

WHAT'S AHEAD

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6

ELECTRONIC STRUCTURE OF ATOMS

6.1 | The Wave Nature of Light



The beginning of the twentieth century was truly one of the most revolutionary periods of scientific discovery. Two theoretical developments caused dramatic changes in our view of the universe. The first, Einstein's theory of relativity, forever changed our views of the relationships between space and time. The second—which will be the focus of this chapter—is *quantum theory*, which explains much of the behavior of electrons in atoms.

We begin by looking at the nature of light and how our description of light was changed by quantum theory. We will explore some of the tools used in *quantum mechanics*, the “new” physics that had to be developed to describe atoms correctly. We will then use quantum theory to describe the arrangements of electrons in atoms—what we call

the **electronic structure** of atoms. We will see that the quantum description of the electronic structure of atoms helps us to understand the arrangement of the elements in the periodic table—why, for example, helium and neon are both unreactive gases, whereas sodium and potassium are both soft, reactive metals.

By the end of this section, you should be able to

- Describe a wave in terms of its wavelength and frequency

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

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

All types of electromagnetic radiation move through a vacuum at 2.998×10^8 m/s, the *speed of light*. All have wave-like characteristics similar to those of waves that move through water. Water waves are the result of energy imparted to the water, perhaps by a dropped stone or the movement of a boat across the water's surface (Figure 6.1). This energy is expressed as the up-and-down movements of the water.

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

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

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

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

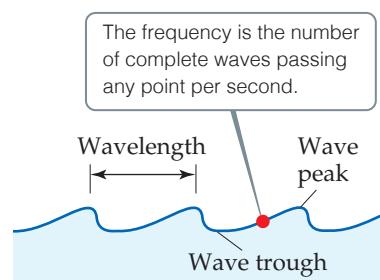
where λ (lambda) is wavelength, ν (nu) is frequency, and c is the speed of light.

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

Frequency is expressed in cycles per second, a unit also called a *hertz* (Hz). Because it is understood that cycles are involved, the units of frequency are normally given simply as “per second,” which is denoted by s^{-1} or /s. For example, a frequency of 698 megahertz (MHz), a typical frequency for a cellular telephone, could be written as 698 MHz, $698,000,000$ Hz, $698,000,000$ s $^{-1}$, or $698,000,000$ /s.



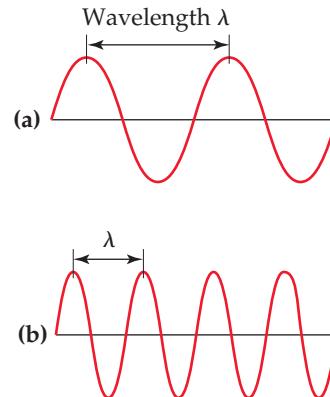
▲ **Figure 6.1 Water waves.** The movement of a boat through the water forms waves. The regular variation of peaks and troughs enables us to sense the motion of the waves away from the boat.



▲ **Figure 6.2 Water waves.** The wavelength is the distance between two adjacent peaks or two adjacent troughs.

Go Figure

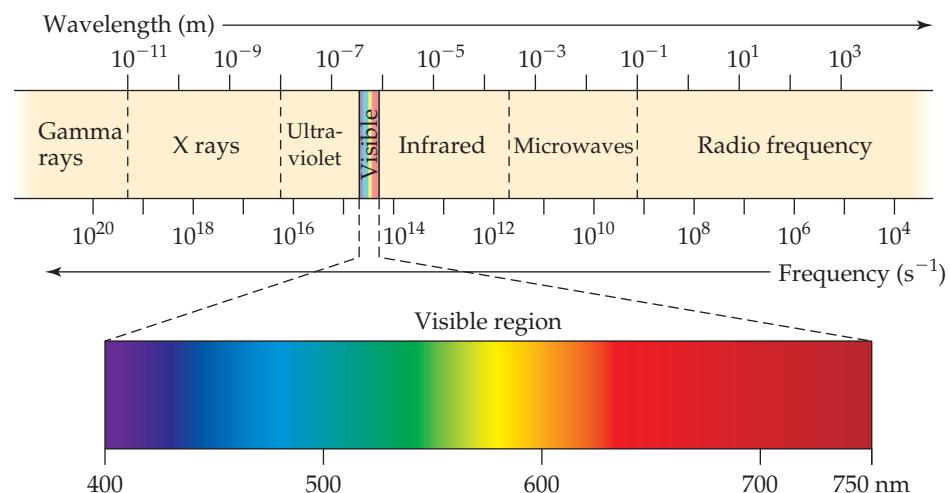
If wave (a) has a wavelength of 2.0 m and a frequency of 1.5×10^8 cycles/s, what are the wavelength and frequency of wave (b)?



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

**Go Figure**

Is the wavelength of a microwave longer or shorter than the wavelength of visible light? By how many orders of magnitude do the two waves differ in wavelength?



▲ **Figure 6.4** The electromagnetic spectrum.* Wavelengths in the spectrum range from very short gamma rays to very long radio waves.

TABLE 6.1 Common Wavelength Units for Electromagnetic Radiation

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

**Sample Exercise 6.1****Concepts of Wavelength and Frequency**

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

SOLUTION

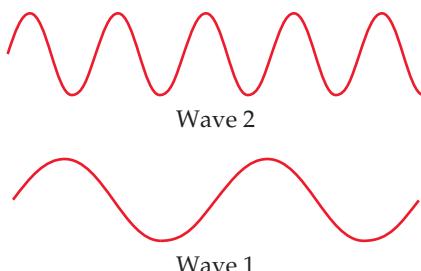
(a) Wave 1 has a longer wavelength (greater distance between peaks). The longer the wavelength, the lower the frequency ($\nu = c/\lambda$). Thus, Wave 1 has the lower frequency, and Wave 2 has the higher frequency.

(b) The electromagnetic spectrum (Figure 6.4) indicates that infrared radiation has a longer wavelength than visible light. Thus, Wave 1 is infrared radiation.

► Practice Exercise

A source of electromagnetic radiation produces infrared light. Which of the following could be the wavelength of the light?

- (a) 3.0 nm (b) 4.7 cm (c) 66.8 m (d) 34.5 μm (e) 16.5 Å



* Based on B. A. Averill and P. Eldredge, *Chemistry: Principles, Patterns, and Applications* 1e, © 2007 Pearson Education, Inc.



Sample Exercise 6.2

Calculating Frequency from Wavelength

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

SOLUTION

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

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

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

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

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

► Practice Exercise

- (a) A laser used in orthopedic spine surgery produces radiation with a wavelength of $2.10 \mu\text{m}$. Calculate the frequency of this radiation. (b) An FM radio station broadcasts electromagnetic radiation at a frequency of 103.4 MHz (megahertz; $1 \text{ MHz} = 10^6 \text{ s}^{-1}$). Calculate the wavelength of this radiation. The speed of light is 2.998×10^8 m/s to four significant figures.

Self-Assessment Exercise

- 6.1** The broadcast frequency of a local radio station is 106.5 MHz. What is the wavelength of the broadcast radio waves?

- (a) 0.355 m
 (b) 2.82 m
 (c) 2.82×10^6 m

Exercises

- 6.2** Label each of the following statements as true or false. For those that are false, correct the statement. (a) Visible light is a form of electromagnetic radiation. (b) Ultraviolet light has longer wavelengths than visible light. (c) X rays travel faster than microwaves. (d) Electromagnetic radiation and sound waves travel at the same speed.
- 6.3** Arrange the following kinds of electromagnetic radiation in order of increasing wavelength: infrared, green light, red light, radio waves, X rays, ultraviolet light.
- 6.4** The wavenumber $\bar{\lambda}$ is the number of waves that exist over a specified distance, very often 1 cm. The wavenumber can easily be calculated by taking the reciprocal of the wavelength.

Give typical wavenumbers for (a) X-rays ($\lambda = 1 \text{ nm}$) (b) visible light ($\lambda = 500 \text{ nm}$) (c) microwaves ($\lambda = 1 \text{ mm}$).

- 6.5** (a) What is the frequency of radiation that has a wavelength of $10 \mu\text{m}$, about the size of a bacterium? (b) What is the wavelength of radiation that has a frequency of $5.50 \times 10^{14} \text{ s}^{-1}$? (c) Would the radiations in part (a) or part (b) be visible to the human eye? (d) What distance does electromagnetic radiation travel in $50.0 \mu\text{s}$?
- 6.6** A laser pointer used in a lecture hall emits light at 650 nm. What is the frequency of this radiation? Using Figure 6.4, predict the color associated with this wavelength.

6.1 (b)



6.2 | Quantized Energy and Photons



White light, a combination of the colors of the visible spectrum, surrounds us and consists of all the wavelengths in the range 400–750 nm. A little more unusual is the light emitted from a laser, which consists of just a single wavelength, a result of a quantized process. In recent times, the application of laser technology has entered many areas of life: bar code readers, levels used in building construction, welding equipment, surgery, mapping, communication, military applications, and spectacular displays put on for our entertainment. The first laser was built in 1960, the name coming from the acronym ‘Light Amplification by Stimulated Emission of Radiation’.

By the end of this section, you should be able to

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

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

Go Figure

Which is at a higher temperature: the part of the nail glowing yellow or the part glowing red?



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

Hot Objects and the Quantization of Energy

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

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

$$E = h\nu$$

[6.2]

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

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

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

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

The Photoelectric Effect and Photons

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

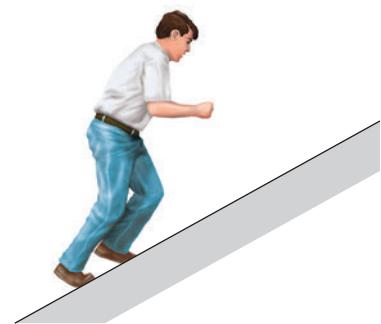
To explain the photoelectric effect, Einstein assumed that the radiant energy striking the metal surface behaves like a stream of tiny energy packets. Each packet, which is like a “particle” of energy, is called a **photon**. Extending Planck's quantum theory, Einstein deduced that each photon must have an energy equal to the Planck constant times the frequency of the light:

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

Thus, radiant energy itself is quantized.

Under the right conditions, photons striking a metal surface can transfer their energy to electrons in the metal. A certain amount of energy—called the *work function*—is required for the electrons to overcome the attractive forces holding them in the metal. If the photons striking the metal have less energy than the work function, the electrons do not acquire sufficient energy to escape from the metal. Increasing the intensity of the light source doesn't lead to emission of electrons from the metal; only changing the frequency of the incoming light has that effect. The intensity (brightness) of the light is related to the number of photons striking the surface per unit time but not to the energy of each photon. When the frequency is such that photons have energy greater than the work function of the particular metal, electrons are emitted; any excess energy of the photon is converted into kinetic energy of the emitted electron. Einstein won the Nobel Prize in Physics in 1921 primarily for his explanation of the photoelectric effect.

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



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

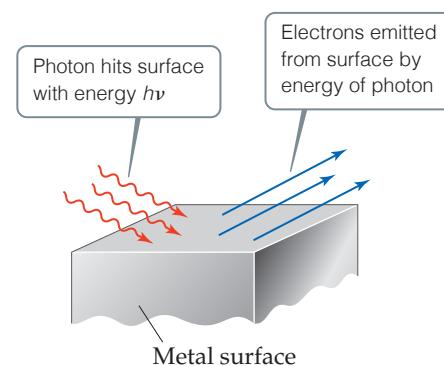


Potential energy of person walking up steps increases in stepwise, quantized manner

▲ Figure 6.6 Quantized versus continuous change in energy.

Go Figure

If the frequency of the incoming light is increased, will the energy of the ejected electrons increase, decrease, or stay the same?



▲ Figure 6.7 The photoelectric effect.



Sample Exercise 6.3

Energy of a Photon

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

SOLUTION

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

Solve The frequency, ν , is calculated from the given wavelength, as shown in Sample Exercise 6.2:

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

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

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

Plan We can use Equation 6.1 to convert the wavelength to frequency: $\nu = c/\lambda$. We can then use Equation 6.3 to calculate energy: $E = h\nu$

$$\nu = (3.00 \times 10^8 \text{ m/s})/(589 \times 10^{-9} \text{ m}) = 5.09 \times 10^{14} \text{ s}^{-1}$$

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

► Practice Exercise

Which of the following expressions correctly gives the energy of a mole of photons with wavelength λ ?

(a) $E = \frac{h}{\lambda}$ (b) $E = N_A \frac{\lambda}{h}$ (c) $E = \frac{hc}{\lambda}$ (d) $E = N_A \frac{h}{\lambda}$ (e) $E = N_A \frac{hc}{\lambda}$

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

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

Self-Assessment Exercise

6.7 Which photon of light has the higher energy?

- (a) UV radiation with a wavelength of 450 nm

(b) A red laser pointer with a wavelength of 635 nm

(c) A microwave oven operating with a wavelength of 12.24 cm

Exercises

6.8 If human height were quantized in 1 cm increments, what would happen to the height of a child as she grows up: (i) the child's height would never change, (ii) the child's height would continuously increase, (iii) the child's height would increase in jumps of 6 cm, or (iv) the child's height would increase in "jumps" of 1 cm at a time?

6.9 (a) Calculate the energy of a photon of electromagnetic radiation whose frequency is $2.94 \times 10^{14} \text{ s}^{-1}$. (b) Calculate the energy of a photon of radiation whose wavelength is 413 nm. (c) What wavelength of radiation has photons of energy 6.06×10^{-19} J?

6.10 (a) Calculate and compare the energy of a photon of wavelength 3.0 mm with that of wavelength 0.3 nm. (b) Use Figure 6.4 to identify the region of the electromagnetic spectrum to which each belongs.

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

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

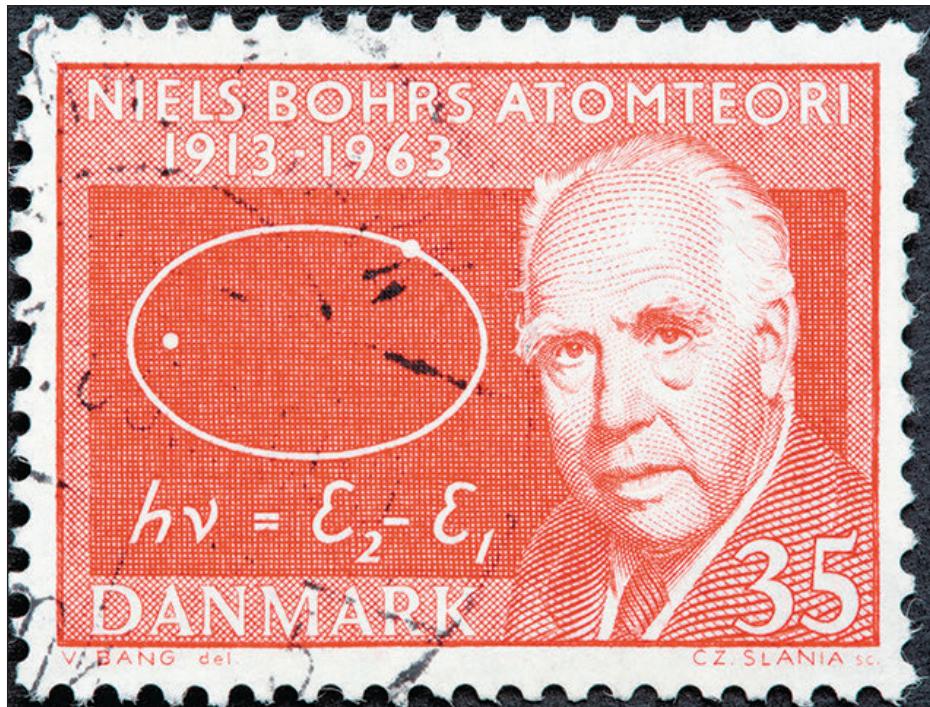
6.13 Molybdenum metal must absorb radiation with an energy higher than 7.22×10^{-19} J (“energy threshold”) before it can eject an electron from its surface via the photoelectric effect. (a) What is the frequency threshold for emission of electrons? (b) What wavelength of radiation will provide a photon of this energy? (c) If molybdenum is irradiated with light of wavelength of 240 nm, what is the maximum possible velocity of the emitted electrons?

6.7 (a)

Answers to Self-Assessment Exercises



6.3 | Line Spectra and the Bohr Model



The work of Planck and Einstein paved the way for understanding how electrons are arranged in atoms. In 1913, the Danish physicist Niels Bohr (1885–1962) offered a theoretical explanation of *line spectra*, another phenomenon that had puzzled scientists during the nineteenth century. We will see that Bohr used the ideas of Planck and Einstein to explain the line spectrum of hydrogen.

By the end of this section, you should be able to

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

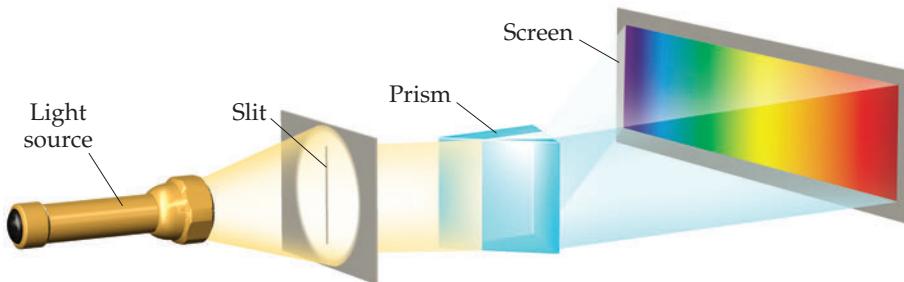
Line Spectra

A particular source of radiant energy may emit a single wavelength, as in the light from a laser. Radiation composed of a single wavelength is *monochromatic*. However, most common radiation sources, including incandescent light bulbs and stars, produce radiation containing many different wavelengths, *polychromatic* radiation. A **spectrum** is

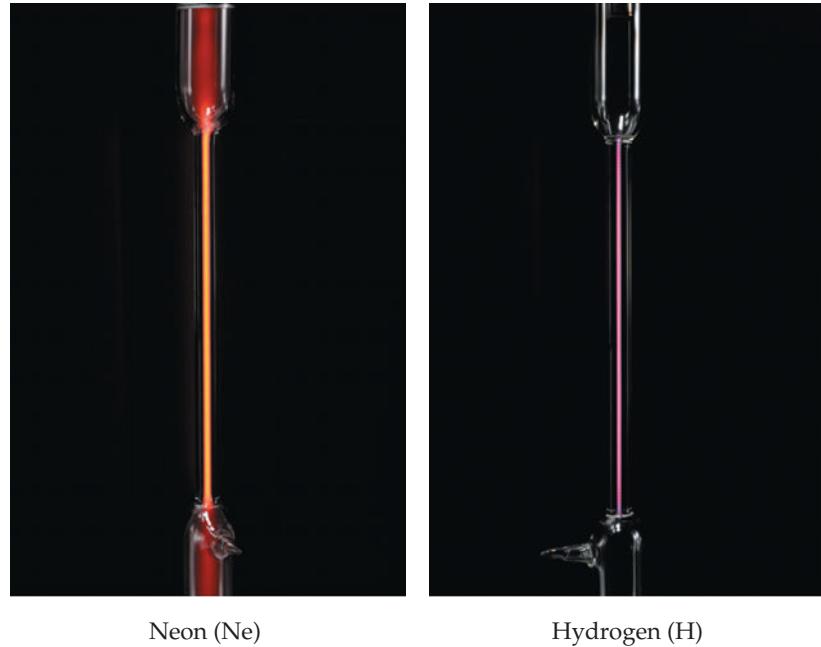
produced when radiation from a polychromatic source is separated into its component wavelengths, as shown in [Figure 6.8](#). The resulting spectrum consists of a continuous range of colors—violet merges into indigo, indigo into blue, and so forth, with no (or very few) blank spots. This rainbow of colors, containing light of all wavelengths, is called a **continuous spectrum**. The most familiar example of a continuous spectrum is the rainbow produced when raindrops or mist acts as a prism for sunlight.

