy levels*, and when an electron in a higher energy level drops (or undergoes a transition) to a lower energy level, a photon is emitted. The energy of the photon equals the difference in energy between the two levels.

Electrons and other particles of matter have both particle and wave properties. For a particle of mass m and speed v , the

wavelength is related to momentum $m\nu$ by the *de Broglie relation*: $\lambda = h/m\nu$. The wave properties of a particle are described by a *wave function*, from which we can get the probability of finding the particle in different regions of space.

Each electron in an atom is characterized by four different quantum numbers. The distribution of an electron in space—its *atomic orbital*—is characterized by three of these quantum numbers: the principal quantum number, the angular momentum quantum number, and the magnetic quantum number. The fourth quantum number (spin quantum number) describes the magnetism of the electron.

Media Summary

Visit the **student website at college.hmco.com/pic/ebbing9e** to help prepare for class, study for quizzes and exams, understand core concepts, and visualize molecular-level interactions. The following media activities are available for this chapter:



Prepare for Class

- **Video Lessons** Mini lectures from chemistry experts
 - CIA Demonstration: Flame Colors
 - The Wave Nature of Light
 - Absorption and Emission
 - The Ultraviolet Catastrophe
 - The Photoelectric Effect
 - The Bohr Model
 - The Wave Nature of Matter
 - The Heisenberg Uncertainty Principle
 - Atomic Orbital Size
 - Atomic Orbital Shapes and Quantum Numbers



Improve Your Grade

- **Visualizations** Molecular-level animations and lab demonstration videos
 - Flame Tests
 - The Line Spectrum of Hydrogen
 - Electromagnetic Waves
 - Refraction of White Light
 - Photoelectric Effect
 - 1s Orbital
 - 2p_x Orbital
 - 2p_y Orbital

$2p_z$ Orbital
 $3d_{x^2-y^2}$ Orbital
 $3d_{xy}$ Orbital
 $3d_{xz}$ Orbital
 $3d_{yz}$ Orbital
 $3d_{z^2}$ Orbital

- **Flashcards** Key terms and definitions
Online Flashcards

Access these resources using the passkey available free with new texts or for purchase separately.

- **Self-Assessment Questions** Additional questions with full worked-out solutions
6 Self-Assessment Questions



ACE the Test

- Multiple-choice quizzes
- 3 ACE Practice Tests

Learning Objectives

7.1 The Wave Nature of Light

- Define the *wavelength* and *frequency* of a wave.
- Relate the wavelength, frequency, and speed of light.
Examples 7.1 and 7.2
- Describe the different regions of the electromagnetic spectrum.

7.2 Quantum Effects and Photons

- State Planck's quantization of vibrational energy.
- Define *Planck's constant* and *photon*.
- Describe the photoelectric effect.
- Calculate the energy of a photon from its frequency or wavelength. **Example 7.3**

7.3 The Bohr Theory of the Hydrogen Atom

- State the postulates of Bohr's theory of the hydrogen atom.
- Relate the energy of a photon to the associated energy levels of an atom.

- Determine the wavelength or frequency of a hydrogen atom transition. **Example 7.4**
- Describe the difference between *emission* and *absorption* of light by an atom.

7.4 Quantum Mechanics

- State the de Broglie relation.
- Calculate the wavelength of a moving particle. **Example 7.5**
- Define *quantum mechanics*.
- State Heisenberg's uncertainty principle.
- Relate the wave function for an electron to the probability of finding it at a location in space.

7.5 Quantum Numbers and Atomic Orbitals

- Define *atomic orbital*.
- Define each of the quantum numbers for an atomic orbital.
- State the rules for the allowed values for each quantum number.
- Apply the rules for quantum numbers. **Example 7.6**
- Describe the shapes of *s*, *p*, and *d* orbitals.

Self-Assessment and Review Questions

7.1 Give a brief wave description of light. What are two characteristics of light waves?

7.2 What is the mathematical relationship among the different characteristics of light waves? State the meaning of each of the terms in the equation.

7.3 Briefly describe the portions of the electromagnetic spectrum, starting with shortest wavelengths and going to longer wavelengths.

7.4 Planck originated the idea that energies can be quantized. What does the term *quantized* mean? What was Planck trying to explain when he was led to the concept of quantization of energy? Give the formula he arrived at and explain each of the terms in the formula.

7.5 In your own words, explain the photoelectric effect. How does the photon concept explain this effect?

7.6 Describe the wave-particle picture of light.

7.7 Give the equation that relates particle properties of light. Explain the meaning of each symbol in the equation.

7.8 Physical theory at the time Rutherford proposed his nuclear model of the atom was not able to explain how this model could give a stable atom. Explain the nature of this difficulty.

7.9 Explain the main features of Bohr's theory. Do these features solve the difficulty alluded to in Question 7.8?

7.10 Explain the process of emission of light by an atom.

7.11 Explain the process of absorption of light by an atom.

7.12 What is the evidence for electron waves? Give a practical application.

7.13 What kind of information does a wave function give about an electron in an atom?

7.14 The atom is sometimes said to be similar to a miniature planetary system, with electrons orbiting the nucleus. What does the uncertainty principle have to say about this view of the atom?

7.15 Bohr described the hydrogen atom as an electron orbiting a hydrogen nucleus. Although certain aspects of his theory are still valid, his theory agreed quantitatively with experiment

only in the case of the hydrogen atom. In what way does quantum mechanics change Bohr's original picture of the hydrogen atom?

7.16 Give the possible values of (a) the principal quantum number, (b) the angular momentum quantum number, (c) the magnetic quantum number, and (d) the spin quantum number.

7.17 What is the notation for the subshell in which $n = 4$ and $l = 3$? How many orbitals are in this subshell?

7.18 What is the general shape of an s orbital? of a p orbital?

7.19 Which of the following statements about a hydrogen atom is false?

- An electron in the $n = 1$ level of the hydrogen atom is in its ground state.
- On average, an electron in the $n = 3$ level is farther from the nucleus than an electron in the $n = 2$ state.
- The wavelength of light emitted when the electron goes from the $n = 3$ level to the $n = 1$ level is the same as the wavelength of light absorbed when the electron goes from the $n = 1$ level to $n = 3$ level.
- An electron in the $n = 1$ level is higher in energy than an electron in the $n = 4$ level.
- Light of greater frequency is required for a transition from the $n = 1$ level to $n = 3$ level than is required for a transition from the $n = 2$ level to $n = 3$ level.

7.20 Which of the following statements is (are) true?

- The product of wavelength and frequency of light is a constant.
- As the energy of electromagnetic radiation increases, its frequency decreases.
- As the wavelength of light increases, its frequency increases.
 - I only
 - II only
 - III only
 - I and III only
 - II and III only

7.21 Of the following possible transitions of an electron in a hydrogen atom, which emits light of the highest energy?

- Transition from the $n = 1$ to the $n = 3$ level
- Transition from the $n = 1$ to the $n = 2$ level
- Transition from the $n = 3$ to the $n = 1$ level
- Transition from the $n = 2$ to the $n = 1$ level
- Transition from the $n = 5$ to the $n = 4$ level

7.22 What wavelength of electromagnetic radiation corresponds to a frequency of $3.46 \times 10^{13} \text{ s}^{-1}$?

- $8.66 \times 10^{-6} \text{ m}$
- $1.15 \times 10^5 \text{ m}$
- $7.65 \times 10^{-29} \text{ m}$
- $9.10 \times 10^{-6} \text{ m}$
- $8.99 \times 10^{-6} \text{ m}$

Concept Explorations

7.23 Light, Energy, and the Hydrogen Atom

- Which has the greater wavelength, blue light or red light?
- How do the frequencies of blue light and red light compare?
- How does the energy of blue light compare with that of red light?
- Does blue light have a greater speed than red light?
- How does the energy of three photons from a blue light source compare with the energy of one photon of blue light from the same source? How does the energy of two photons corresponding to a wavelength of 451 nm (blue light) compare with the energy of three photons corresponding to a wavelength of 704 nm (red light)?
- A hydrogen atom with an electron in its ground state interacts with a photon of light with a wavelength of $1.22 \times 10^{-6} \text{ m}$. Could the electron make a transition from the ground state to a higher energy level? If it does make a transition, indicate which one. If no transition can occur, explain.
- If you have one mole of hydrogen atoms with their electrons in the $n = 1$ level, what is the minimum number of photons you would need to interact with these atoms in order to have all of their electrons promoted to the $n = 3$ level? What wavelength of light would you need to perform this experiment?

7.24 Investigating Energy Levels

Consider the hypothetical atom X that has one electron like the H atom but has different energy levels. The energies of an electron in an X atom are described by the equation

$$E = -\frac{R_{\text{H}}}{n^3}$$

where R_{H} is the same as for hydrogen ($2.179 \times 10^{-18} \text{ J}$). Answer the following questions, *without calculating energy values*.

- How would the ground-state energy levels of X and H compare?
- Would the energy of an electron in the $n = 2$ level of H be higher or lower than that of an electron in the $n = 2$ level of X? Explain your answer.
- How do the spacings of the energy levels of X and H compare?
- Which would involve the emission of a higher frequency of light, the transition of an electron in an H atom from the $n = 5$ to the $n = 3$ level or a similar transition in an X atom?
- Which atom, X or H, would require more energy to completely remove its electron?
- A photon corresponding to a particular frequency of blue light produces a transition from the $n = 2$ to the $n = 5$ level of a hydrogen atom. Could this photon produce the same transition ($n = 2$ to $n = 5$) in an atom of X? Explain.

Conceptual Problems

7.25 Consider two beams of the same yellow light. Imagine that one beam has its wavelength doubled; the other has its frequency doubled. Which of these two beams is then in the ultraviolet region?

7.26 Some infrared radiation has a wavelength that is 1000 times larger than that of a certain visible light. This visible light has a frequency that is 1000 times smaller than that of some X radiation. How many times more energy is there in a photon of this X radiation than there is in a photon of the infrared radiation?

7.27 One photon of green light has less than twice the energy of two photons of red light. Consider two hypothetical experiments. In one experiment, potassium metal is exposed to one photon of green light; in another experiment, potassium metal is exposed to two photons of red light. In one of these experiments, no electrons are ejected by the photoelectric effect (no matter how many times this experiment is repeated). In the other experiment, at least one electron was observed to be ejected. What is the maximum number of electrons that could be ejected during this other experiment, one or two?

7.28 An atom in its ground state absorbs a photon (photon 1), then quickly emits another photon (photon 2). One of these photons corresponds to ultraviolet radiation, whereas the other one corresponds to red light. Explain what is happening. Which electromagnetic radiation, ultraviolet or red light, is associated with the emitted photon (photon 2)?

7.29 Three emission lines involving three energy levels in an atom occur at wavelengths x , $1.5x$, and $3.0x$ nanometers. Which wavelength corresponds to the transition from the highest to the lowest of the three energy levels?

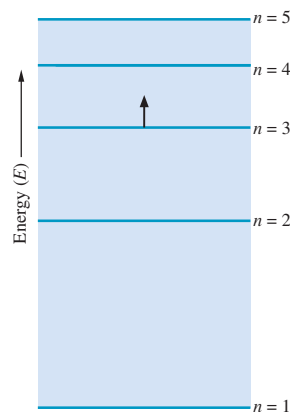
7.30 An atom emits yellow light when an electron makes the transition from the $n = 5$ to the $n = 1$ level. In separate experiments, suppose you bombarded the $n = 1$ level of this atom with red light, yellow light (obtained from the previous emission), and blue light. In which experiment or experiments would the electron be promoted to the $n = 5$ level?

7.31 Which of the following particles has the longest wavelength?

- an electron traveling at x meters per second
- a proton traveling at x meters per second
- a proton traveling at $2x$ meters per second

7.32 Imagine a world in which the rule for the l quantum number is that values start with 1 and go up to n . The rules for the n and m_l quantum numbers are unchanged from those of our world. Write the quantum numbers for the first two shells (i.e., $n = 1$ and $n = 2$).

7.33 Given the following energy level diagram for an atom that contains an electron in the $n = 3$ level, answer the following questions.



- Which transition of the electron will emit light of the lowest frequency?
- Using only those levels depicted in the diagram, which transition of the electron would require the highest-frequency light?
- If the transition from the $n = 3$ level to the $n = 1$ level emits green light, what color light is absorbed when an electron makes the transition from the $n = 1$ to $n = 3$ level?

7.34 The following shapes each represent an orbital of an atom in a hypothetical universe. The small circle is the location of the nucleus in each orbital.



- If you placed an electron in each orbital, which one would be higher in energy?
- When an electron makes a transition from the orbital represented on the right to the orbital on the left, would you expect energy to be absorbed or released?
- Draw a sketch of an orbital of the same type that would be higher in energy than either of the two pictured orbitals.

Practice Problems

Electromagnetic Waves

7.35 Radio waves in the AM region have frequencies in the range 530 to 1700 kilocycles per second (530 to 1700 kHz). Calculate the wavelength corresponding to a radio wave of frequency $1.365 \times 10^6/\text{s}$ (that is, 1365 kHz).

7.36 Microwaves have frequencies in the range 10^9 to $10^{12}/\text{s}$ (cycles per second), equivalent to between 1 gigahertz and 1

terahertz. What is the wavelength of microwave radiation whose frequency is $1.258 \times 10^{10}/\text{s}$?

7.37 Light with a wavelength of 478 nm lies in the blue region of the visible spectrum. Calculate the frequency of this light.

7.38 Calculate the frequency associated with light of wavelength 656 nm. (This corresponds to one of the wavelengths of light emitted by the hydrogen atom.)

7.39 At its closest approach, Mars is 56 million km from Earth. How long would it take to send a radio message from a space probe of Mars to Earth when the planets are at this closest distance?

7.40 The space probe *Pioneer 11* was launched April 5, 1973, and reached Jupiter in December 1974, traveling a distance of 998 million km. How long did it take an electromagnetic signal to travel to Earth from *Pioneer 11* when it was near Jupiter?

7.41 The meter was defined in 1963 as the length equal to 1,650,763.73 wavelengths of the orange-red radiation emitted by the krypton-86 atom (the meter has since been redefined). What is the wavelength of this transition? What is the frequency?

7.42 The second is defined as the time it takes for 9,192,631,770 wavelengths of a certain transition of the cesium-133 atom to pass a fixed point. What is the frequency of this electromagnetic radiation? What is the wavelength?

Photons

7.43 What is the energy of a photon corresponding to radio waves of frequency $1.365 \times 10^6/\text{s}$?

7.44 What is the energy of a photon corresponding to microwave radiation of frequency $1.258 \times 10^{10}/\text{s}$?

7.45 The green line in the atomic spectrum of thallium has a wavelength of 535 nm. Calculate the energy of a photon of this light.

7.46 Indium compounds give a blue-violet flame test. The atomic emission responsible for this blue-violet color has a wavelength of 451 nm. Obtain the energy of a single photon of this wavelength.

7.47 A particular transition of the rubidium atom emits light whose frequency is 3.84×10^{14} Hz. (Hz is the abbreviation for *hertz*, which is equivalent to the unit $1/\text{s}$, or s^{-1} .) Is this light in the visible spectrum? If so, what is the color of the light? (See Figure 7.5.)

7.48 Barium atoms have a particular transition that emits light of frequency 5.41×10^{14} Hz. (Hz is the abbreviation for *hertz*, which is equivalent to the unit $1/\text{s}$, or s^{-1} .) Is this light in the visible spectrum? If so, what is the color of the light? (See Figure 7.5.)

Bohr Theory

7.49 An electron in a hydrogen atom in the level $n = 5$ undergoes a transition to level $n = 3$. What is the frequency of the emitted radiation?

7.50 Calculate the frequency of electromagnetic radiation emitted by the hydrogen atom in the electron transition from $n = 4$ to $n = 3$.

7.51 The first line of the Lyman series of the hydrogen atom emission results from a transition from the $n = 2$ level to the $n = 1$ level. What is the wavelength of the emitted photon? Using Figure 7.5, describe the region of the electromagnetic spectrum in which this emission lies.

7.52 What is the wavelength of the electromagnetic radiation emitted from a hydrogen atom when the electron undergoes the transition $n = 5$ to $n = 4$? In what region of the spectrum does this line occur? (See Figure 7.5.)

7.53 Calculate the shortest wavelength of the electromagnetic radiation emitted by the hydrogen atom in undergoing a transition from the $n = 6$ level.

7.54 Calculate the longest wavelength of the electromagnetic radiation emitted by the hydrogen atom in undergoing a transition from the $n = 7$ level.

7.55 What is the difference in energy between the two levels responsible for the violet emission line of the calcium atom at 422.7 nm?

7.56 What is the difference in energy between the two levels responsible for the ultraviolet emission line of the magnesium atom at 285.2 nm?

de Broglie Waves

Note: Masses of the electron, proton, and neutron are listed on the inside back cover of this book.

7.57 What is the wavelength of a neutron traveling at a speed of 4.15 km/s? (Neutrons of these speeds are obtained from a nuclear pile.)

7.58 What is the wavelength of a proton traveling at a speed of 6.58 km/s? What would be the region of the spectrum for electromagnetic radiation of this wavelength?

7.59 At what speed must an electron travel to have a wavelength of 10.0 pm?

7.60 At what speed must a neutron travel to have a wavelength of 12.0 pm?

7.61 What is the de Broglie wavelength of a 145-g baseball traveling at 30.0 m/s (67.1 mph)? Is the wavelength much smaller or much larger than the diameter of an atom (on the order of 100 pm)?

7.62 What is the de Broglie wavelength of an oxygen molecule, O_2 , traveling at 521 m/s? Is the wavelength much smaller or much larger than the diameter of an atom (on the order of 100 pm)?

Atomic Orbitals

7.63 If the n quantum number of an atomic orbital is 4, what are the possible values of l ? If the l quantum number is 3, what are the possible values of m_l ?

7.64 The n quantum number of an atomic orbital is 6. What are the possible values of l ? What are the possible values of m_l if the l quantum number is 5?

7.65 How many subshells are there in the M shell? How many orbitals are there in the f subshell?

7.66 How many subshells are there in the N shell? How many orbitals are there in the g subshell?

7.67 Give the notation (using letter designations for l) for the subshells denoted by the following quantum numbers.

- a. $n = 6, l = 2$ c. $n = 4, l = 3$
b. $n = 5, l = 4$ d. $n = 6, l = 1$

7.68 Give the notation (using letter designations for l) for the subshells denoted by the following quantum numbers.

- a. $n = 3, l = 2$
b. $n = 4, l = 0$
c. $n = 4, l = 1$
d. $n = 5, l = 3$

7.69 Explain why each of the following sets of quantum numbers would not be permissible for an electron, according to the rules for quantum numbers.

