



Anyone who is not shocked by quantum mechanics has not understood it.

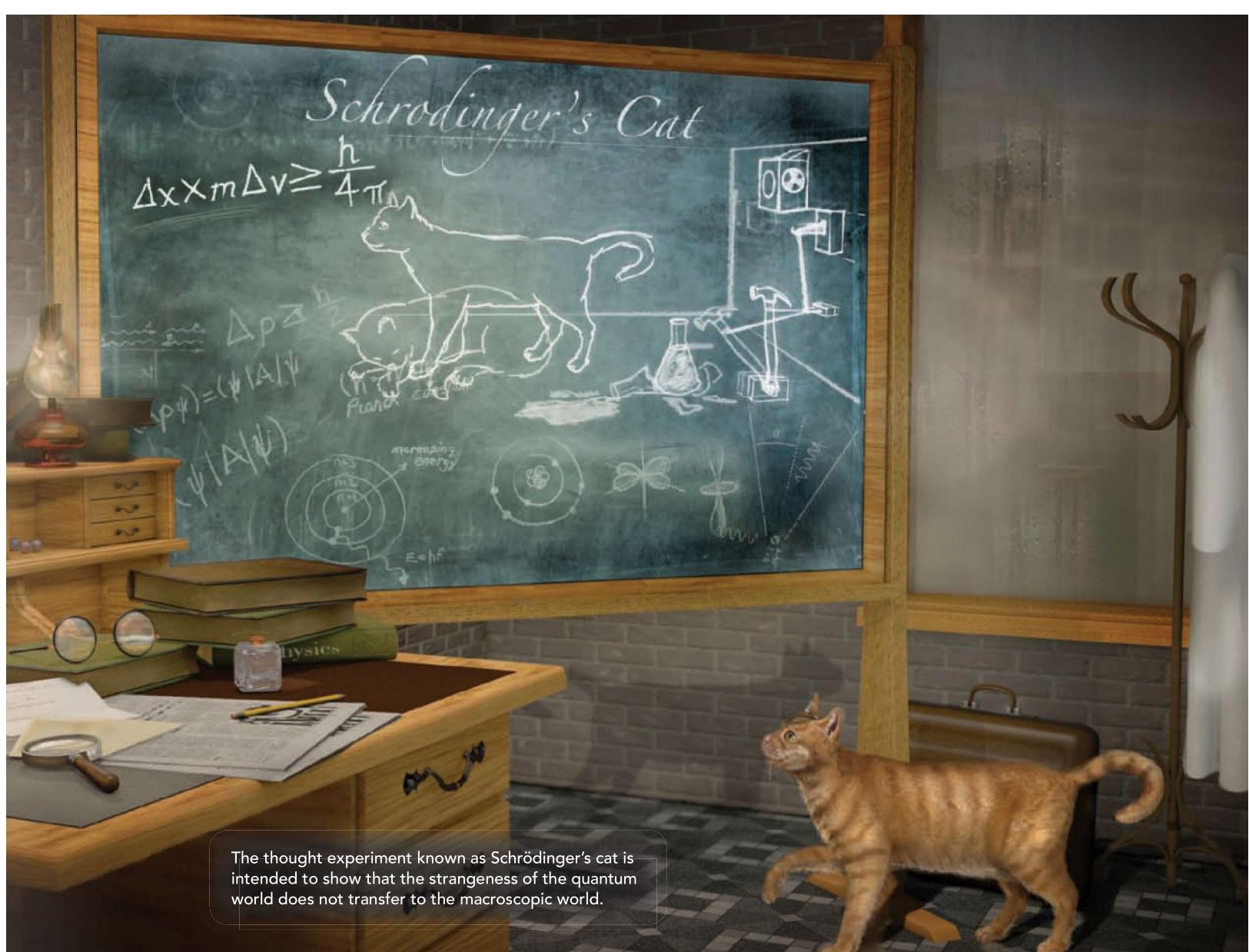
—NIELS BOHR (1885–1962)

CHAPTER

8

The Quantum-Mechanical Model of the Atom

The early part of the twentieth century revolutionized how we think about physical reality. Before then, all descriptions of the behavior of matter were deterministic—the present conditions completely determining the future. The new theory of quantum mechanics suggested that for subatomic particles—electrons, neutrons, and protons—the present does NOT completely determine the future. For example, if you shoot one electron down a path and measure where it lands, a second electron shot down the same path under the same conditions will most likely land in a different place! Several gifted scientists, including Albert Einstein, Niels Bohr, Louis de Broglie, Max Planck, Werner Heisenberg, P. A. M. Dirac, and Erwin Schrödinger, developed quantum-mechanical theory; they also realized its strangeness. Bohr said, “Anyone who is not shocked by quantum mechanics has not understood it.” Schrödinger wrote, “I don’t like it, and I’m sorry I ever had anything to do with it.” Albert Einstein disbelieved the very theory he helped develop, stating, “God does not play dice with the universe.” In fact, Einstein attempted to disprove quantum mechanics—without success—until he died. Today, quantum mechanics forms the foundation of chemistry—explaining the periodic table and chemical bonding—as well as providing the practical basis for lasers, computers, and countless other applications.



The thought experiment known as Schrödinger's cat is intended to show that the strangeness of the quantum world does not transfer to the macroscopic world.

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8.1 Schrödinger's Cat

Atoms and the particles that compose them are unimaginably small. Electrons have a mass of less than a trillionth of a trillionth of a gram, and a size so small that it is immeasurable. A single speck of dust contains more electrons than the number of people who have existed on Earth over all the centuries of time. Electrons are *small* in the absolute sense of the word—they are among the smallest particles that compose matter. And yet, as we have seen in the preceding chapters, an atom's electrons determine many

of its chemical and physical properties. If we are to understand these properties, we must try to understand electrons.

In the early twentieth century, scientists discovered that the *absolutely small* (or *quantum*) world of the electron behaves differently than the *large* (or *macroscopic*) world that we are used to observing. Chief among these differences is the idea that, when unobserved, *absolutely small particles like electrons can be in two different states at the same time*. For example, through a process called radioactive decay (see Chapter 21) an atom can emit small (that is, *absolutely small*) energetic particles from its nucleus. In the macroscopic world, something either emits an energetic particle or it doesn't. In the quantum world, however, the unobserved atom can be in a state in which it is doing both—emitting the particle and not emitting the particle—simultaneously. At first, this seems absurd. The absurdity resolves itself, however, upon observation. When we set out to measure the emitted particle, the act of measurement actually forces the atom into one state or the other.

Early twentieth-century physicists struggled with this idea. Austrian physicist Erwin Schrödinger (1887–1961), in an attempt to demonstrate that this quantum strangeness could never transfer itself to the macroscopic world, published a paper in 1935 that contained a thought experiment about a cat, now known as Schrödinger's cat. In the thought experiment, the imaginary cat is put into a steel chamber that contains radioactive atoms such as the atom described in the previous paragraph. The chamber is equipped with a mechanism that, upon the emission of an energetic particle by one of the radioactive atoms, causes a hammer to break a flask of hydrocyanic acid, a poison. If the flask breaks, the poison is released and the cat dies.

Now here comes the absurdity: if the steel chamber is closed, the whole system remains unobserved, and the radioactive atom is in a state in which it has both emitted the particle and not emitted the particle (with equal probability). Therefore, the cat is both dead and undead. Schrödinger put it this way: “[the steel chamber would have] *in it the living and dead cat (pardon the expression) mixed or smeared out in equal parts.*” When the chamber is opened, the act of observation forces the entire system into one state or the other: the cat is either dead or alive, not both. However, while unobserved, the cat is both dead and alive. The absurdity of the both dead and undead cat in Schrödinger's thought experiment was meant to demonstrate how quantum strangeness does not transfer to the macroscopic world.

In this chapter, we examine the **quantum-mechanical model** of the atom, a model that explains the strange behavior of electrons. In particular, we focus on how the model describes electrons as they exist within atoms, and how those electrons determine the chemical and physical properties of elements. You have already learned much about those properties. You know, for example, that some elements are metals and that others are nonmetals. You know that the noble gases are chemically inert and that the alkali metals are chemically reactive. You know that sodium tends to form $1+$ ions and that fluorine tends to form $1-$ ions. But we have not explored *why*. The quantum-mechanical model explains why. In doing so, it explains the modern periodic table and provides the basis for our understanding of chemical bonding.

WATCH NOW!