Not all radiation sources produce a continuous spectrum. When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colors of light ([Figure 6.9](#)). The light emitted by neon gas is the familiar red-orange glow of many “neon” lights, whereas sodium vapor emits the yellow light characteristic of some streetlights. When light coming from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectra ([Figure 6.10](#)). Each colored line in such spectra represents light of one wavelength. A spectrum containing radiation of only specific wavelengths is called a **line spectrum**.

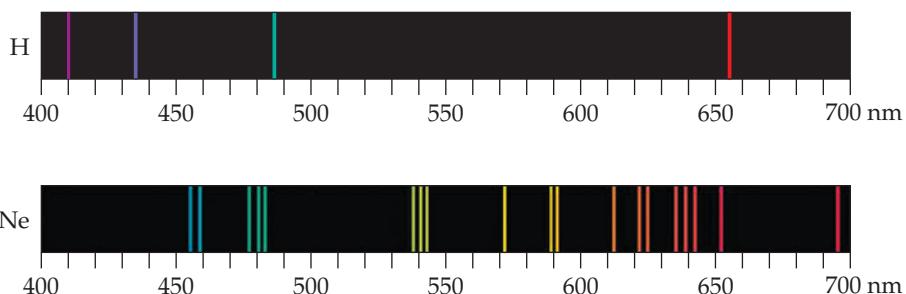
► Figure 6.8 Creating a spectrum. A continuous visible spectrum is produced when a narrow beam of white light is passed through a prism. The white light could be sunlight or light from an incandescent lamp.



► Figure 6.9 Atomic emission of hydrogen and neon. Different gases emit light of different characteristic colors when an electric current is passed through them.



► Figure 6.10 Line spectra of hydrogen and neon. The colored lines occur at wavelengths present in the emission. The black regions are wavelengths for which no light is produced in the emission.



When scientists first detected the line spectrum of hydrogen in the mid-1800s, they were fascinated by its simplicity. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red) were observed (Figure 6.10). In 1885, a Swiss schoolteacher named Johann Balmer showed that the wavelengths of these four lines fit an intriguingly simple formula that relates the wavelengths to integers. Later, additional lines were found in the ultraviolet and infrared regions of hydrogen's line spectrum. Soon Balmer's equation was extended to a more general one, called the *Rydberg equation*, which allows us to calculate the wavelengths of all the spectral lines of hydrogen:

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

In this formula, λ is the wavelength of a spectral line, R_H is the *Rydberg constant* ($1.096776 \times 10^7 \text{ m}^{-1}$), and n_1 and n_2 are positive integers, with n_2 being larger than n_1 . How could the remarkable simplicity of this equation be explained? It took nearly 30 more years to answer this question.

Bohr's Model

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

Bohr based his model on three postulates:

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

The Energy States of the Hydrogen Atom

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

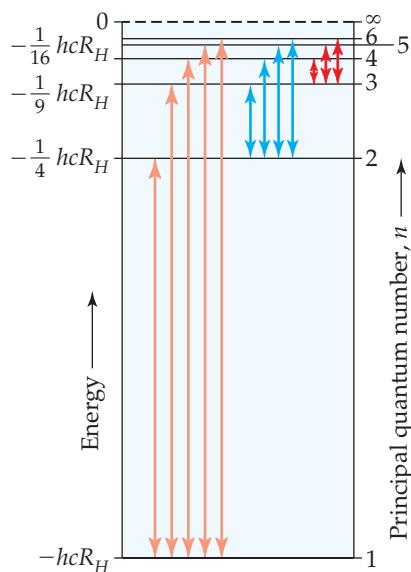
$$E = (-hcR_H) \left(\frac{1}{n^2} \right) = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n^2} \right) \quad [6.5]$$

where h , c , and R_H are the Planck constant, the speed of light, and the Rydberg constant, respectively. The integer n , which can have whole-number values of $1, 2, 3, \dots, \infty$, is called the **principal quantum number**.

Each allowed orbit corresponds to a different value of n . The radius of the orbit gets larger as n increases. Thus, the first allowed orbit (the one closest to the nucleus) has $n = 1$, the next allowed orbit (the one second closest to the nucleus) has $n = 2$, and so forth. The electron in the hydrogen atom can be in any allowed orbit, and Equation 6.5 tells us the energy the electron has in each allowed orbit.

Go Figure

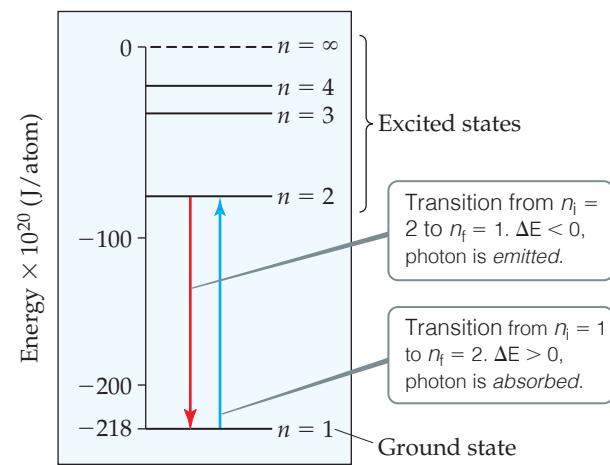
If the transition of an electron from the $n = 3$ state to the $n = 2$ state results in emission of visible light, is the transition from the $n = 2$ state to the $n = 1$ state more likely to result in the emission of infrared or ultraviolet radiation?



▲ Figure 6.11 Energy levels in the hydrogen atom from the Bohr model. The arrows refer to the transitions of the electron from one allowed energy state to another. The states shown are those for which $n = 1$ through $n = 6$ and the state for $n = \infty$ for which the energy, E , equals zero.

Go Figure

Which transition will lead to the emission of light with longer wavelength, $n = 3$ to $n = 2$, or $n = 4$ to $n = 3$?



▲ Figure 6.12 Change in energy states for absorption and emission of a photon in a hydrogen atom.

Note that the energies of the electron given by Equation 6.5 are negative for all values of n . The lower (more negative) the energy is, the more stable the atom is. The energy is lowest (most negative) for $n = 1$. As n gets larger, the energy becomes less negative and therefore increases. We can liken the situation to a ladder in which the rungs are numbered from the bottom. The higher one climbs (the greater the value of n), the higher the energy. The lowest-energy state ($n = 1$, analogous to the bottom rung) is called the **ground state** of the atom. When the electron is in a higher-energy state ($n = 2$ or higher), the atom is said to be in an **excited state**. Figure 6.11 shows the allowed energy levels for the hydrogen atom for several values of n .

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

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

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

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

Let's consider a case in which the electron jumps from an initial state with principal quantum number n_i and energy E_i to a final state with principal quantum number n_f and energy E_f . Using Equation 6.5, we see that the change in energy for this transition is

$$\Delta E = E_f - E_i = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad [6.6]$$

What is the significance of the sign of ΔE ? Notice that ΔE is positive when n_f is greater than n_i . That makes sense to us because that means the electron is jumping to a higher-energy orbit. Conversely, ΔE is negative when n_f is less than n_i ; the electron is falling in energy to a lower-energy orbit.

As noted earlier, transitions from one allowed state to another will involve a photon. *The energy of the photon (E_{photon}) must equal the difference in energy between the two states (ΔE)*. When ΔE is positive, a photon must be *absorbed* as the electron jumps to a higher energy. When ΔE is negative, a photon is *emitted* as the electron falls to a lower-energy level. In both cases, the energy of the photon must match the energy difference between the states. Because the frequency ν is always a positive number, the energy of the photon ($h\nu$) must always be positive. Thus, the sign of ΔE tells us whether the photon is absorbed or emitted:

$$\Delta E > 0 (n_f > n_i): \text{Photon absorbed with } E_{\text{photon}} = h\nu = \Delta E$$

$$\Delta E < 0 (n_f < n_i): \text{Photon emitted with } E_{\text{photon}} = h\nu = -\Delta E \quad [6.7]$$

These two situations are summarized in Figure 6.12. We see that Bohr's model of the hydrogen atom leads to the conclusion that only the specific frequencies of light that satisfy Equation 6.7 can be absorbed or emitted by the atom.

Let's see how to apply these concepts by considering a transition in which the electron moves from $n_i = 3$ to $n_f = 1$. From Equation 6.6 we have

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

The value of ΔE is negative—that makes sense because the electron is falling from a higher-energy orbit ($n = 3$) to a lower-energy orbit ($n = 1$). A photon is *emitted* during this transition, and the energy of the photon is equal to $E_{\text{photon}} = h\nu = -\Delta E = +1.94 \times 10^{-18} \text{ J}$.

Knowing the energy of the emitted photon, we can calculate either its frequency or its wavelength. For the wavelength, we combine Equations 6.1 ($\lambda = c/\nu$) and 6.3 ($E_{\text{photon}} = h\nu$) to obtain

$$\lambda = \frac{c}{\nu} = \frac{hc}{E_{\text{photon}}} = \frac{hc}{-\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{+1.94 \times 10^{-18} \text{ J}} = 1.02 \times 10^{-7} \text{ m}$$

Thus, a photon of wavelength $1.02 \times 10^{-7} \text{ m}$ (102 nm) is *emitted*.

We are now in a position to understand the remarkable simplicity of the line spectra of hydrogen, first discovered by Balmer. We recognize that the line spectra are the result of emission, so $E_{\text{photon}} = h\nu = hc/\lambda = -\Delta E$ for these transitions. Combining Equations 6.5 and 6.6, we see that

$$E_{\text{photon}} = \frac{hc}{\lambda} = -\Delta E = hcR_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ (for emission)}$$

which gives us

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

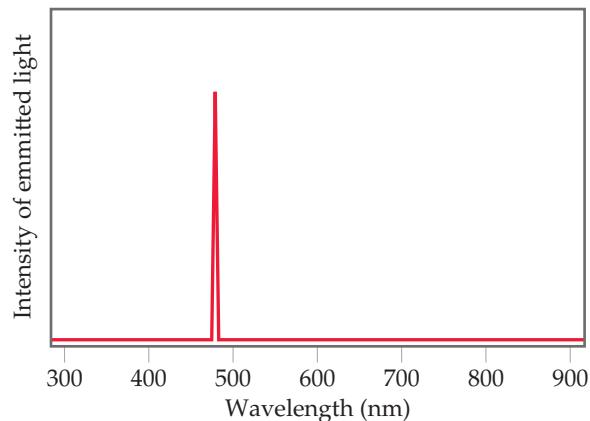
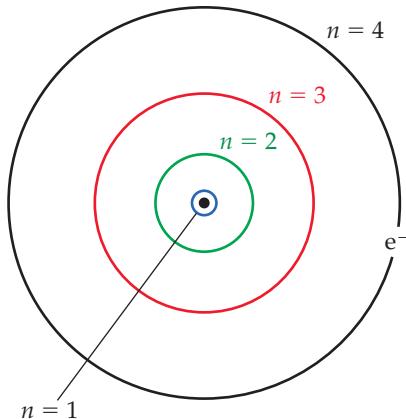
Thus, the existence of discrete spectral lines can be attributed to the quantized jumps of electrons between energy levels.

Sample Exercise 6.4

Electronic Transitions in the Hydrogen Atom

In the Bohr model of the hydrogen atom, electrons are confined to orbits with fixed radii, and those radii can be calculated. The radii of the first four orbits are 0.53, 2.12, 4.76, and 8.46 Å, respectively, as depicted here.

- (a) If an electron makes a transition from the $n_i = 4$ level to a lower-energy level, $n_f = 3, 2$, or 1 , which transition would produce a photon with the shortest wavelength?
- (b) What are the energy and wavelength of such a photon, and in which region of the electromagnetic spectrum does it lie?
- (c) The image on the right shows the output of a detector that measures the intensity of light emitted from a sample of hydrogen atoms that have been excited so that each atom begins with an electron in the $n = 4$ state. What is the final state, n_f , of the transition being detected?



SOLUTION

Analyze We are asked to determine the energy and wavelength associated with various transitions involving an electron relaxing from the $n = 4$ state of the hydrogen atom to one of three lower-energy states.

Plan Given the integers representing the initial and final states of the electron, we can use Equation 6.6 to calculate the energy of the photon emitted and then use the relationships $E = h\nu$ and $c = \nu\lambda$ to convert energy to wavelength. The photon with the highest energy will have the shortest wavelength because photon energy is inversely proportional to wavelength.

Solve

- (a) The wavelength of a photon is related to its energy through the relationship $E = h\nu = hc/\lambda$. Hence, the photon with the smallest wavelength will have the largest energy. The energy levels of the electron orbits decrease as n decreases.

- (b) We first calculate the energy of the photon using Equation 6.6 with $n_i = 4$ and $n_f = 1$:

The electron loses the most energy on transitioning from the $n_i = 4$ state to the $n_f = 1$ state, and the photon emitted in that transition has the highest energy and the smallest wavelength.

$$\Delta E = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = -2.04 \times 10^{-18} \text{ J}$$

$$E_{\text{photon}} = -\Delta E = 2.04 \times 10^{-18} \text{ J}$$

Next we rearrange Planck's relationship to calculate the frequency of the emitted photon.

Finally, we use the frequency to determine the wavelength.

Light with this wavelength falls in the ultraviolet region of the electromagnetic spectrum.

- (c) From the graph, we estimate the wavelength of the photon to be approximately 480 nm. Starting from the wavelength, it is easiest to estimate n_f using Equation 6.4:

Rearranging:

So $n_f = 2$, and the photons seen by the detector are those emitted when an electron transitions from the $n_f = 4$ to the $n_f = 2$ state.

Check Referring back to Figure 6.11, we confirm that the $n = 4$ to $n = 1$ transition should have the largest energy of the three possible transitions.

$$\nu = E/h = (2.04 \times 10^{-18} \text{ J}) / (6.626 \times 10^{-34} \text{ J}\cdot\text{s}) = 3.02 \times 10^{15} \text{ s}^{-1}$$

$$\lambda = c/\nu = (2.998 \times 10^8 \text{ m/s}) / (3.02 \times 10^{15} \text{ s}^{-1}) \\ = 9.72 \times 10^{-8} \text{ m} = 97.2 \text{ nm}$$

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

$$\frac{1}{n_f^2} = \frac{1}{n_i^2} + \frac{1}{R_H \lambda} = \frac{1}{4^2} + \frac{1}{(1.097 \times 10^7 \text{ m}^{-1})(480 \times 10^{-9} \text{ m})} \\ \frac{1}{n_f^2} = 0.25$$

► Practice Exercise

In the top part of Figure 6.10, the four lines in the H atom spectrum are due to transitions from a level for which $n_i > 2$ to the $n_f = 2$ level. What is the value of n_i for the red line in the spectrum? (a) 3 (b) 4 (c) 5 (d) 6 (e) 7

Limitations of the Bohr Model

Although the Bohr model explains the line spectrum of the hydrogen atom, it can not explain the spectra of other atoms, except in a crude way. Bohr also avoided the problem of why the negatively charged electron would not just fall into the positively charged nucleus, by simply assuming it would not happen. Furthermore, we will see that Bohr's model of an electron orbiting the nucleus at a fixed distance is not a realistic picture. As we will see in Section 6.4, the electron exhibits wave-like properties, a fact that any acceptable model of electronic structure must accommodate.

As it turns out, the Bohr model was only an important step along the way toward the development of a more comprehensive model. What is most significant about Bohr's model is that it introduces two important ideas that are also incorporated into our current model:

1. Electrons exist only in certain discrete energy levels, which are described by quantum numbers.
2. Energy is involved in the transition of an electron from one level to another.

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

Self-Assessment Exercise

6.14 Which transition would result in emission of the shortest wavelength photon?

- (a) from $n = 4$ to $n = 2$
- (b) from $n = 6$ to $n = 4$

(c) from $n = 10$ to $n = 6$

(d) from $n = 100$ to $n = 10$

Exercises

6.15 Does the hydrogen atom “expand” or “contract” when an electron is excited from the $n = 1$ state to the $n = 3$ state?

6.16 Is energy emitted or absorbed when the following electronic transitions occur in hydrogen? (a) from $n = 3$ to $n = 2$, (b) from an orbit of radius 0.846 nm to one of radius 0.212 nm, (c) an electron adds to the H^+ ion and ends up in the $n = 2$ shell?

6.17 (a) Using Equation 6.5, calculate the energy of an electron in the hydrogen atom when $n = 3$ and when $n = 6$. Calculate the wavelength of the radiation released when an electron moves from $n = 6$ to $n = 3$. (b) Is this line in the visible region of the electromagnetic spectrum?

6.18 The visible emission lines observed by Balmer all involved $n_f = 2$. (a) Which of the following is the best explanation of why the lines with $n_f = 3$ are not observed in the visible portion of the spectrum: (i) Transitions to $n_f = 3$ are not allowed

to happen, (ii) transitions to $n_f = 3$ emit photons in the infrared portion of the spectrum, (iii) transitions to $n_f = 3$ emit photons in the ultraviolet portion of the spectrum, or (iv) transitions to $n_f = 3$ emit photons that are at exactly the same wavelengths as those to $n_f = 2$. (b) Calculate the wavelengths of the first three lines in the Balmer series—those for which $n_i = 3, 4$, and 5—and identify these lines in the emission spectrum shown in Figure 6.10.