- $n = 1, l = 0, m_l = 0, m_s = +1$
- $n = 1, l = 3, m_l = +3, m_s = +\frac{1}{2}$
- $n = 3, l = 2, m_l = +3, m_s = -\frac{1}{2}$
- $n = 0, l = 1, m_l = 0, m_s = +\frac{1}{2}$
- $n = 2, l = 1, m_l = -1, m_s = +\frac{3}{2}$

General Problems

7.71 The blue line of the strontium atom emission has a wavelength of 461 nm. What is the frequency of this light? What is the energy of a photon of this light?

7.72 The barium atom has an emission with wavelength 554 nm (green). Calculate the frequency of this light and the energy of a photon of this light.

7.73 The energy of a photon is 4.10×10^{-19} J. What is the wavelength of the corresponding light? What is the color of this light?

7.74 The energy of a photon is 3.34×10^{-19} J. What is the wavelength of the corresponding light? What is the color of this light?

7.75 The photoelectric work function of a metal is the minimum energy needed to eject an electron by irradiating the metal with light. For calcium, this work function equals 4.34×10^{-19} J. What is the minimum frequency of light for the photoelectric effect in calcium?

7.76 The photoelectric work function for magnesium is 5.90×10^{-19} J. (The work function is the minimum energy needed to eject an electron from the metal by irradiating it with light.) Calculate the minimum frequency of light required to eject electrons from magnesium.

7.77 Light of wavelength 345 nm shines on a piece of calcium metal. What is the speed of the ejected electron? (Light energy greater than that of the work function of calcium ends up as kinetic energy of the ejected electron. See Problem 7.75 for the definition of work function and its value for calcium.)

7.78 Light of wavelength 276 nm shines on a piece of magnesium metal. What is the speed of the ejected electron? (Light energy greater than that of the work function of magnesium ends up as kinetic energy of the ejected electron. See Problem 7.76 for the definition of work function and its value for magnesium.)

7.79 Calculate the wavelength of the Balmer line of the hydrogen spectrum in which the initial n quantum number is 5 and the final n quantum number is 2.

7.80 Calculate the wavelength of the Balmer line of the hydrogen spectrum in which the initial n quantum number is 6 and the final n quantum number is 2.

7.81 One of the lines in the Balmer series of the hydrogen atom emission spectrum is at 397 nm. It results from a transition from an upper energy level to $n = 2$. What is the principal quantum number of the upper level?

7.82 A line of the Lyman series of the hydrogen atom spectrum has the wavelength 9.50×10^{-8} m. It results from a transition

7.70 State which of the following sets of quantum numbers would be possible and which impossible for an electron in an atom.

- $n = 2, l = 0, m_l = 0, m_s = +\frac{1}{2}$
- $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$
- $n = 0, l = 0, m_l = 0, m_s = -\frac{1}{2}$
- $n = 2, l = 1, m_l = -1, m_s = +\frac{1}{2}$
- $n = 2, l = 1, m_l = -2, m_s = +\frac{1}{2}$

from an upper energy level to $n = 1$. What is the principal quantum number of the upper level?

7.83 A hydrogen-like ion has a nucleus of charge $+Ze$ and a single electron outside this nucleus. The energy levels of these ions are $-Z^2 R_H/n^2$ (where Z = atomic number). Calculate the wavelength of the transition from $n = 3$ to $n = 2$ for He^+ , a hydrogen-like ion. In what region of the spectrum does this emission occur?

7.84 What is the wavelength of the transition from $n = 5$ to $n = 3$ for Li^{2+} ? In what region of the spectrum does this emission occur? Li^{2+} is a hydrogen-like ion. Such an ion has a nucleus of charge $+Ze$ and a single electron outside this nucleus. The energy levels of the ion are $-Z^2 R_H/n^2$, where Z is the atomic number.

7.85 An electron microscope employs a beam of electrons to obtain an image of an object. What energy must be imparted to each electron of the beam to obtain a wavelength of 10.0 pm? Obtain the energy in electron volts (eV) ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$).

7.86 Neutrons are used to obtain images of the hydrogen atoms in molecules. What energy must be imparted to each neutron in a neutron beam to obtain a wavelength of 10.0 pm? Obtain the energy in electron volts (eV) ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$).

7.87 What is the number of different orbitals in each of the following subshells?

- 3d
- 4f
- 4p
- 5s

7.88 What is the number of different orbitals in each of the following subshells?

- 6g
- 4f
- 6s
- 5p

7.89 List the possible subshells for the $n = 6$ shell.

7.90 List the possible subshells for the $n = 7$ shell.

7.91 What are gamma rays? How does the gamma radiation of foods improve their shelf life?

7.92 How can gamma rays that are used in food irradiation be produced? Does such irradiated food show any radioactivity?

7.93 The word *laser* is an acronym meaning *light amplification by stimulated emission of radiation*. What is the stimulated emission of radiation?

7.94 Explain how lasers are used to “read” a compact disc.

7.95 Explain the concept of quantum mechanical tunneling.

7.96 Explain how the probe in a scanning tunneling microscope scans a sample on the surface of a metal.

Strategy Problems

7.97 What wavelength of electromagnetic radiation corresponds to a frequency of $7.76 \times 10^9 \text{ s}^{-1}$? Note that Planck's constant is $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$, and the speed of light is $3.00 \times 10^8 \text{ m/s}$.

7.98 AM radio stations broadcast at frequencies between 530 kHz and 1700 kHz. ($1 \text{ kHz} = 10^3 \text{ s}^{-1}$.) For a station broadcasting at $1.69 \times 10^3 \text{ kHz}$, what is the energy of this radio wave? Note that Planck's constant is $6.63 \times 10^{-34} \text{ J}\cdot\text{s}$, and the speed of light is $3.00 \times 10^8 \text{ m/s}$.

7.99 The photoelectric *work function* of a metal is the minimum energy required to eject an electron by shining light on the metal. The work function of calcium is $4.60 \times 10^{-19} \text{ J}$. What is the longest wavelength of light (in nanometers) that can cause an electron to be ejected from calcium metal.

7.100 Calculate the shortest wavelength of *visible* light (in nanometers) seen in the spectrum of the hydrogen atom. What are the principal quantum numbers for the levels in this transition? Does Figure 7.11 include all visible lines?

7.101 Light of wavelength $1.03 \times 10^{-7} \text{ m}$ is emitted when an electron in an excited level of a hydrogen atom undergoes a transition to the $n = 1$ level. What is the region of the spectrum of this light? What is the principal quantum number of the excited level?

7.102 It requires 799 kJ of energy to break one mole of carbon-oxygen double bonds in carbon dioxide. What wavelength of light does this correspond to per bond? Is there any transition in the hydrogen atom that has at least this quantity of energy in one photon?

7.103 The root-mean-square speed of an oxygen molecule, O_2 , at 21°C is 479 m/s. Calculate the de Broglie wavelength for an O_2 molecule traveling at this speed. How does this wavelength compare with the approximate length of this molecule, which is about 242 pm? (For this comparison, state the wavelength as a percentage of the molecular length).

7.104 A particular microwave oven delivers 800 watts. (A watt is a unit of power, which is the joules of energy delivered, or used, per second.) If the oven uses microwave radiation of wavelength 12.2 cm, how many photons of this radiation are required to heat 1.00 g of water 1.00°C , assuming that all of the photons are absorbed?

7.105 For each of the following combinations of quantum numbers, make changes that produce an allowed combination. Count 3 for each change of n , 2 for each change of l , and 1 for each change of m_l . What is the lowest possible count that you can obtain?

a. $n = 3, l = 0, m_l = -2$ c. $n = 3, l = 3, m_l = -3$

b. $n = 5, l = 5, m_l = 4$ d. $n = 5, l = 6, m_l = 3$

7.106 The term *degeneracy* means the number of different quantum states of an atom or molecule having the same energy. For example, the degeneracy of the $n = 2$ level of the hydrogen atom is 4 (a $2s$ quantum state, and three different $2p$ states). What is the degeneracy of the $n = 5$ level?

Cumulative-Skills Problems

7.107 The energy required to dissociate the Cl_2 molecule to Cl atoms is 239 kJ/mol Cl_2 . If the dissociation of a Cl_2 molecule were accomplished by the absorption of a single photon whose energy was exactly the quantity required, what would be its wavelength (in meters)?

7.108 The energy required to dissociate the H_2 molecule to H atoms is 432 kJ/mol H_2 . If the dissociation of an H_2 molecule were accomplished by the absorption of a single photon whose energy was exactly the quantity required, what would be its wavelength (in meters)?

7.109 A microwave oven heats by radiating food with microwave radiation, which is absorbed by the food and converted to heat. Suppose an oven's radiation wavelength is 12.5 cm. A container with 0.250 L of water was placed in the oven, and the temperature of the water rose from 20.0°C to 100.0°C . How many photons of this microwave radiation were required? Assume that all the energy from the radiation was used to raise the temperature of the water.

7.110 Warm objects emit electromagnetic radiation in the infrared region. Heat lamps employ this principle to generate infrared radiation. Water absorbs infrared radiation with wavelengths near $2.80 \mu\text{m}$. Suppose this radiation is absorbed by the water and converted to heat. A 1.00-L sample of water absorbs infrared radiation, and its temperature increases from 20.0°C to 30.0°C . How many photons of this radiation are used to heat the water?

7.111 Light with a wavelength of 425 nm fell on a potassium surface, and electrons were ejected at a speed of $4.88 \times 10^5 \text{ m/s}$. What energy was expended in removing an electron from the metal? Express the answer in joules (per electron) and in kilojoules per mole (of electrons).

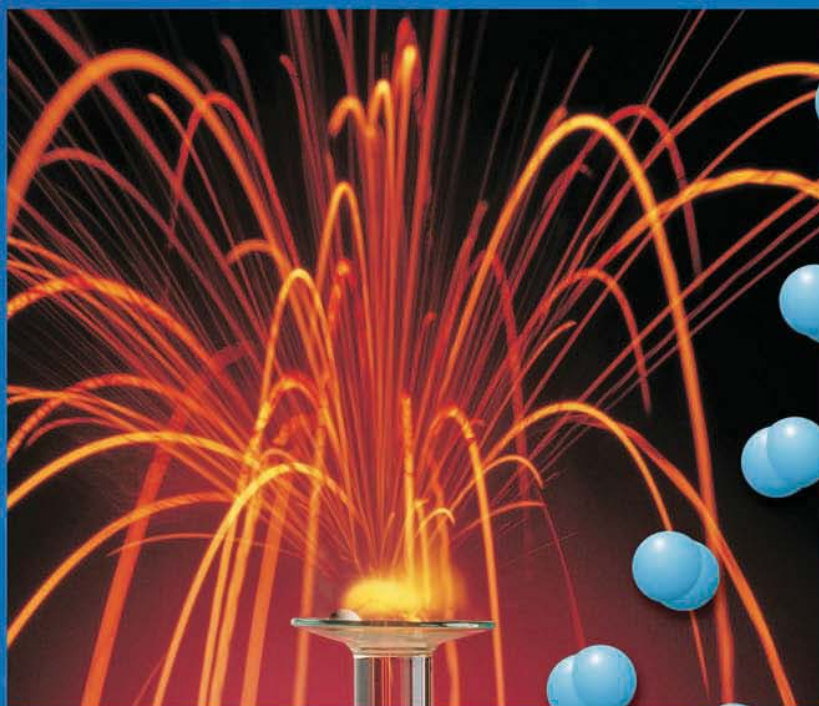
7.112 Light with a wavelength of 405 nm fell on a strontium surface, and electrons were ejected. If the speed of an ejected electron is $3.36 \times 10^5 \text{ m/s}$, what energy was expended in removing the electron from the metal? Express the answer in joules (per electron) and in kilojoules per mole (of electrons).

7.113 When an electron is accelerated by a voltage difference, the kinetic energy acquired by the electron equals the voltage times the charge on the electron. Thus, one volt imparts a kinetic energy of $1.602 \times 10^{-19} \text{ volt-coulombs}$, which equals $1.602 \times 10^{-19} \text{ J}$. What is the wavelength associated with electrons accelerated by $4.00 \times 10^3 \text{ volts}$?

7.114 When an electron is accelerated by a voltage difference, the kinetic energy acquired by the electron equals the voltage times the charge on the electron. Thus, one volt imparts a kinetic energy of $1.602 \times 10^{-19} \text{ volt-coulombs}$, or $1.602 \times 10^{-19} \text{ J}$. What is the wavelength for electrons accelerated by $1.00 \times 10^4 \text{ volts}$?

8

Electron Configurations and Periodicity



Sodium metal reacts vigorously with water to produce hydrogen gas (which catches fire); other Group 1A metals similarly react with water. The other product is sodium hydroxide, which is used in products such as oven cleaner and soap.

Contents and Concepts

Electronic Structure of Atoms

- 8.1 Electron Spin and the Pauli Exclusion Principle
- 8.2 Building-Up Principle and the Periodic Table
- 8.3 Writing Electron Configurations Using the Periodic Table
- 8.4 Orbital Diagrams of Atoms; Hund's Rule

In the previous chapter, you learned that we characterize an atomic orbital by four quantum numbers: n , l , m_l , and m_s . In the first section, we look further at electron spin; then we discuss how electrons are distributed among the possible orbitals of an atom.

Periodicity of the Elements

- 8.5 Mendeleev's Predictions from the Periodic Table
- 8.6 Some Periodic Properties
- 8.7 Periodicity in the Main-Group Elements

You learned how the periodic table can be explained by the periodicity of the ground-state configurations of the elements. Now we will look at various aspects of the periodicity of the elements.

Marie Curie, a Polish-born French chemist, and her husband, Pierre, announced the discovery of radium in 1898 (Figure 8.1). They had separated a very radioactive mixture from pitchblende, an ore of uranium. This mixture was primarily a compound of barium. When the mixture was heated in a flame, however, it gave a new atomic line spectrum, in addition to the spectrum for barium. The Curies based their discovery of a new element on this finding. It took them four more years to obtain a pure compound of radium. Radium, like uranium, is a radioactive element. But in most of its chemical and physical properties, radium is similar to the non-radioactive element barium. It was this similarity that made the final separation of the new element so difficult.

Chemists had long known that groups of elements have similar properties. In 1869 Dmitri Mendeleev found that when the elements were arranged in a particular way, they fell into columns, with elements in the same column displaying similar properties. Thus, Mendeleev placed beryllium, calcium, strontium, and barium in one column. Now, with the Curies' discovery, radium was added to this column.

Mendeleev's arrangement of the elements, the *periodic table*, was originally based on the observed chemical and physical properties of the elements and their compounds. We now explain this arrangement in terms of the electronic structure of atoms. In this chapter we will

■ See pages 321–322 for the Media Summary.

look at this electronic structure and its relationship to the periodic table of elements.



FIGURE 8.1 ▲

Marie Skłodowska Curie (1867–1934), with Pierre Curie

Marie Skłodowska Curie, born in Warsaw, Poland, began her doctoral work with Henri Becquerel soon after he discovered the spontaneous radiation emitted by uranium salts. She found this radiation to be an atomic property and coined the word *radioactivity* for it. In 1903 the Curies and Becquerel were awarded the Nobel Prize in physics for their discovery of radioactivity. Three years later, Pierre Curie was killed in a carriage accident. Marie Curie continued their work on radium and in 1911 was awarded the Nobel Prize in chemistry for the discovery of polonium and radium and the isolation of pure radium metal. This was the first time a scientist had received two Nobel awards. (Since then two others have been so honored.)

Electronic Structure of Atoms

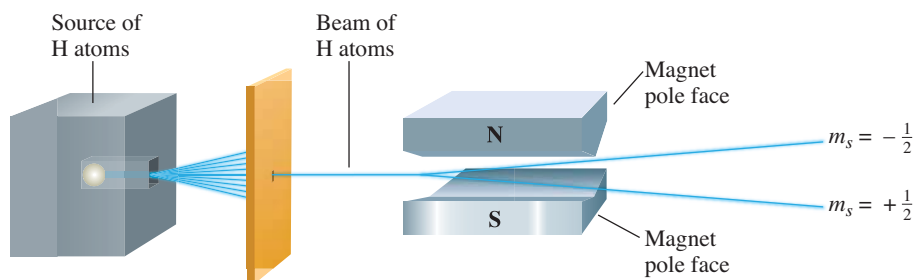
In Chapter 7 we found that an electron in an atom has four quantum numbers— n , l , m_l , and m_s —associated with it. The first three quantum numbers characterize the orbital that describes the region of space where an electron is most likely to be found; we say that the electron “occupies” this orbital. The spin quantum number, m_s , describes the spin orientation of an electron. In the first section, we will look further at electron spin; then we will discuss how electrons are distributed among the possible orbitals of an atom.

8.1 Electron Spin and the Pauli Exclusion Principle

Otto Stern and Walther Gerlach first observed electron spin magnetism in 1921. They directed a beam of silver atoms into the field of a specially designed magnet. The same experiment can be done with hydrogen atoms. The beam of hydrogen atoms is split into two by the magnetic field; half of the atoms are bent in one direction and

FIGURE 8.2 ▶**The Stern–Gerlach experiment**

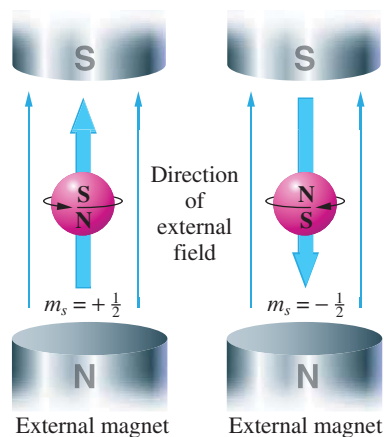
The diagram shows the experiment using hydrogen atoms (simpler to interpret theoretically), although the original experiment employed silver atoms. A beam of hydrogen atoms (shown in blue) is split into two by a nonuniform magnetic field. One beam consists of atoms each with an electron having $m_s = +\frac{1}{2}$; the other beam consists of atoms each having an electron with $m_s = -\frac{1}{2}$.



half in the other (see Figure 8.2). The fact that the atoms are affected by the laboratory magnet shows that they themselves act as magnets.

The beam of hydrogen atoms is split into two because the electron in each atom behaves as a tiny magnet with only two possible orientations. In effect, the electron acts as though it were a ball of spinning charge (Figure 8.3), and, like a circulating electric charge, the electron would create a magnetic field. Electron spin, however, is subject to a quantum restriction on the possible directions of the spin axis. The resulting directions of spin magnetism correspond to spin quantum numbers $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$. <

Protons and many nuclei also have spin. See the Instrumental Methods essay at the end of this section.