KEY CONCEPT VIDEO 8.2

 The Nature of Light

8.2

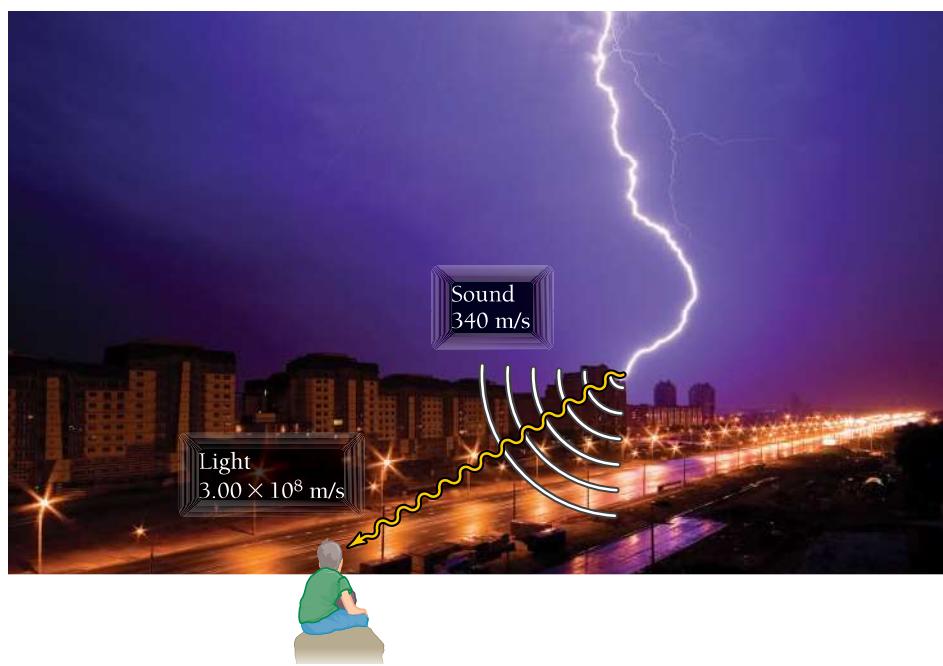
The Nature of Light

Before we explore electrons and their behavior within the atom, we must understand some of the properties of light. As quantum mechanics developed, light was (surprisingly) found to have many characteristics in common with electrons. Chief among these is the *wave-particle duality* of light. Certain properties of light are best described by thinking of it as a wave, while other properties are best described by thinking of it as a particle. In this section, we first explore light's dual nature (its wave behavior and its particle behavior), and then turn to electrons to see that they too display the same wave-particle duality.

The Wave Nature of Light

Light is **electromagnetic radiation**, a type of energy embodied in oscillating electric and magnetic fields. A *magnetic field* is a region of space where a magnetic particle experiences a force (think of the space around a magnet). An *electric field* is a region of space where an electrically charged particle experiences a force. A proton, for example, has an electric field around it. If you bring another charged particle into that field, that particle will experience a force.

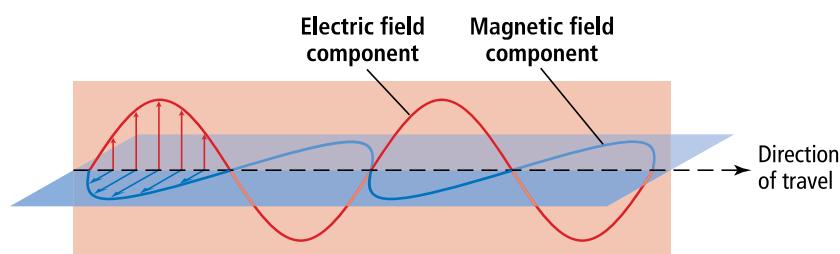
We can describe electromagnetic radiation as a wave composed of oscillating, mutually perpendicular electric and magnetic fields propagating through space, as shown in Figure 8.1▼. In a vacuum, these waves move at a constant speed of 3.00×10^8 m/s (186,000 mi/s)—fast enough to circle Earth in one-seventh of a second. This great speed is the reason for the delay between the moment when you see a firework in the sky and the moment when you hear the sound of its explosion. The light from the exploding firework reaches your eye almost instantaneously. The sound, traveling much more slowly (340 m/s), takes longer. The same thing happens in a thunderstorm—you see the flash of lightning immediately, but the sound of thunder takes a few seconds to reach you. (The sound of thunder is delayed by five seconds for each mile between you and its origin.)



◀ Because light travels nearly a million times faster than sound, the flash of lightning reaches your eyes before the roll of thunder reaches your ears.

Electromagnetic Radiation

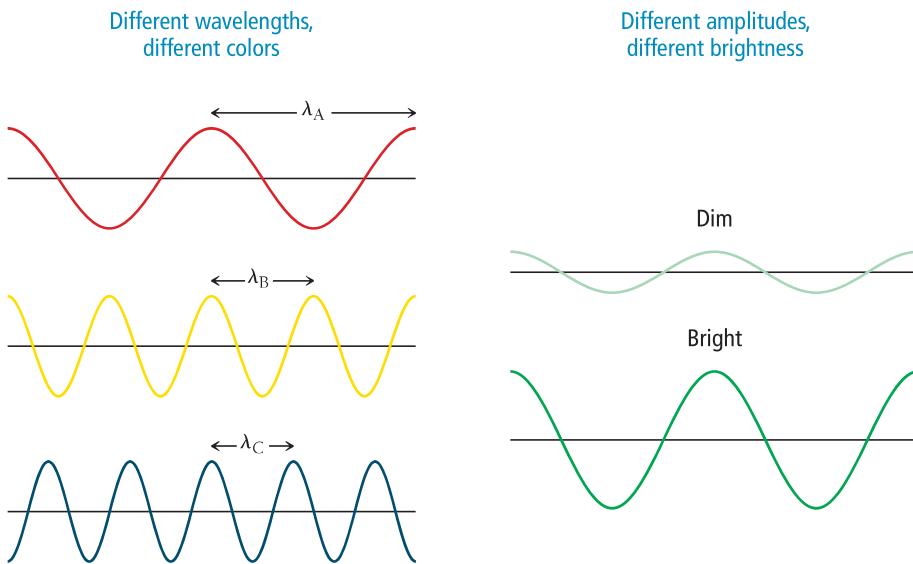
Electromagnetic radiation can be described as a wave composed of electric and magnetic fields that oscillate in perpendicular planes.



◀ FIGURE 8.1 Electromagnetic Radiation

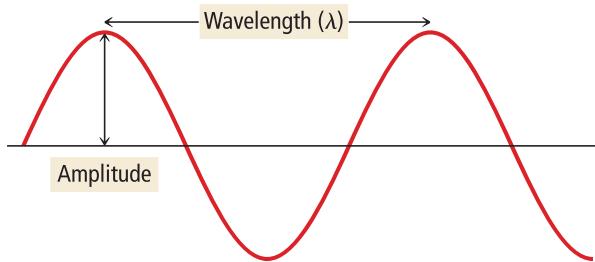
► FIGURE 8.2 Wavelength and Amplitude

Wavelength and amplitude are independent properties. The wavelength of light determines its color. The amplitude, or intensity, determines its brightness.



The symbol λ is the Greek letter lambda, pronounced "lamb-duh."

We characterize a wave by its *amplitude* and its *wavelength*. In the graphical representation shown here, the **amplitude** of the wave is the vertical height of a crest (or depth of a trough). The amplitude of the electric and magnetic field waves in light determines the light's *intensity* or brightness—the greater the amplitude, the greater the intensity. The **wavelength (λ)** of the wave is the distance between adjacent crests (or any two analogous points) and is measured in units such as meters, micrometers, or nanometers. Amplitude and wavelength can vary independently of one another, as shown in Figure 8.2▲.



The symbol ν is the Greek letter nu, pronounced "noo."

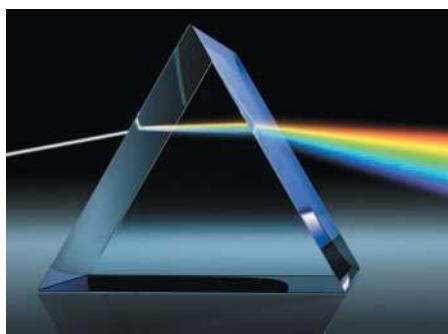
Like all waves, light is also characterized by its **frequency (ν)**, the number of cycles (or wave crests) that pass through a stationary point in a given period of time. The units of frequency are cycles per second (cycle/s) or simply s^{-1} . An equivalent unit of frequency is the hertz (Hz), defined as 1 cycle/s. The frequency of a wave is directly proportional to the speed at which the wave is traveling—the faster the wave, the greater the number of crests that pass a fixed location per unit time. Frequency is also *inversely* proportional to the wavelength (λ)—the farther apart the crests, the lower the number of crests that pass a fixed location per unit time. For light, therefore, we can write the equation:

$$\nu = \frac{c}{\lambda} \quad [8.1]$$

where the speed of light, c , and the wavelength, λ , are both expressed in the same unit of distance. Wavelength and frequency represent different ways of specifying the same information—if we know one, we can readily calculate the other.