6.19 One of the emission lines of the hydrogen atom has a wavelength of 94.974 nm. (a) In what region of the electromagnetic spectrum is this emission found? (b) Determine the initial and final values of n associated with this emission.

6.20 Order the following transitions in the hydrogen atom from smallest to largest frequency of light absorbed: $n = 3$ to $n = 7$, $n = 4$ to $n = 8$, $n = 2$ to $n = 5$, and $n = 1$ to $n = 3$.

6.14 (a)

Answers to Self-Assessment Exercise



6.4 | The Wave Behavior of Matter



Sometimes, things are not what they seem! A movie film is based on motion and change yet slow the film down enough and it becomes evident it is made of a

progression of still pictures. We live in a macroscopic world where every object is composed of millions upon millions of atoms. Dial down to an atomic scale and we glimpse another realm.

By the end of this section, you should be able to

- Appreciate that a wave–particle duality and position–momentum uncertainty become significant when dealing with electrons.

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

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

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

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

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



Sample Exercise 6.5

Matter Waves

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

SOLUTION

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

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

Solve

Using the value of the Planck constant:

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$

we have the following:

$$\begin{aligned} \lambda &= \frac{h}{mv} \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})}{(9.11 \times 10^{-31} \text{ kg})(5.97 \times 10^6 \text{ m/s})} \left(\frac{1 \text{ kg}\cdot\text{m}^2/\text{s}^2}{1 \text{ J}} \right) \\ &= 1.22 \times 10^{-10} \text{ m} = 0.122 \text{ nm} = 122 \text{ pm} \end{aligned}$$

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

moving at a speed of $2.3 \times 10^2 \text{ m/s}$. List the three objects in order from shortest to longest de Broglie wavelength.

- (a) i < iii < ii (b) ii < iii < i (c) iii < ii < i (d) i < ii < iii
(e) iii < i < ii

► Practice Exercise

Consider the following three moving objects: (i) a golf ball with a mass of 45.9 g moving at a speed of 50.0 m/s, (ii) An electron moving at a speed of $3.50 \times 10^5 \text{ m/s}$, (iii) A neutron

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

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

The Uncertainty Principle

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

The German physicist Werner Heisenberg (Figure 6.14) proposed that the dual nature of matter places a fundamental limitation on how precisely we can know both the location and the momentum of an object at a given instant. The limitation becomes important only when we deal with matter at the subatomic level (that is, with masses as small as that of an electron). Heisenberg's principle is called the **uncertainty principle**. When applied to the electrons in an atom, this principle states that it is impossible for us to know simultaneously both the exact momentum of an electron and its exact location in space.

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

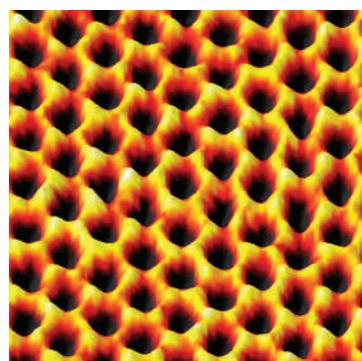
$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi} \quad [6.9]$$

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

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

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

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



▲ Figure 6.13 Electrons as waves.
Transmission electron micrograph of graphene, which has a hexagonal honeycomb arrangement of carbon atoms. Each of the bright yellow "mountains" indicates a carbon atom.



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

A CLOSER LOOK Measurement and the Uncertainty Principle

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

To measure an object, we must disturb it, at least a little, with our measuring device. Imagine using a flashlight to locate a large rubber ball in a dark room. You see the ball when the light from the flashlight bounces off the ball and strikes your eyes. When a beam of photons strikes an object of this size, it does not alter its position or momentum to any practical extent. Imagine, however, that you wish to locate an electron by similarly bouncing light off it into some detector. Objects can be located to an accuracy no greater than the wavelength of the radiation used. Thus, if we want an accurate position measurement for an electron, we must use a short wavelength. This means that photons of high energy

must be employed. The more energy the photons have, the more momentum they impart to the electron when they strike it, which changes the electron's motion in an unpredictable way. The attempt to measure accurately the electron's position introduces considerable uncertainty in its momentum; the act of measuring the electron's position at one moment makes our knowledge of its future position inaccurate.

Suppose, then, that we use photons of longer wavelength. Because these photons have lower energy, the momentum of the electron is not so appreciably changed during measurement, but at the same time the longer wavelength limits the accuracy with which the electron's position can be determined. This is the essence of the uncertainty principle: *There is an uncertainty in simultaneously knowing both the position and the momentum of the electron that cannot be reduced beyond a certain minimum level.* The more accurately one is known, the less accurately the other is known.

Although we can never know the exact position and momentum of the electron, we can talk about the probability of its being at certain locations in space. In Section 6.5, we introduce a model of the atom that provides the probability of finding electrons of specific energies at certain positions in atoms.

Related Exercises: 6.25, 6.75, 6.105, 6.106

Self-Assessment Exercises

- 6.21** Is this statement true or false: *when considering a small fast moving object such as an electron, we can never measure both its position and velocity with great accuracy?*

- (a) True
(b) False

- 6.22** Is this statement true or false: *the wave-particle duality becomes significant with objects the size of an electron?*

- (a) True
(b) False

Exercises

- 6.23** Use the de Broglie relationship to determine the wavelengths of the following objects: (a) an 85 kg person skiing at 50 km/hr, (b) a 10.0 g bullet fired at 250 m/s, (c) a lithium atom of mass 11.5×10^{-27} kg moving at 2.5×10^5 m/s.
- 6.24** Neutron diffraction is an important technique for determining the structures of molecules. Calculate the velocity of a neutron needed to achieve a wavelength of 125 pm. (Refer to the inside cover for the mass of the neutron.)

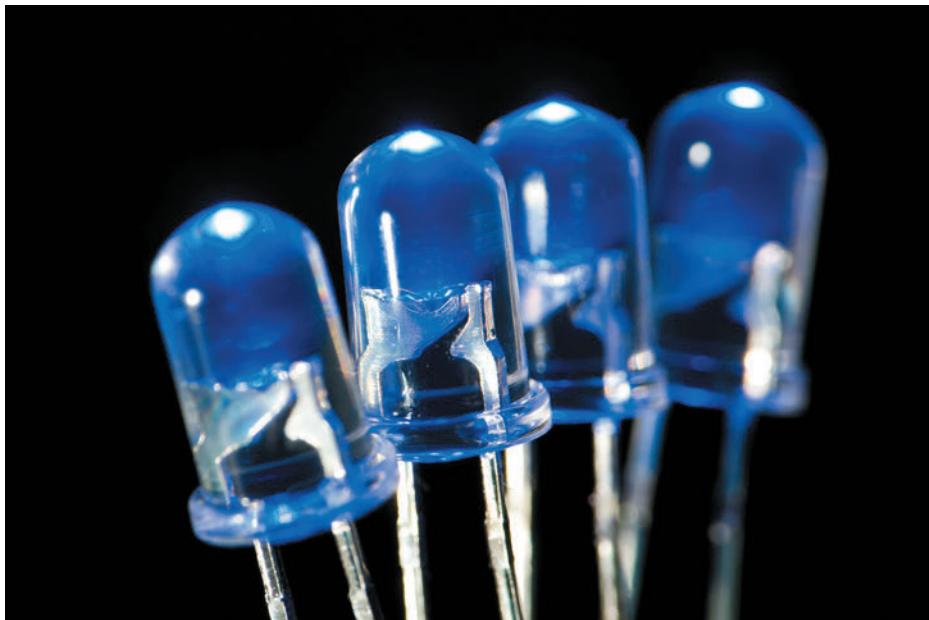
- 6.25** Using Heisenberg's uncertainty principle, calculate the uncertainty in the position of (a) a 1.50-mg mosquito moving at a speed of 1.40 m/s if the speed is known to within ± 0.01 m/s; (b) a proton moving at a speed of $(5.00 \pm 0.01) \times 10^4$ m/s. (The mass of a proton is given in the table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

6.21 (a) 6.22 (a)

Answers to Self-Assessment Exercise



6.5 | Quantum Mechanics and Atomic Orbitals



Quantum theory led to the explosion in technological developments in the twentieth century, including remarkable new light sources, such as light-emitting diodes (LEDs), which are now being used as high-quality, low-energy-consumption light sources in many applications, and lasers, which have revolutionized so many aspects of our lives. Quantum theory also led to the development of the solid-state electronics that are at the heart of computers, cellular telephones, and countless other electronic devices.

By the end of this section, you should be able to

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

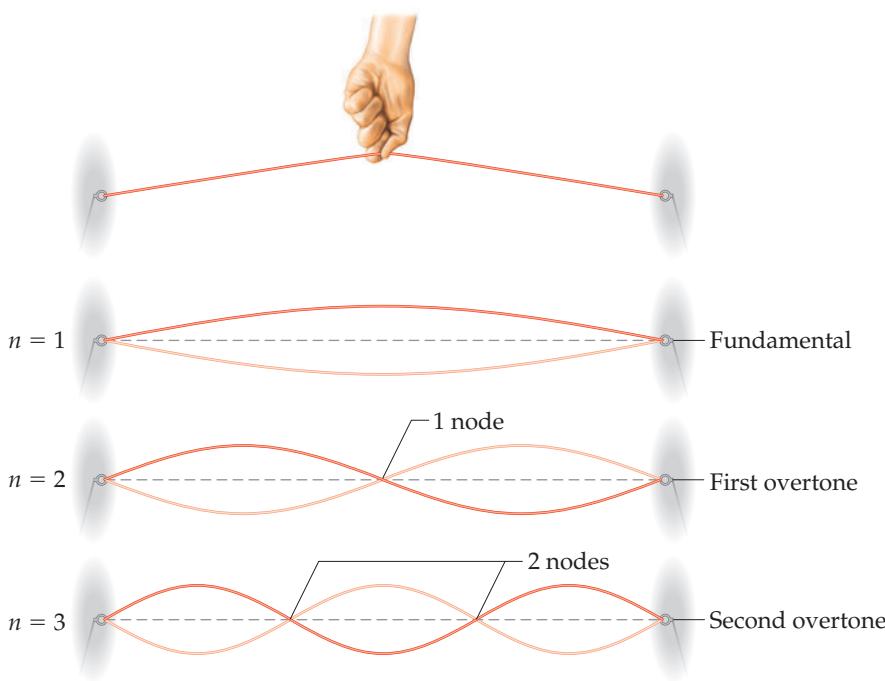
In 1926, the Austrian physicist Erwin Schrödinger (1887–1961) proposed an equation, now known as *Schrödinger's wave equation*, that incorporates both the wave-like and particle-like behaviors of the electron. His work opened a new approach to dealing with subatomic particles, an approach known as *quantum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

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

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

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

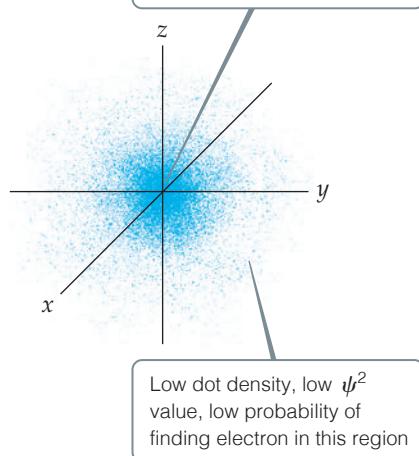
► **Figure 6.15** Standing waves in a vibrating string.



Go Figure

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

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



▲ **Figure 6.16** Electron-density distribution.

This rendering represents the probability, ψ^2 , of finding the electron in a hydrogen atom in its ground state. The origin of the coordinate system is at the nucleus.

According to the uncertainty principle, if we know the momentum of the electron with high accuracy, our simultaneous knowledge of its location is very uncertain. Thus, we cannot hope to specify the exact location of an individual electron around the nucleus. Rather, we must be content with a kind of statistical knowledge. We therefore speak of the *probability* that the electron will be in a certain region of space at a given instant. As it turns out, the square of the wave function, ψ^2 , at a given point in space represents the probability that the electron will be found at that location. For this reason, ψ^2 is called either the **probability density** or the **electron density**.

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

Orbitals and Quantum Numbers

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

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

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

A CLOSER LOOK Thought Experiments and Schrödinger's Cat

The revolutions in scientific thinking caused by the theory of relativity and quantum theory not only changed science; it also caused deep changes in how we understand the world around us. Before relativity and quantum theory, the prevailing physical theories were inherently *deterministic*: Once the specific conditions of an object were given (position, velocity, forces acting on the object), we could determine exactly the position and motion of the object at any time in the future. These theories, from Newton's laws to Maxwell's theory of electromagnetism, successfully described physical phenomena such as motion of the planets, the trajectories of projectiles, and the diffraction of light.

Relativity and quantum theory both challenged the deterministic view of the universe, and did so in a way that caused a great deal of uneasiness among even the scientists who were developing the theories. One of the common methods scientists used to test these new theories was through so-called thought experiments. Thought experiments are hypothetical scenarios that can lead to paradoxes within a given theory. Let's briefly discuss one of these thought experiments that was used to test ideas within quantum theory.

Quantum theory caused a great deal of discussion with respect to its nondeterministic description of matter. We have touched on two such areas in this chapter. First, we have seen that the descriptions of light and matter have become less distinct—light has particle-like properties and matter has wave-like properties. The description of matter that results—in which we can talk only about the probability of an electron being at a certain place as opposed to knowing exactly where it is—was very bothersome to many. Einstein, for example, famously said that “God doesn’t play dice with the world”* about this probabilistic description. Heisenberg’s uncertainty principle, which

assures that we can’t know the position and momentum of a particle exactly, also raised many philosophical questions—so many, in fact, that Heisenberg wrote a book entitled *Physics and Philosophy* in 1958.

One of the most famous thought experiments put forward in the early days of the quantum theory was formulated by Schrödinger and is now known as “Schrödinger’s cat.” This experiment called into question whether a system could have multiple acceptable wave functions prior to observation of the system. In other words, if we don’t actually observe a system, can we know anything about the state it is in? In this paradox, a hypothetical cat is placed in a sealed box with an apparatus that will randomly trigger a lethal dose of poison to the cat (as morbid as that sounds). According to some interpretations of quantum theory, until the box is opened and the cat is observed, the cat must be considered simultaneously alive and dead.

Schrödinger posed this paradox to point out weaknesses in some interpretations of quantum results, but the paradox has led instead to a continuing and lively debate about the fate and meaning of Schrödinger’s cat. In 2012, the Nobel Prize in Physics was awarded to Serge Haroche of France and David Wineland of the United States for their ingenious methods for observing the quantum states of photons or particles without having the act of observation destroy the states. In so doing, they observed what is generally called the “cat state” of the systems, in which the photon or particle exists simultaneously in two different quantum states. A puzzling paradox, indeed, but one that might ultimately lead to new ways to harness the simultaneous states to create so-called quantum computers and more accurate clocks.

Related Exercise: 6.106

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

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

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

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

The collection of orbitals with the same value of n is called an **electron shell**. All the orbitals that have $n = 3$, for example, are said to be in the third shell. The set of orbitals that have the same n and l values is called a **subshell**. Each subshell is designated by a number (the value of n) and a letter (s , p , d , or f , corresponding to the value of l). For example, the orbitals that have $n = 3$ and $l = 2$ are called $3d$ orbitals and are in the $3d$ subshell.

*Hermanns, William, *Einstein and the Poet: In Search of the Cosmic Man*, 1st edition, Branden Books, 1983.

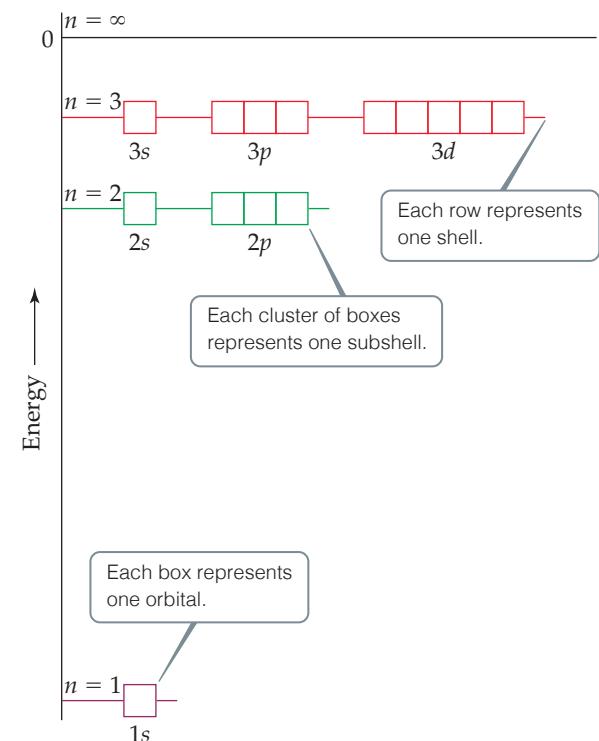
**The letters come from the words *sharp*, *principal*, *diffuse*, and *fundamental*, which were used to describe certain features of spectra before quantum mechanics was developed.

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

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

Go Figure

Are the energies of the $n = 1$, 2 , and 3 shells shown here the same as or different from those of the Bohr model of the atom shown in Figure 6.11?



$n = 1$ shell has one orbital

$n = 2$ shell has two subshells composed of four orbitals
 $n = 3$ shell has three subshells composed of nine orbitals

▲ Figure 6.17 Energy levels in the hydrogen atom.

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

1. *The shell with principal quantum number n consists of exactly n subshells.* Each subshell corresponds to a different allowed value of l from 0 to $(n - 1)$. Thus, the first shell ($n = 1$) consists of only one subshell, the $1s$ ($l = 0$); the second shell ($n = 2$) consists of two subshells, the $2s$ ($l = 0$) and $2p$ ($l = 1$); the third shell consists of three subshells, $3s$, $3p$, and $3d$, and so forth.
2. *Each subshell consists of a specific number of orbitals.* Each orbital corresponds to a different allowed value of m_l . For a given value of l , there are $(2l + 1)$ allowed values of m_l , ranging from $-l$ to $+l$. Thus, each s ($l = 0$) subshell consists of one orbital; each p ($l = 1$) subshell consists of three orbitals; each d ($l = 2$) subshell consists of five orbitals, and so forth.
3. *The total number of orbitals in a shell is n^2 , where n is the principal quantum number of the shell.* The resulting number of orbitals for the shells—1, 4, 9, 16—is related to a pattern seen in the periodic table: We see that the number of elements in the rows of the periodic table—2, 8, 18, and 32>equals twice these numbers. We will discuss this relationship further in Section 6.9.