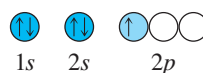
**FIGURE 8.3** ▲**A representation of electron spin**

The two possible spin orientations are indicated by the models. By convention, the spin direction is given as shown by the large arrow on the spin axis. Electrons behave as tiny bar magnets, as shown in the figure.

Electron Configurations and Orbital Diagrams

An **electron configuration** of an atom is a *particular distribution of electrons among available subshells*. The notation for a configuration lists the subshell symbols, one after the other, with a superscript giving the number of electrons in that subshell. For example, a configuration of the lithium atom (atomic number 3) with two electrons in the $1s$ subshell and one electron in the $2s$ subshell is written $1s^2 2s^1$.

The notation for a configuration gives the number of electrons in each subshell, but we use a *diagram to show how the orbitals of a subshell are occupied by electrons*. It is called an **orbital diagram**. An orbital is represented by a circle. Each group of orbitals in a subshell is labeled by its subshell notation. An electron in an orbital is shown by an arrow; the arrow points up when $m_s = +\frac{1}{2}$ and down when $m_s = -\frac{1}{2}$. The orbital diagram



shows the electronic structure of an atom in which there are two electrons in the $1s$ subshell, or orbital (one electron with $m_s = +\frac{1}{2}$, the other with $m_s = -\frac{1}{2}$); two electrons in the $2s$ subshell ($m_s = +\frac{1}{2}$, $m_s = -\frac{1}{2}$); and one electron in the $2p$ subshell ($m_s = +\frac{1}{2}$). The electron configuration is $1s^2 2s^2 2p^1$.

Pauli Exclusion Principle

Not all of the conceivable arrangements of electrons among the orbitals of an atom are physically possible. The **Pauli exclusion principle**, which summarizes experimental observations, states that *no two electrons in an atom can have the same four quantum numbers*. If one electron in an atom has the quantum numbers $n = 1$, $l = 0$, $m_l = 0$, and $m_s = +\frac{1}{2}$, no other electron can have these same quantum numbers. In other words, you cannot place two electrons with the same value of m_s in a $1s$ orbital. The orbital diagram



is not a possible arrangement of electrons.

Instrumental Methods



Nuclear Magnetic Resonance (NMR)

You have just seen that electrons have a spin and as a result behave like tiny magnets. Protons and neutrons similarly have spins. Therefore, depending on the arrangement of protons and neutrons, a nucleus could have

spin. A nucleus with spin will act like a bar magnet, similar to the electron although many times smaller in magnitude. Examples of nuclei with spin are hydrogen-1 (proton), carbon-13 (but carbon-12, the most abundant nuclide of carbon, has no spin), and fluorine-19.

Although nuclear magnetism is much smaller than that of electrons, with the correct equipment it is easily seen and in fact forms the basis of *nuclear magnetic resonance* (NMR) spectroscopy, one of the most important methods for determining molecular structure. Nuclear magnetism also forms the basis of the medical diagnostic tool *magnetic resonance imaging*, or MRI (Figure 8.4).

The essential features of NMR can be seen if you consider the proton. Like the electron, the proton has two spin states. In the absence of a magnetic field, these spin states have the same energy, but in the field of a strong magnet (external field), they have different energies. The state in which the proton magnetism is aligned with the external field, so the south pole of the proton magnet faces the north pole of the external magnet, will have lower energy. The state in which the proton magnet is turned 180° , with its south pole facing the south pole of the external magnet, will have higher energy. Now if a

proton in the lower spin state is irradiated with electromagnetic waves of the proper frequency (in which the photon has energy equal to the difference in energy of the spin states), the proton will change to the higher spin state. The frequency absorbed by the proton depends on the magnitude of the magnetic field. For the magnets used in these instruments, the radiation lies in the radio-frequency range. Frequencies commonly used are 300 MHz and 900 MHz.

Figure 8.5 shows a diagram of an NMR spectrometer. It consists of a sample in the field of a variable electromagnet and near two coils, one a radio wave transmitter and the other a receiver coil perpendicular to the transmitter coil (so that the receiver will not pick up the signal from the transmitter). Suppose the transmitter radiates waves of 300 MHz. If the sample absorbs these radio waves, protons will undergo transitions from the lower to the higher spin state. Once protons are in the higher energy state, they tend to lose energy, going back to the lower spin state and radiating 300-MHz radio waves. Thus, the sample acts like a transmitter, but one with coils in various directions, so the signal can be detected by the receiver coil.

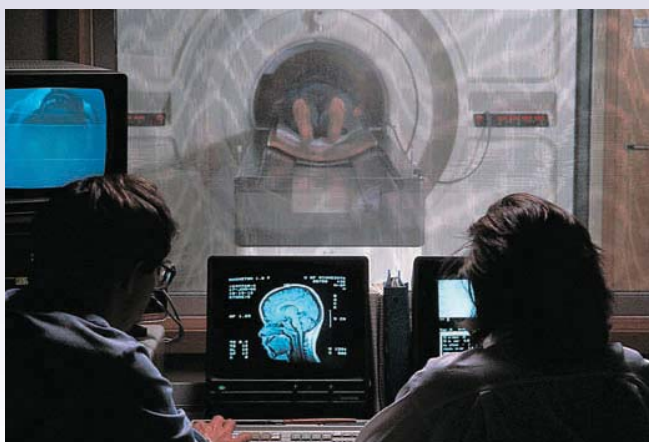
In general, the sample will not absorb at the chosen frequency. But you can change the energy difference between spin states, and therefore the frequency that is absorbed by the sample, by increasing or decreasing the magnitude of the external magnetic field using small coils on the magnet pole faces. In so doing you can, in effect, “tune” the sample, or bring it into “resonance” with the transmitter frequency. (Alternatively, many modern instruments vary the transmitter frequency to obtain resonance.)

Because each proton in a substance is surrounded by electrons that have their own magnetic fields, the magnetic

FIGURE 8.4 ▶

Magnetic resonance imaging

A patient's head is placed in a large magnet and subjected to a radio pulse. Proton spin transitions give rise to a radio wave emission that can be analyzed electronically and converted by computer to a two-dimensional image of a plane portion of the brain. Paul C. Lauterbur, a chemist at the University of Illinois (Urbana), and Sir Peter Mansfield, University of Nottingham (UK), won the Nobel Prize in Physiology or Medicine in 2003 for their work in the early 1970s in developing MRI.



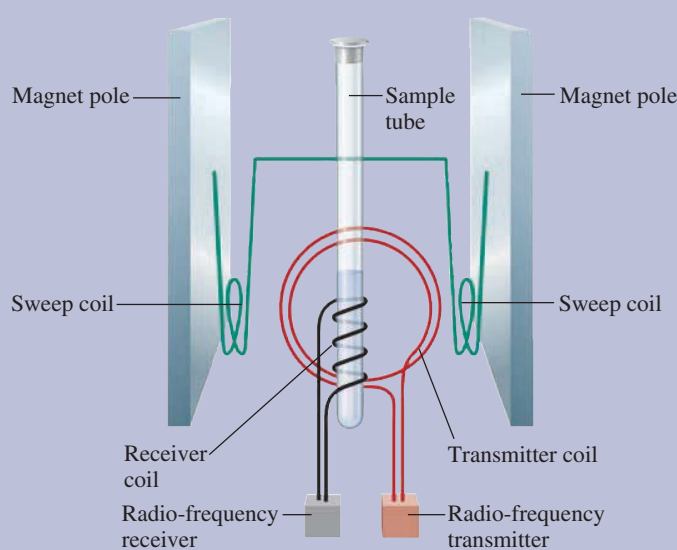
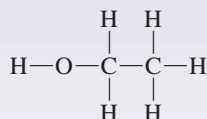


FIGURE 8.5 ▲
Nuclear magnetic resonance spectrometer

A sample in the tube is in a magnetic field, which can be varied by changing the electric current in the *sweep* coils (shown in green). A radio-frequency transmitter radiates radio waves from a coil (shown in red) to the sample. The sample absorbs these waves if the radio frequency corresponds to the difference in energy of the sample's nuclear spin states. When the nuclear spins go back to the ground state, the sample emits radio waves, which are detected by the receiver coil (in black).

environment of a proton depends to some extent on the bonding, or chemical, environment in which the proton is involved. So, the external magnetic field needed to bring a proton into resonance with the 300-MHz radiation, say, varies with the chemical (bonding) environment. A spectrum is produced by recording the magnetic field (or frequency) at which the protons in a molecule produce a resonance signal. Figure 8.6 shows a high-resolution NMR spectrum of ethanol.

Ethanol, whose molecular structure is



has protons in three different chemical environments: a proton bonded to an oxygen atom (H—O—), the protons in a —CH₂— group, and the protons in a —CH₃ group. Each of these three types of protons shows up as a

peak or, as we will see, a group of peaks in the NMR spectrum. The position of the center of a group of peaks for a given proton relative to some standard is referred to as the *chemical shift* for that proton, because it depends on the chemical environment of the proton. By measuring the area under the peaks for a given type of proton (usually done electronically by the spectrometer), a researcher can discover the number of protons of that type, effectively giving the chemist structural information about the molecule.

As we noted earlier, a given proton may give rise to several peaks in a high-resolution spectrum. (At low resolution, these separate peaks may appear as only one for each proton.) For example, the protons for the —CH₂— group of ethanol give four closely spaced peaks. These peaks arise because of the interaction of the proton spins on this group with those protons on the adjacent —CH₃ group. The number of peaks (four) for the —CH₂— group is one more than the number of protons on the adjacent group (three).

NMR spectroscopy is one of the most important tools a chemist has in determining the identity of a substance and its molecular structure. The method is quick and can yield such information as the chemical bonding environment of the protons and the number of protons having a given environment. It can also give information about other nuclei, such as carbon-13.

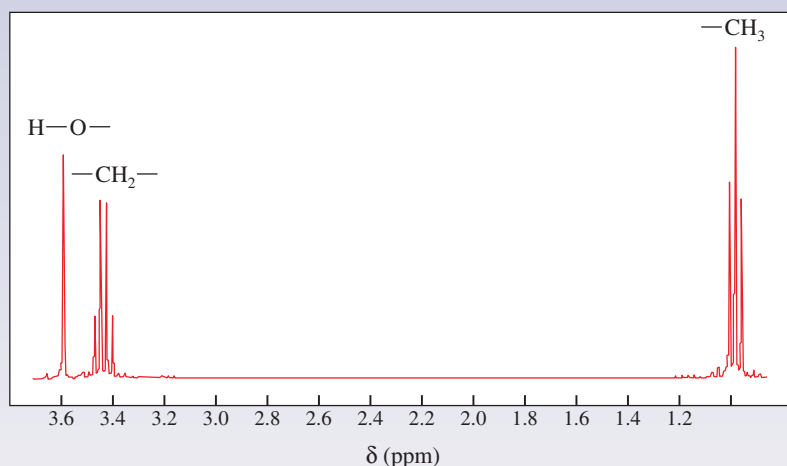


FIGURE 8.6 ▲
High-resolution NMR spectrum of ethanol, CH₃CH₂OH

The protons of a given type occur as a peak or closely spaced group of peaks. The position of the center of such a group of peaks relative to some standard is referred to as the *chemical shift*. The peaks within a group arise from the interaction of the spins between protons of one type with those of another type.

■ See Problems 8.85 and 8.86.

Because there are only two possible values of m_s , an orbital can hold no more than two electrons—and then only if the two electrons have different spin quantum numbers. In an orbital diagram, an orbital with two electrons must be written with arrows pointing in opposite directions. The two electrons are said to have opposite spins. We can restate the Pauli exclusion principle:

Pauli exclusion principle: An orbital can hold at most two electrons, and then only if the electrons have opposite spins.

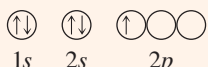

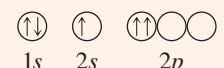
Each subshell holds a maximum of twice as many electrons as the number of orbitals in the subshell. Thus, a $2p$ subshell, which has three orbitals (with $m_l = -1, 0$, and $+1$), can hold a maximum of six electrons. The maximum number of electrons in various subshells is given in the following table.

Subshell	Number of Orbitals	Maximum Number of Electrons
s ($l = 0$)	1	2
p ($l = 1$)	3	6
d ($l = 2$)	5	10
f ($l = 3$)	7	14

Example 8.1

Applying the Pauli Exclusion Principle

Which of the following orbital diagrams or electron configurations are possible and which are impossible, according to the Pauli exclusion principle? Explain.

- a.  b. 
- c.  d. $1s^3 2s^1$
- e. $1s^2 2s^1 2p^7$ f. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

Problem Strategy In any orbital diagram, make sure that each orbital contains no more than two electrons, which have opposite spins. In any electron configuration, make sure that an orbital of given l contains no more than $2(2l + 1)$ electrons (there are $2l + 1$ different orbitals of given l , and each of these orbitals can hold two electrons).

Solution a. **Possible** orbital diagram. b. **Impossible** orbital diagram; there are three electrons in the $2s$ orbital. c. **Impossible** orbital diagram; there are two electrons in a $2p$ orbital with the same spin. d. **Impossible** electron configuration; there are three electrons in the $1s$ subshell (one orbital). e. **Impossible** electron configuration; there are seven electrons in the $2p$ subshell (which can hold only six electrons). f. **Possible**. Note that the $3d$ subshell can hold as many as ten electrons.

Answer Check The overarching idea here is that each orbital in an atom can hold a maximum of only two electrons, and then only if the two electrons have opposite spins. For example, a p subshell has three orbitals and therefore holds a maximum of six electrons.

(continued)

(continued)

Exercise 8.1

Look at the following orbital diagrams and electron configurations.

Which are possible and which are not, according to the Pauli exclusion principle? Explain.

- a. \uparrow \uparrow \circ \circ \circ b. \uparrow \uparrow $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$
 1s 2s 2p 1s 2s 2p
- c. $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\uparrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ d. $1s^2 2s^2 2p^4$
 1s 2s 2p
- e. $1s^2 2s^4 2p^2$ f. $1s^2 2s^2 2p^6 3s^2 3p^{10} 3d^{10}$

■ See Problems 8.41, 8.42, 8.43, and 8.44.

8.2

Building-Up Principle and the Periodic Table

The transition of the sodium atom from the excited state $1s^2 2s^2 2p^6 3p^1$ to the ground state $1s^2 2s^2 2p^6 3s^1$ is accompanied by the emission of yellow light at 589 nm. Excited states of an atom are needed to describe its spectrum.

Every atom has an infinite number of possible electron configurations. The configuration associated with the lowest energy level of the atom corresponds to a quantum-mechanical state called the *ground state*. Other configurations correspond to *excited states*, associated with energy levels other than the lowest. For example, the ground state of the sodium atom is known from experiment to have the electron configuration $1s^2 2s^2 2p^6 3s^1$. The electron configuration $1s^2 2s^2 2p^6 3p^1$ represents an excited state of the sodium atom. <

The chemical properties of an atom are related primarily to the electron configuration of its ground state. Table 8.1 lists the experimentally determined ground-state

TABLE 8.1

Ground-State Electron Configurations of Atoms $Z = 1$ to 36*

Z	Element	Configuration	Z	Element	Configuration
1	H	$1s^1$	19	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
2	He	$1s^2$	20	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
3	Li	$1s^2 2s^1$	21	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
4	Be	$1s^2 2s^2$	22	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
5	B	$1s^2 2s^2 2p^1$	23	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
6	C	$1s^2 2s^2 2p^2$	24	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
7	N	$1s^2 2s^2 2p^3$	25	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
8	O	$1s^2 2s^2 2p^4$	26	Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
9	F	$1s^2 2s^2 2p^5$	27	Co	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
10	Ne	$1s^2 2s^2 2p^6$	28	Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
11	Na	$1s^2 2s^2 2p^6 3s^1$	29	Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
12	Mg	$1s^2 2s^2 2p^6 3s^2$	30	Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
13	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	31	Ga	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$
14	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	32	Ge	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
15	P	$1s^2 2s^2 2p^6 3s^2 3p^3$	33	As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
16	S	$1s^2 2s^2 2p^6 3s^2 3p^4$	34	Se	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$
17	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$	35	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
18	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$	36	Kr	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

*A complete table appears in Appendix D.

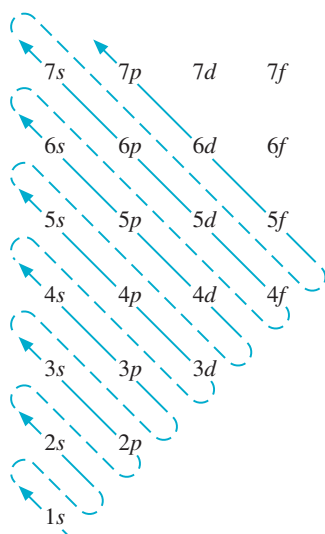


FIGURE 8.7 ▲
A mnemonic diagram for the building-up order (diagonal rule)

You obtain this diagram by writing the subshell(s) in rows, each row having subshell(s) of given n . Within each row, you arrange the subshell(s) by increasing l . (You can stop after writing the nf subshell(s), since no known elements contain g or higher subshell(s).) Now, starting with the $1s$ subshell(s), draw a series of diagonals, as shown. The building-up order is the order in which these diagonals strike the subshell(s).

The quantum numbers and characteristics of orbitals were discussed in Section 7.5.

electron configurations of atoms $Z = 1$ to $Z = 36$. (A complete table appears in Appendix D.)

Building-Up Principle (Aufbau Principle)

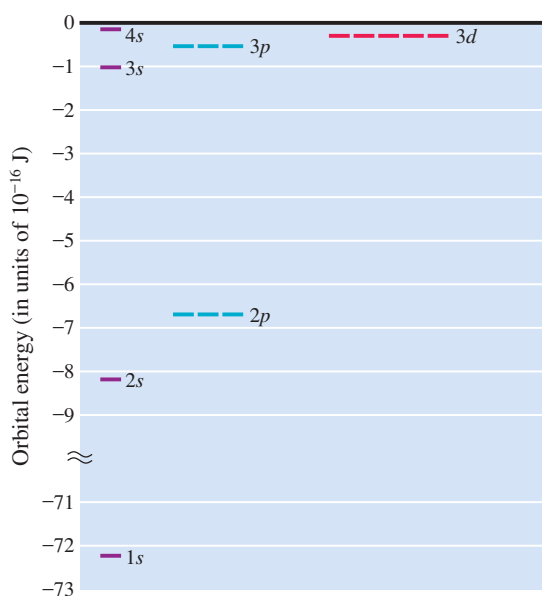
Most of the configurations in Table 8.1 can be explained in terms of the **building-up principle** (or **Aufbau principle**), a scheme used to reproduce the electron configurations of the ground states of atoms by successively filling subshells with electrons in a specific order (the building-up order). Following this principle, you obtain the electron configuration of an atom by successively filling subshells in the following order: $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f$. This order reproduces the experimentally determined electron configurations (with some exceptions, which we will discuss later). You need not memorize this order. As you will see, you can very easily obtain it from the periodic table. (You can also reproduce this order from the mnemonic diagram shown in Figure 8.7.)