For *visible light*—light that can be seen by the human eye—wavelength (or, alternatively, frequency) determines color. White light, produced by the sun or by a lightbulb, contains a spectrum of wavelengths and therefore a spectrum of colors. We see these colors—red, orange, yellow, green, blue, indigo, and violet—in a rainbow or when white light passes through a prism (Figure 8.3►). Red light, with a wavelength of about 750 nanometers (nm), has the longest wavelength of visible light; violet light, with a wavelength of about 400 nm, has the shortest. The presence of a variety of wavelengths in white light is responsible for the way we perceive colors in objects. When a substance absorbs some colors while reflecting others, it appears colored. For example, a red shirt

$$\text{nano} = 10^{-9}$$



▲ FIGURE 8.3 Components of White Light

Light We can pass white light through a prism and decompose it into its constituent colors, each with a different wavelength. The array of colors makes up the spectrum of visible light.



▲ FIGURE 8.4 The Color of an Object

Object A red shirt is red because it reflects predominantly red light while absorbing most other colors.

appears red because it reflects predominantly red light while absorbing most other colors (Figure 8.4▲). Our eyes see only the reflected light, making the shirt appear red.

WAVE NATURE OF LIGHT Which statement best describes the differences between a bright green laser and a dim red laser?

- (a) The two lasers emit light of the same frequency, and the light from the green laser has a greater amplitude.
- (b) The two lasers emit light of different frequencies, and the light from the green laser has a smaller amplitude.
- (c) The two lasers emit light of different frequencies, and the light from the green laser has a greater amplitude.

8.1

Cc
Conceptual Connection

ANSWER NOW!



EXAMPLE 8.1 Wavelength and Frequency

Calculate the wavelength (in nm) of the red light emitted by a barcode scanner that has a frequency of $4.62 \times 10^{14} \text{ s}^{-1}$.

SOLUTION

You are given the frequency of the light and asked to find its wavelength. Use Equation 8.1, which relates frequency to wavelength. You can convert the wavelength from meters to nanometers by using the conversion factor between the two ($1 \text{ nm} = 10^{-9} \text{ m}$).

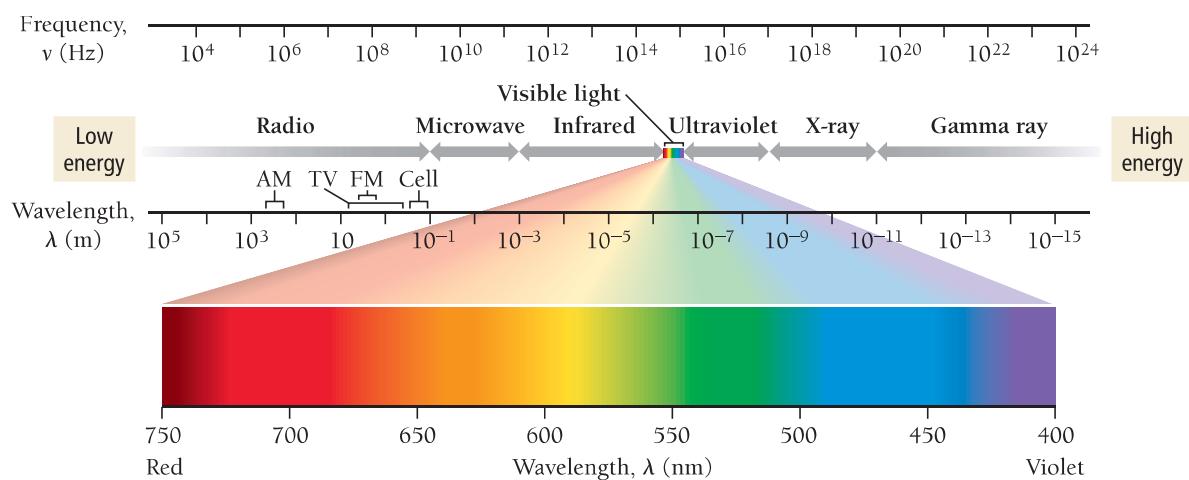
$$\begin{aligned} v &= \frac{c}{\lambda} \\ \lambda &= \frac{c}{v} = \frac{3.00 \times 10^8 \text{ m/s}}{4.62 \times 10^{14} \text{ s}} \\ &= 6.49 \times 10^{-7} \text{ m} \\ &= 6.49 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 649 \text{ nm} \end{aligned}$$

FOR PRACTICE 8.1 A laser dazzles the audience in a rock concert by emitting green light with a wavelength of 515 nm. Calculate the frequency of the light.

The Electromagnetic Spectrum

Visible light makes up only a tiny portion of the entire **electromagnetic spectrum**, which includes all wavelengths of electromagnetic radiation. Figure 8.5► shows the main regions of the electromagnetic spectrum, ranging in wavelength from 10^{-15} m (gamma rays) to 10^5 m (radio waves). In Figure 8.5, short-wavelength, high-frequency radiation is on the right, and long-wavelength, low-frequency radiation is on the left.

The Electromagnetic Spectrum



▲ FIGURE 8.5 The Electromagnetic Spectrum The right side of the spectrum consists of high-energy, high-frequency, short-wavelength radiation. The left side consists of low-energy, low-frequency, long-wavelength radiation. Visible light constitutes a small segment in the middle.

We will discuss gamma rays in more detail in Chapter 21.



▲ To produce a medical X-ray, short-wavelength electromagnetic radiation passes through the skin and creates an image of bones and internal organs.



▲ Warm objects emit infrared light, which is invisible to the eye but can be captured on film or by detectors to produce an infrared photograph.

We will see later in this section that short-wavelength light inherently has greater energy than long-wavelength light (because of the particle nature of light). The most energetic forms of electromagnetic radiation have the shortest wavelengths. The form of electromagnetic radiation with the shortest wavelength is the **gamma (γ) ray**. Gamma rays are produced by the sun, other stars, and certain unstable atomic nuclei on Earth. Excessive exposure to gamma rays is dangerous to humans because the high energy of gamma rays can damage biological molecules.

Next on the electromagnetic spectrum, with longer wavelengths than gamma rays, are **X-rays**, familiar to us from their medical use. X-rays pass through many substances that block visible light and are therefore used to image bones and internal organs. Like gamma rays, X-rays are sufficiently energetic to damage biological molecules. Although several annual medical X-rays are relatively harmless, too much exposure to X-rays increases cancer risk.

Sandwiched between X-rays and visible light in the electromagnetic spectrum is **ultraviolet (UV) radiation**, most familiar to us as the component of sunlight that produces a sunburn or suntan. Though not as energetic as gamma rays or X-rays, ultraviolet light still carries enough energy to damage biological molecules. Excessive exposure to ultraviolet light increases the risk of skin cancer and cataracts and causes premature wrinkling of the skin.

Next on the spectrum is **visible light**, ranging from violet (shorter wavelength, higher energy) to red (longer wavelength, lower energy). Visible light—at low to moderate intensity—does not carry enough energy to damage biological molecules. It does, however, cause certain molecules in our eyes to change their shape, sending a signal to our brains that results in our ability to see.

Beyond visible light lies **infrared (IR) radiation**. The heat you feel when you place your hand near a hot object is infrared radiation. All warm objects, including human bodies, emit infrared light. Although infrared light is invisible to our eyes, infrared sensors can detect it and are often employed in night vision technology to help people “see” in the dark.

Beyond infrared light, at longer wavelengths still, are **microwaves**, used for radar and in microwave ovens. Although microwave radiation has longer wavelengths and therefore lower energies than visible or infrared light, it is efficiently absorbed by water and can therefore heat substances that contain water. The longest wavelengths on the electromagnetic spectrum are those of **radio waves**, which are used to transmit the signals responsible for AM and FM radio, cellular telephone, television, and other forms of communication.

ELECTROMAGNETIC RADIATION

Arrange the following types of electromagnetic radiation in order of increasing wavelength: visible, X-ray, infrared.

- (a) X-ray < visible < infrared
- (b) X-ray < infrared < visible
- (c) visible < infrared < X-ray
- (d) infrared < X-ray < visible



ANSWER NOW!