Figure 6.17 shows the relative energies of the hydrogen atom orbitals through $n = 3$. Each box represents an orbital, and orbitals of the same subshell, such as the three $2p$ orbitals, are grouped together. When the electron occupies the lowest-energy orbital ($1s$), the hydrogen atom is said to be in its *ground state*. When the electron occupies any other orbital, the atom is in an *excited state*. (The electron can be excited to a higher-energy orbital by absorption of a photon of appropriate energy.) At ordinary temperatures, essentially all hydrogen atoms are in the ground state.



Sample Exercise 6.6

Subshells of the Hydrogen Atom



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

SOLUTION

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

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

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

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

► Practice Exercise

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

Self-Assessment Exercise

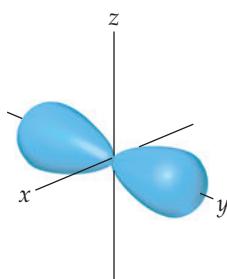
- 6.26** Which set of quantum numbers is a valid description of an orbital?

- (a) $n = 2; l = 2; m_l = 0$
 (b) $n = 0; l = 2; m_l = 2$

- (c) $n = 3; l = 2; m_l = 1$
 (d) $n = 2; l = 0; m_l = 1$

Exercises

- 6.27** Classify the following statements as either true or false:
 (a) In a contour representation of an orbital, such as the one shown here for a 2p orbital, the electron is confined to move about the nucleus on the outer surface of the shape. (b) The probability density $[\psi(r)]^2$ gives the probability of finding the electron at a specific distance from the nucleus.



- 6.28** (a) For $n = 4$, what are the possible values of l ? (b) For $l = 2$, what are the possible values of m_l ? (c) If m_l is 2, what are the possible values for l ?
6.29 Give the numerical values of n and l corresponding to each of the following orbital designations: (a) 3p, (b) 2s, (c) 4f, (d) 5d.
6.30 A certain orbital of the hydrogen atom has $n = 4$ and $l = 3$. (a) What are the possible values of m_l for this orbital? (b) What are the possible values of m_s for the orbital?
6.31 Which of the following represent impossible combinations of n and l ? (a) 1p, (b) 4s, (c) 5f, (d) 2d

6.26 (c)

Answers to Self-Assessment Exercise



6.6 | Representations of Orbitals



Watching the waves break on the shore of a large lake or at the seaside can be both fascinating and relaxing. We can, perhaps, imagine waves of different sorts—a wave in one dimension might be represented by the shape of a plucked guitar string or a moving skipping rope. A wave in two dimensions is typified by the ripples in a pond after a stone has been thrown into the water. For a wave in three dimensions, think of the surface of a balloon that is pulsing in size. To simplify the situation, we may draw a cross-section of the wave as a snapshot in time, but we should always bear in mind that waves are in motion.

By the end of this section, you should be able to

- Recognize the shape and size of orbitals of a given n and l quantum number

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

The s Orbitals

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

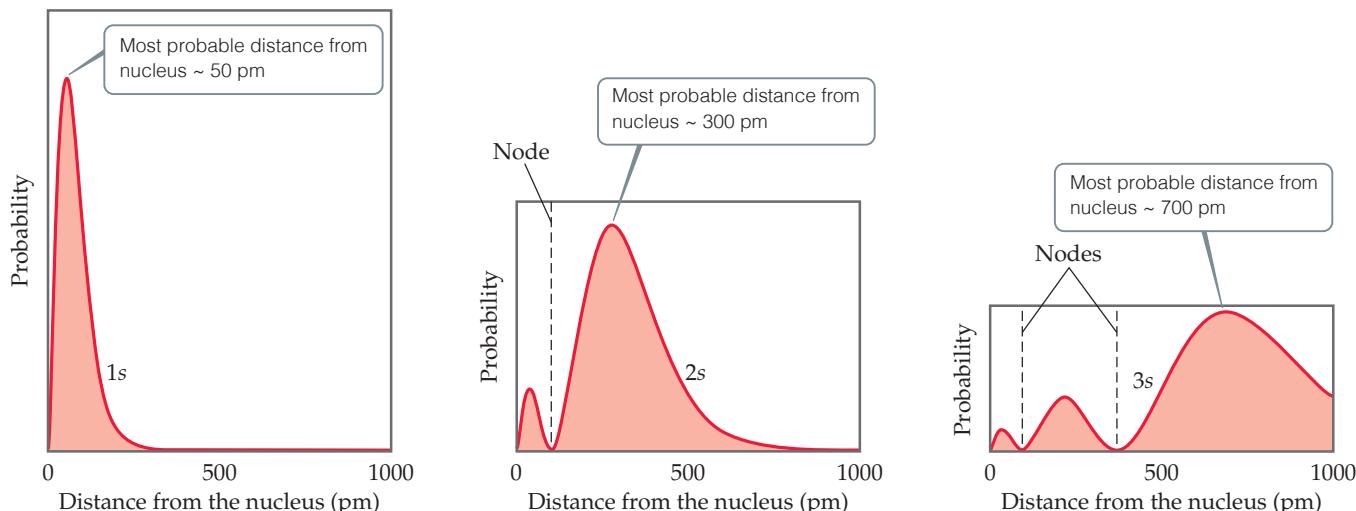
Recall that the l quantum number for the s orbitals is 0; therefore, the m_l quantum number must be 0. Thus, for each value of n , there is only one s orbital. So how do s orbitals differ as the value of n changes? For example, how does the electron-density distribution of the hydrogen atom change when the electron is excited from the $1s$ orbital to the $2s$ orbital? To address this question, we will look at the *radial probability density*, which is the probability that the electron is at a specific distance from the nucleus.

Figure 6.18 shows the radial probability densities for the $1s$, $2s$, and $3s$ orbitals of hydrogen as a function of r , the distance from the nucleus—each resulting curve is the **radial probability function** for the orbital. Three features of these plots are noteworthy: the number of peaks, the number of points at which the probability function goes to zero (called **nodes**), and how spread out the distribution is, which gives a sense of the size of the orbital.

For the $1s$ orbital, we see that the probability rises rapidly as we move away from the nucleus, maximizing at about 50 pm. Thus, when the electron occupies the $1s$ orbital, it is *most likely* to be found this distance from the nucleus*—we still use the probabilistic

Go Figure

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



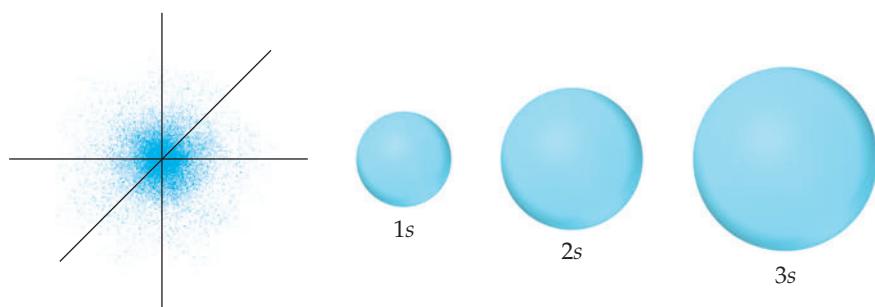
▲ Figure 6.18 Radial probability functions for the 1s, 2s, and 3s orbitals of hydrogen. These plots show the probability of finding the electron as a function of distance from the nucleus. As n increases, the most likely distance at which to find the electron (the highest peak) moves farther from the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

description, consistent with the uncertainty principle. Notice also that in the 1s orbital the probability of finding the electron at a distance greater than about 300 pm from the nucleus is essentially zero.

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

1. For an ns orbital, the number of peaks is equal to n , with the outermost peak being larger than inner ones.
2. For an ns orbital, the number of nodes is equal to $n - 1$.
3. As n increases, the electron density becomes more spread out; that is, there is a greater probability of finding the electron further from the nucleus.

One widely used method of representing orbital *shape* is to draw a boundary surface that encloses some substantial portion, say 90%, of the electron density for the orbital. This type of drawing is called a *contour representation*, and the contour representations for the s orbitals are spheres (Figure 6.19). All the orbitals have the same shape, but they differ in size, becoming larger as n increases, reflecting the fact that the electron density becomes more spread out as n increases. Although the details of how electron density varies within a given contour representation are lost in these representations, this is not a



(a) An electron density model

(b) Contour models

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

*In the quantum-mechanical model, the most probable distance at which to find the electron in the 1s orbital is actually 52.9 pm, the same as the radius of the orbit predicted by Bohr for $n = 1$. The distance 52.9 pm is often called the Bohr radius.

A CLOSER LOOK Probability Density and Radial Probability Functions

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

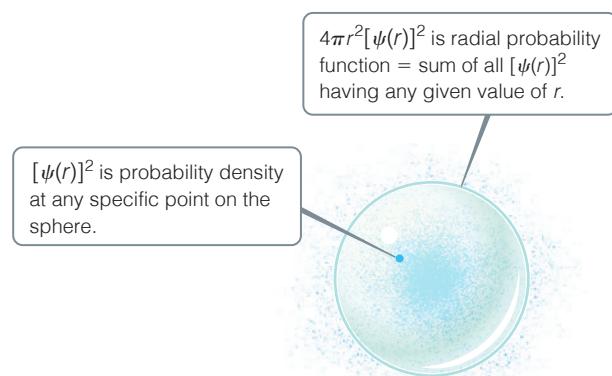
The radial probability function, which we used in Figure 6.18, differs from the probability density. The radial probability function equals the *total* probability of finding the electron at all the points at any distance r from the nucleus. In other words, to calculate this function, we need to "add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

Let's examine the difference between probability density and radial probability function more closely. **Figure 6.21** shows plots of $[\psi(r)]^2$ as a function of r for the 1s, 2s, and 3s orbitals of the hydrogen atom. You will notice that these plots look distinctly different from the radial probability functions shown in Figure 6.18.

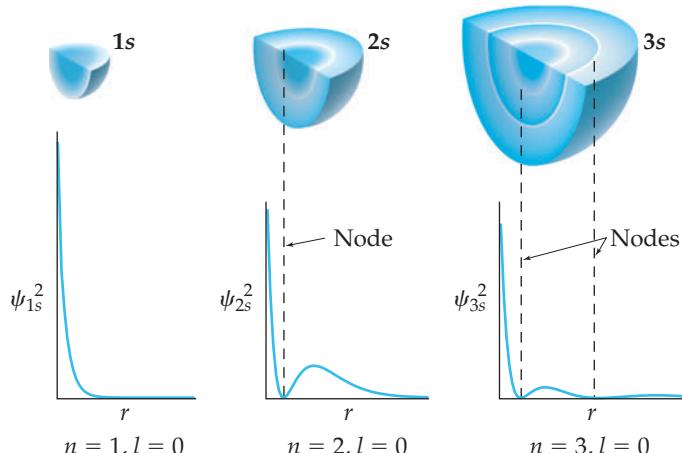
As shown in Figure 6.20, the collection of points a distance r from the nucleus is the surface of a sphere of radius r . The probability density *at each point* on that spherical surface is $[\psi(r)]^2$. To add up all the individual probability densities requires calculus and so is beyond the scope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

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

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



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



▲ Figure 6.21 Probability density $[\psi(r)]^2$ in the 1s, 2s, and 3s orbitals of hydrogen.

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

Related Exercises: 6.34, 6.76, 6.82, 107

serious disadvantage. For qualitative discussions, the most important features of orbitals are shape and relative size, which are adequately displayed by contour representations.

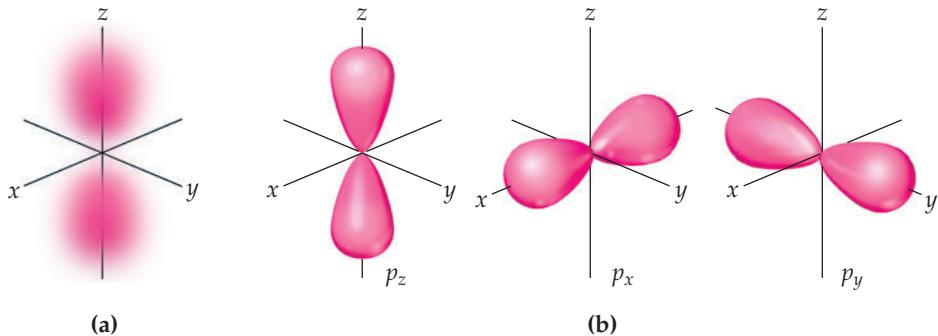
The p Orbitals

Recall that the orbitals for which $l = 1$ are the *p* orbitals. Each *p* subshell has three orbitals, corresponding to the three allowed values of m_l : -1, 0, and 1. The distribution of electron density for a $2p$ orbital is shown in **Figure 6.22(a)**. The electron density is not distributed spherically as in an *s* orbital. Instead, the density is concentrated in two regions on either side of the nucleus, separated by a node at the nucleus. We say that this dumbbell-shaped orbital has two *lobes*. Recall that we are making no statement of how the electron is moving within the orbital. **Figure 6.22(a)** portrays only the *averaged* distribution of the electron density in a $2p$ orbital.

Beginning with the $n = 2$ shell, each shell has three *p* orbitals (Table 6.2), one for each allowed value of m_l . Thus, there are three $2p$ orbitals, three $3p$ orbitals, and so forth. Each set of *p* orbitals has the dumbbell shapes shown in **Figure 6.22(a)** for the $2p$ orbitals. For each value of n , the three *p* orbitals have the same size and shape but differ from one another in spatial orientation. We usually represent *p* orbitals by drawing the shape and orientation of their wave functions, as shown in the contour representations in

 Go Figure

Each p orbital has what is called a nodal plane, a plane or sheet where the probability density goes to zero. For which of the orbitals below is the yz plane a nodal plane?



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

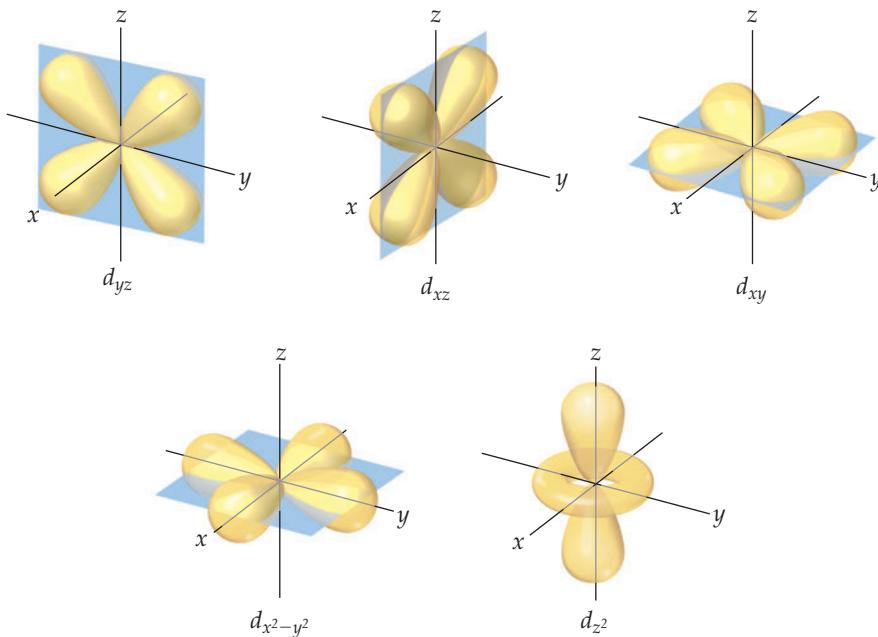
Figure 6.22(b). It is convenient to label these as p_x , p_y , and p_z orbitals. The letter subscript indicates the Cartesian axis along which the orbital is oriented. Thus, we see that two orbitals with the same value of n and l , but different values of m_l , differ from each other in the way they are oriented in space.* Like s orbitals, p orbitals increase in size as we move from $2p$ to $3p$ to $4p$, and so forth.

The d and f Orbitals

When n is 3 or greater, we encounter the d orbitals (for which $l = 2$). There are five $3d$ orbitals, five $4d$ orbitals, and so forth, because in each shell there are five possible values for the m_l quantum number: $-2, -1, 0, 1$, and 2 . The different d orbitals in a given shell have different shapes and orientations in space, as shown in Figure 6.23. Four of

 Go Figure

How many nodal planes, two-dimensional sheets where the probability density goes to zero, are there for the d_{xy} orbital?



▲ Figure 6.23 Contour representations of the five d orbitals.

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

the d -orbital contour representations have a “four-leaf clover” shape, with four lobes, and each lies primarily in a plane. The d_{xy} , d_{xz} , and d_{yz} orbitals lie in the xy , xz , and yz planes, respectively, with the lobes oriented *between* the axes. The lobes of the $d_{x^2-y^2}$ orbital also lie in the xy plane, but the lobes lie *along* the x and y axes. The d_{z^2} orbital looks very different from the other four: It has two lobes along the z axis and a “doughnut” in the xy plane. Even though the d_{z^2} orbital looks different from the other d orbitals, it has the same energy as the other four d orbitals. The representations in Figure 6.23 are commonly used for all d orbitals, regardless of the principal quantum number.

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

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

Self-Assessment Exercise

6.32 How many nodes does a $5s$ orbital have?

(a) 4

(b) 5

(c) 6

Exercises

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

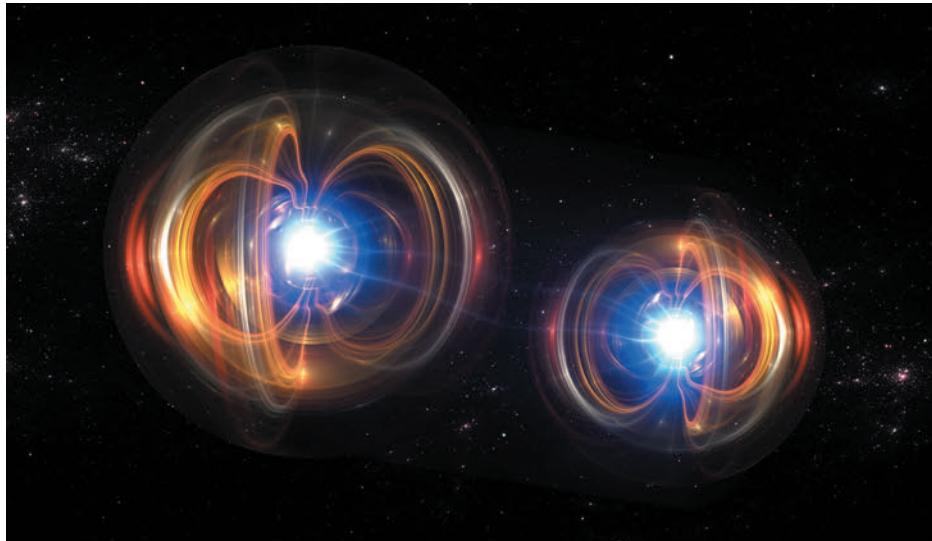
6.34 (a) What are the similarities of and differences between the $1s$ and $2s$ orbitals of the hydrogen atom? (b) In what sense does a $2p$ orbital have directional character? Compare the “directional” characteristics of the p_x and $d_{x^2-y^2}$ orbitals.