The building-up order corresponds for the most part to increasing energy of the subshells. You might expect this. By filling orbitals of lowest energy first, you usually get the lowest total energy (ground state) of the atom. Recall that the energy of an orbital depends only on the quantum numbers n and l . (The energy of the H atom, however, depends only on n .) Orbitals with the same n and l but different m_l —that is, different orbitals of the same subshell—have the same energy. The energy depends primarily on n , increasing with its value. For example, a $3s$ orbital has greater energy than a $2s$ orbital. Except for the H atom, the energies of orbitals with the same n increase with the l quantum number. A $3p$ orbital has slightly greater energy than a $3s$ orbital. The orbital of lowest energy is $1s$; next higher are $2s$ and $2p$, then $3s$ and $3p$. The order of these subshells by energy, from $1s$ to $3p$, follows the building-up order as listed earlier.

When subshells have nearly the same energy, however, the building-up order is not strictly determined by the order of their energies. The ground-state configurations, which we are trying to predict by the building-up order, are determined by the *total* energies of the atoms. The total energy of an atom depends not only on the energies of the subshells but also on the energies of interaction among the different subshells. It so happens that for all elements with $Z = 21$ or greater, the energy of the $3d$ subshell is lower than the energy of the $4s$ subshell (Figure 8.8), which is opposite to the

FIGURE 8.8 ►
Orbital energies for the scandium atom ($Z = 21$)

Note that in the scandium atom, unlike the hydrogen atom, the subshells for each n are spread apart in energy. Thus, the $2p$ energy is above the $2s$. Similarly, the $n = 3$ subshells are spread to give the order $3s < 3p < 3d$. The $3d$ subshell energy is now just below the $4s$. (Values for this figure were calculated from theory by Charlotte F. Fischer, Vanderbilt University.)



building-up order. You need the building-up order to predict the electron configurations of the ground states of atoms.

Now you can see how to reproduce the electron configurations of Table 8.1 using the building-up principle. Remember that the number of electrons in a neutral atom equals the atomic number Z . (The nuclear charge is $+Z$.) In the case of the simplest atom, hydrogen ($Z = 1$), you obtain the ground state by placing the single electron into the $1s$ orbital, giving the configuration $1s^1$ (this is read as “one-ess-one”). Now you go to helium ($Z = 2$). The first electron goes into the $1s$ orbital, as in hydrogen, followed by the second electron, because any orbital can hold two electrons. The configuration is $1s^2$. Filling the $n = 1$ shell creates a very stable configuration, and as a result, helium is chemically unreactive.

You continue this way through the elements, each time increasing Z by 1 and adding another electron. You obtain the configuration of an atom from that of the preceding element by adding an electron into the next available orbital, following the building-up order. In lithium ($Z = 3$), the first two electrons give the configuration $1s^2$, like helium, but the third electron goes into the next higher orbital in the building-up order, because the $1s$ orbital is now filled. This gives the configuration $1s^2 2s^1$. In beryllium ($Z = 4$), the fourth electron fills the $2s$ orbital, giving the configuration $1s^2 2s^2$.

Using the abbreviation [He] for $1s^2$, the configurations are

$Z = 3$ lithium $1s^2 2s^1$ or [He] $2s^1$

$Z = 4$ beryllium $1s^2 2s^2$ or [He] $2s^2$

With boron ($Z = 5$), the electrons begin filling the $2p$ subshell. You get

$Z = 5$ boron $1s^2 2s^2 2p^1$ or [He] $2s^2 2p^1$

$Z = 6$ carbon $1s^2 2s^2 2p^2$ or [He] $2s^2 2p^2$

⋮

⋮

$Z = 10$ neon $1s^2 2s^2 2p^6$ or [He] $2s^2 2p^6$

Having filled the $2p$ subshell, you again find a particularly stable configuration. Neon is chemically unreactive as a result.

With sodium ($Z = 11$), the $3s$ orbital begins to fill. Using the abbreviation [Ne] for $1s^2 2s^2 2p^6$, you have

$Z = 11$ sodium $1s^2 2s^2 2p^6 3s^1$ or [Ne] $3s^1$

$Z = 12$ magnesium $1s^2 2s^2 2p^6 3s^2$ or [Ne] $3s^2$

Then the $3p$ subshell begins to fill.

$Z = 13$ aluminum $1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne] $3s^2 3p^1$

⋮

⋮

$Z = 18$ argon $1s^2 2s^2 2p^6 3s^2 3p^6$ or [Ne] $3s^2 3p^6$

With the $3p$ subshell filled, a stable configuration has been attained; argon is an unreactive element.

Now the $4s$ orbital begins to fill. You get [Ar] $4s^1$ for potassium ($Z = 19$) and [Ar] $4s^2$ for calcium ($Z = 20$) ([Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$). At this point the $3d$ subshell begins to fill. You get [Ar] $3d^1 4s^2$ for scandium ($Z = 21$), [Ar] $3d^2 4s^2$ for titanium ($Z = 22$), and [Ar] $3d^3 4s^2$ for vanadium ($Z = 23$). *Note that we have written the configurations with subshells arranged in order by shells.* This generally places the subshells in order by energy and puts the subshells involved in chemical reactions at the far right. <

Let us skip to zinc ($Z = 30$). The $3d$ subshell has filled; the configuration is [Ar] $3d^{10} 4s^2$. Now the $4p$ subshell begins to fill, starting with gallium ($Z = 31$),

Although the building-up order reproduces the ground-state electron configurations, it has no other significance. The order by n (and then by l within a given n), however, generally places the most easily ionized orbitals at the far right. For example, the electron configuration of Fe (in order by shells) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. The $4s$ electrons ionize first.

configuration $[\text{Ar}]3d^{10}4s^24p^1$, and ending with krypton ($Z = 36$), configuration $[\text{Ar}]3d^{10}4s^24p^6$.

Electron Configurations and the Periodic Table

By this time you can see a pattern develop among the ground-state electron configurations of the atoms. This pattern explains the periodic table, which was briefly described in Section 2.5. Consider helium, neon, argon, and krypton, elements in Group VIIIA of the periodic table. Neon, argon, and krypton have configurations in which a p subshell has just filled. (Helium has a filled $1s$ subshell; no $1p$ subshell is possible.)

helium	$1s^2$
neon	$1s^22s^22p^6$
argon	$1s^22s^22p^63s^23p^6$
krypton	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$

These elements are the first members of the group called *noble gases* because of their relative unreactivity.

Look now at the configurations of beryllium, magnesium, and calcium, members of the group of *alkaline earth metals* (Group IIA), which are similar, moderately reactive elements.

beryllium	$1s^22s^2$	or	$[\text{He}]2s^2$
magnesium	$1s^22s^22p^63s^2$	or	$[\text{Ne}]3s^2$
calcium	$1s^22s^22p^63s^23p^64s^2$	or	$[\text{Ar}]4s^2$

Each of these configurations consists of a **noble-gas core**, that is, an *inner-shell configuration corresponding to one of the noble gases*, plus two outer electrons with an ns^2 configuration.

The elements boron, aluminum, and gallium (Group IIIA) also have similarities. Their configurations are

boron	$1s^22s^22p^1$	or	$[\text{He}]2s^22p^1$
aluminum	$1s^22s^22p^63s^23p^1$	or	$[\text{Ne}]3s^23p^1$
gallium	$1s^22s^22p^63s^23p^63d^{10}4s^24p^1$	or	$[\text{Ar}]3d^{10}4s^24p^1$

Boron and aluminum have noble-gas cores plus three electrons with the configuration ns^2np^1 . Gallium has an additional filled $3d$ subshell. *The noble-gas core together with $(n - 1)d^{10}$ electrons* is often referred to as a **pseudo-noble-gas core**, because these electrons usually are not involved in chemical reactions.

An electron in an atom outside the noble-gas or pseudo-noble-gas core is called a **valence electron**. Such electrons are primarily involved in chemical reactions, and similarities among the configurations of valence electrons (the *valence-shell configurations*) account for similarities of the chemical properties among groups of elements.

Figure 8.9 shows a periodic table with the valence-shell configurations included. Note the similarity in electron configuration within any group (column) of elements. This similarity explains what chemists since Mendeleev have known—the properties of elements in any group are similar.

The *main-group* (or *representative*) *elements* all have valence-shell configurations $ns^a np^b$, with some choice of a and b . (b could be equal to 0.) In other words, the outer s or p subshell is being filled. Similarly, in the *d-block transition elements* (often called simply *transition elements* or *transition metals*), a d subshell is being filled. In the *f-block transition elements* (or *inner transition elements*), an

Main-Group Elements <i>s</i> subshell fills														Main-Group Elements <i>p</i> subshell fills									
IA														VIII A									
1 H 1s ¹														2 He 1s ²									
3 Li 2s ¹														4 Be 2s ²									
11 Na 3s ¹														18 Ar 3s ² 3p ⁶									
19 K 4s ¹														36 Kr 4s ² 4p ⁶									
37 Rb 5s ¹														54 Xe 5s ² 5p ⁶									
55 Cs 6s ¹														87 Fr 7s ¹									
89 Ac 6d ¹ 7s ²														103 La 5f ¹ 6d ¹ 7s ²									
91 Pa 5f ² 6d ¹ 7s ²														105 Db 6d ³ 7s ²									
93 Np 5f ⁴ 6d ¹ 7s ²														107 Bh 6d ⁵ 7s ²									
95 Am 5f ⁷ 7s ²														109 Mt 6d ⁷ 7s ²									
97 Bk 5f ⁹ 7s ²														111 Rg 6d ⁹ 7s ²									
99 Es 5f ¹¹ 7s ²														113 Uut 7s ³ 7p ¹									
101 Md 5f ¹³ 7s ²														115 Uup 7s ³ 7p ³									
103 La 5f ¹ 6d ¹ 7s ²														117 Uus 7s ³ 7p ⁵									
105 Db 6d ³ 7s ²														119 Uuo 7s ³ 7p ⁵									
107 Bh 6d ⁵ 7s ²														121 Ubu 7s ³ 7p ⁵									
109 Mt 6d ⁷ 7s ²														123 Ubu 7s ³ 7p ⁵									
111 Rg 6d ⁹ 7s ²														125 Ubu 7s ³ 7p ⁵									
113 Uut 7s ³ 7p ¹														127 Ubu 7s ³ 7p ⁵									
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Instrumental Methods



X Rays, Atomic Numbers, and Orbital Structure (Photoelectron Spectroscopy)

In 1913 Henry G. J. Moseley, a student of Rutherford, used the technique of x-ray spectroscopy (just discovered by Max von Laue) to determine the atomic numbers of the elements. X rays are

produced in a cathode-ray tube when the electron beam (cathode ray) falls on a metal target. The explanation for the production of x rays is as follows: When an electron in the cathode ray hits a metal atom in the target, it can (if it has sufficient energy) knock an electron from an inner shell of the atom. This produces a metal ion with an electron missing from an inner orbital. The electron configuration is unstable, and an electron from an orbital of higher energy drops into the half-filled orbital and a photon is emitted. The photon corresponds to electromagnetic radiation in the x-ray region.

The energies of the inner orbitals of an atom and the energy changes between them depend on the nuclear charge, $+Z$. Therefore, the photon energies $h\nu$ and the frequencies ν of emitted x rays depend on the atomic number Z of the metal atom in the target. Figure 8.10 shows the x-ray spectra Moseley obtained with various metal targets. The direct dependence of the x-ray spectrum on atomic number provides an unequivocal way of deciding whether a substance is a pure element or not.

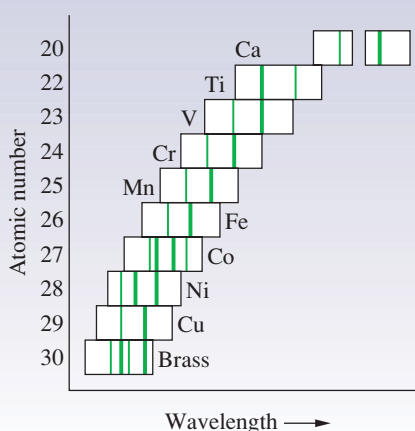
A related technique, *x-ray photoelectron spectroscopy*, experimentally confirms our theoretical view of the orbital structure of the atom. Instead of irradiating a sample with an electron beam and analyzing the frequencies of emitted x rays, you irradiate a sample with x rays and analyze the kinetic energies of ejected electrons. In other words, you observe the *photoelectric effect* on the sample (see Section 7.2).

As an example of photoelectron spectroscopy, consider a sample of neon gas (Ne atoms). Suppose the sample

FIGURE 8.10 ►

X-ray spectra of the elements calcium to zinc, obtained by Moseley

Each line results from an emission of given wavelength. Because of the volatility of zinc, Moseley used brass (a copper–zinc alloy) to observe the spectrum of zinc. Note the copper lines in brass. Also note how the lines progress to the right (indicating increasing wavelength or decreasing energy difference) with decreasing atomic number. (From J. J. Lagowski, *The Structure of Atoms* (Boston: Houghton Mifflin, 1964), Figure 26, p. 80. Used by permission.)



Concept Check 8.1

Imagine a world in which the Pauli principle is “No more than one electron can occupy an atomic orbital, irrespective of its spin.” How many elements would there be in the second row of the periodic table, assuming that nothing else is different about this world?

8.3 Writing Electron Configurations Using the Periodic Table

To discuss bonding and the chemistry of the elements coherently, you must be able to reproduce the atomic configurations with ease, following the building-up principle. All you need is some facility in recall of the building-up order of subshells.

is irradiated with x rays of a specific frequency great enough to remove a 1s electron from the neon atom. Part of the energy of the x-ray photon, $h\nu$, is used to remove the electron from the atom. (This is the *ionization energy*, $I.E.$, for that electron.) The remaining energy appears as kinetic energy, E_k , of the ejected electron. From the law of conservation of energy, you can write

$$E_k = h\nu - I.E.$$

Because $h\nu$ is fixed, E_k will depend linearly on $I.E.$, the ionization energy.

If you look at the electrons ejected from neon, you find that they have kinetic energies related to the ionization energies from all possible orbitals (1s, 2s, and 2p) in the atom. When you scan the various kinetic energies of ejected electrons, you see a spectrum with peaks corresponding to the different occupied orbitals (see Figure 8.11A). These ionization energies are approximately equal to the positive values of the orbital energies (Figure 8.11B), so this spectrum provides direct experimental verification of the discrete energy levels associated with the electrons of the atom.

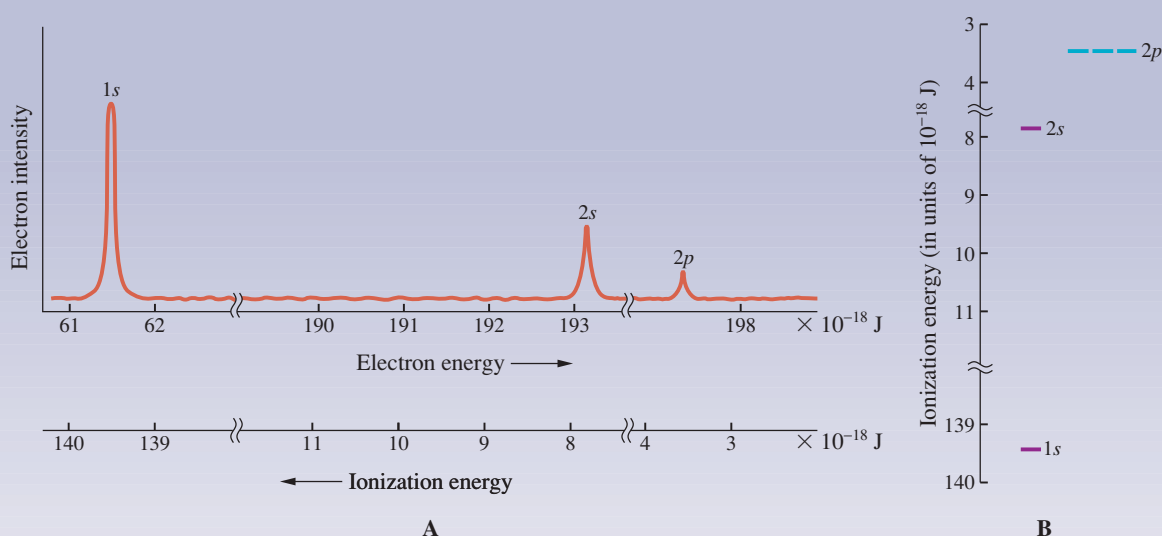


FIGURE 8.11 ▲

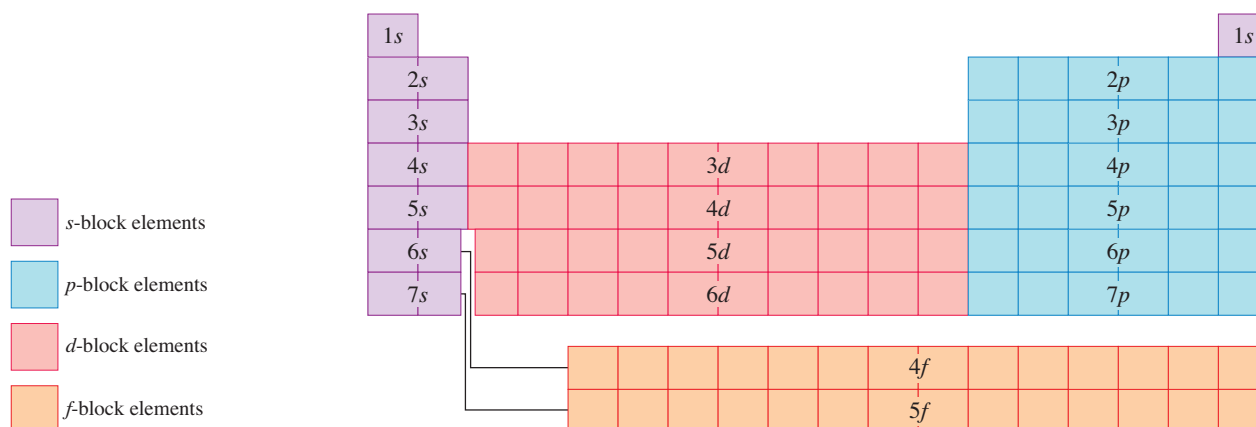
X-ray photoelectron spectrum of neon

(A) Each peak shows the energy of the ejected electrons. The energy of each x-ray photon is 200.9×10^{-18} J. (B) The energy-level diagram for neon. The transitions that occur in the photoelectron spectrum are to $n = \infty$, where the energy = 0.