CHEMISTRY AND MEDICINE

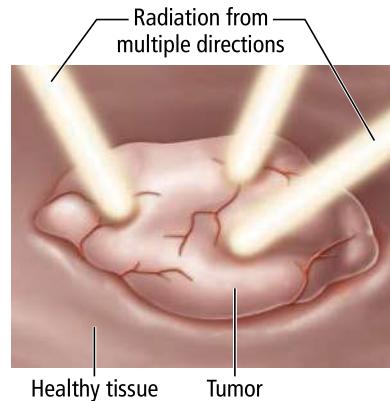
Radiation Treatment for Cancer

X-rays and gamma rays are sometimes called *ionizing radiation* because their short wavelengths correspond to high energies that can ionize atoms and molecules. When ionizing radiation interacts with biological molecules, it can permanently change or even destroy them. Consequently, we normally try to limit our exposure to ionizing radiation. However, doctors use ionizing radiation to destroy molecules within unwanted cells such as cancer cells.

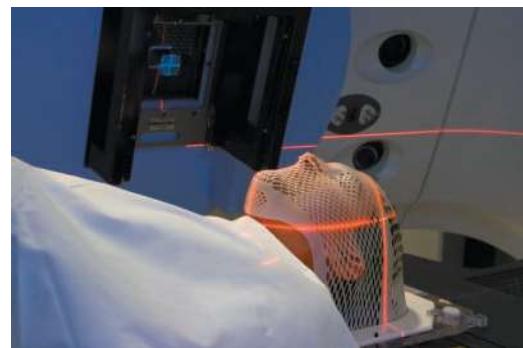
In radiation therapy (also called radiotherapy) doctors aim X-ray or gamma-ray beams at cancerous tumors (groups of cells that divide uncontrollably and invade surrounding healthy tissue). The ionizing radiation damages the molecules within the tumor's cells that carry genetic information—information necessary for the cell to grow and divide. Consequently, the cell dies or stops dividing. Ionizing radiation also damages molecules in healthy cells, but cancerous cells divide more quickly than normal cells, making them more susceptible to genetic damage. Nonetheless, harm to healthy tissues during radiation therapy treatments can result in side effects such as fatigue, skin lesions, hair loss, and organ damage. Medical workers try to reduce such effects by appropriate shielding (of healthy tissue) and by targeting the tumor from multiple directions, minimizing the exposure of healthy cells while maximizing the exposure of cancerous cells.

Another side effect of exposing healthy cells to radiation is that the healthy cells may become cancerous. If a treatment for cancer may cause cancer, why do we continue to use it? In radiation therapy, as in most other disease therapies, there is an associated risk. We take risks all the time, many of them for lesser reasons. For example, every time we fly in an airplane or drive in a car, we risk injury or even death. Why? Because we perceive the benefit—the convenience of being able to travel a significant distance in a short time—to be worth the relatively small risk. The situation is similar in cancer therapy, or any other medical therapy for that matter. The benefit of cancer therapy (possibly curing a cancer that might otherwise kill you) is worth the risk (a slight increase in the chance of developing a future cancer).

QUESTION Why is visible light (by itself) not used to destroy cancerous tumors?



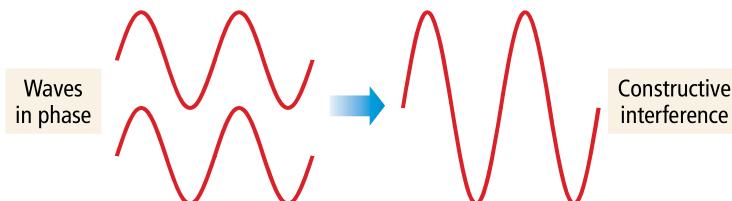
▲ During radiation therapy, a tumor is targeted from multiple directions in order to minimize the exposure of healthy cells while maximizing the exposure of cancerous cells.



▲ In radiation therapy, highly energetic gamma rays are aimed at cancerous tumors.

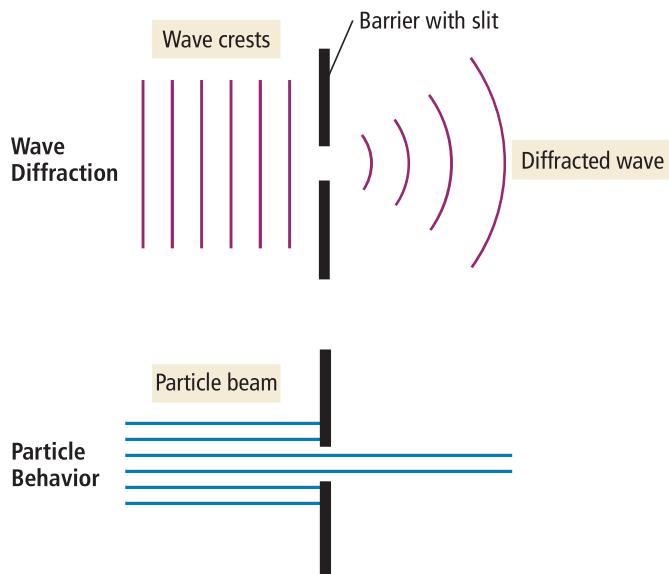
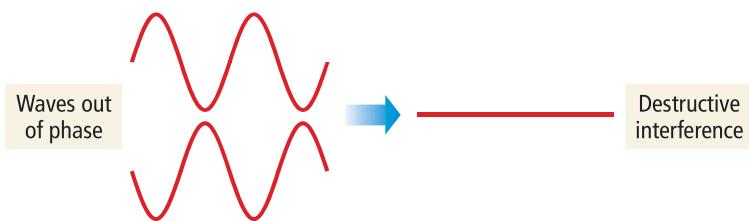
Interference and Diffraction

Waves, including electromagnetic waves, interact with each other in a characteristic way called **interference**: they cancel each other out or build each other up, depending on their alignment upon interaction. For example, if two waves of equal amplitude are *in phase* when they interact—that is, they align with overlapping crests—a wave with twice the amplitude results. This is called **constructive interference**.



▲ When a reflected wave meets an incoming wave near the shore, the two waves interfere constructively for an instant, producing a large-amplitude spike.

On the other hand, if two waves are completely *out of phase* when they interact—that is, they align so that the crest from one source overlaps with the trough from the other source—the waves cancel by **destructive interference**.



▲ FIGURE 8.6 Diffraction In this view from above, we can see how a wave bends, or diffracts, when it encounters an obstacle or slit with a size comparable to its wavelength. When a wave passes through a small opening, it spreads out. Particles, by contrast, do not diffract; they simply pass through the opening.

The term *classical*, as in classical electromagnetic theory or classical mechanics, refers to descriptions of matter and energy before the advent of quantum mechanics.

Waves also exhibit a characteristic behavior called **diffraction** (Figure 8.6◀). When a wave encounters an obstacle or a slit that is comparable in size to its wavelength, it bends (or *diffRACTS*) around it. The diffraction of light through two slits separated by a distance comparable to the wavelength of the light, coupled with interference, results in an *interference pattern*, illustrated in Figure 8.7▶. Each slit acts as a new wave source, and the two new waves interfere with each other. The resulting pattern is a series of bright and dark lines that can be viewed on a screen (or recorded on a film) placed a short distance behind the slits. At the center of the screen, the two waves travel equal distances and interfere constructively to produce a bright line. A small distance away from the center in either direction, the two waves travel slightly different distances, so they are out of phase. At the point where the difference in distance is one-half of one wavelength, the interference is destructive and a dark line appears on the screen. A bit farther away from the center we see constructive interference again because the difference between the paths is one whole wavelength. The end result is the interference pattern shown by the light and dark bars in Figure 8.7. Notice that interference results from the ability of a wave to diffract through two slits—an inherent property of waves.

The Particle Nature of Light

Prior to the early 1900s, and especially after the discovery of the diffraction of light, light was thought to be purely a wave phenomenon. Its behavior was described adequately by classical electromagnetic theory, which treated the electric and magnetic fields that constitute light as waves propagating through space. However, a number of discoveries brought the classical view into question. Chief among these discoveries was the *photoelectric effect*.