(That is, in what direction or region of space is the electron density concentrated?) (c) What can you say about the average distance from the nucleus of an electron in a $2s$ orbital as compared with a $3s$ orbital? (d) For the hydrogen atom, list the following orbitals in order of increasing energy (that is, most stable ones first): $4f$, $6s$, $3d$, $1s$, $2p$.

6.32 (a)

Answers to Self-Assessment Exercise

6.7 | Many-Electron Atoms



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

By the end of this section, you should be able to

- Explain how and why the energies of the orbitals are different in a many-electron atom from those in the hydrogen atom.

Orbitals and Their Energies

We can describe the electronic structure of a many-electron atom by using the orbitals we described for the hydrogen atom in Table 6.2. Thus, the orbitals of a many-electron atom are designated $1s$, $2p_x$, and so forth (Table 6.2) and have the same general shapes as the corresponding hydrogen orbitals.

Although the shapes of the orbitals of a many-electron atom are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, n (Figure 6.17). For instance, in a hydrogen atom, the $3s$, $3p$, and $3d$ subshells all have the same energy. In a many-electron atom, however, the energies of the various subshells in a given shell are *different* because of electron–electron repulsions. To explain why this happens, we must consider the forces between the electrons and how these forces are affected by the shapes of the orbitals. We will, however, forgo this analysis until Chapter 7.

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

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

Electron Spin and the Pauli Exclusion Principle

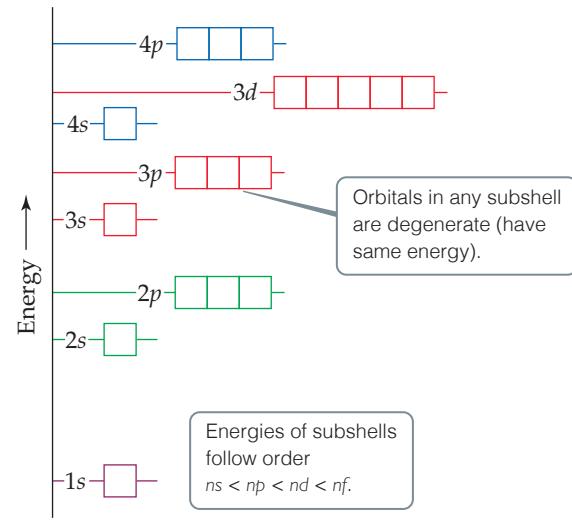
We have now seen that we can use hydrogen-like orbitals to describe many-electron atoms. What, however, determines which orbitals the electrons occupy? That is, how do the electrons of a many-electron atom populate the available orbitals? To answer this question, we must consider an additional property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

When scientists studied the line spectra of many-electron atoms in great detail, they noticed a very puzzling feature: Lines that were originally thought to be single were actually closely spaced pairs. This meant, in essence, that there were twice as many energy levels as there were “supposed” to be. In 1925, the Dutch physicists George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978) proposed a solution to this dilemma. They postulated that electrons have an intrinsic property, called **electron spin**, that causes each electron to behave as if it were a tiny sphere spinning on its own axis.

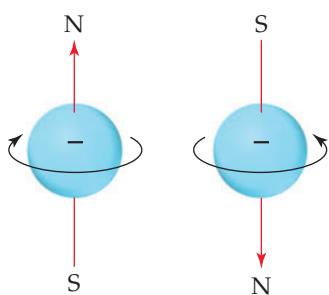
By now, it may not surprise you to learn that electron spin is quantized. This observation led to the assignment of a new quantum number for the electron, in addition to n , l , and m_l , which we have

Go Figure

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



▲ **Figure 6.24** General energy ordering of orbitals for a many-electron atom.



▲ Figure 6.25 Electron spin. The electron behaves as if it were spinning about an axis, thereby generating a magnetic field whose direction depends on the direction of spin. The two directions for the magnetic field correspond to the two possible values for the spin quantum number, m_s . The magnetic fields that emanate from materials, like iron, arise because there are more electrons with one spin direction than the other.

already discussed. This new quantum number, the **spin magnetic quantum number**, is denoted m_s (the subscript s stands for *spin*). Two possible values are allowed for m_s , $+\frac{1}{2}$ or $-\frac{1}{2}$, which were first interpreted as indicating the two opposite directions in which the electron can spin. A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields (**Figure 6.25**).^{*} These two opposite magnetic fields lead to the splitting of spectral lines into closely spaced pairs.

Electron spin is crucial for understanding the electronic structures of atoms. In 1925, the Austrian-born physicist Wolfgang Pauli (1900–1958) discovered the principle that governs the arrangement of electrons in many-electron atoms. The **Pauli exclusion principle** states that *no two electrons in an atom can have the same set of four quantum numbers n , l , m_l , and m_s* . For a given orbital, the values of n , l , and m_l are fixed. Thus, if we want to put more than one electron in an orbital and satisfy the Pauli exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two such values, we conclude that *an orbital can hold a maximum of two electrons and they must have opposite spins*. This restriction allows us to index the electrons in an atom, giving their quantum numbers and thereby defining the region in space where each electron is most likely to be found. It also provides the key to understanding the remarkable structure of the periodic table of the elements.

Self-Assessment Exercise

- 6.35** what is the maximum number of electrons that can occupy a $3d$ subshell?

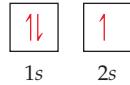
- (a) 3
(b) 5
(c) 10

Exercises

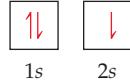
- 6.36** (a) For an He^+ ion, do the $2s$ and $2p$ orbitals have the same energy? If not, which orbital has a lower energy? (b) If we add one electron to form the He atom, would your answer to part (a) change?

- 6.37** Two possible electron configurations for an Li atom are shown here. (a) Does either configuration violate the Pauli exclusion principle? (b) Does either configuration violate Hund's rule? (c) In the absence of an external magnetic field, can we say that one electron configuration has a lower energy than the other? If so, which one has the lowest energy?

Configuration A



Configuration B



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

6.35 (c)

Answers to Self-Assessment Exercise

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

6.8 | Electron Configurations



The line spectrum of hydrogen can only be seen if the light from a hydrogen discharge tube is passed through a prism, or similar device. What we see is the amalgamation of the different wavelengths emitted by hydrogen—a pale purple color. Colored fireworks represent the atomic emission spectrum of different elements. If we were to pass their light through a prism, we would see a different line spectrum for each different element present. We can measure the spectrum and use it to test our theories of electron configuration. So, while quantum mechanics may appear theoretical, we can validate the predictions it makes in the study of spectroscopy.

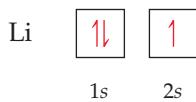
By the end of this section, you should be able to

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

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

The most stable electron configuration—the ground state—is that in which the electrons are in the lowest possible energy states. If there were no restrictions on the possible values for the quantum numbers of the electrons, all the electrons would crowd into the 1s orbital because it is the lowest in energy (Figure 6.24). The Pauli exclusion principle tells us, however, that there can be at most two electrons in any single orbital. Thus, *the orbitals are filled in order of increasing energy, with no more than two electrons per orbital*. For example, consider the lithium atom, which has three electrons. (Recall that the number of electrons in a neutral atom equals its atomic number.) The 1s orbital can accommodate two of the electrons. The third one goes into the next lowest-energy orbital, the 2s.

We can represent any electron configuration by writing the symbol for the occupied subshell and adding a superscript to indicate the number of electrons in that subshell. For example, for lithium we write $1s^22s^1$ (read “1s two, 2s one”). We can also show the arrangement of the electrons as

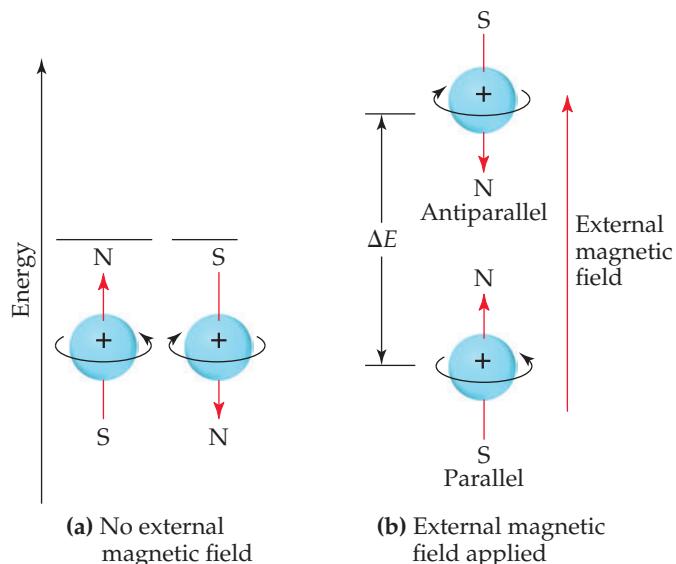


CHEMISTRY AND LIFE Nuclear Spin and Magnetic Resonance Imaging

A major challenge facing medical diagnosis is seeing inside the human body. Until recently, this was accomplished primarily by X-ray technology. X rays do not, however, give well-resolved images of overlapping physiological structures, and sometimes fail to discern diseased or injured tissue. Moreover, because X rays are high-energy radiation, they potentially can cause physiological harm, even in low doses. An imaging technique developed in the 1980s called *magnetic resonance imaging (MRI)* does not have these disadvantages.

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

A spinning hydrogen nucleus acts like a tiny magnet. In the absence of external effects, the two spin states have the same energy. However, when the nuclei are placed in an external magnetic field,

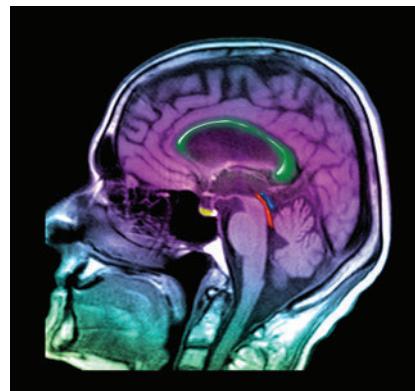


▲ Figure 6.26 Nuclear spin. Like electron spin, nuclear spin generates a small magnetic field and has two allowed values. (a) In the absence of an external magnetic field, the two spin states have the same energy. (b) When an external magnetic field is applied, the spin state in which the spin direction is parallel to the direction of the external field is lower in energy than the spin state in which the spin direction is antiparallel to the field direction. The energy difference, ΔE , is in the radio frequency portion of the electromagnetic spectrum.

they can align either parallel or opposed (antiparallel) to the field, depending on their spin. The parallel alignment is lower in energy than the antiparallel one by a certain amount, ΔE (Figure 6.26). If the nuclei are irradiated with photons having energy equal to ΔE , the spin of the nuclei can be “flipped,” that is, excited from the parallel to the antiparallel alignment. Detection of the flipping of nuclei between the two spin states leads to an NMR spectrum. The radiation used in an NMR experiment is in the radiofrequency range, typically 100 to 900 MHz, which is far less energetic per photon than X rays.

Because hydrogen is a major constituent of aqueous body fluids and fatty tissue, the hydrogen nucleus is the most convenient one for study by MRI. In MRI a person’s body is placed in a strong magnetic field. By irradiating the body with pulses of radiofrequency radiation and using sophisticated detection techniques, medical technicians can image tissue at specific depths in the body, giving pictures with spectacular detail (Figure 6.27). The ability to sample at different depths allows the technicians to construct a three-dimensional picture of the body.

MRI has had such a profound influence on the modern practice of medicine that Paul Lauterbur, a chemist, and Peter Mansfield, a physicist, were awarded the 2003 Nobel Prize in Physiology or Medicine for their discoveries concerning MRI. The major drawback of this technique is expense: The current cost of a new standard MRI instrument for clinical applications is typically \$1.5 million. In the 2000s, a new technique was developed, called *prepolarized MRI*, that requires much less expensive equipment and will lead to an even greater application of this important diagnostic tool.



▲ Figure 6.27 MRI image. This image of a human head, obtained using magnetic resonance imaging, shows a normal brain, airways, and facial tissues.

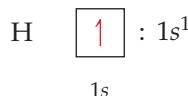
In this representation, which we call an **orbital diagram**, each orbital is denoted by a box and each electron by a half arrow. A half arrow pointing up (\uparrow) represents an electron with a positive spin magnetic quantum number ($m_s = +\frac{1}{2}$), and a half arrow pointing down (\downarrow)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

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

Hund's Rule

Consider now how the electron configurations of the elements change as we move from element to element across the periodic table.

Hydrogen Hydrogen has one electron, which occupies the 1s orbital in its ground state:



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

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

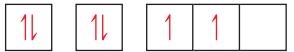


The two electrons present in helium complete the filling of the first shell. This arrangement represents a very stable configuration, as is evidenced by the chemical inertness of helium.

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

Beryllium and Boron The element that follows lithium is beryllium; its electron configuration is $1s^22s^2$ (Table 6.3). Boron, atomic number 5, has the electron configuration $1s^22s^22p^1$. The fifth electron must be placed in a $2p$ orbital because the $2s$ orbital is filled. Because all three of the $2p$ orbitals are of equal energy, it does not matter which $2p$ orbital we place this fifth electron in.

TABLE 6.3 Electron Configurations of Several Lighter Elements

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

Carbon With the next element, carbon, we encounter a new situation. We know that the sixth electron must go into a $2p$ orbital. However, does this new electron go into the $2p$ orbital that already has one electron or into one of the other two $2p$ orbitals?

Hund's rule states that when filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized.

This means that electrons occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell all have the same spin magnetic quantum number. Electrons arranged in this way are said to have *parallel spins*. For a carbon atom to achieve its lowest energy, therefore, the two $2p$ electrons must have the same spin. For this to happen, the electrons must be in different $2p$ orbitals, as shown in Table 6.3. Thus, a carbon atom in its ground state has two unpaired electrons.

Nitrogen, Oxygen, Fluorine Similarly, for nitrogen in its ground state, Hund's rule requires that the three $2p$ electrons singly occupy each of the three $2p$ orbitals. This is the only way that all three electrons can have the same spin. For oxygen and fluorine, we place four and five electrons, respectively, in the $2p$ orbitals. To achieve this, we pair up electrons in the $2p$ orbitals, as we will see in Sample Exercise 6.7.

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

Condensed Electron Configurations

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



The symbol $[\text{Ne}]$ represents the electron configuration of the ten electrons of neon, $1s^22s^22p^6$. Writing the electron configuration as $[\text{Ne}]3s^1$ focuses attention on the

Sample Exercise 6.7

Orbital Diagrams and Electron Configurations



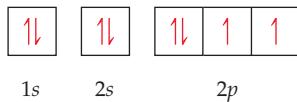
Draw the orbital diagram for the electron configuration of oxygen, atomic number 8. How many unpaired electrons does an oxygen atom possess?

SOLUTION

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

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

of the three electrons already in a $2p$ orbital, so that the orbital diagram is



The corresponding electron configuration is written $1s^22s^22p^4$. The atom has two unpaired electrons.

► Practice Exercise

How many of the elements in the second row of the periodic table (Li through Ne) will have at least one unpaired electron in their electron configurations?

- (a) 3 (b) 4 (c) 5 (d) 6 (e) 7

outermost electron of the atom, which is the one largely responsible for how sodium behaves chemically.

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



We refer to the electrons represented by the bracketed symbol as the *noble-gas core* of the atom. More usually, these inner-shell electrons are referred to as the **core electrons**. The electrons given after the noble-gas core are called the *outer-shell electrons*. The outer-shell electrons include the electrons involved in chemical bonding, which are called the **valence electrons**. For the elements with atomic number of 30 or less, all of the outer-shell electrons are valence electrons. By comparing the condensed electron configurations of lithium and sodium, we can appreciate why these two elements are so similar chemically. They have the same type of electron configuration in the outermost occupied shell. Indeed, all the members of the alkali metal group (1) have a single *s* valence electron beyond a noble-gas configuration (Figure 6.28).

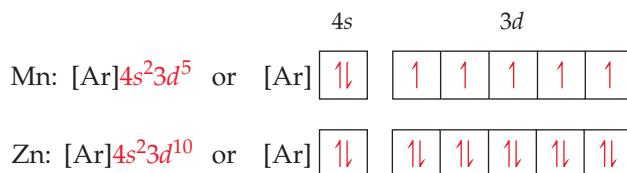
Transition Metals

The noble-gas element argon ($1s^22s^22p^63s^23p^6$) marks the end of the row started by sodium. The element following argon in the periodic table is potassium (K), atomic number 19. In all its chemical properties, potassium is clearly a member of the alkali metal group. The experimental facts about the properties of potassium leave no doubt that the outermost electron of this element occupies an *s* orbital. But this means that the electron with the highest energy has *not* gone into a *3d* orbital, which we might expect it to do. Because the *4s* orbital is lower in energy than the *3d* orbital (Figure 6.24), the condensed electron configuration of potassium is



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

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



Once all the *3d* orbitals have been filled with two electrons each, the *4p* orbitals begin to be occupied until the completed octet of outer electrons ($4s^24p^6$) is reached with krypton (Kr), atomic number 36, another of the noble gases. Rubidium (Rb) marks the beginning of the fifth row. Refer again to the periodic table on the front-inside cover. Notice that this row is in every respect like the preceding one, except that the value for *n* is greater by 1.

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

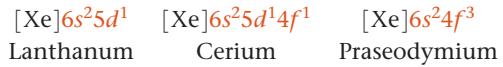
▲ Figure 6.28 The condensed electron configurations of the alkali metals (Group 1 in the periodic table).

The Lanthanides and Actinides

The sixth row of the periodic table begins with Cs and Ba, which have $[Xe]6s^1$ and $[Xe]6s^2$ configurations, respectively. Notice, however, that the periodic table then has a break, with elements 57–70 placed below the main portion of the table. This break point is where we begin to encounter a new set of orbitals, the $4f$.