■ See Problems 8.87 and 8.88.

One approach is to recall the structure of the periodic table. Because that structure is basic, it offers a sound way to remember the building-up order. There is a definite pattern to the order of filling of the subshells as you go through the elements in the periodic table, and from this you can write the building-up order. Figure 8.12 shows a periodic table stressing this pattern. For example, in the violet-colored area, an ns subshell is being filled. In the blue-colored area, an np subshell is being filled. The value of n is obtained from the period (row) number. In the red area, an $(n - 1)d$ subshell is being filled.

You read the building-up order by starting with the first period, in which the 1s subshell is being filled. In the second period, you have 2s (violet area); then, staying in the same period but jumping across, you have 2p (blue area). In the third period, you have 3s and 3p; in the fourth period, 4s (violet area), 3d (red area), and 4p (blue area). This

**FIGURE 8.12** ▲**A periodic table illustrating the building-up order**

The colored areas of elements show the different subshells that are filling with those elements.

pattern should become clear enough to visualize with a periodic table that is not labeled with the subshells, such as the one on the inside front cover of this book. The detailed method is illustrated in the next example. (An alternative way to reconstruct the building-up order of subshells is to write the diagram in Figure 8.7.)

Note on writing electron configurations of atoms: If you write the configuration of an atom with its subshells arranged by shells, the orbitals will usually be in order by energy, with the subshells used to describe chemical reactions at the far right. For example, the configuration of Br would be written $[\text{Ar}]3d^{10}4s^24p^5$. However, you will also see the orbitals in a configuration written in the building-up order, which is an empirical order that has been found to reproduce most of the atomic configurations. The configuration of Br would be written $[\text{Ar}]4s^23d^{10}4p^5$. Ask your instructor whether he or she has a preference.

Example 8.2**Determining the Configuration of an Atom Using the Building-Up Principle**

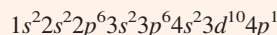
Use the building-up principle to obtain the configuration for the ground state of the gallium atom ($Z = 31$). Give the configuration in complete form (do not abbreviate for the core). What is the valence-shell configuration?

Problem Strategy Write the subshells in their building-up order. You can use any periodic table to do this. All you have to remember is the pattern in which subshells are filled as you progress through the table (Figure 8.12). Go through the periods, starting with hydrogen, writing the subshells that are being filled, and stopping with the element whose configuration you want (gallium in this example). Then you distribute the electrons (equal to the atomic number of the element) to the subshells. The valence-shell configuration includes only the subshells outside the noble-gas or pseudo-noble-gas core.

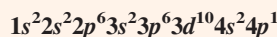
Solution From a periodic table, you get the following building-up order:

	1s	2s 2p	3s 3p	4s 3d 4p
Period:	first	second	third	fourth

Now you fill the subshells with electrons, remembering that you have a total of 31 electrons to distribute. You get



Or, if you rearrange the subshells by shells, you write



The valence-shell configuration is $4s^2 4p^1$.

(continued)

(continued)

Answer Check The principal quantum number of the valence shell must equal the period of the element. If your answer is not consistent with this, examine your work for error. Here, gallium is in period 4, and the principal quantum number of the valence shell is 4.

Exercise 8.2

Use the building-up principle to obtain the electron configuration for the ground state of the manganese atom ($Z = 25$).

■ See Problems 8.47, 8.48, 8.49, and 8.50.

In many cases, you need only the configuration of the outer electrons. You can determine this from the position of the element in the periodic table. Recall that the valence-shell configuration of a main-group element is $ns^a np^b$, where n , the principal quantum number of the outer shell, also equals the period number for the element. The total number of valence electrons, which equals $a + b$, can be obtained from the group number. For example, gallium is in Period 4, so $n = 4$. It is in Group IIIA, so the number of valence electrons is 3. This gives the valence-shell configuration $4s^2 4p^1$. The configuration of outer shells of a transition element is obtained in a similar fashion. The next example gives the details.

Example 8.3**Determining the Configuration of an Atom Using the Period and Group Numbers**

What are the configurations for the outer electrons of a. tellurium, $Z = 52$, and b. nickel, $Z = 28$?

Problem Strategy Find the period and the group number (the Roman numeral) of the element for the atom. Note whether it is a main-group or a transition element.

If the atom is that of a main-group element, the valence configuration is $ns^a np^b$, where n equals the period of the element and $a + b$ equals the group number (which equals the number of valence electrons). Distribute these electrons to the ns orbital; then distribute any remaining electrons to the np orbitals.

If the atom is that of a transition element, the outer-shell configuration is $(n - 1)d^{a-2} ns^2$, where n equals the period and a is the group number—except for Group VIIIB, which has three columns. For Group VIIIB, count 8, 9, then 10 for successive columns, which then equals a .

Solution a. You locate tellurium in a periodic table and find it to be in Period 5, Group VIA. Thus, it is a main-group element, and the outer subshells are $5s$ and $5p$. These subshells contain six electrons, because the group is VIA. The valence-shell configuration is $5s^2 5p^4$. b. Nickel is a Period 4 transition element, in which

the general form of the outer-shell configuration is $3d^{a-2} 4s^2$. To determine a, you note that it equals the Roman numeral group number up to iron (8). After that you count Co as 9 and Ni as 10. Hence, the outer-shell configuration is $3d^8 4s^2$.

Answer Check

Note whether the configuration does follow the general form, either for a main-group element or a transition element. Check that the principal quantum number, n , equals the period of the element. For a main-group element, the total number of valence electrons should equal the group number. For a transition element, the number of electrons in the outer shell equals a .

Exercise 8.3

Using the periodic table on the inside front cover, write the valence-shell configuration of arsenic (As).

■ See Problems 8.51, 8.52, 8.53, and 8.54.

Exercise 8.4

The lead atom has the ground-state configuration $[\text{Xe}]4f^{14}5d^{10}6s^2 6p^2$. Find the period and group for this element. From its position in the periodic table, would you classify lead as a main-group element, a transition element, or an inner transition element?

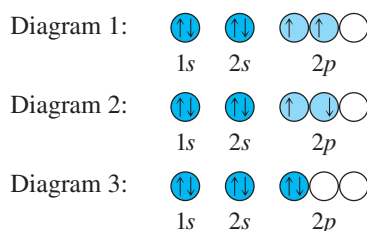
■ See Problems 8.55 and 8.56.

Concept Check 8.2

Two elements in Period 3 are adjacent to one another in the periodic table. The ground-state atom of one element has only s electrons in its valence shell; the other one has at least one p electron in its valence shell. Identify the elements.

8.4 Orbital Diagrams of Atoms; Hund's Rule

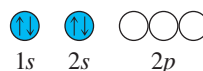
In discussing the ground states of atoms, we have not yet described how the electrons are arranged within each subshell. There may be several different ways of arranging electrons in a particular configuration. Consider the carbon atom ($Z = 6$) with the ground-state configuration $1s^2 2s^2 2p^2$. Three possible arrangements are given in the following orbital diagrams.



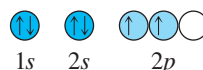
These orbital diagrams show different states of the carbon atom. Each state has a different energy and, as you will see, different magnetic characteristics.

Hund's Rule

In about 1927, Friedrich Hund discovered an empirical rule determining the lowest-energy arrangement of electrons in a subshell. **Hund's rule** states that *the lowest-energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before pairing electrons*. Let us see how this would apply to the carbon atom, whose ground-state configuration is $1s^2 2s^2 2p^2$. The first four electrons go into the $1s$ and $2s$ orbitals.

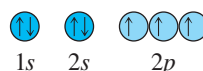


The next two electrons go into separate $2p$ orbitals, with both electrons having the same spin, following Hund's rule.

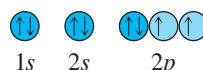


We see that the orbital diagram corresponding to the lowest energy is the one we previously labeled Diagram 1.

To apply Hund's rule to the oxygen atom, whose ground-state configuration is $1s^2 2s^2 2p^4$, we place the first seven electrons as follows:



The last electron is paired with one of the $2p$ electrons to give a doubly occupied orbital. The orbital diagram for the ground state of the oxygen atom is



In the following example, Hund's rule is used to determine the orbital diagram for the ground state of a more complicated atom. Table 8.2 gives orbital diagrams for the ground states of the first ten elements.

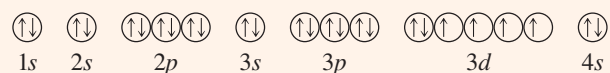
Example 8.4**Applying Hund's Rule**

Write an orbital diagram for the ground state of the iron atom.

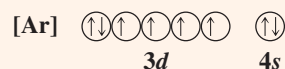
Problem Strategy First obtain the electron configuration, as described in Example 8.2. Then draw circles for the orbitals of each subshell. A filled subshell should have doubly occupied orbitals (two electrons with opposite spins). For a partially filled subshell, apply Hund's rule, putting electrons into separate orbitals with the same spin (either all up or all down) before pairing electrons.

Solution The electron configuration of the iron atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. All the subshells except the $3d$ are filled. In placing the six electrons in the $3d$ subshell, you note that the first five go into separate $3d$ orbitals with their spin arrows in the same direction. The sixth

electron must doubly occupy a $3d$ orbital. The orbital diagram is



You can write this diagram in abbreviated form using [Ar] for the argon-like core of the iron atom:



Answer Check Check that you have started with the correct configuration for the atom. Then note that you have followed Hund's rule for a partially filled subshell.

Exercise 8.5

Write an orbital diagram for the ground state of the phosphorus atom ($Z = 15$). Write all orbitals.

■ See Problems 8.57 and 8.58.

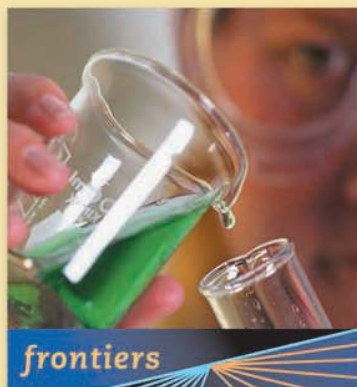
TABLE 8.2**Orbital Diagrams for the Ground States of Atoms from $Z = 1$ to $Z = 10$**

Atom	Z	Configuration	Orbital Diagram		
			1s	2s	2p
Hydrogen	1	$1s^1$			
Helium	2	$1s^2$			
Lithium	3	$1s^2 2s^1$			
Beryllium	4	$1s^2 2s^2$			
Boron	5	$1s^2 2s^2 2p^1$			
Carbon	6	$1s^2 2s^2 2p^2$			
Nitrogen	7	$1s^2 2s^2 2p^3$			
Oxygen	8	$1s^2 2s^2 2p^4$			
Fluorine	9	$1s^2 2s^2 2p^5$			
Neon	10	$1s^2 2s^2 2p^6$			

Magnetic Properties of Atoms

The magnetic properties of a substance can reveal certain information about the arrangement of electrons in an atom (or molecule). Although an electron in an atom behaves like a small magnet, the magnetic attractions from two electrons that are opposite in spin cancel each other. As a result, an atom that has only doubly occupied orbitals has no net spin magnetism. However, an atom with *unpaired* electrons—that is, with an excess of one kind of spin—does exhibit a net magnetism.

A Chemist Looks at . . .



Levitating Frogs and People

Have you ever seen a magic act in which a person rises above the stage in apparent defiance of gravity? Magicians have often included such acts of “levitation” as part of their performances.

Of course, magical levitation uses tricks to deceive you. But levitation can be done, without tricks, using the known laws of electromagnetism.

Recently, researchers wanted to demonstrate that you can levitate almost anything if you have the proper magnetic field. They placed a frog within the magnetic field of a powerful electromagnet (which consists of an electric current flowing through a coil of wire). The frog floated in midair above the coil, at the point where the upward repulsion of the frog from the magnetic field just balanced the downward force of gravity (Figure 8.13).

We don’t usually think of things such as frogs as being magnetic. In fact, most materials, including most substances in a biological organism, are diamagnetic. They contain pairs of electrons, in which the magnetism of each electron in a pair offsets the equal and opposite magnetism of the other electron. You might expect diamagnetic materials to be nonmagnetic because of this balance of opposite electron spins. But when you place a diamagnetic material in an external magnetic field, its electrons move so as to induce, or generate, a smaller magnetic field that is

opposite in direction to the external field. This results in a repulsive force between the diamagnetic material and the external field. The repulsive force, though generally small, can be easily observed if the external magnet is large enough. Although, with a sufficiently large magnet, it would be possible to levitate a person as well as a frog, the researchers don’t plan to do that.



FIGURE 8.13 ▲

Levitation of a frog

A frog placed in a powerful magnetic field, generated by a current flowing through a water-cooled coil of wire, appears to float in midair in defiance of gravity. The frog contains materials that are diamagnetic (composed of electron pairs), which are repelled by the magnetic field.

■ See Problems 8.89 and 8.90.

The strong, permanent magnetism seen in iron objects is called ferromagnetism and is due to the cooperative alignment of electron spins in many iron atoms. Paramagnetism is a much weaker effect. Nevertheless, paramagnetic substances can be attracted to a strong magnet. Liquid oxygen is composed of paramagnetic O_2 molecules. When poured over a magnet, the liquid clings to the poles. (See Figure 10.29.)

The magnetic properties of an atom can be observed. The most direct way is to determine whether the atomic substance is attracted to the field of a strong magnet. A **paramagnetic substance** is a substance that is weakly attracted by a magnetic field, and this attraction is generally the result of unpaired electrons. < For example, sodium vapor has been found experimentally to be paramagnetic. The explanation is that the vapor consists primarily of sodium atoms, each containing an unpaired electron. (The configuration is $[Ne]3s^1$.) A **diamagnetic substance** is a substance that is not attracted by a magnetic field or is very slightly repelled by such a field. This property generally means that the substance has only paired electrons. Mercury vapor is found experimentally to be diamagnetic. The explanation is that mercury vapor consists of mercury atoms, with the electron configuration $[Xe]4f^{14}5d^{10}6s^2$, which has only paired electrons.

We expect the different orbital diagrams presented at the beginning of this section for the $1s^2 2s^2 2p^2$ configuration of the carbon atom to have different magnetic properties. Diagram 1, predicted by Hund’s rule to be the ground state, would give a

magnetic atom, whereas the other diagrams would not. If we could prepare a vapor of carbon atoms, it should be attracted to a magnet. (It should be paramagnetic.) It is difficult to prepare a vapor of free carbon atoms in sufficient concentration to observe a result. However, the visible-ultraviolet spectrum of carbon atoms can be obtained easily from dilute vapor. From an analysis of this spectrum, it is possible to show that the ground-state atom is magnetic, which is consistent with the prediction of Hund's rule.

Periodicity of the Elements

You have seen that the periodic table that Mendeleev discovered in 1869 can be explained by the periodicity of the ground-state electron configurations of the atoms. Now we will look at various aspects of the periodicity of the elements.

8.5 Mendeleev's Predictions from the Periodic Table

One of Mendeleev's periodic tables is reproduced in Figure 8.14. Though somewhat different from modern tables, it shows essentially the same arrangement. In this early form of the periodic table, within each column some elements were placed toward the left side and some toward the right. With some exceptions, the elements on a given side have similar properties. Mendeleev left spaces in his periodic table for what he felt were undiscovered elements. There are blank spaces in his row 5—for example, one directly under aluminum and another under silicon (looking at just the elements on the right side of the column). By writing the known elements in this row with their atomic weights, he could determine approximate values (between the known ones) for the missing elements (values in parentheses).

Cu Zn — — As Se Br
63 amu 65 amu (68 amu) (72 amu) 75 amu 78 amu 80 amu

The Group III element directly under aluminum Mendeleev called eka-aluminum, with the symbol Ea. (*Eka* is the Sanskrit word meaning “first”; thus eka-aluminum is the first element under aluminum.) The known Group III elements have oxides of the form R_2O_3 , so Mendeleev predicted that eka-aluminum would have an oxide with the formula Ea_2O_3 .

The physical properties of this undiscovered element could be predicted by comparing values for the neighboring known elements. For eka-aluminum Mendeleev

FIGURE 8.14 ▶

Mendeleev's periodic table

This one was published in 1872.

T a b e l l e II.								
Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O_3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	B=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	—
9	(—)	—	—	—	—	—	—	—
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	—
12	—	—	—	Th=231	—	U=240	—	—

predicted a density of 5.9 g/cm^3 , a low *melting point* (the temperature at which a substance melts), and a high *boiling point* (the temperature at which a substance boils).

In 1874 the French chemist Paul-Émile Lecoq de Boisbaudran found two previously unidentified lines in the atomic spectrum of a sample of sphalerite (a zinc sulfide, ZnS , mineral). Realizing he was on the verge of a discovery, Lecoq de Boisbaudran quickly prepared a large batch of the zinc mineral, from which he isolated a gram of a new element. He called this new element gallium. The properties of gallium were remarkably close to those Mendeleev predicted for eka-aluminum.

<i>Property</i>	<i>Predicted for Eka-Aluminum</i>	<i>Found for Gallium</i>
Atomic weight	68 amu	69.7 amu
Formula of oxide	Ea_2O_3	Ga_2O_3
Density of the element	5.9 g/cm^3	5.91 g/cm^3
Melting point of the element	Low	30.1°C
Boiling point of the element	High	1983°C

The predictive power of Mendeleev's periodic table was demonstrated again when scandium (eka-boron) was discovered in 1879 and germanium (eka-silicon) in 1886. Both elements had properties remarkably like those predicted by Mendeleev. These early successes won acceptance for the organizational and predictive power of the periodic table.

8.6 Some Periodic Properties

The electron configurations of the atoms display a periodic variation with increasing atomic number (nuclear charge). As a result, the elements show periodic variations of physical and chemical behavior. The **periodic law** states that *when the elements are arranged by atomic number, their physical and chemical properties vary periodically*. In this section, we will look at three physical properties of an atom: atomic radius, ionization energy, and electron affinity. These three quantities, especially ionization energy and electron affinity, are important in discussions of chemical bonding (the subject of Chapter 9).

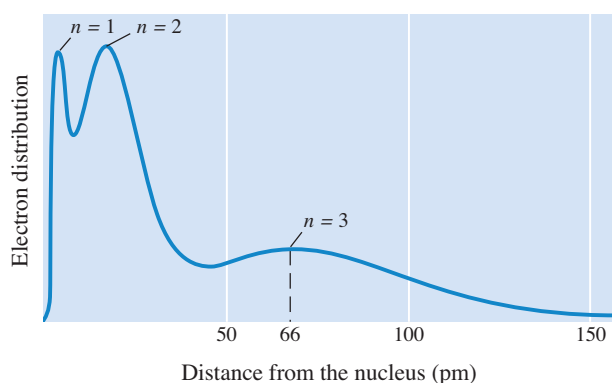


FIGURE 8.15 ▲

Electron distribution for the argon atom

This is a radial distribution, showing the probability of finding an electron at a given distance from the nucleus. The distribution shows three maxima, for the $n = 1$, $n = 2$, and $n = 3$ shells. The outermost maximum occurs at 66 pm; then the distribution falls steadily, becoming negligibly small after several hundred picometers.