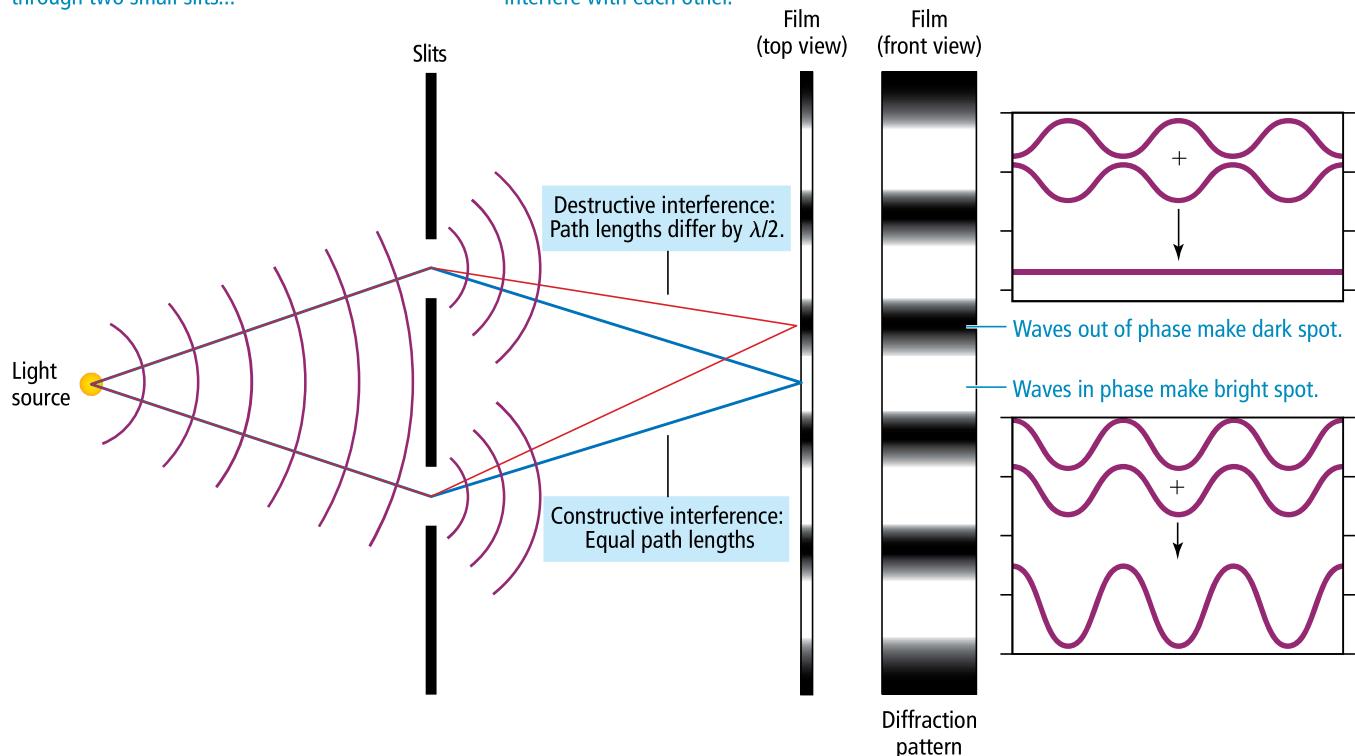
The **photoelectric effect** is the observation that many metals emit electrons when light shines upon them, as shown in Figure 8.8▶. Classical electromagnetic theory attributed this effect to the transfer of energy from the light to an electron in the metal, which resulted in the dislodgment of the electron. According to this explanation, only the amplitude (intensity) of the light affects the emission of electrons, not the wavelength. In other words, according to the classical description, the rate at which electrons leave the metal due to the photoelectric effect increases with increasing intensity of the light. A dim light was expected to result in a *lag time* between the initial shining of the light and the subsequent emission of an electron. The lag time would be the minimum amount of time required for the dim light to transfer sufficient energy to the electron to dislodge it.

The experimental results, however, did not support the classical prediction. Scientists found that a high-frequency, low-intensity light produces electrons *without* the

Interference from Two Slits

When a beam of light passes through two small slits...

...the two resulting waves interfere with each other.

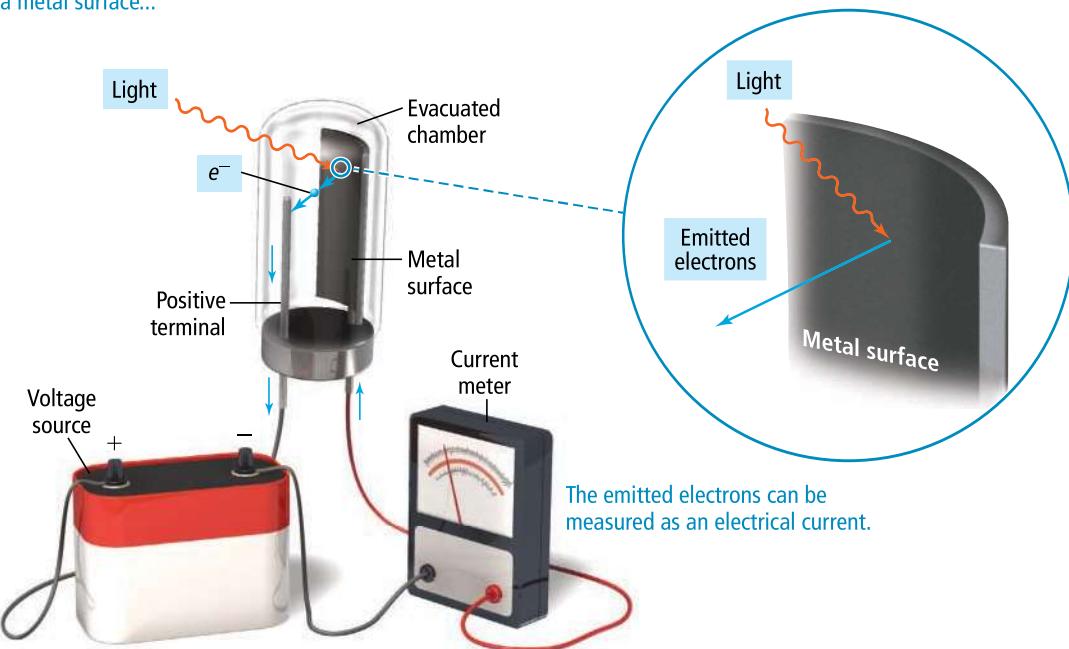


▲ FIGURE 8.7 Interference from Two Slits Whether the interference is constructive or destructive at any given point depends on the difference in the path lengths traveled by the waves.

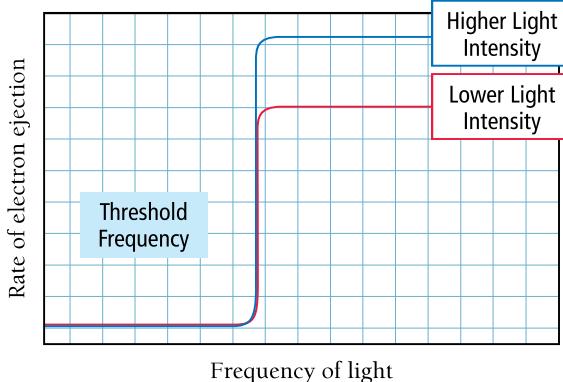
The Photoelectric Effect

When sufficiently energetic light shines on a metal surface...

...the surface emits electrons.



▲ FIGURE 8.8 The Photoelectric Effect



▲ FIGURE 8.9 The Photoelectric Effect A plot of the electron ejection rate versus frequency of light for the photoelectric effect.

Einstein was not the first to suggest that energy was quantized. Max Planck (1858–1947) used the idea in 1900 to account for certain characteristics of radiation from hot bodies.

The energy of a photon is directly proportional to its frequency and inversely proportional to its wavelength.

predicted lag time. Furthermore, the light used to dislodge electrons in the photoelectric effect exhibits a *threshold frequency*, below which no electrons are emitted from the metal, no matter how long the light shines on the metal. Figure 8.9 is a graph of the rate of electron ejection from the metal versus the frequency of light used. Notice that increasing the intensity of the light does not change the threshold frequency. In other words, low-frequency (long-wavelength) light *does not* eject electrons from a metal regardless of its intensity or its duration. But high-frequency (short-wavelength) light *does* eject electrons, even if its intensity is low. What could explain this odd behavior?

In 1905, Albert Einstein (1879–1955) proposed a bold explanation for the photoelectric effect: *light energy must come in packets*. According to Einstein, the amount of energy (E) in a light packet depends on its frequency (ν) according to the following equation:

$$E = h\nu \quad [8.2]$$

where h , called *Planck's constant*, has the value $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$. A *packet* of light is called a **photon** or a **quantum** of light. Since $\nu = c/\lambda$, the energy of a photon can also be expressed in terms of wavelength as follows:

$$E = \frac{hc}{\lambda} \quad [8.3]$$

Unlike classical electromagnetic theory, in which light was viewed purely as a wave whose intensity was *continuously variable*, Einstein suggested that light was *lumpy*. From this perspective, a beam of light is *not* a wave propagating through space, but a shower of particles (photons), each with energy $h\nu$.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 8.2

EXAMPLE 8.2 Photon Energy

A nitrogen gas laser pulse with a wavelength of 337 nm contains 3.83 mJ of energy. How many photons does it contain?

SORT You are given the wavelength and total energy of a light pulse and asked to find the number of photons it contains.