There are seven degenerate $4f$ orbitals, corresponding to the seven allowed values of m_l , ranging from 3 to –3. Thus, it takes 14 electrons to fill the $4f$ orbitals completely. The 14 elements corresponding to the filling of the $4f$ orbitals are known as either the **lanthanide elements** or the **rare earth elements**. These elements are set below the other elements to avoid making the periodic table unduly wide. The properties of the lanthanide elements are all quite similar, and these elements occur together in nature. For many years it was virtually impossible to separate them from one another.

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



Because La has a single $5d$ electron, it is sometimes placed below yttrium (Y) as the first member of the third series of transition elements; Ce is then placed as the first member of the lanthanides. Based on its chemical properties, however, La can be considered the first element in the lanthanide series. Arranged this way, there are fewer apparent exceptions to the regular filling of the $4f$ orbitals among the subsequent members of the series.

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

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

Self-Assessment Exercise

- 6.39** What is the condensed electron configuration of Se?

(a) $[Ar]4s^23d^{10}4p^4$

(b) $[Ar]4s^24d^{10}4p^4$

(c) $[Ar]4s^25d^{10}4p^4$

Exercises

- 6.40** (a) What are “valence electrons”? (b) What are “core electrons”? (c) What does each box in an orbital diagram represent? (d) What object is represented by the half arrows in an orbital diagram? What does the direction of the arrow signify?
- 6.41** Write the condensed electron configurations for the following atoms, using the appropriate noble-gas core abbreviations: (a) Cs, (b) Ni, (c) Se, (d) Cd, (e) U, (f) Pb.
- 6.42** Identify the specific element that corresponds to each of the following electron configurations and indicate the number

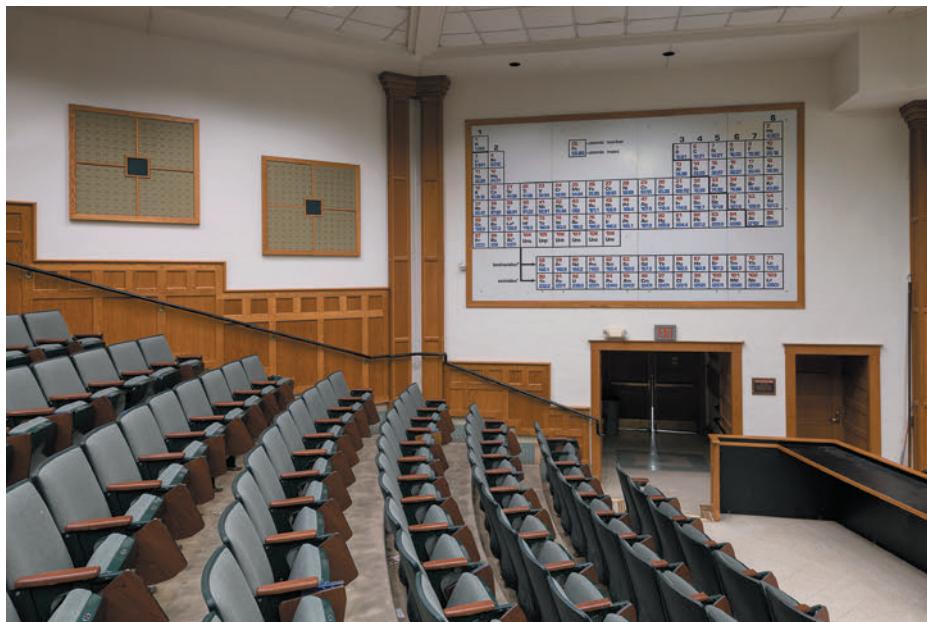
of unpaired electrons for each: (a) $1s^22s^2$, (b) $1s^22s^22p^4$, (c) $[Ar]4s^13d^5$, (d) $[Kr]5s^24d^{10}5p^4$.

- 6.43** The following do not represent valid ground-state electron configurations for an atom either because they violate the Pauli exclusion principle or because orbitals are not filled in order of increasing energy. Indicate which of these two principles is violated in each example. (a) $[Ne]3s^23p^63d^5$ (b) $[Xe]6s^3$ (c) $1s^23s^1$.

6.39 (a)



6.9 | Electron Configurations and the Periodic Table



In almost every chemistry lecture theatre and teaching space, there is a periodic table. It plays a central role in our thinking about chemistry. The pattern it portrays reflects the electron configuration of the atoms and hence the chemistry they undergo. It is our ‘road map’ to understanding the reactivity of the elements.

By the end of this section, you should be able to

- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom

We just saw that the electron configurations of the elements correspond to their locations in the periodic table. Thus, elements in the same column of the table have related outer-shell (valence) electron configurations. As **Table 6.4** shows, for example, all Group 2 elements have an ns^2 outer configuration, and all Group 13 elements have an ns^2np^1 outer configuration, with the value of n increasing as we move down each column.

In Table 6.2 we saw that the total number of orbitals in each shell equals n^2 : 1, 4, 9, or 16. Because we can place two electrons in each orbital, each shell accommodates up to $2n^2$ electrons: 2, 8, 18, or 32. We see that the overall structure of the periodic table reflects these electron numbers: Each row of the table has 2, 8, 18, or 32 elements in it. As shown in **Figure 6.29**, the periodic table can be further divided into four blocks based on the filling order of orbitals. On the left are *two* blue columns of elements. These elements, known as the alkali metals (Group 1) and alkaline earth metals (Group 2), are

TABLE 6.4 Electron Configurations of Group 2 and 13 Elements

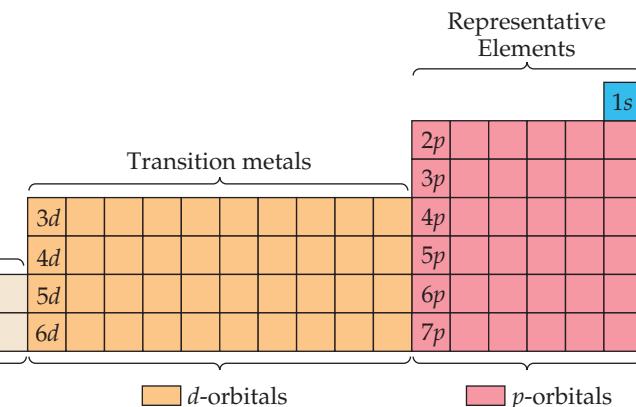
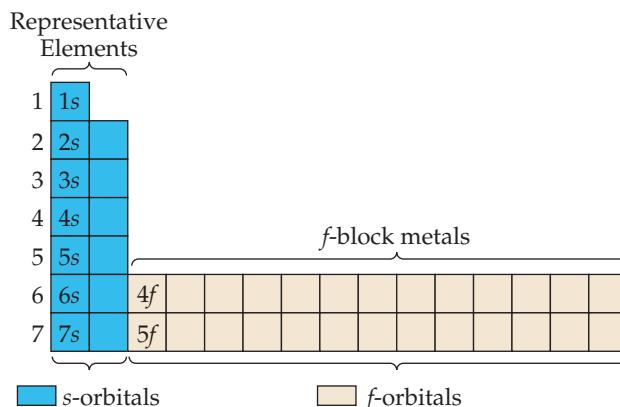
Group 2

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

Group 13

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

▼ Figure 6.29 Regions of the periodic table. The order in which electrons are added to orbitals is read left to right beginning in the top-left corner.

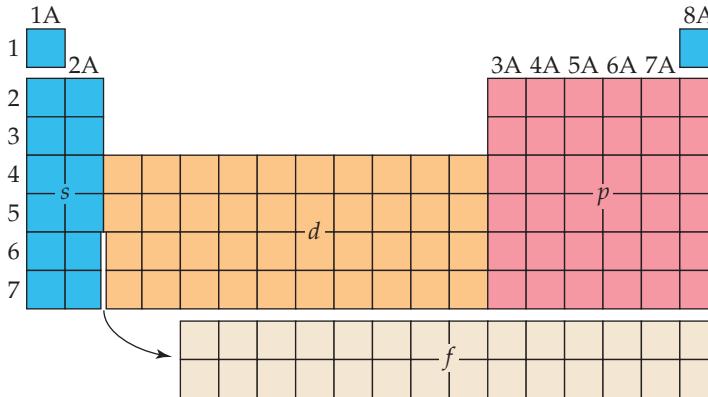


those in which the valence *s* orbitals are being filled. These two columns make up the *s* block of the periodic table.

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

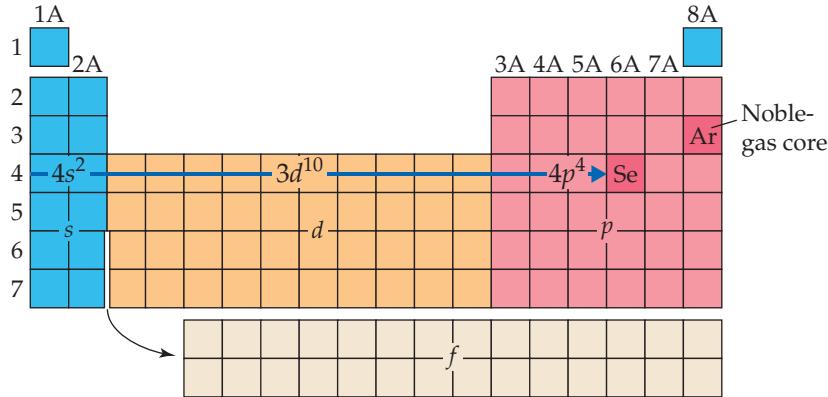
The orange block in Figure 6.29 has *ten* columns containing the **transition metals**. These are the elements in which the valence *d* orbitals are being filled and make up the *d* block.

The elements in the two tan rows containing *14* columns are the ones in which the valence *f* orbitals are being filled and make up the *f* block. Consequently, these elements are often referred to as the ***f*-block metals**. In most tables, the *f* block is positioned below the periodic table to save space:



The number of columns in each block corresponds to the maximum number of electrons that can occupy each kind of subshell. Recall that 2, 6, 10, and 14 are the numbers of electrons that can fill the *s*, *p*, *d*, and *f* subshells, respectively. Thus, the *s* block has 2 columns, the *p* block has 6, the *d* block has 10, and the *f* block has 14. Recall also that 1*s* is the first *s* subshell, 2*p* is the first *p* subshell, 3*d* is the first *d* subshell, and 4*f* is the first *f* subshell, as Figure 6.29 shows. Using these facts, you can write the electron configuration of an element based merely on its position in the periodic table. Remember: *The periodic table is your best guide to the order in which orbitals are filled.*

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



Because K is in the fourth period and the *s* block, we begin with the 4*s* electrons, meaning our first two outer electrons are written $4s^2$. We then move into the *d* block, which begins with the 3*d* electrons. (The principal quantum number in the *d* block is always

one less than that of the preceding elements in the *s* block, as seen in Figure 6.29.) Traversing the *d* block adds ten electrons, $3d^{10}$. Finally, we move into the *p* block, whose principal quantum number is always the same as that of the *s* block. Counting the squares as we move across the *p* block to Se tells us that we need four electrons, $4p^4$. The electron configuration for Se is therefore $[Ar]4s^23d^{10}4p^4$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[Ar]3d^{10}4s^24p^4$.

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

Sample Exercise 6.8

Electron Configurations for a Group

What is the characteristic valence electron configuration of the Group 17 elements, the halogens?

SOLUTION

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

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



The electron configuration for chlorine, the second halogen, is



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

► Practice Exercise

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

Sample Exercise 6.9

Electron Configurations from the Periodic Table

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

SOLUTION

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

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

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

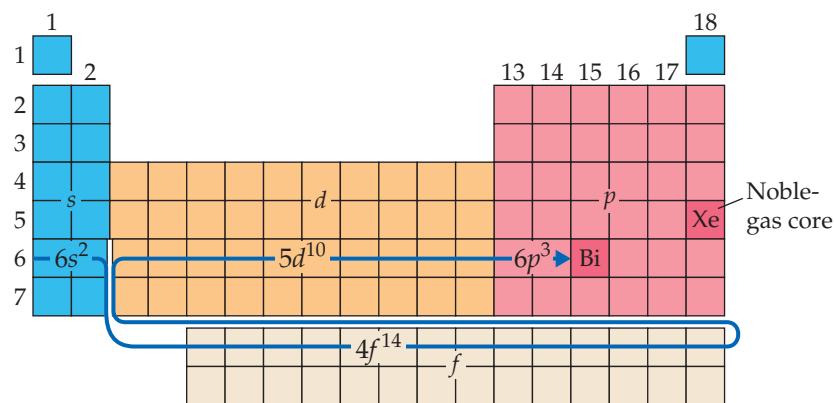
With element 71, we move into the third row of the *d* block. Because the first row of the *d* block is *3d*, the

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

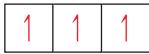
Moving from element 80 to element 81 puts us into the *p* block in the *6p* subshell. (Remember that the principal quantum number in the *p* block is the same as that in the *s* block.) Moving across to Bi requires three electrons: $6p^3$. Putting the parts together, we obtain the condensed electron configuration: $[\text{Xe}]6s^24f^{14}5d^{10}6p^3$. This configuration can also be written with the subshells arranged in order of increasing principal quantum number: $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$.

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

Continued



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



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

► Practice Exercise

A certain atom has a [noble gas] $5s^24d^{10}5p^4$ electron configuration. Which element is it?

- (a) Cd (b) Te (c) Sm (d) Hg (e) More information is needed

Figure 6.30 gives, for all the elements, the ground-state electron configurations for the outer-shell electrons. You can use this figure to check your answers as you practice writing electron configurations. We have written these configurations with orbitals listed in order of increasing principal quantum number. As we saw in Sample Exercise 6.9, the orbitals can also be listed in order of filling, as they would be read off of the periodic table.

Figure 6.30 allows us to reexamine the concept of *valence electrons*. Notice, for example, that as we proceed from Cl ([Ne] $3s^23p^5$) to Br ([Ar] $3d^{10}4s^24p^5$) we add a complete subshell of $3d$ electrons to the electrons beyond the [Ar] core. Although the $3d$ electrons are outer-shell electrons, they are not involved in chemical bonding and are therefore not considered valence electrons. Thus, we consider only the $4s$ and $4p$ electrons of Br to be valence electrons. Similarly, if we compare the electron configurations of Ag (element 47) and Au (element 79), we see that Au has a completely full $4f^{14}$ subshell beyond its noble-gas core, but those $4f$ electrons are not involved in bonding. In general, *for representative elements we do not consider the electrons in completely filled d or f subshells to be valence electrons, and for transition elements we do not consider the electrons in a completely filled f subshell to be valence electrons.*

Anomalous Electron Configurations

The electron configurations of certain elements appear to violate the rules we have just discussed. For example, Figure 6.30 shows that the electron configuration of chromium (element 24) is [Ar] $3d^54s^1$ rather than the [Ar] $3d^44s^2$ configuration we might expect. Similarly, the configuration of copper (element 29) is [Ar] $3d^{10}4s^1$ instead of [Ar] $3d^94s^2$.

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

 Go Figure

A friend tells you that her favorite element has an electron configuration of [noble gas] $6s^24f^{14}5d^6$. Which element is it?

▲ Figure 6.30 Outer-shell electron configurations of the elements.

Sample Integrative Exercise

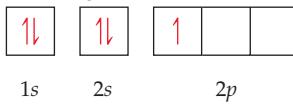
Putting Concepts Together

Boron, atomic number 5, occurs naturally as two isotopes, ^{10}B and ^{11}B , with natural abundances of 19.9% and 80.1%, respectively. **(a)** In what ways do the two isotopes differ from each other? Does the electronic configuration of ^{10}B differ from that of ^{11}B ? **(b)** Draw the orbital diagram for an atom of ^{11}B . Which electrons are the valence electrons? **(c)** Indicate three ways in which the 1s electrons in boron differ from its 2s electrons. **(d)** Elemental boron reacts with fluorine to form BF_3 , a gas. Write a balanced chemical equation for the reaction of solid boron with fluorine gas. **(e)** ΔH_f° for $\text{BF}_3(g)$ is -1135.6 kJ/mol . Calculate the standard enthalpy change in the reaction of boron with fluorine. **(f)** Will the mass percentage of F be the same in $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$? If not, why is that the case?

SOLUTION

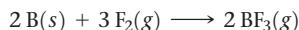
- (a) The two isotopes of boron differ in the number of neutrons in the nucleus. Each of the isotopes contains five protons, but ^{10}B contains five neutrons, whereas ^{11}B contains six neutrons. The two isotopes of boron have identical electron configurations, $1s^22s^22p^1$, because each has five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

(b) The complete orbital diagram is



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

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



(e) $\Delta H^\circ = 2(-1135.6) - [0 + 0] = -2271.2 \text{ kJ}$. The reaction is strongly exothermic.

(f) As we saw in Equation 3.10 (Section 3.3), the mass percentage of an element in a substance depends on the formula weight of the substance. The formula weights of $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$ are different because of the difference in the masses of the two isotopes (the isotope masses of ^{10}B and ^{11}B are 10.01294 and 11.00931 amu, respectively). The denominators in Equation 3.10 would therefore be different for the two isotopes, whereas the numerators would remain the same.

Chapter Summary and Key Terms

WAVELENGTHS AND FREQUENCIES OF LIGHT (INTRODUCTION AND SECTION 6.1)

The **electronic structure** of an atom describes the energies and arrangement of electrons around the atom. Much of what is known about the electronic structure of atoms was obtained by observing the interaction of light with matter.

Visible light and other forms of **electromagnetic radiation** (also known as radiant energy) move through a vacuum at the speed of light, $c = 2.998 \times 10^8 \text{ m/s}$. Electromagnetic radiation has both electric and magnetic components that vary periodically in wave-like fashion. The wave characteristics of radiant energy allow it to be described in terms of **wavelength**, λ , and **frequency**, ν , which are interrelated: $\lambda\nu = c$.

QUANTIZED ENERGY AND PHOTONS (SECTION 6.2) Planck proposed that the minimum amount of radiant energy that an object can gain or lose is related to the frequency of the radiation: $E = h\nu$. This smallest quantity is called a **quantum** of energy. The constant h is called the **Planck constant**: $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$.

In the quantum theory, energy is quantized, meaning that it can have only certain allowed values. Einstein used the quantum theory to explain the **photoelectric effect**, the emission of electrons from metal surfaces when exposed to light. He proposed that light behaves as if it consists of quantized energy packets called **photons**. Each photon carries energy, $E = h\nu$.

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

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

WAVE BEHAVIOR OF MATTER (SECTION 6.4) De Broglie proposed that matter, such as electrons, should exhibit wave-like properties. This hypothesis of **matter waves** was proved experimentally by observing the diffraction of electrons. An object has a characteristic wavelength that depends on its **momentum**, mv : $\lambda = h/mv$.