Atomic Radius

An atom does not have a definite size, because the statistical distribution of electrons does not abruptly end but merely decreases to very small values as the distance from the nucleus increases. This can be seen in the plot of the electron distribution for the argon atom, shown in Figure 8.15. Consequently, atomic size must be defined in a somewhat arbitrary manner, so various measures of atomic size exist. The atomic radii plotted in Figure 8.16 and also represented in Figure 8.17 are *covalent radii*, which are obtained from measurements of distances

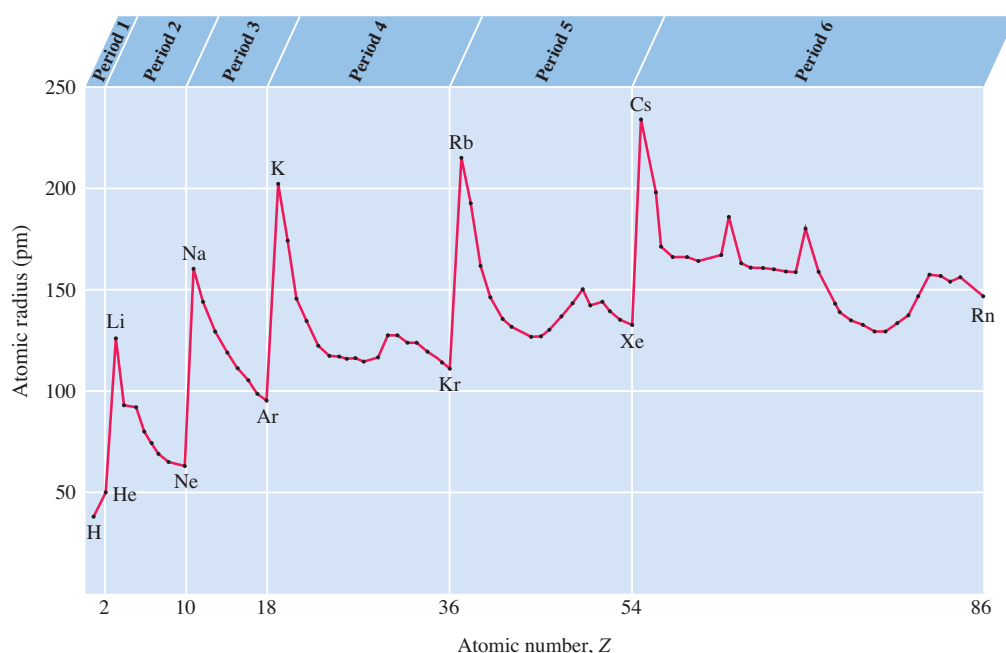
between the nuclei of atoms in the chemical bonds of molecular substances. (The determination and use of covalent radii are discussed in Chapter 9.)

Figures 8.16 and 8.17 show the following general trends in size of atomic radii:

1. Within each period (horizontal row), the atomic radius tends to decrease with increasing atomic number (nuclear charge). The largest atom in a period is a Group IA atom and the smallest is a noble-gas atom.
2. Within each group (vertical column), the atomic radius tends to increase with the period number.

FIGURE 8.16 ▶**Atomic radius (covalent radius) versus atomic number**

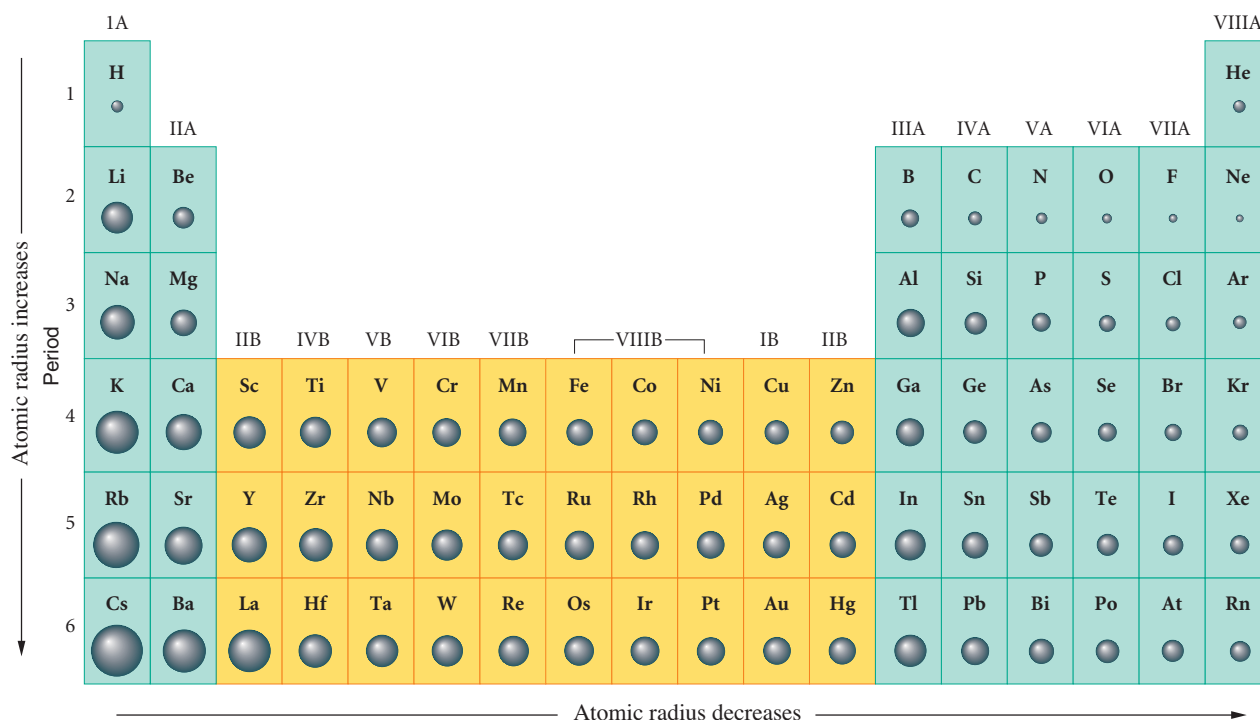
Note that the curve is periodic (tends to repeat). Each period of elements begins with the Group IA atom, and the atomic radius tends to decrease until the Group VIIIA atom. (Values for He, Ne, and Ar are estimated because there are no known compounds.)



The atomic radius increases greatly going from any noble-gas atom to the following Group IA atom, giving the curve in Figure 8.16 a saw-tooth appearance. A similar diagram is obtained for other measures of atomic size.

FIGURE 8.17 ▼**Representation of atomic radii (covalent radii) of the main-group elements**

Note the trends within each period and each group.



increasing the effective nuclear charge reduces the size of the orbital by pulling the electrons inward. The **effective nuclear charge** is the positive charge that an electron experiences from the nucleus, equal to the nuclear charge but reduced by any shielding or screening from any intervening electron distribution. Consider the effective nuclear charge on the 2s electron in the lithium atom (configuration $1s^2 2s^1$). The nuclear charge is $3e$, but the effect of this charge on the 2s electron is reduced by the distribution of the two 1s electrons lying between the nucleus and the 2s electron (roughly, each core electron reduces the nuclear charge by $1e$).

Consider a given period of elements. The principal quantum number of the outer orbitals remains constant. However, the effective nuclear charge increases, because the nuclear charge increases and the number of core electrons remains constant. Consequently, the size of the outermost orbital and, therefore, the radius of the atom decrease with increasing Z in any period.

Now consider a given column of elements. The effective nuclear charge remains nearly constant (approximately equal to e times the number of valence electrons), but n gets larger. You observe that the atomic radius increases.

Example 8.5

Determining Relative Atomic Sizes from Periodic Trends

Refer to a periodic table and use the trends noted for size of atomic radii to arrange the following in order of increasing atomic radius: Al, C, Si.

Problem Strategy The general trends in atomic radius are that it decreases left to right in a period and that it increases from top to bottom of a group. Compare any two elements in the same period, or in the same group, to decide which of the two is smaller. From this, decide the order of the elements.

Solution Note that C is above Si in Group IVA. Therefore, the radius of C is smaller than that of Si (the

atomic radius increases going down a group of elements). Note that Al and Si are in the same period. Therefore, the radius of Si is smaller than that of Al (radius decreases with Z in a period). Hence the order of elements by increasing radius is C, Si, Al.

Answer Check After you have decided on the order of the atoms, check that the atomic radius does indeed increase, left to right, as asked for in the problem.

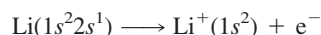
Exercise 8.6

Using a periodic table, arrange the following in order of increasing atomic radius: Na, Be, Mg.

■ See Problems 8.61 and 8.62.

Ionization Energy

The **first ionization energy** (or **first ionization potential**) of an atom is the minimum energy needed to remove the highest-energy (that is, the outermost) electron from the neutral atom in the gaseous state. (When the unqualified term *ionization energy* is used, it generally means first ionization energy.) For the lithium atom, the first ionization energy is the energy needed for the following process (electron configurations are in parentheses):



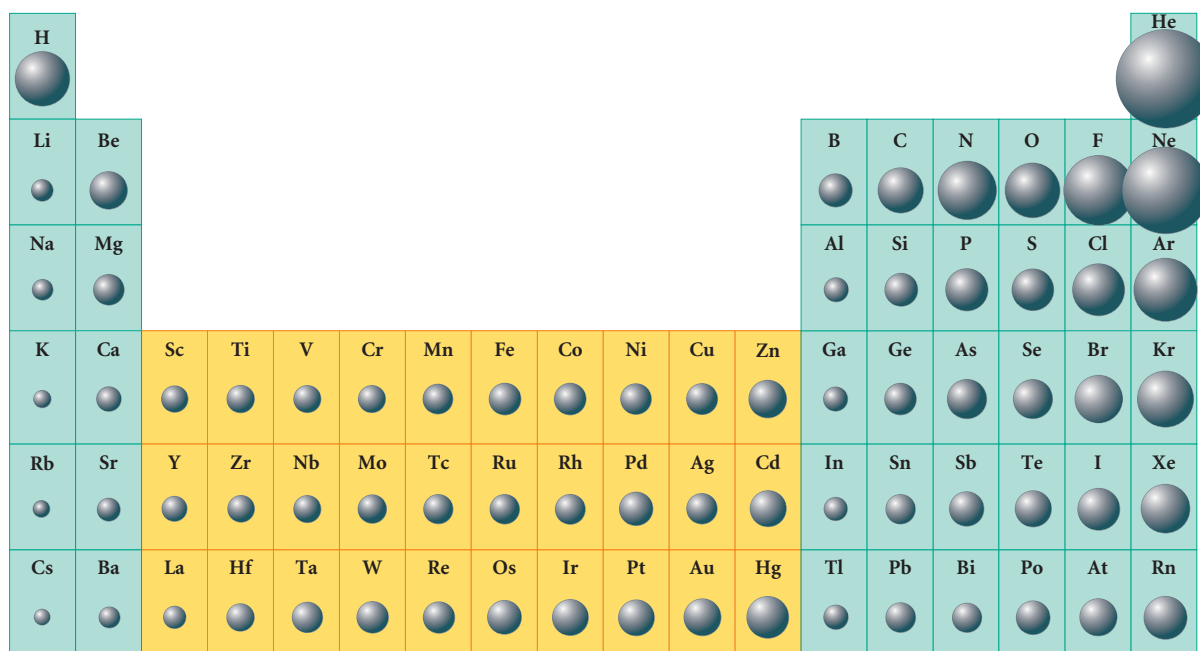
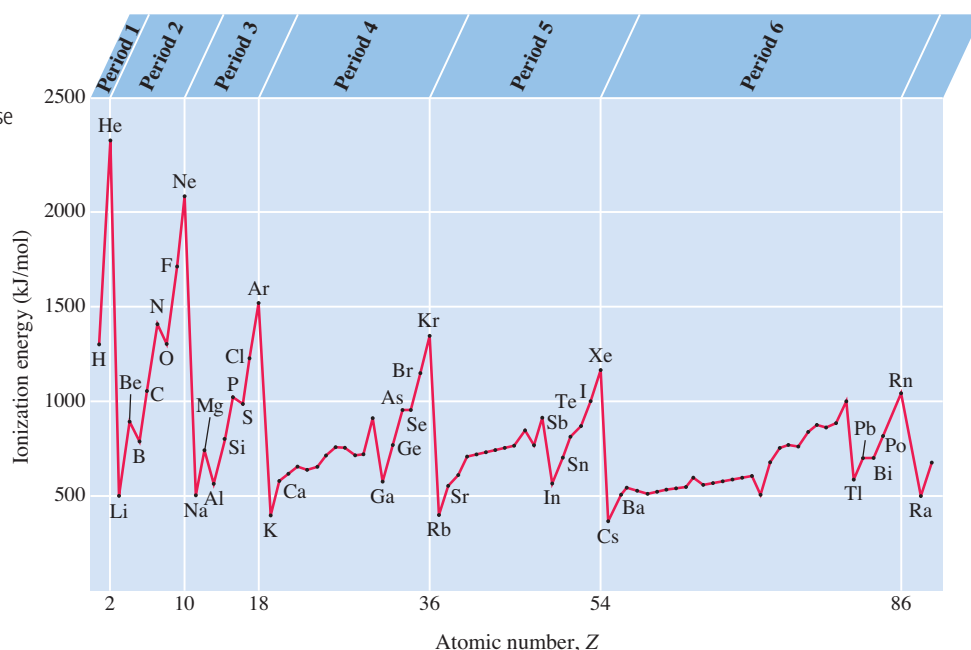
Values of this energy are usually quoted for one mole of atoms (6.02×10^{23} atoms). The ionization energy of the lithium atom is 520 kJ/mol. <

Ionization energies display a periodic variation when plotted against atomic number, as Figure 8.18 shows. Within any period, values tend to increase with atomic number. Thus, the lowest values in a period are found for the Group IA elements (*alkali metals*). It is characteristic of reactive metals such as these to lose electrons easily. The

Ionization energies are often measured in electron volts (eV). This is the amount of energy imparted to an electron when it is accelerated through an electrical potential of one volt. One electron volt is equivalent to 96.5 kJ/mol. (This is an easy conversion to remember; it is approximately one hundred kilojoules per mole.)

FIGURE 8.18**Ionization energy versus atomic number**

Top: Note that the values tend to increase within each period, except for small drops in ionization energy at the Group IIIA and VIA elements. Large drops occur when a new period begins. *Bottom:* Note the trends within each period. The size of the sphere for each atom indicates the relative magnitude of ionization energy.



largest ionization energies in any period occur for the noble-gas elements. In other words, a noble-gas atom loses electrons with difficulty, which is partly responsible for the stability of the noble-gas configurations and the unreactivity of the noble gases.

This general trend—increasing ionization energy with atomic number in a given period—can be explained as follows: The energy needed to remove an electron from the outer shell is proportional to the effective nuclear charge divided by the average distance between electron and nucleus. (This distance is inversely proportional to the effective nuclear charge.) Hence, the ionization energy is proportional to the square of the effective nuclear charge and increases going across a period.

Small deviations from this general trend occur. A IIIA element (ns^2np^1) has smaller ionization energy than the preceding IIA element (ns^2). Apparently, the np electron of the IIIA element is more easily removed than one of the ns electrons of the preceding IIA element. Also note that a VIA element (ns^2np^4) has smaller ionization energy than the preceding VA element. As a result of electron repulsion, it is easier to remove an electron from the doubly occupied np orbital of the VIA element than from a singly occupied orbital of the preceding VA element.

Ionization energies tend to decrease going down any column of main-group elements. This is because atomic size increases going down the column.

Example 8.6**Determining Relative Ionization Energies from Periodic Trends**

Using a periodic table only, arrange the following elements in order of increasing ionization energy: Ar, Se, S.

Problem Strategy The general trends in (first) ionization energy are that it increases from left to right in a period and that it decreases from top to bottom of a group. Compare any two elements in the same period, or in the same group, to decide which of the two is smaller. From this, decide the order of the elements.

Solution Note that Se is below S in Group VIA. Therefore, the ionization energy of Se should be less than that of S. Also, S and Ar are in the same period,

with Z increasing from S to Ar. Therefore, the ionization energy of S should be less than that of Ar. Hence the order is **Se, S, Ar**.

Answer Check After you have decided on the order of the atoms, check that the ionization energy does indeed increase, left to right, as asked for in the problem.

Exercise 8.7 The first ionization energy of the chlorine atom is 1251 kJ/mol. Without looking at Figure 8.18, state which of the following values would be the more likely ionization energy for the iodine atom. Explain. a. 1000 kJ/mol. b. 1400 kJ/mol.

■ See Problems 8.63 and 8.64.

The electrons of an atom can be removed successively. The energies required at each step are known as the *first* ionization energy, the *second* ionization energy, and so forth. Table 8.3 lists the successive ionization energies of the first ten elements. Note that the ionization energies for a given element increase as more electrons are removed. The first and second ionization energies of beryllium (electron configuration $1s^22s^2$) are 899 kJ/mol and 1757 kJ/mol, respectively. The first ionization energy

TABLE 8.3**Successive Ionization Energies of the First Ten Elements (kJ/mol)***

Element	First	Second	Third	Fourth	Fifth	Sixth	Seventh
H	1312						
He	2372	5250					
Li	520	7298	11,815				
Be	899	1757	14,848	21,006			
B	801	2427	3660	25,025	32,826		
C	1086	2353	4620	6222	37,829	47,276	
N	1402	2857	4578	7475	9445	53,265	64,358
O	1314	3388	5300	7469	10,989	13,326	71,333
F	1681	3374	6020	8407	11,022	15,164	17,867
Ne	2081	3952	6122	9370	12,177	15,238	19,998

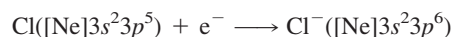
*Ionization energies to the right of a vertical line correspond to removal of electrons from the core of the atom.

is the energy needed to remove a $2s$ electron from the Be atom. The second ionization energy is the energy needed to remove a $2s$ electron from the positive ion Be^+ . Its value is greater than that of the first ionization energy because the electron is being removed from a positive ion, which strongly attracts the electron.