STRATEGIZE In the first part of the conceptual plan, calculate the energy of an individual photon from its wavelength.

In the second part, divide the total energy of the pulse by the energy of a photon to determine the number of photons in the pulse.

SOLVE To execute the first part of the conceptual plan, convert the wavelength to meters and substitute it into the equation to calculate the energy of a 337-nm photon.

GIVEN: $E_{\text{pulse}} = 3.83 \text{ mJ}$
 $\lambda = 337 \text{ nm}$

FIND: number of photons

CONCEPTUAL PLAN

$$\lambda \rightarrow E_{\text{photon}}$$

$$E = \frac{hc}{\lambda}$$

$$\frac{E_{\text{pulse}}}{E_{\text{photon}}} = \text{number of photons}$$

RELATIONSHIPS USED $E = hc/\lambda$ (Equation 8.3)

SOLUTION

$$\lambda = 337 \text{ nm} \times \frac{10^{-9} \text{ m}}{1 \text{ nm}} = 3.37 \times 10^{-7} \text{ m}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \frac{\text{m}}{\text{s}})}{3.37 \times 10^{-7} \text{ m}}$$

$$= 5.8985 \times 10^{-19} \text{ J}$$

To execute the second part of the conceptual plan, convert the energy of the pulse from mJ to J. Then divide the energy of the pulse by the energy of a photon to obtain the number of photons.

$$3.83 \text{ mJ} \times \frac{10^{-3} \text{ J}}{1 \text{ mJ}} = 3.83 \times 10^{-3} \text{ J}$$

$$\text{number of photons} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{3.83 \times 10^{-3} \text{ J}}{5.8985 \times 10^{-19} \text{ J}}$$

$$= 6.49 \times 10^{15} \text{ photons}$$

CHECK The units of the answer, photons, are correct. The magnitude of the answer (10^{15}) is reasonable. Photons are small particles, and any macroscopic collection must contain a large number of them.

FOR PRACTICE 8.2 A 100-watt lightbulb radiates energy at a rate of 100 J/s. (The watt, a unit of power, or energy over time, is defined as 1 J/s.) If all of the light emitted has a wavelength of 525 nm, how many photons are emitted per second? (Assume three significant figures in this calculation.)

FOR MORE PRACTICE 8.2 The energy required to dislodge electrons from sodium metal via the photoelectric effect is 275 kJ/mol. What wavelength in nm of light has sufficient energy per photon to dislodge an electron from the surface of sodium?

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 8.3

EXAMPLE 8.3 Wavelength, Energy, and Frequency



Arrange these three types of electromagnetic radiation—visible light, X-rays, and microwaves—in order of increasing

- (a) wavelength. (b) frequency. (c) energy per photon.

SOLUTION

Examine Figure 8.5 and note that X-rays have the shortest wavelength, followed by visible light and then microwaves.

(a) wavelength
X-rays < visible < microwaves

Since frequency and wavelength are inversely proportional—the longer the wavelength, the shorter the frequency—the ordering with respect to frequency is the reverse of the ordering with respect to wavelength.

(b) frequency
microwaves < visible < X-rays

Energy per photon decreases with increasing wavelength but increases with increasing frequency; therefore, the ordering with respect to energy per photon is the same as for frequency.

(c) energy per photon
microwaves < visible < X-rays

FOR PRACTICE 8.3 Arrange these three colors of visible light—green, red, and blue—in order of increasing

- (a) wavelength. (b) frequency. (c) energy per photon.

Einstein's idea that light is quantized elegantly explains the photoelectric effect. The emission of electrons from the metal depends on whether or not a single photon has sufficient energy (as given by $h\nu$) to dislodge a single electron. For an electron bound to the metal with binding energy ϕ , the threshold frequency is reached when the energy of the photon is equal to ϕ .

The symbol ϕ is the Greek letter phi, pronounced "fi."

Threshold frequency condition

$$h\nu = \phi$$

Energy of photon Binding energy of emitted electron

Low-frequency light does not eject electrons because no single photon has the minimum energy necessary to dislodge the electron. We can draw an analogy between a photon ejecting an electron from a metal surface and a ball breaking a glass window. In this analogy, low-frequency photons are like ping-pong balls—a ping-pong ball thrown at a glass window does not break it (just as a low-frequency photon does not eject an electron). Increasing the *intensity* of low-frequency light is like increasing the number of

ping-pong balls thrown at the window—doing so simply increases the number of low-energy photons but does not produce any single photon with sufficient energy. In contrast, increasing the *frequency* of the light, even at low intensity, *increases the energy of each photon*. In our analogy, a high-frequency photon is like a baseball—a baseball thrown at a glass window breaks it (just as a high-frequency photon dislodges an electron with no lag time).

As the frequency of the light increases past the threshold frequency, the excess energy of the photon (beyond what is needed to dislodge the electron) transfers to the electron in the form of kinetic energy. The kinetic energy (KE) of the ejected electron, therefore, is the difference between the energy of the photon ($h\nu$) and the binding energy of the electron, as given by the equation:

$$KE = h\nu - \phi$$

Although the quantization of light explained the photoelectric effect, the wave explanation of light continued to have explanatory power as well, depending on the circumstances of the particular observation. So the principle that slowly emerged (albeit with some measure of resistance) is what we now call the *wave-particle duality of light*. Sometimes light appears to behave like a wave, at other times like a particle. Which behavior we observe depends on the particular experiment.

ANSWER NOW!



8.3

Cc
Conceptual Connection

THE PHOTOELECTRIC EFFECT

We shine light of three different wavelengths—325 nm, 455 nm, and 632 nm—on a metal surface and record the following observations for each wavelength, labeled A, B, and C:

Observation A: No photoelectrons were observed.

Observation B: Photoelectrons with a kinetic energy of 155 kJ/mol were observed.

Observation C: Photoelectrons with a kinetic energy of 51 kJ/mol were observed.

Which observation corresponds to the 325 nm light?

- (a) Observation A (b) Observation B (c) Observation C



▲ The familiar red light from a neon sign is emitted by neon atoms that have absorbed electrical energy, which the atoms reemit as visible radiation.

8.3

Atomic Spectroscopy and the Bohr Model

The discovery of the particle nature of light began to break down the division that existed in nineteenth-century physics between electromagnetic radiation, which was thought of as a wave phenomenon, and the small particles (protons, neutrons, and electrons) that compose atoms, which were thought to follow Newton's laws of motion. Just as the photoelectric effect suggested the particle nature of light, so certain observations about atoms began to suggest a wave nature for particles. The most important of these observations came from *atomic spectroscopy*, the study of the electromagnetic radiation absorbed and emitted by atoms.

When an atom absorbs energy—in the form of heat, light, or electricity—it often reemits that energy as light. For example, a neon sign is composed of one or more glass tubes filled with neon gas. When an electric current is passed through the tube, the neon atoms absorb some of the electrical energy and reemit it as the familiar red light of a neon sign. If the atoms in the tube are different (that is, not neon), they emit light of a different color. In other words, atoms of each element emit light of a characteristic color. Mercury atoms, for example, emit light that appears blue, helium atoms emit light that appears violet, and hydrogen atoms emit light that appears reddish (Figure 8.10►).

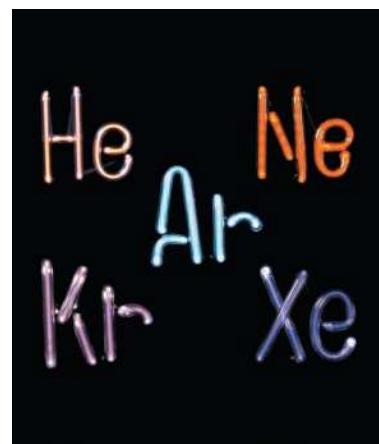
Remember that the color of visible light is determined by its wavelength. Closer inspection of the light emitted by various atoms reveals that it contains several distinct wavelengths. We can separate the light emitted by a single element in a glass tube into its constituent wavelengths by passing it through a prism (just like we separate the white

light from a lightbulb), as shown in Figure 8.11▼. The result is a series of bright lines called an **emission spectrum**. The emission spectrum of a particular element is always the same—it consists of the same bright lines at the same characteristic wavelengths. We can use the emission spectrum to identify the element. For example, light arriving from a distant star contains the emission spectra of the elements that compose the star. Analysis of the light allows us to identify the elements present in the star.