Discovery of the wave properties of the electron led to Heisenberg's **uncertainty principle**, which states that there is an inherent limit to the accuracy with which the position and momentum of a particle can be measured simultaneously.

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

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

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

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

MANY-ELECTRON ATOMS (SECTION 6.7) In many-electron atoms, different subshells of the same electron shell have different energies. For a given value of n , the energy of the subshells increases as the value of l increases: $ns < np < nd < nf$. Orbitals within the same subshell are **degenerate**, meaning they have the same energy.

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

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

two $2p$ electrons have the same spin and must occupy two different $2p$ orbitals.

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

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

Learning Outcomes After studying this chapter, you should be able to:

- Calculate the wavelength of electromagnetic radiation given its frequency or its frequency given its wavelength. (Section 6.1)
Related Exercises: 6.5, 6.6, 6.59,
- Order the common kinds of radiation in the electromagnetic spectrum according to their wavelengths or energy. (Section 6.1)
Related Exercises: 6.2, 6.3, 6.57, 6.58
- Explain what photons are and be able to calculate their energies given either their frequency or wavelength. (Section 6.2)
Related Exercises: 6.9, 6.11, 6.12, 6.62
- Explain how line spectra relate to the idea of quantized energy states of electrons in atoms. (Section 6.3)
Related Exercises: 6.18, 6.67, 6.70, 6.71
- Calculate the wavelength of a moving object. (Section 6.4)
Related Exercises: 6.23, 6.24, 6.73, 6.74
- Explain how the uncertainty principle limits how precisely we can specify the position and the momentum of subatomic particles such as electrons. (Section 6.4) *Related Exercises: 6.25, 6.75*
- Relate the quantum numbers to the number and type of orbitals and recognize the different orbital shapes. (Section 6.5)
Related Exercises: 6.28, 6.29, 6.31, 6.80
- Interpret radial probability function graphs for atomic orbitals. (Section 6.6) *Related Exercises: 6.27, 6.76, 6.82*
- Explain how and why the energies of the orbitals are different in a many-electron atom from those in the hydrogen atom (Section 6.7) *Related Exercises: 6.36, 6.83*
- Draw an energy-level diagram for the orbitals in a many-electron atom and describe how electrons populate the orbitals in the ground state of an atom, using the Pauli exclusion principle and Hund's rule. (Section 6.8)
Related Exercises: 6.37, 6.54
- Use the periodic table to write condensed electron configurations and determine the number of unpaired electrons in an atom. (Section 6.9) *Related Exercises: 6.41, 6.42, 6.87, 6.88*

Key Equations

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

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

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

$$\lambda = h/mv \quad [6.8]$$

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

light as a wave: λ = wavelength in meters, ν = frequency in s^{-1} , c = speed of light ($2.998 \times 10^8 \text{ m/s}$)

light as a particle (photon): E = energy of photon in joules, h = Planck constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), ν = frequency in s^{-1}

energies of the allowed states of the hydrogen atom: h = Planck constant; c = speed of light; R_{H} = Rydberg constant ($1.096776 \times 10^7 \text{ m}^{-1}$); $n = 1, 2, 3, \dots$ (any positive integer)

matter as a wave: λ = wavelength, h = Planck constant, m = mass of object in kg, v = speed of object in m/s

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

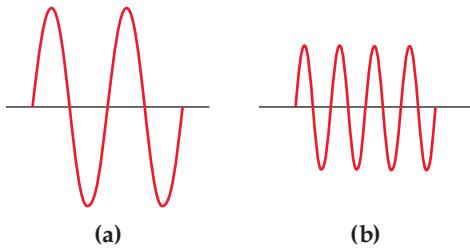
Exercises

Visualizing Concepts

- 6.44** The speed of sound in dry air at 20 °C is 343 m/s and the lowest frequency sound wave that the human ear can detect is approximately 20 Hz. (a) What is the wavelength of such a sound wave? (b) What would be the frequency of electromagnetic radiation with the same wavelength? (c) What type of electromagnetic radiation would that correspond to? [Section 6.1]

- 6.45** A popular kitchen appliance produces electromagnetic radiation with a frequency of 2450 MHz. With reference to Figure 6.4, answer the following: (a) Estimate the wavelength of this radiation. (b) Would the radiation produced by the appliance be visible to the human eye? (c) If the radiation is not visible, do photons of this radiation have more or less energy than photons of visible light? (d) Which of the following is the appliance likely to be? (i) A toaster oven, (ii) A microwave oven, or (iii) An electric hotplate. [Section 6.1]

- 6.46** The following diagrams represent two electromagnetic waves, drawn on the same scale. (a) Which wave has a longer wavelength? (b) Which wave has a higher frequency? (c) Which wave has a higher energy? [Section 6.2]



- 6.47** Stars do not all have the same temperature. The color of light emitted by stars is characteristic of the light emitted by hot objects. Telescopic photos of three stars are shown: (i) the Sun, which is classified as a *yellow* star, (ii) Rigel, in the constellation Orion, which is classified as a *blue-white* star, and (iii) Betelgeuse, also in Orion, which is classified as a *red* star. (a) Place these three stars in order of increasing temperature. (b) Which of the following principles is relevant to your choice of answer for part (a): The uncertainty principle, the photoelectric effect, blackbody radiation, or line spectra? [Section 6.2]



(i) Sun

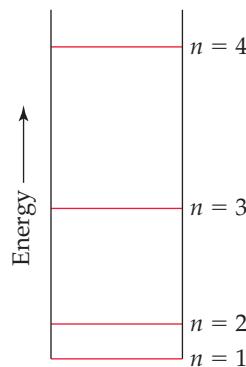
(ii) Rigel

(iii) Betelgeuse

- 6.48** The familiar phenomenon of a rainbow results from the diffraction of sunlight through raindrops. (a) Does the wavelength of light increase or decrease as we proceed outward from the innermost band of the rainbow? (b) Does the frequency of light increase or decrease as we proceed outward? [Section 6.3]

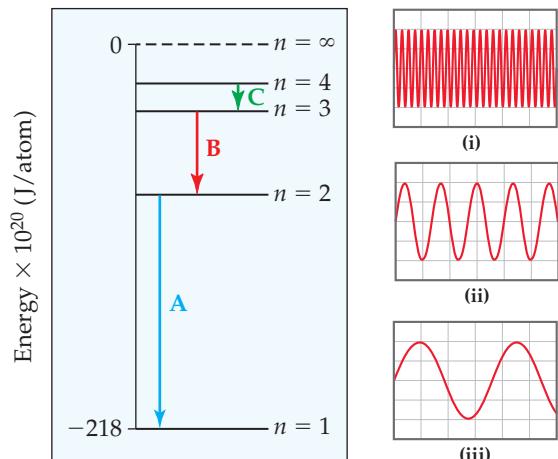


- 6.49** A certain quantum-mechanical system has the energy levels shown in the accompanying diagram. The energy levels are indexed by a single quantum number n that is an integer. (a) As drawn, which quantum numbers are involved in the transition that requires the most energy? (b) Which quantum numbers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



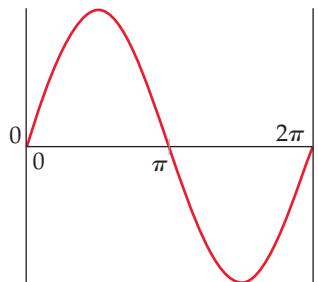
- 6.50** Consider the three electronic transitions in a hydrogen atom shown here, labeled A, B, and C.

- (a) Three electromagnetic waves, all drawn on the same scale, are also shown. Each corresponds to one of the transitions. Which electromagnetic wave (i), (ii), or (iii), is associated with electronic transition C?

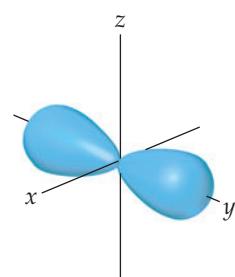


- (b) Calculate the energy of the photon emitted for each transition.
(c) Calculate the wavelength of the photon emitted for each transition. Do any of these transitions lead to the emission of visible light? If so which one(s)? [Section 6.3]

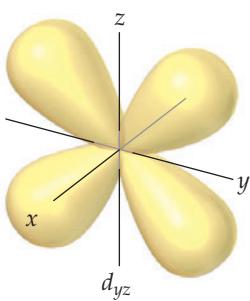
- 6.51** Consider a fictitious one-dimensional system with one electron. The wave function for the electron, as shown here, is $\psi(x) = \sin x$ from $x = 0$ to $x = 2\pi$. **(a)** Sketch the probability density, $\psi^2(x)$, from $x = 0$ to $x = 2\pi$. **(b)** At what value or values of x will there be the greatest probability of finding the electron? **(c)** What is the probability that the electron will be found at $x = \pi$? What is such a point in a wave function called? [Section 6.5]



- 6.52** The contour representation of one of the orbitals for the $n = 3$ shell of a hydrogen atom is shown here. **(a)** What is the quantum number l for this orbital? **(b)** How do we label this orbital? **(c)** In which of the following ways would you modify this sketch if the value of the magnetic quantum number, m_l , were to change? **(i)** It would be drawn larger, **(ii)** the number of lobes would change, **(iii)** the lobes of the orbital would point in a different direction, **(iv)** there would be no change in the sketch. [Section 6.6]



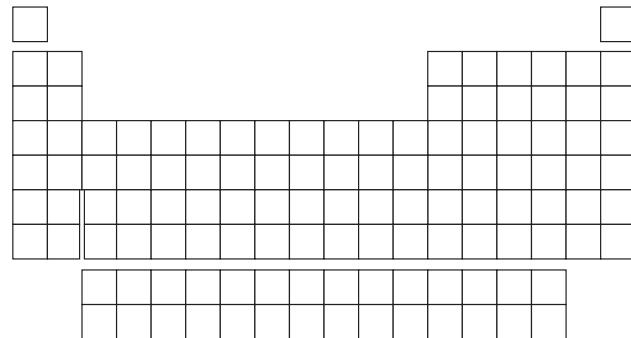
- 6.53** The accompanying drawing shows a contour plot for a d_{yz} orbital. Consider the quantum numbers that could potentially correspond to this orbital. **(a)** What is the smallest possible value of the principal quantum number, n ? **(b)** What is the value of the angular momentum quantum number, l ? **(c)** What is the largest possible value of the magnetic quantum number, m_l ? **(d)** The probability density goes to zero along which of the following planes: xy , xz , or yz ?



- 6.54** Four possible electron configurations for a nitrogen atom are shown here, but only one schematic represents the correct configuration for a nitrogen atom in its ground state. Which one is the correct electron configuration? Which configurations violate the Pauli exclusion principle? Which configurations violate Hund's rule? [Section 6.8]

| | | | |
|-----------------|----|----|----|
| Configuration A | | | |
| | 1s | 2s | 2p |
| Configuration B | | | |
| | 1s | 2s | 2p |
| Configuration C | | | |
| | 1s | 2s | 2p |
| Configuration D | | | |
| | 1s | 2s | 2p |

- 6.55** State where in the periodic table these elements appear:
- (a)** elements with the valence-shell electron configuration ns^2np^5
 - (b)** elements that have three unpaired p electrons
 - (c)** an element whose valence electrons are $4s^24p^1$
 - (d)** the d -block elements [Section 6.9]



The Wave Nature of Light (Section 6.1)

- 6.56** Carbon dioxide in the atmosphere absorbs energy in the $4.0\text{--}4.5\text{ }\mu\text{m}$ range of the spectrum. **(a)** Calculate the frequency of the $4.0\text{ }\mu\text{m}$ radiation. **(b)** In what region of the electromagnetic spectrum does this radiation occur?

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

- 6.58** List the following types of electromagnetic radiation in order of descending wavelength: **(a)** UV lights used in tanning salons ($300\text{--}400\text{ nm}$); **(b)** radiation from an FM radio station at 93.1 MHz on the dial; **(c)** radiation from mobile phones ($450\text{--}2100\text{ MHz}$); **(d)** the yellow light from sodium vapor streetlights; **(e)** the red light of a light-emitting diode, such as in an appliance's display.

- 6.59** **(a)** What is the frequency of radiation whose wavelength is 0.86 nm ? **(b)** What is the wavelength of radiation that has a frequency of $6.4 \times 10^{11}\text{ s}^{-1}$? **(c)** Would the radiations in part (a) or part (b) be detected by an X-ray detector? **(d)** What distance does electromagnetic radiation travel in 0.38 ps ?

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

Quantized Energy and Photons (Section 6.2)

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

- 6.62** **(a)** A green laser pointer emits light with a wavelength of 532 nm . What is the frequency of this light? **(b)** What is the energy of one of these photons? **(c)** The laser pointer emits light because electrons in the material are excited (by a battery) from their ground state to an upper excited state. When the electrons return to the ground state, they lose the excess energy in the form of 532-nm photons. What is the energy gap between the ground state and excited state in the laser material?

- 6.63** An AM radio station broadcasts at 1000 kHz and its FM partner broadcasts at 100 MHz. Calculate and compare the energy of the photons emitted by these two radio stations.
- 6.64** The energy from radiation can be used to rupture chemical bonds. A minimum energy of 192 kJ/mol is required to break the bromine–bromine bond in Br_2 . What is the longest wavelength of radiation that possesses the necessary energy to break the bond? What type of electromagnetic radiation is this?
- 6.65** A stellar object is emitting radiation at 3.0 mm. **(a)** What type of electromagnetic spectrum is this radiation? **(b)** If a detector is capturing 3.0×10^8 photons per second at this wavelength, what is the total energy of the photons detected in 1 day?
- 6.66** Titanium metal requires light with a maximum wavelength of 286 nm to emit electrons. **(a)** What is the minimum energy of the photons necessary to emit electrons from titanium via the photoelectric effect? **(b)** What is the frequency of this radiation? **(c)** Is it possible to eject electrons from titanium metal using infrared light? **(d)** If titanium is irradiated with light of wavelength 276 nm, what is the maximum possible kinetic energy of the emitted electrons?

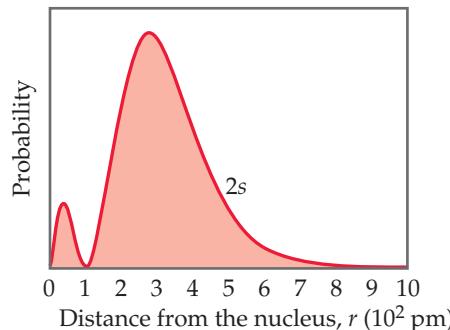
Bohr's Model; Matter Waves (Sections 6.3 and 6.4)

- 6.67** Classify each of the following statements as either true or false: **(a)** A hydrogen atom in the $n = 3$ state can emit light at only two specific wavelengths, **(b)** a hydrogen atom in the $n = 2$ state is at a lower energy than one in the $n = 1$ state, and **(c)** the energy of an emitted photon equals the energy difference of the two states involved in the emission.
- 6.68** Indicate whether energy is emitted or absorbed when the following electronic transitions occur in hydrogen: **(a)** from $n = 2$ to $n = 3$, **(b)** from an orbit of radius 0.529 to one of radius 0.476 nm, **(c)** from the $n = 9$ to the $n = 6$ state.
- 6.69** Consider a transition of the electron in the hydrogen atom from $n = 8$ to $n = 3$. **(a)** Is ΔE for this process positive or negative? **(b)** Determine the wavelength of light that is associated with this transition. Will the light be absorbed or emitted? **(c)** In which portion of the electromagnetic spectrum is the light in part (b)?
- 6.70** The Lyman series of emission lines of the hydrogen atom are those for which $n_f = 1$. **(a)** Determine the region of the electromagnetic spectrum in which the lines of the Lyman series are observed. **(b)** Calculate the wavelengths of the first three lines in the Lyman series—those for which $n_i = 2, 3$, and 4.
- 6.71** The hydrogen atom can absorb light of wavelength 1094 nm. **(a)** In what region of the electromagnetic spectrum is this absorption found? **(b)** Determine the initial and final values of n associated with this absorption.
- 6.72** Place the following transitions of the hydrogen atom in order from shortest to longest wavelength of the photon emitted: $n = 5$ to $n = 2$, $n = 4$ to $n = 3$, $n = 8$ to $n = 4$, and $n = 4$ to $n = 2$.
- 6.73** Among the elementary subatomic particles of physics is the muon, which decays within a few microseconds after formation. The muon has a rest mass 206.8 times that of an electron. Calculate the de Broglie wavelength associated with a muon traveling at 8.85×10^5 cm/s.
- 6.74** The electron microscope has been widely used to obtain highly magnified images of biological and other types of materials. When an electron is accelerated through a particular potential field, it attains a speed of 9.47×10^6 m/s. What is the characteristic wavelength of this electron? Is the wavelength comparable to the size of atoms?
- 6.75** Calculate the uncertainty in the position of **(a)** an electron moving at a speed of $(3.00 \pm 0.01) \times 10^5$ m/s, **(b)** a neutron moving at this same speed. (The masses of an electron and

a neutron are given in the table of fundamental constants in the inside cover of the text.) **(c)** Based on your answers to parts (a) and (b), which can we know with greater precision, the position of the electron or of the neutron?

Quantum Mechanics and Atomic Orbitals (Sections 6.5 and 6.6)

- 6.76** The radial probability function for a 2s orbital is shown here.



Classify the following statements as either true or false: **(a)** There are two maxima in this function because one electron spends most of its time at an approximate distance of 50 pm from the nucleus and the other electron spends most of its time at an approximate distance of 300 pm from the nucleus. **(b)** The radial probability function shown here and the probability density $[\psi(r)]^2$ both go to zero at the same distance from the nucleus, approximately 100 pm. **(c)** For an s orbital, the number of radial nodes is equal to the principal quantum number, n .

- 6.77** How many unique combinations of the quantum numbers l and m_l are there when **(a)** $n = 1$, **(b)** $n = 5$?
- 6.78** Give the values for n , l , and m_l for **(a)** each orbital in the 3p subshell, **(b)** each orbital in the 4f subshell.
- 6.79** A hydrogen atom orbital has $n = 4$ and $m_l = -2$. **(a)** What are the possible values of l for this orbital? **(b)** What are the possible values of m_s for the orbital?
- 6.80** For the table that follows, write which orbital goes with the quantum numbers. Don't worry about x, y, z subscripts. If the quantum numbers are not allowed, write "not allowed."