Note that there is a large jump in value from the second ionization energy of Be (1757 kJ/mol) to the third ionization energy (14,848 kJ/mol). The second ionization energy corresponds to removing a valence electron (from the $2s$ orbital), which is relatively easy. The third ionization energy corresponds to removing an electron from the core of the atom (from the $1s$ orbital)—that is, from a noble-gas configuration ($1s^2$). A vertical line in Table 8.3 separates the energies needed to remove valence electrons from those needed to remove core electrons. For each element, a large increase in ionization energy occurs when this line is crossed. The large increase results from the fact that once the valence electrons are removed, a stable noble-gas configuration is obtained. Further ionizations become much more difficult. We will see in Chapter 9 that metal atoms often form compounds by losing valence electrons; core electrons are not significantly involved in the formation of compounds.

Electron Affinity

When a neutral atom in the gaseous state picks up an electron to form a stable negative ion, energy is released. For example, a chlorine atom can pick up an electron to give a chloride ion, Cl^- , and 349 kJ/mol of energy is released. You write the process as follows, with electron configurations noted in parentheses:



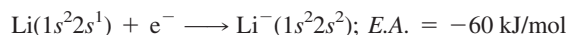
The **electron affinity** is the energy change for the process of adding an electron to a neutral atom in the gaseous state to form a negative ion. If the negative ion is stable (does not spontaneously disintegrate into the neutral atom and free electron), the energy change for its formation is a negative number. Thus, the electron affinity of Cl is -349 kJ/mol. Large negative numbers such as this indicate that a very stable negative ion is formed. Small negative numbers indicate that a less stable ion is formed. Table 8.4 gives the electron affinities of the main-group elements. <

Electron affinities are also defined with positive values for the formation of stable ions.

TABLE 8.4		Electron Affinities of the Main-Group Elements (kJ/mol)*				
Period	IA	IIIA	IVA	VA	VIA	VIIA
1	H −73					
2	Li −60	B −27	C −122	N 0	O −141	F −328
3	Na −53	Al −44	Si −134	P −72	S −200	Cl −349
4	K −48	Ga −30	Ge −120	As −77	Se −195	Br −325
5	Rb −47	In −30	Sn −121	Sb −101	Te −190	I −295
6	Cs −45	Tl −30	Pb −110	Bi −110	Po −180	At −270

*Atoms of the alkaline earth metals (Group IIA) and the noble gases (Group VIIIA) do not form stable negative ions.

Electron affinities, *E.A.*, have a periodic variation, just as atomic radii and ionization energies do, though somewhat more complicated. To see this variation, consider each of the main groups of elements beginning with Group IA. All of the Group IA elements have small negative electron affinities. When you add an electron to a lithium atom, for example, it goes into the $2s$ orbital to form a moderately stable negative ion, releasing energy.

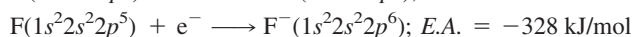
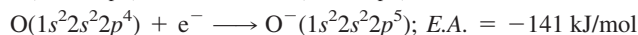
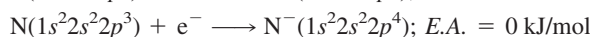
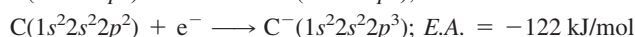
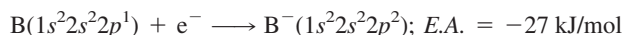


None of the Group IIA elements form stable negative ions; that is, the electron affinities of these elements are positive. Each of the atoms has a filled ns subshell, so that if you were to add an electron, it would have to go into the next higher energy subshell (np). Instead of releasing energy, the atom would absorb energy. For example,



(For a similar reason, the Group VIIIA elements also do not form stable negative ions.)

From Group IIIA to Group VIIA, the added electron goes into the np subshell of the valence shell. With the exception of the Group VA elements, the electron affinities tend toward more negative values as you progress to the right through these elements in any period (more energy is released and stabler negative ions are formed). The electron affinity of a Group VA element is generally less negative than the preceding Group IVA element. Note the trend in electron affinities in the following:



Broadly speaking, the general trend is toward more negative electron affinities from left to right in any period. Note especially that the Group VIA and Group VIIA elements have the largest negative electron affinities of any of the main-group elements. Therefore, these elements have compounds containing monatomic anions (such as F^- and O^{2-}).

Exercise 8.8

Without looking at Table 8.4 but using the general comments in this section, decide which has the larger negative electron affinity, C or F.

■ See Problems 8.65 and 8.66.

Concept Check 8.3

Given the following information for element E, identify the element's group in the periodic table: The electron affinity of E is positive (that is, it does not form a stable negative ion). The first ionization energy of E is less than the second ionization energy, which in turn is very much less than its third ionization energy.

8.7 Periodicity in the Main-Group Elements

The chemical and physical properties of the main-group elements clearly display periodic character. For instance, as pointed out in Section 2.5, the metallic elements lie to the left of the “staircase” line in the periodic table (see inside front cover), nonmetals

lie to the right, and the metalloids (with intermediate characteristics) lie along this line. So, as you move left to right in any row of the periodic table, the metallic character of the elements decreases. As you progress down a column, however, the elements tend to increase in metallic character.

These variations of metallic–nonmetallic character can be attributed in part to variations in the ionization energies of the corresponding atoms. Elements with low ionization energy tend to be metallic, whereas those with high ionization energy tend to be nonmetallic. As you saw in the previous section, ionization energy is a periodic property, so it is not surprising that the metallic–nonmetallic character of an element is similarly periodic.

The basic–acidic behavior of the oxides of the elements is a good indicator of the metallic–nonmetallic character of the elements. Oxides are classified as basic or acidic depending on their reactions with acids and bases. A **basic oxide** is *an oxide that reacts with acids*. Most metal oxides are basic. An **acidic oxide** is *an oxide that reacts with bases*. Most nonmetal oxides are acidic oxides. An **amphoteric oxide** is *an oxide that has both basic and acidic properties*.

In the following brief descriptions of the main-group elements, we will note the metallic–nonmetallic behavior of the elements, as well as the basic–acidic character of the oxides. Although elements in a given group are expected to be similar, the degree of similarity does vary among the groups. The alkali metals (Group IA) show marked similarities, as do the halogens (Group VIIA). On the other hand, the Group IVA elements range from a nonmetal (carbon) at the top of the column to a metal (lead) at the bottom. In either case, however, the changes from one element in a column to the next lower one are systematic, and the periodic table helps us to correlate these systematic changes.

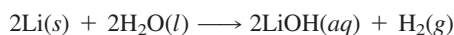
Hydrogen ($1s^1$)

Although the electron configuration of hydrogen would seem to place the element in Group IA, its properties are quite different, and it seems best to consider this element as belonging in a group by itself. The element is a colorless gas composed of H_2 molecules. <

At very high pressures, however, hydrogen is believed to have metallic properties.

Group IA Elements, the Alkali Metals (ns^1)

The *alkali metals* are soft and reactive, with the reactivities increasing as you move down the column of elements. All of the metals react with water to produce hydrogen.



The vigor of the reaction increases from lithium (moderate) to rubidium (violent). All of the alkali metals form basic oxides with the general formula R_2O .

Group IIA Elements, the Alkaline Earth Metals (ns^2)

The *alkaline earth metals* are also chemically reactive but much less so than the alkali metals. Reactivities increase going down the group. The alkaline earth metals form basic oxides with the general formula RO .

Group IIIA Elements (ns^2np^1)

Groups IA and IIA exhibit only slight increases in metallic character down a column, but with Group IIIA we see a significant increase. The first Group IIIA element, boron, is a metalloid. Other elements in this group—aluminum, gallium, indium, and thallium—are metals. (Gallium is a curious metal; it melts readily in the palm of the hand—see Figure 8.19.)



FIGURE 8.19 ▲

Gallium

This metal melts from the heat of a hand.

The oxides in this group have the general formula R_2O_3 . Boron oxide, B_2O_3 , is an acidic oxide; aluminum oxide, Al_2O_3 , and gallium oxide, Ga_2O_3 , are amphoteric oxides. The change in the oxides from acidic to amphoteric to basic is indicative of an increase in metallic character of the elements.

Group IVA Elements (ns^2np^2)

This group shows the most distinct change in metallic character. It begins with the nonmetal carbon, C, followed by the metalloids silicon, Si, and germanium, Ge, and then the metals tin, Sn, and lead, Pb. Both tin and lead were known to the ancients. <

All the elements in this group form oxides with the general formula RO_2 , which progress from acidic to amphoteric. Carbon dioxide, CO_2 , an acidic oxide, is a gas. (Carbon also forms the monoxide, CO.) Silicon dioxide, SiO_2 , an acidic oxide, exists as quartz and white sand (particles of quartz). Germanium dioxide, GeO_2 , is acidic, though less so than silicon dioxide. Tin dioxide, SnO_2 , an amphoteric oxide, is found as the mineral cassiterite, the principal ore of tin. Lead dioxide, PbO_2 , is amphoteric. Lead has a more stable monoxide, PbO . Figure 8.20 shows oxides of some Group IVA elements.

Bronze, one of the first alloys (metallic mixtures) used by humans, contains about 90% copper and 10% tin. Bronze melts at a lower temperature than copper but is much harder.



FIGURE 8.20 ▲

Oxides of some Group IVA elements

Powdered lead monoxide (yellow), lead dioxide (dark brown), tin dioxide (white), and crystalline silicon dioxide (clear quartz).

Group VA Elements (ns^2np^3)

The Group VA elements also show the distinct transition from nonmetal (nitrogen, N, and phosphorus, P) to metalloid (arsenic, As, and antimony, Sb) to metal (bismuth, Bi). Nitrogen occurs as a colorless, odorless, relatively unreactive gas with N_2 molecules; white phosphorus is a white, waxy solid with P_4 molecules. Gray arsenic is a brittle solid with metallic luster; antimony is a brittle solid with a silvery, metallic luster. Bismuth is a hard, lustrous metal with a pinkish tinge.

The Group VA elements form oxides with empirical formulas R_2O_3 and R_2O_5 . In some cases, the molecular formulas are twice these formulas—that is, R_4O_6 and R_4O_{10} . Nitrogen has the acidic oxides N_2O_3 and N_2O_5 , although it also has other, better known oxides, such as NO. Phosphorus has the acidic oxides P_4O_6 and P_4O_{10} . Arsenic has the acidic oxides As_2O_3 and As_2O_5 ; antimony has the amphoteric oxides Sb_2O_3 and Sb_2O_5 ; and bismuth has the basic oxide Bi_2O_3 .

Group VIA Elements, the Chalcogens (ns^2np^4)

These elements, the *chalcogens* (pronounced kal'-ke-jens), show the transition from nonmetal (oxygen, O, sulfur, S, and selenium, Se) to metalloid (tellurium, Te) to metal (polonium, Po). Oxygen occurs as a colorless, odorless gas with O_2 molecules. It also has an allotrope, ozone, with molecular formula O_3 . Sulfur is a brittle, yellow solid with molecular formula S_8 . Tellurium is a shiny gray, brittle solid; polonium is a silvery metal.

Sulfur, selenium, and tellurium form oxides with the formulas RO_2 and RO_3 . (Sulfur burns in air to form sulfur dioxide; see Figure 8.21.) These oxides, except for TeO_2 , are acidic; TeO_2 is amphoteric. Polonium has an oxide PoO_2 , which is amphoteric, though more basic in character than TeO_2 .

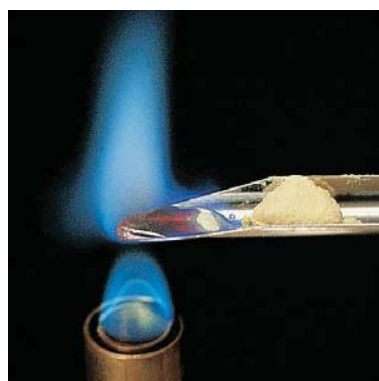


FIGURE 8.21 ▲

Burning sulfur

The combustion of sulfur in air gives a blue flame. The product is primarily sulfur dioxide, detectable by its acrid odor.

Group VIIA Elements, the Halogens (ns^2np^5)

The *halogens* are reactive nonmetals with the general molecular formula X_2 , where X symbolizes a halogen. Fluorine, F_2 , is a pale yellow gas; chlorine, Cl_2 , a pale greenish yellow gas; bromine, Br_2 , a reddish brown liquid; and iodine, I_2 , a bluish black

**FIGURE 8.22** ▲**The halogens**

From left to right, the flasks contain chlorine, bromine, and iodine. (Bromine and iodine were warmed to produce the vapors; bromine is normally a reddish brown liquid and iodine a bluish black solid.)

solid that has a violet vapor (see Figure 8.22). Little is known about the chemistry of astatine, At, because all isotopes are radioactive with very short half-lives. (The half-life of a radioactive isotope is the time it takes for half of the isotope to decay, or break down, to another element.) It might be expected to be a metalloid.

Each halogen forms several compounds with oxygen; these are generally unstable, acidic oxides.

Group VIIIA Elements, the Noble Gases (ns^2np^6)

The Group VIIIA elements exist as gases consisting of uncombined atoms. For a long time these elements were thought to be chemically inert, because no compounds were known. Then, in the early 1960s, several compounds of xenon were prepared. Now compounds are also known for argon, krypton, and radon. These elements are known as the *noble gases* because of their relative unreactivity.

Concept Check 8.4

A certain element is a metalloid that forms an acidic oxide with the formula R_2O_5 . Identify the element.

A Checklist for Review**Important Terms****electron configuration** (8.1)**orbital diagram** (8.1)**Pauli exclusion principle** (8.1)**building-up (Aufbau) principle** (8.2)**noble-gas core** (8.2)**pseudo-noble-gas core** (8.2)**valence electron** (8.2)**Hund's rule** (8.4)**paramagnetic substance** (8.4)**diamagnetic substance** (8.4)**periodic law** (8.6)**effective nuclear charge** (8.6)**first ionization energy (first ionization potential)** (8.6)**electron affinity** (8.6)**basic oxide** (8.7)**acidic oxide** (8.7)**amphoteric oxide** (8.7)**Summary of Facts and Concepts**

To understand the similarities that exist among the members of a group of elements, it is necessary to know the *electron configurations* for the ground states of atoms. Only those arrangements of electrons allowed by the *Pauli exclusion principle* are possible. The ground-state configuration of an atom represents the electron arrangement that has the lowest total energy. This arrangement can be reproduced by the *building-up principle* (Aufbau principle), where electrons fill the subshells in particular order (the building-up order) consistent with the Pauli exclusion principle. The arrangement of electrons in partially filled subshells is governed by *Hund's rule*.

Elements in the same group of the periodic table have similar valence-shell configurations. As a result, chemical and physical properties of the elements show periodic behavior. *Atomic radii*, for example, tend to decrease across any period (left to right) and increase down any group (top to bottom). *First ionization energies* tend to increase across a period and decrease down a group. *Electron affinities* of the Group VIA and Group VIIA elements have large negative values.

Media Summary

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Understanding Electron Spin
Electron Shielding

Electron Configurations Through Neon
Electron Configurations Beyond Neon
Periodic Relationships
Periodic and Atomic Sizes
Ionization Energy

Electron Affinity
 Transition Metals and Nonmetals
 Hydrogen, Alkali Metals, and Alkaline Earth Metals



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- **Visualizations** Molecular-level animations and lab demonstration videos
- Orbital Energies
- Periodic Table Trends
- Determining the Atomic Radius of a Nonmetal (Carbon)
- Determining the Atomic Radius of a Nonmetal (Chlorine)
- Determining the Atomic Radius of a Metal (Molybdenum)

- **Tutorials** Animated examples and interactive activities
Aufbau Principle

- **Flashcards** Key terms and definitions
Online Flashcards

- **Self-Assessment Questions** Additional questions with full worked-out solutions
6 Self-Assessment Questions



ACE the Test

- Multiple-choice quizzes
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Access these resources using the passkey available free with new texts or for purchase separately.

Learning Objectives

8.1 Electron Spin and the Pauli Exclusion Principle

- Define *electron configuration* and *orbital diagram*.
- State the Pauli exclusion principle.
- Apply the Pauli exclusion principle. **Example 8.1**

8.2 Building-Up Principle and the Periodic Table

- Define *building-up principle*.
- Define *noble-gas core*, *pseudo-noble-gas core*, and *valence electron*.
- Define *main-group element* and (*d-block* and *f-block*) *transition element*.

8.3 Writing Electron Configurations Using the Periodic Table

- Determine the configuration of an atom using the building-up principle. **Example 8.2**
- Determine the configuration of an atom using the period and group numbers. **Example 8.3**

8.4 Orbital Diagrams of Atoms; Hund's Rule

- State Hund's rule.
- Apply Hund's rule. **Example 8.4**
- Define *paramagnetic substance* and *diamagnetic substance*.

8.5 Mendeleev's Predictions from the Periodic Table

- Describe how Mendeleev predicted the properties of undiscovered elements.

8.6 Some Periodic Properties

- State the periodic law.
- State the general periodic trends in size of atomic radii.
- Define *effective nuclear charge*.
- Determine relative atomic sizes from periodic trends. **Example 8.5**
- State the general periodic trends in ionization energy.
- Define *first ionization energy*.
- Determine relative ionization energies from periodic trends. **Example 8.6**
- Define *electron affinity*.
- State the broad general trend in electron affinity across any period.

8.7 Periodicity in the Main-Group Elements

- Define *basic oxide*, *acidic oxide*, and *amphoteric oxide*.
- State the main group corresponding to an *alkali metal*, an *alkaline earth metal*, a *chalcogen*, a *halogen*, and a *noble gas*.
- Describe the change in metallic/nonmetallic character (or reactivities) in going through any main group of elements.

Self-Assessment and Review Questions

- 8.1** Describe the experiment of Stern and Gerlach. How are the results for the hydrogen atom explained?
- 8.2** Describe the model of electron spin given in the text. What are the restrictions on electron spin?

- 8.3** How does the Pauli exclusion principle limit the possible electron configurations of an atom?
- 8.4** What is the maximum number of electrons that can occupy a *g* subshell ($l = 4$)?