Notice the differences between a white light spectrum and the emission spectra of hydrogen, helium, and barium (shown in Figure 8.11). The white light spectrum is *continuous*, meaning that there are no sudden interruptions in the intensity of the light as a function of wavelength—the spectrum consists of light of all wavelengths. The emission spectra of hydrogen, helium, and barium, however, are not continuous—they consist of bright lines at specific wavelengths, with complete darkness in between. That is, only certain discrete wavelengths of light are present. Classical physics could not explain why these spectra consisted of discrete lines. In fact, according to classical physics, an atom composed of an electron orbiting a nucleus should emit a continuous white light spectrum. Even more problematic, the electron should lose energy as it emits the light and spirals into the nucleus. According to classical physics, an atom should not even be stable.

Johannes Rydberg (1854–1919), a Swedish mathematician, analyzed many atomic spectra and developed an equation that predicts the wavelengths of the hydrogen emission spectrum. However, his equation (shown in the margin) gives little insight into *why* atomic spectra are discrete, *why* atoms are stable, or *why* his equation works.

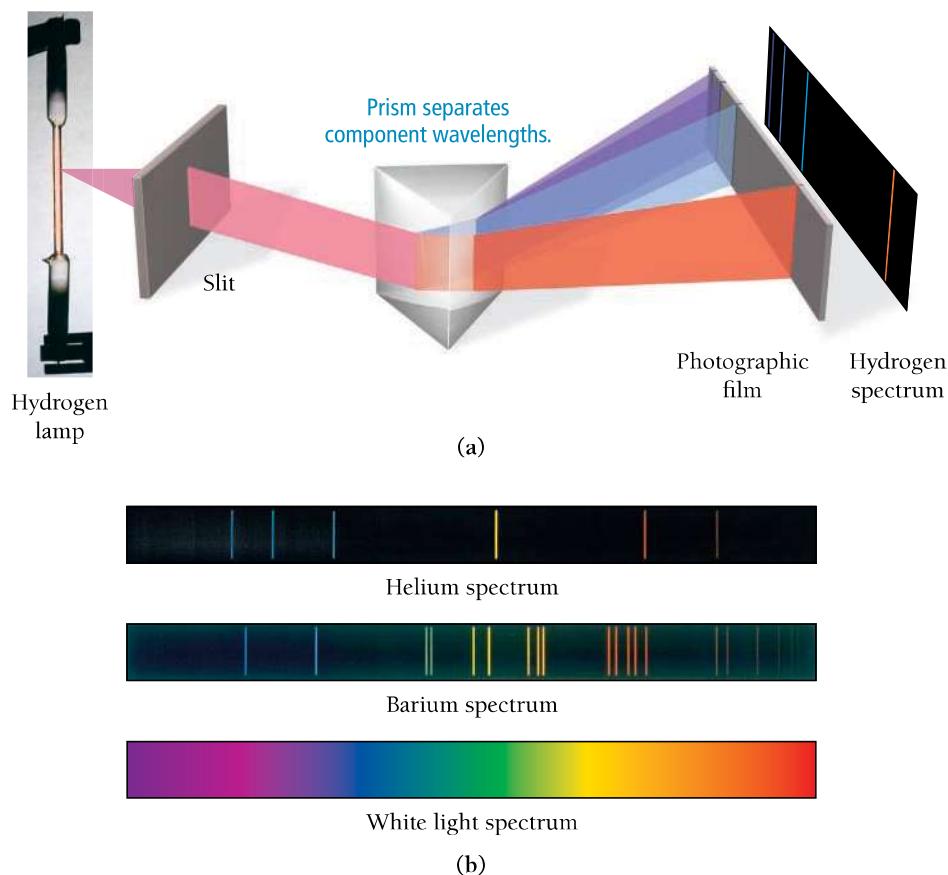
The Danish physicist Niels Bohr (1885–1962) attempted to develop a model for the hydrogen atom that explained its atomic spectrum. In his model, the electron travels



▲ FIGURE 8.10 Light emitted from various elements. Each element emits a characteristic color.

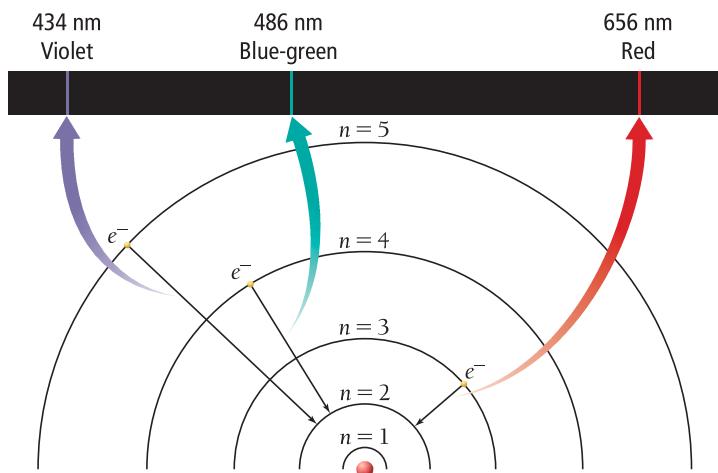
The Rydberg equation is $1/\lambda = R(1/m^2 - 1/n^2)$, where R is the Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$) and m and n are integers.

Emission Spectra



▲ FIGURE 8.11 Emission Spectra (a) The light emitted from a hydrogen, helium, or barium lamp consists of specific wavelengths that can be separated by passing the light through a prism. (b) The resulting bright lines constitute an emission spectrum characteristic of the element that produced it.

The Bohr Model and Emission Spectra



▲ FIGURE 8.12 The Bohr Model for the Hydrogen Atom

According to the Bohr model, each spectral line is produced when an electron falls from one stable orbit, or stationary state, to another of lower energy.

around the nucleus in circular orbit (analogous to those of the planets around the sun). However, in contrast to planetary orbits—which theoretically can exist at any distance from the sun—Bohr’s orbits exist only at specific, fixed distances from the nucleus. The energy of each Bohr orbit is also fixed, or *quantized*. Bohr called these orbits *stationary states* and suggested that, although they obey the laws of classical mechanics, they also possess “a peculiar, mechanically unexplainable, stability.” Scientists now know that the stationary states were really manifestations of the wave nature of the electron, which we will expand upon shortly. Bohr further proposed that, in contradiction to classical electromagnetic theory, an electron orbiting the nucleus in a stationary state emits no radiation. It is only when an electron jumps, or makes a *transition*, from one stationary state to another that radiation is emitted or absorbed (Figure 8.12◀).



CHEMISTRY IN YOUR DAY

Atomic Spectroscopy, a Bar Code for Atoms

When you check out of the grocery store, a laser scanner reads the bar code on the items that you buy. Each item has a unique code that identifies the item and its price. Similarly, each element in the periodic table has a spectrum unlike that of any other element. For example, Figure 8.13▼ shows the emission spectra of oxygen and neon. (In Figure 8.11, we saw the emission spectra of hydrogen, helium, and barium.) Notice that each spectrum is unique and, as such, can be used to identify the substance.

The presence of intense lines in the spectra of a number of metals is the basis for *flame tests*, simple tests used to identify elements in ionic compounds in the absence of a precise analysis of a compound’s spectrum. For example, the emission spectrum of sodium features two closely spaced, bright yellow lines. When a crystal of a sodium salt (or a drop of a solution containing a sodium salt) is put into a flame, the flame glows bright yellow (Figure 8.14▶). As Figure 8.14 shows, other metals exhibit similarly characteristic colors in flame tests. Each color represents an especially bright spectral emission line (or a combination of two or more such lines). Similar emissions form the basis of the colors seen in fireworks.

Although the emission of light from elements is easier to detect, the absorption of light by elements is even more commonly used for purposes of identification. Whereas emission spectra consist of bright lines on a dim background, absorption spectra consist of dark lines (absorbed light) on a bright background (Figure 8.15▶). An absorption spectrum is measured by passing white light through a sample and observing what wavelengths are *missing* due to absorption by the sample. Notice that, in the spectrum of mercury shown in Figure 8.15, the absorption lines are at the same wavelengths as the emission lines. This is because the processes that produce them are mirror images. In emission, an electron makes a transition from a higher-energy level to a lower-energy one. In absorption, the transition is between the same two energy levels, but from the lower level to the higher one.



▲ Fireworks typically contain the salts of such metals as sodium, calcium, strontium, barium, and copper. Emissions from these elements produce the brilliant colors of pyrotechnic displays.