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

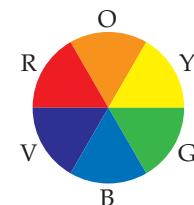
- 6.81** Sketch the shape and orientation of the following types of orbitals: **(a)** p_x , **(b)** d_{z^2} , **(c)** $d_{x^2-y^2}$.
- 6.82** **(a)** With reference to Figure 6.18, what is the relationship between the number of nodes in an s orbital and the value of the principal quantum number? **(b)**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

Many-Electron Atoms and Electron Configurations (Sections 6.7–6.9)

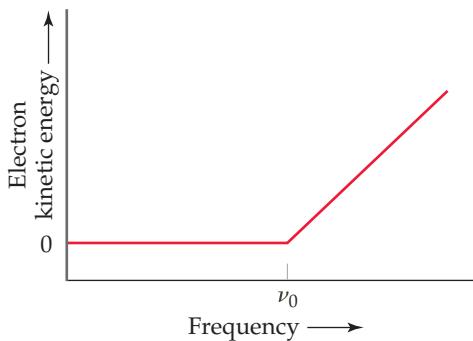
- 6.83** (a) The average distance from the nucleus of a $3s$ electron in a chlorine atom is smaller than that for a $3p$ electron. In light of this fact, which orbital is higher in energy? (b) Would you expect it to require more or less energy to remove a $3s$ electron from the chlorine atom, as compared with a $2p$ electron?
- 6.84** An experiment called the Stern–Gerlach experiment helped establish the existence of electron spin. In this experiment, a beam of silver atoms is passed through a magnetic field, which deflects half of the silver atoms in one direction and half in the opposite direction. The separation between the two beams increases as the strength of the magnetic field increases. (a) What is the electron configuration for a silver atom? (b) Would this experiment work for a beam of cadmium (Cd) atoms? (c) Would this experiment work for a beam of fluorine (F) atoms?
- 6.85** What is the maximum number of electrons in an atom that can have the following quantum numbers? (a) $n = 3, m_l = -1$; (b) $n = 4, l = 2$; (c) $n = 4, l = 3, m_l = -2$; (d) $n = 5, l = 2, m_l = 0$.
- 6.86** For each element, indicate the number of valence electrons, core electrons, and unpaired electrons in the ground state: (a) sodium, (b) sulfur, (c) fluorine.
- 6.87** Write the condensed electron configurations for the following atoms and indicate how many unpaired electrons each has: (a) Mg, (b) Ge, (c) Br, (d) V, (e) Y, (f) Lu.
- 6.88** Identify the group of elements that corresponds to each of the following generalized electron configurations and indicate the number of unpaired electrons for each:
- (a) [noble gas] ns^2np^5
 - (b) [noble gas] $ns^2(n-1)d^2$
 - (c) [noble gas] $ns^2(n-1)d^{10}np^1$
 - (d) [noble gas] $ns^2(n-2)f^6$
- 6.89** The following electron configurations represent excited states. Identify the element and write its ground-state condensed electron configuration. (a) $1s^22s^22p^43s^1$, (b) $[\text{Ne}]3s^13p^44p^1$, (c) $[\text{Ar}]4s^23d^64p^1$.

Additional Exercises

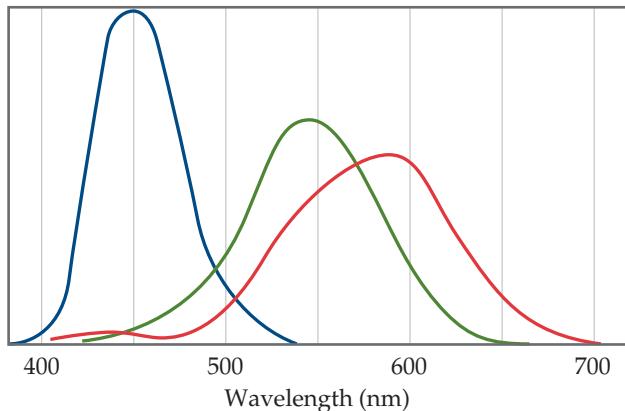
- 6.90** Consider the two waves shown here, which we will consider to represent two electromagnetic radiations:
- What is the wavelength of wave A? Of wave B?
 - What is the frequency of wave A? Of wave B?
 - Identify the regions of the electromagnetic spectrum to which waves A and B belong.
-
- 6.91** If a sample of calcium chloride is introduced into a non-luminous flame, the color of the flame turns to orange ("flame test"). The light is emitted because calcium atoms become excited; their return to the ground state results in light emission. (a) The wavelength of this emitted light is 422.7 nm. Calculate its frequency. (b) What is the energy of 1.00 mol of these photons (a mole of photons is called an Einstein)? (c) Calculate the energy gap between the excited and ground states for the calcium atom.
- 6.92** Certain elements emit light of a specific wavelength when they are burned or heated in a non-luminous flame. Historically, chemists used such emission wavelengths to determine whether specific elements were present in a sample. Some characteristic wavelengths for a few of the elements are given in the following table:
- | | | | |
|----|----------|----|----------|
| Ag | 328.1 nm | Fe | 372.0 nm |
| Au | 267.6 nm | K | 404.7 nm |
| Ba | 455.4 nm | Mg | 285.2 nm |
| Ca | 422.7 nm | Na | 589.6 nm |
| Cu | 324.8 nm | Ni | 341.5 nm |
- (a) Determine which of these emissions occur in the ultraviolet part of the spectrum. (b) Which emission has the highest frequency?
- 6.93** In January 2006, the *New Horizons* space probe was launched from Earth with the mission to perform a flyby study of Pluto. The arrival at the dwarf planet was estimated to happen after nine years, in 2015. The distance between Earth and Pluto varies depending on the location of the planets in their orbits, but at their closest, the distance is 4.2 billion kilometers (2.6 billion miles). Calculate the minimum amount of time it takes for a transmitted signal from Pluto to reach the Earth.
- 6.94** The rays of the Sun that cause tanning and burning are in the ultraviolet portion of the electromagnetic spectrum. These rays are categorized by wavelength. So-called UV-A radiation has wavelengths in the range of 320–380 nm, whereas UV-B radiation has wavelengths in the range of 290–320 nm. (a) Calculate the frequency of light that has a wavelength of 380 nm. (b) Calculate the energy of a mole of 380 nm photons. (c) Which are more energetic, photons of UV-A radiation or photons of UV-B radiation? (d) The UV-B radiation from the Sun is considered a more important cause of sunburn in humans than UV-A radiation. Is this observation consistent with your answer to part (c)?
- 6.95** The watt is the derived SI unit of power, the measure of energy per unit time: $1 \text{ W} = 1 \text{ J/s}$. A semiconductor laser in a DVD player has an output wavelength of 650 nm and a power level of 5.0 mW. How many photons strike the DVD surface during the playing of a DVD 90 minutes in length?
- 6.96** Carotenoids are yellow, orange, and red pigments synthesized by plants. The observed color of an object is not the color of light it absorbs but rather the complementary color, as described by a color wheel such as the one shown here. On this wheel, complementary colors are across from each other. (a) Based on this wheel, what color is absorbed most strongly if a plant is orange? (b) If a particular carotenoid absorbs photons at 455 nm, what is the energy of the photon?



- 6.97** In an experiment to study the photoelectric effect, a scientist measures the kinetic energy of ejected electrons as a function of the frequency of radiation hitting a metal surface. She obtains the following plot. The point labeled “ ν_0 ” corresponds to light with a wavelength of 542 nm. **(a)** What is the value of ν_0 in s^{-1} ? **(b)** What is the value of the work function of the metal in units of kJ/mol of ejected electrons? **(c)** Note that when the frequency of the light is greater than ν_0 , the plot shows a straight line with a nonzero slope. What is the slope of this line segment?



- 6.98** Consider a transition in which the electron of a hydrogen atom is excited from $n = 1$ to $n = \infty$. **(a)** What is the end result of this transition? **(b)** What is the wavelength of light that must be absorbed to accomplish this process? **(c)** What will occur if light with a shorter wavelength than that in part (b) is used to excite the hydrogen atom? **(d)** How are the results of parts (b) and (c) related to the plot shown in Exercise 6.97?
- 6.99** The human retina has three types of receptor cones, each sensitive to a different range of wavelengths of visible light, as shown in this figure (the colors are merely to differentiate the three curves from one another; they do not indicate the actual colors represented by each curve):



- (a)** Estimate the energies of photons with wavelengths at the maximum for each type of cone. **(b)** The color of the sky is due to scattering of solar light by the molecules of the atmosphere. Lord Rayleigh was one of the first to study scattering of this kind. He showed that the amount of scattering for very small particles such as molecules is inversely proportional to the fourth power of the wavelength. Estimate the ratio of the scattering efficiency of light at the wavelength of the maximum for the “blue” cones, as compared with that for the “green” cones. **(c)** Explain why the sky appears blue even though all wavelengths of solar light are scattered by the atmosphere.

- 6.100** The series of emission lines of the hydrogen atom for which $n_f = 4$ is called the *Brackett series*. **(a)** Determine the region of the electromagnetic spectrum in which the lines of the Brackett series are observed. **(b)** Calculate the wavelengths

of the first three lines in the Brackett series—those for which $n_i = 5, 6$, and 7.

- 6.101** When the spectrum of light from the Sun is examined in high resolution in an experiment similar to that illustrated in Figure 6.8, dark lines are evident. These are called Fraunhofer lines, after the scientist who studied them extensively in the early nineteenth century. Altogether, about 25,000 lines have been identified in the solar spectrum between 1000 nm and 295 nm. The Fraunhofer lines are attributed to absorption of certain wavelengths of the Sun’s “white” light by gaseous elements in the Sun’s atmosphere. **(a)** Describe the process that causes absorption of specific wavelengths of light from the solar spectrum. **(b)** To determine which Fraunhofer lines belong to a given element, say, neon, what experiments could a scientist conduct here on Earth?

- 6.102** Determine whether each of the following sets of quantum numbers for the hydrogen atom are valid. If a set is not valid, indicate which of the quantum numbers has a value that is not valid:
- (a)** $n = 3, l = 3, m_l = 2, m_s = +\frac{1}{2}$
(b) $n = 4, l = 3, m_l = -3, m_s = +\frac{1}{2}$
(c) $n = 3, l = 1, m_l = 2, m_s = +\frac{1}{2}$
(d) $n = 5, l = 0, m_l = 0, m_s = 0$
(e) $n = 2, l = 1, m_l = 1, m_s = -\frac{1}{2}$

- 6.103** Bohr’s model can be used for hydrogen-like ions—ions that have only one electron, such as He^+ and Li^{2+} . **(a)** Why is the Bohr model applicable to Li^{2+} ions but not to neutral Li atoms? **(b)** The ground-state energies of B^{4+} , C^{5+} , and N^{6+} are tabulated as follows:

| Atom or ion | B^{4+} | C^{5+} | N^{6+} |
|--------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Ground-state | $-5.45 \times 10^{-17} \text{ J}$ | $-7.85 \times 10^{-17} \text{ J}$ | $-1.07 \times 10^{-16} \text{ J}$ |

By examining these numbers, propose a relationship between the ground-state energy of hydrogen-like systems and the nuclear charge, Z . (*Hint:* Divide by the ground-state energy of hydrogen $-2.18 \times 10^{-18} \text{ J}$) **(c)** Use the relationship you derive in part (b) to predict the ground-state energy of the Be^{3+} ion.

- 6.104** An electron is accelerated through an electric potential to a kinetic energy of $1.6 \times 10^{-15} \text{ J}$. What is its characteristic wavelength? [*Hint:* Recall that the kinetic energy of a moving object is $E = \frac{1}{2}mv^2$, where m is the mass of the object and v is the speed of the object.]

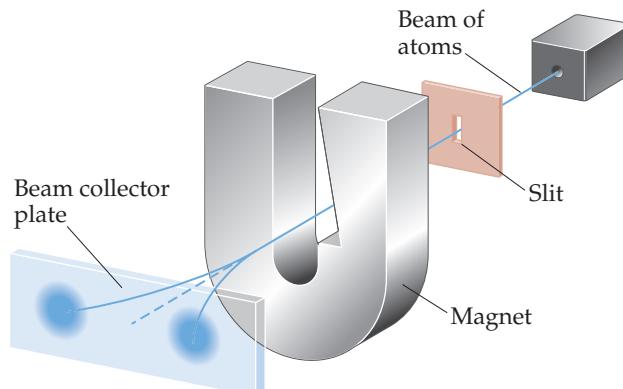
- 6.105** In the television series *Star Trek*, the transporter beam is a device used to “beam down” people from the *Starship Enterprise* to another location, such as the surface of a planet. The writers of the show put a “Heisenberg compensator” into the transporter beam mechanism. Explain why such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

- 6.106** As discussed in the A Closer Look box on “Measurement and the Uncertainty Principle,” the essence of the uncertainty principle is that we can’t make a measurement without disturbing the system that we are measuring. **(a)** Why can’t we measure the position of a subatomic particle without disturbing it? **(b)** How is this concept related to the paradox discussed in the Closer Look box on “Thought Experiments and Schrödinger’s Cat”?

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

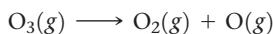
- 6.108** For orbitals that are symmetric but not spherical, the contour representations (as in Figures 6.22 and 6.23) suggest where nodal planes exist (that is, where the electron density is zero). For example, the p_x orbital has a node wherever $x = 0$. This equation is satisfied by all points on the yz plane, so this plane is called a nodal plane of the p_x orbital. **(a)** Determine the nodal plane of the p_z orbital. **(b)** What are the two nodal planes of the d_{xy} orbital? **(c)** What are the two nodal planes of the $d_{x^2-y^2}$ orbital?
- 6.109** Suppose that the spin quantum number, m_s , could have *three* allowed values instead of two. How would this affect the number of elements in the first four rows of the periodic table?
- 6.110** Using the periodic table as a guide, write the condensed electron configuration and determine the number of unpaired electrons for the ground state of **(a)** Cl, **(b)** Al, **(c)** Zr, **(d)** As, **(e)** Sb, **(f)** W.
- 6.111** Scientists have speculated that element 126 might have a moderate stability, allowing it to be synthesized and characterized. Predict what the condensed electron configuration of this element might be.
- 6.112** In the experiment shown schematically with this question, a beam of neutral atoms is passed through a magnetic field. Atoms that have unpaired electrons are deflected in different directions in the magnetic field depending on the value of the electron spin quantum number. In the experiment illustrated,

we envision that a beam of hydrogen atoms splits into two beams. **(a)** What is the significance of the observation that the single beam splits into two beams? **(b)** What do you think would happen if the strength of the magnet were increased? **(c)** What do you think would happen if the beam of hydrogen atoms were replaced with a beam of helium atoms? Why? **(d)** The relevant experiment was first performed by Otto Stern and Walter Gerlach in 1921. They used a beam of Ag atoms in the experiment. By considering the electron configuration of a silver atom, explain why the single beam splits into two beams.



Integrative Exercises

- 6.113** Microwave ovens use microwave radiation to heat food. The energy of the microwaves is absorbed by water molecules in food and then transferred to other components of the food. **(a)** Suppose that the microwave radiation has a wavelength of 10 cm. How many photons are required to heat 200 mL of water from 25 to 75 °C? **(b)** Suppose the microwave's power is 1000 W (1 watt = 1 joule-second). How long would you have to heat the water in part (a)?
- 6.114** The stratospheric ozone (O_3) layer helps to protect us from harmful ultraviolet radiation. It does so by absorbing ultraviolet light and falling apart into an O_2 molecule and an oxygen atom, a process known as photodissociation.



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

- 6.115** The discovery of hafnium, element number 72, provided a controversial episode in chemistry. G. Urbain, a French chemist, claimed in 1911 to have isolated an element number 72 from a sample of rare earth (elements 58–71) compounds. However, Niels Bohr believed that hafnium was more likely to be found along with zirconium than with the rare earths. D. Coster and G. von Hevesy, working in Bohr's laboratory in Copenhagen, showed in 1922 that element 72 was present in a sample of Norwegian zircon, an ore of zirconium. (The name *hafnium* comes from the Latin name for Copenhagen, *Hafnia*). **(a)** How would you use electron configuration arguments to justify Bohr's prediction? **(b)** Zirconium, hafnium's neighbor in Group 4, can be produced as a metal by reduction of solid $ZrCl_4$ with molten sodium metal. Write a balanced chemical equation

for the reaction. Is this an oxidation-reduction reaction? If yes, what is reduced and what is oxidized? **(c)** Solid zirconium dioxide, ZrO_2 , reacts with chlorine gas in the presence of carbon. The products of the reaction are $ZrCl_4$ and two gases, CO_2 and CO in the ratio 1:2. Write a balanced chemical equation for the reaction. Starting with a 55.4 g sample of ZrO_2 , calculate the mass of $ZrCl_4$ formed, assuming that ZrO_2 is the limiting reagent and assuming 100% yield. **(d)** Using their electron configurations, account for the fact that Zr and Hf form chlorides MCl_4 and oxides MO_2 .

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

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

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



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

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

the electron has mass? In what sense is it consistent with proposals preceding Thomson's work that the cathode rays are a wave phenomenon?

- 6.118** The two most common isotopes of uranium are ^{235}U and ^{238}U . **(a)** Compare the number of protons, the number of electrons, and the number of neutrons in atoms of these two isotopes. **(b)** Using the periodic table in the front-inside cover, write the electron configuration for a U atom.

- (c)** Compare your answer to part (b) to the electron configuration given in Figure 6.29. How can you explain any differences between these two electron configurations? **(d)** ^{238}U undergoes radioactive decay to ^{234}Th . How many protons, electrons, and neutrons are gained or lost by the ^{238}U atom during this process? **(e)** Examine the electron configuration for Th in Figure 6.30. Are you surprised by what you find? Explain.

Design an Experiment

In this chapter, we have learned about the *photoelectric effect* and its impact on the formulation of light as photons. We have also seen that some anomalous electron configurations of the elements are particularly favorable if each atom has one or more half-filled shell, such as the case for the Cr atom with its $[\text{Ar}]4s^13d^5$ electron configuration. Let's suppose it is hypothesized that it requires more energy to remove an electron from a metal that has atoms with one or more half-filled shells than from those that do not. **(a)** Design a series of experiments involving the photoelectric effect that would test the

hypothesis. **(b)** What experimental apparatus would be needed to test the hypothesis? It's not necessary that you name actual equipment but rather that you imagine how the apparatus would work—think in terms of the types of measurements that would be needed, and what capability you would need in your apparatus. **(c)** Describe the type of data you would collect and how you would analyze the data to see whether the hypothesis were correct. **(d)** Could your experiments be extended to test the hypothesis for other parts of the periodic table, such as the lanthanide or actinide elements?