- 8.5** List the orbitals in order of increasing orbital energy up to and including $3p$ orbitals.
- 8.6** Define each of the following: noble-gas core, pseudo-noble-gas core, valence electron.
- 8.7** Give two different possible orbital diagrams for the $1s^2 2s^2 2p^4$ configuration of the oxygen atom, one of which should correspond to the ground state. Label the diagram for the ground state.
- 8.8** Define the terms *diamagnetic substance* and *paramagnetic substance*. Does the ground-state oxygen atom give a diamagnetic or a paramagnetic substance? Explain.
- 8.9** What kind of subshell is being filled in Groups IA and IIA? in Groups IIIA to VIIIA? in the transition elements? in the lanthanides and actinides?
- 8.10** How was Mendeleev able to predict the properties of gallium before it was discovered?
- 8.11** Describe the major trends that emerge when atomic radii are plotted against atomic number. Describe the trends observed when first ionization energies are plotted against atomic number.
- 8.12** What atom has the smallest radius among the alkaline earth elements?
- 8.13** What main group in the periodic table has elements with the most negative electron affinities for each period? What electron configurations of neutral atoms have only unstable negative ions?
- 8.14** The ions Na^+ and Mg^{2+} occur in chemical compounds, but the ions Na^{2+} and Mg^{3+} do not. Explain.
- 8.15** Describe the major trends in metallic character observed in the periodic table of the elements.
- 8.16** Distinguish between an acidic and a basic oxide. Give examples of each.
- 8.17** What is the name of the alkali metal atom with valence-shell configuration $5s^1$?
- 8.18** What would you predict for the atomic number of the halogen under astatine in the periodic table?
- 8.19** List the elements in Groups IIIA to VIA in the same order as in the periodic table. Label each element as a metal, a metalloid, or a nonmetal. Does each column of elements display the expected trend of increasing metallic characteristics?
- 8.20** For the list of elements you made for Question 8.19, note whether the oxides of each element are acidic, basic, or amphoteric.
- 8.21** Write an equation for the reaction of potassium metal with water.
- 8.22** From what is said in Section 8.7 about Group IIA elements, list some properties of barium.
- 8.23** Give the names and formulas of two oxides of carbon.
- 8.24** Match each description in the left column with the appropriate element in the right column.
- | | |
|--|------------------|
| a. A waxy, white solid, normally stored under water | Sulfur |
| b. A yellow solid that burns in air | Sodium |
| c. A reddish brown liquid | White phosphorus |
| d. A soft, light metal that reacts vigorously with water | Bromine |
- 8.25** Phosphorus has _____ unpaired electrons.
a. 1 b. 2 c. 3 d. 4 e. 5
- 8.26** Which of the following atoms, designated by their electron configurations, has the *highest* ionization energy?
- $[\text{Ne}]3s^2 3p^2$
 - $[\text{Ne}]3s^2 3p^3$
 - $[\text{Ar}]3d^{10} 4s^2 4p^3$
 - $[\text{Kr}]4d^{10} 5s^2 5p^3$
 - $[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^3$
- 8.27** When trying to remove electrons from Be, which of the following sets of ionization energy makes the most sense going from first to third ionization energy?
- First IE 900 KJ/mol, second IE 1750 kJ/mol, third IE 15,000 kJ/mol
 - First IE 1750 KJ/mol, second IE 900 kJ/mol, third IE 15,000 kJ/mol
 - First IE 15,000 KJ/mol, second IE 1750 kJ/mol, third IE 900 kJ/mol
 - First IE 900 KJ/mol, second IE 15,000 kJ/mol, third IE 22,000 kJ/mol
 - First IE 900 KJ/mol, second IE 1750 kJ/mol, third IE 1850 kJ/mol
- 8.28** Consider the following orderings.
- $\text{Al} < \text{Si} < \text{P} < \text{S}$
 - $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr}$
 - $\text{I} < \text{Br} < \text{Cl} < \text{F}$
- Which of these give(s) a correct trend in atomic size?
- I only
 - II only
 - III only
 - I and II only
 - II and III only

Concept Explorations

8.29 Periodic Properties I

A hypothetical element, X, has the following ionization energy values:

- First ionization energy: 900 kJ/mol
- Second ionization energy: 1750 kJ/mol
- Third ionization energy: 14,900 kJ/mol
- Fourth ionization energy: 21,000 kJ/mol

Another element, Y, has the following ionization energy values:

- First ionization energy: 1200 kJ/mol
- Second ionization energy: 2500 kJ/mol
- Third ionization energy: 19,900 kJ/mol
- Fourth ionization energy: 26,000 kJ/mol

- To what family of the periodic table would element X be most likely to belong? Explain?

- b. What charge would you expect element X to have when it forms an ion?
- c. If you were to place elements X and Y into the periodic table, would element Y be in the same period as element X? If not in the same period, where might they be relative to each other in the periodic table?
- d. Would an atom of Y be smaller or larger than an atom of X? Explain your reasoning.

8.30 Periodic Properties II

Consider two hypothetical elements, W and Z. Element W has an electron affinity of -300 kJ/mol, and element Z has an electron affinity of -75 kJ/mol.

- a. If you have a W^- ion and a Z^- ion, from which ion would it require more energy to remove an electron? Explain your answer.
- b. If elements W and Z are in the same period of the periodic table, which atom would you expect to have the greater atomic radius? Why?
- c. Assuming that the elements are in the same period, which element would you expect to have the smaller first ionization energy?
- d. Do the valence electrons in element Z feel a greater effective nuclear charge than those in element W? Explain how you arrived at your answer.

Conceptual Problems

8.31 Suppose that the Pauli exclusion principle were “No more than two electrons can have the same four quantum numbers.” What would be the electron configurations of the ground states for the first six elements of the periodic table, assuming that, except for the Pauli principle, the usual building-up principle held?

8.32 Imagine a world in which all quantum numbers, except the l quantum number, are as they are in the real world. In this imaginary world, l begins with 1 and goes up to n (the value of the principal quantum number). Assume that the orbitals fill in the order by n , then l ; that is, the first orbital to fill is for $n = 1$, $l = 1$; the next orbital to fill is for $n = 2$, $l = 1$, and so forth. How many elements would there be in the first period of the periodic table?

8.33 Two elements in Period 5 are adjacent to one another in the periodic table. The ground-state atom of one element has only s electrons in its valence shell; the other has at least one d electron in an unfilled shell. Identify the elements.

8.34 Two elements are in the same column of the periodic table, one above the other. The ground-state atom of one element has two s electrons in its outer shell, and no d electrons anywhere in its configuration. The other element has d electrons in its configuration. Identify the elements.

8.35 You travel to an alternate universe where the atomic orbitals are different from those on earth, but all other aspects of the atoms are the same. In this universe, you find that the first (lowest energy) orbital is filled with three electrons and the second orbital can hold a maximum of nine electrons. You discover an element Z that has five electrons in its atom. Would you expect Z to be more likely to form a cation or an anion? Indicate a possible charge on this ion.

8.36 Would you expect to find an element having both a very large (positive) first ionization energy and an electron affinity that is much less than zero (large but negative)? Explain.

8.37 Two elements are in the same group, one following the other. One is a metalloid; the other is a metal. Both form oxides of the formula RO_2 . The first is acidic; the next is amphoteric. Identify the two elements.

8.38 A metalloid has an acidic oxide of the formula R_2O_3 . The element has no oxide of the formula R_2O_5 . What is the name of the element?

8.39 Given the following information, identify the group from the periodic table that contains elements that behave like main-group element “E.”

- The electron affinity of E is greater than zero.
- The ionization energy (IE) trend for element E is: first ionization energy $<$ second ionization energy \lll third ionization energy.
- Samples of E are lustrous and are good electrical conductors.

8.40 A hypothetical element A has the following properties:

First ionization energy: 850 kJ/mol

Second ionization energy: 1700 kJ/mol

Third ionization energy: 13,999 kJ/mol

- If you were to react element A with oxygen, what would be the chemical formula of the resulting compound?
- Write the balanced chemical reaction of A reacting with oxygen to give the product from part a.
- Would you expect the product of the chemical reaction of A with oxygen to be a basic, an acidic, or an amphoteric oxide?

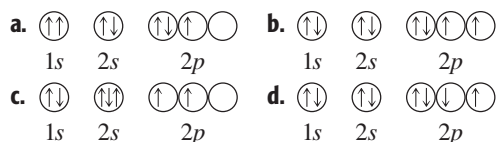
Practice Problems

Pauli Exclusion Principle

8.41 Which of the following orbital diagrams are allowed by the Pauli exclusion principle? Explain how you arrived at this decision. Give the electron configuration for the allowed ones.

- a. $1s \uparrow \downarrow$ $2s \uparrow \downarrow$ $2p \uparrow \uparrow \uparrow$
- b. $1s \uparrow \downarrow$ $2s \uparrow \downarrow$ $2p \uparrow \uparrow \uparrow$
- c. $1s \uparrow \uparrow$ $2s \uparrow \downarrow$ $2p \uparrow \downarrow \uparrow$
- d. $1s \uparrow \downarrow$ $2s \uparrow \uparrow$ $2p \uparrow \uparrow \uparrow$

8.42 Which of the following orbital diagrams are allowed and which are not allowed by the Pauli exclusion principle? Explain. For those that are allowed, write the electron configuration.



8.43 Which of the following electron configurations are possible? Explain why the others are not.

- a. $1s^1 2s^2 2p^7$ b. $1s^2 2s^2 2p^6 3s^3 3d^7$
 c. $1s^2 2s^2 2p^5$ d. $1s^2 2s^2 2p^6 3s^2 3d^8$

8.44 Choose the electron configurations that are possible from among the following. Explain why the others are impossible.

- a. $1s^2 2s^1 2p^6$ b. $1s^2 2s^2 2p^8$
 c. $1s^2 2s^3 2p^6 3s^2 3p^6 3d^7$ d. $1s^2 2s^2 2p^6 3s^1 3d^9$

8.45 Write all of the possible orbital diagrams for the electron configuration $1s^2 2p^1$. (There are six different diagrams.)

8.46 Give the different orbital diagrams for the configuration $1s^1 2p^1$. (There are twelve different diagrams.)

Building-Up Principle and Hund's Rule

8.47 Give the electron configuration of the ground state of iodine, using the building-up principle.

8.48 Use the building-up principle to obtain the ground-state configuration of phosphorus.

8.49 Use the building-up principle to obtain the electron configuration of the ground state of manganese.

8.50 Give the electron configuration of the ground state of cobalt, using the building-up principle.

8.51 Bromine is a Group VIIA element in Period 4. Deduce the valence-shell configuration of bromine.

8.52 Antimony is a Group VA element in Period 5. Write the valence-shell configuration of antimony.

8.53 Zirconium is a Group IVB element in Period 5. What would you expect for the valence-shell configuration of zirconium?

8.54 Titanium is a Group IVB element in Period 4. What would you expect for the configuration of outer electrons of manganese?

General Problems

8.69 Write the complete ground-state electron configuration of the strontium atom, Sr, using the building-up principle.

8.70 Write the complete ground-state electron configuration of the tin atom, Sn, using the building-up principle.

8.71 Obtain the valence-shell configuration of the polonium atom, Po, using the position of this atom in the periodic table.

8.55 Thallium has the ground-state configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$. Give the group and period for this element. Classify it as a main-group, a *d*-transition, or an *f*-transition element.

8.56 The configuration for the ground state of iridium is $[\text{Xe}]4f^{14}5d^76s^2$. What are the group and period for this element? Is it a main-group, a *d*-transition, or an *f*-transition element?

8.57 Write the orbital diagram for the ground state of cobalt. The electron configuration is $[\text{Ar}]3d^74s^2$.

8.58 Write the orbital diagram for the ground state of terbium. The electron configuration is $[\text{Xe}]4f^96s^2$.

8.59 Write an orbital diagram for the ground state of the potassium atom. Is the atomic substance diamagnetic or paramagnetic?

8.60 Write an orbital diagram for the ground state of the calcium atom. Is the atomic substance diamagnetic or paramagnetic?

Periodic Trends

8.61 Order the following elements by increasing atomic radius according to what you expect from periodic trends: Se, S, As.

8.62 Using periodic trends, arrange the following elements in order of increasing atomic radius: O, P, S.

8.63 Using periodic trends, arrange the following elements by increasing ionization energy: Ar, Na, Cl, Al.

8.64 Arrange the following elements in order of increasing ionization energy: Mg, Ca, S. Do not look at Figure 8.18.

8.65 From what you know in a general way about electron affinities, state which member of each of the following pairs has the greater negative value: (a) As, Br (b) F, Li.

8.66 From what you know in a general way about electron affinities, state which member of each of the following pairs has the greater negative value: (a) Cl, S (b) Se, K.

8.67 If potassium chlorate has the formula KClO_3 , what formula would you expect for lithium bromate?

8.68 Write the simplest formulas expected for two oxides of selenium.

8.72 Obtain the valence-shell configuration of the thallium atom, Tl, using the position of this atom in the periodic table.

8.73 Write the orbital diagram for the ground state of the arsenic atom. Give all orbitals.

8.74 Write the orbital diagram for the ground state of the germanium atom. Give all orbitals.

8.75 For eka-lead, predict the electron configuration, whether the element is a metal or nonmetal, and the formula of an oxide.

8.76 For eka-bismuth, predict the electron configuration, whether the element is a metal or nonmetal, and the formula of an oxide.

8.77 From Figure 8.18, predict the first ionization energy of francium ($Z = 87$).

8.78 From Figure 8.18, predict the first ionization energy of astatine ($Z = 85$).

8.79 Write the orbital diagram corresponding to the ground state of Nb, whose configuration is $[\text{Kr}]4d^45s^1$.

8.80 Write the orbital diagram for the ground state of ruthenium. The configuration is $[\text{Kr}]4d^75s^1$.

8.81 Match each set of characteristics on the left with an element in the column at the right.

- | | |
|---|----------------------------|
| a. A reactive nonmetal; the atom has a large negative electron affinity | Sodium (Na) |
| b. A soft metal; the atom has low ionization energy | Antimony (Sb) |
| c. A metalloid that forms an oxide of formula R_2O_3 | Argon (Ar) |
| d. A chemically unreactive gas | Chlorine (Cl_2) |

8.82 Match each element on the right with a set of characteristics on the left.

- | | |
|---|---------------------------|
| a. A reactive, pale yellow gas; the atom has a large negative electron affinity | Oxygen (O_2) |
| b. A soft metal that reacts with water to produce hydrogen | Gallium (Ga) |
| c. A metal that forms an oxide of formula R_2O_3 | Barium (Ba) |
| d. A colorless gas; the atom has a moderately large negative electron affinity | Fluorine (F_2) |

8.83 Find the electron configuration of the element with $Z = 23$. From this, give its group and period in the periodic table. Classify the element as a main-group, a d -block transition, or an f -block transition element.

8.84 Find the electron configuration of the element with $Z = 33$. From this, give its group and period in the periodic table. Is this a main-group, a d -block transition, or an f -block transition element?

8.85 What property of an atom does nuclear magnetic resonance depend on? What frequency range of the electromagnetic spectrum does NMR use?

8.86 Explain the origin of the “chemical shift” seen for a proton in a molecule.

8.87 Explain how x rays are produced when an electron beam falls on a metal target.

8.88 Describe how x-ray photoelectron spectroscopy is done. What kind of information is obtained from photoelectron spectroscopy?

8.89 How is it possible for a diamagnetic material to be levitated by a magnetic field?

8.90 Researchers have shown that it is possible to levitate diamagnetic materials. What animal did they use in their experiments to show this?

Strategy Problems

8.91 A metallic element, M, reacts vigorously with water to form a solution of MOH. If M is in Period 5, what is the ground-state electron configuration of the atom?

8.92 A nonmetallic element, R, burns brightly in air to give the oxide R_4O_{10} . If R is in Period 3, what is the ground-state valence-shell configuration of the atom?

8.93 The ground-state electron configuration of an atom is $1s^22s^22p^63s^23p^4$. What is the valence-shell configuration of the atom in the same group, but in Period 5?

8.94 An atom of an element has the following ground-state configuration: $[\text{Xe}]4f^{14}5d^96s^1$. Using this configuration, give the symbol of the element. Explain your reasoning.

8.95 An atom of an element has the following ground-state configuration: $[\text{Kr}]4d^{10}5s^25p^b$. If the element is in Group VIA, what is the symbol of the element? What is b ?

8.96 A main-group atom in Period 5 has the following orbital diagram for its valence shell (ground state): $\uparrow\downarrow \quad \uparrow\uparrow\uparrow\uparrow$.

What is the symbol for the element? Write the formula of the oxide containing the most oxygen.

8.97 Write the orbital diagram for the ground-state valence electrons of the main-group atom in Period 5 that has the smallest radius. Explain how you got this answer.

8.98 Using the periodic table, decide which of the following atoms you expect to have the largest radius: H, Sc, As, Br, V, K. Why?

8.99 An atom easily loses two electrons to form the ion R^{+2} . The element, which is in Period 6, forms the oxides RO and RO_2 . Give the orbital diagram for the ground-state valence shell of the element that immediately follows R in the periodic table.

8.100 List three elements in order of increasing ionization energy. Two of the elements should be halogens (but not F), and the other should be Se.

Cumulative-Skills Problems

8.101 A 2.50-g sample of barium reacted completely with water. What is the equation for the reaction? How many milliliters of dry H_2 evolved at 21°C and 748 mmHg?

8.102 A sample of cesium metal reacted completely with water, evolving 48.1 mL of dry H_2 at 19°C and 768 mmHg. What is the equation for the reaction? What was the mass of cesium in the sample?

8.103 What is the formula of radium oxide? What is the percentage of radium in this oxide?

8.104 What is the formula of hydrogen telluride? What is the percentage of tellurium in this compound?

8.105 How much energy would be required to ionize 5.00 mg of Na(g) atoms to $\text{Na}^+(\text{g})$ ions? The first ionization energy of Na atoms is 496 kJ/mol.

8.106 How much energy is evolved when 2.65 mg of Cl(g) atoms adds electrons to give $\text{Cl}^-(\text{g})$ ions?

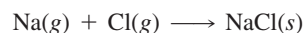
8.107 Using the Bohr formula for the energy levels, calculate the energy required to raise the electron in a hydrogen atom from $n = 1$ to $n = \infty$. Express the result for 1 mol H atoms. Because the $n = \infty$ level corresponds to removal of the electron from the atom, this energy equals the ionization energy of the H atom.

8.108 Calculate the ionization energy of the He^+ ion in kJ/mol (this would be the second ionization energy of He). See Problem 8.107. The Bohr formula for the energy levels of an ion consisting of a nucleus of charge Z and a single electron is $-R_{\text{H}}Z^2/n^2$.

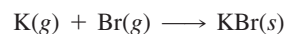
8.109 The lattice energy of an ionic solid such as NaCl is the enthalpy change ΔH° for the process in which the solid changes to ions. For example,



Assume that the ionization energy and electron affinity are ΔH values for the processes defined by those terms. The ionization energy of Na is 496 kJ/mol. Use this, the electron affinity from Table 8.4, and the lattice energy of NaCl to calculate ΔH for the following process:



8.110 Calculate ΔH for the following process:



The lattice energy of KBr is 689 kJ/mol, and the ionization energy of K is 419 kJ/mol. The electron affinity of Br is given in Table 8.4. See Problem 8.109.