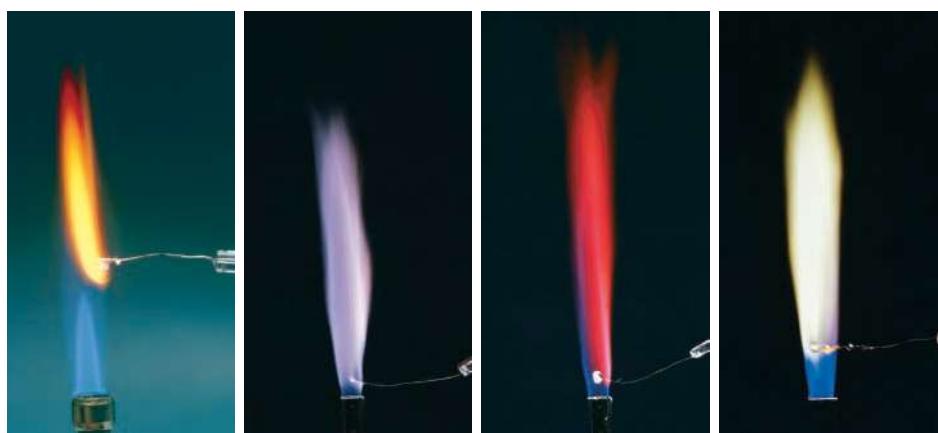
Oxygen



Neon



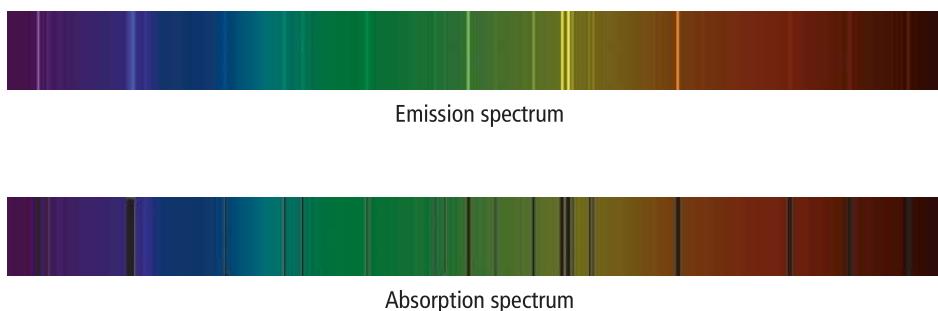
▲ FIGURE 8.13 Emission Spectra of Oxygen and Neon The emission spectrum of each element is unique, and we can use it to identify the element.



◀ FIGURE 8.14 Flame Tests (from left to right) for Sodium, Potassium, Lithium, and Barium We can identify elements by the characteristic color of the light they produce when heated. The colors derive from especially bright lines in their emission spectra.

Absorption spectrometers, found in most chemistry laboratories, typically plot the intensity of absorption as a function of wavelength. Such plots are useful both for identifying substances (qualitative analysis) and for determining the concentration of substances (quantitative analysis). Quantitative analysis is possible because the amount of light absorbed by a sample depends on the concentration of the absorbing substance within the sample. For example, we can determine the concentration of Ca^{2+} in a hard water sample by measuring the quantity of light absorbed by the calcium ion at its characteristic wavelength.

In spite of its initial success in explaining the line spectrum of hydrogen, the Bohr model left many unanswered questions. It did, however, serve as an intermediate model between a classical view of the electron and a fully quantum-mechanical view, and therefore has great historical and conceptual importance. Nonetheless, it was ultimately replaced by a more complete quantum-mechanical theory that fully incorporated the wave nature of the electron.



◀ FIGURE 8.15 Emission and Absorption Spectrum of Mercury Elements absorb light of the same wavelengths that they radiate when heated. When these wavelengths are subtracted from a beam of white light, the result is a pattern of dark lines corresponding to an absorption spectrum.

The transitions between stationary states in a hydrogen atom are quite unlike transitions in the macroscopic world. The electron is *never* observed *between states*; it is observed only in one state or another. The emission spectrum of an atom consists of discrete lines because the stationary states exist only at specific, fixed energies. The energy of the photon emitted when an electron makes a transition from one stationary state to another is the energy difference between the two stationary states. Transitions between stationary states that are closer together, therefore, produce light of lower energy (longer wavelength) than transitions between stationary states that are farther apart.

8.4

The Wave Nature of Matter: The de Broglie Wavelength, the Uncertainty Principle, and Indeterminacy

The heart of quantum-mechanical theory is the wave nature of the electron, first proposed by Louis de Broglie (1892–1987) in 1924 and confirmed by experiments in 1927. It seemed incredible at the time, but electrons—which were then thought of only as particles and known to have mass—also have a wave nature. The wave nature of the electron is seen most clearly in its diffraction. If an electron beam is aimed at two closely

WATCH NOW!

KEY CONCEPT VIDEO 8.4
The Wave Nature of Matter

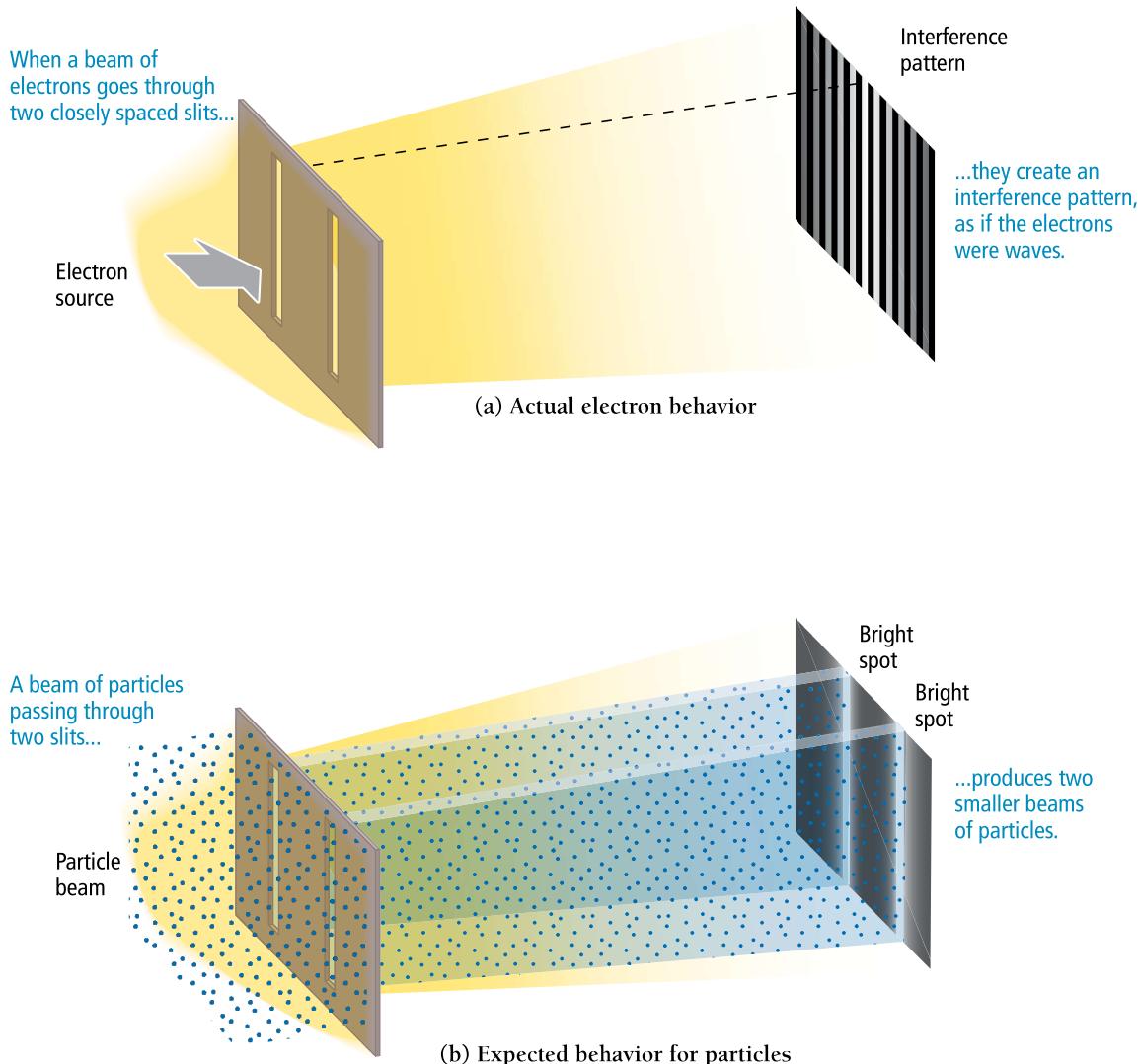
The Davisson–Germer experiment of 1927 provided the first evidence of electron wave properties. In this experiment, electrons were observed to undergo diffraction by a metal crystal.

For interference to occur, the spacing of the slits has to be on the order of atomic dimensions.

spaced slits, and a series (or array) of detectors is arranged to detect the electrons after they pass through the slits, an interference pattern similar to that observed for light (see Figure 8.6) is recorded behind the slits (Figure 8.16(a)). The detectors at the center of the array (midway between the two slits) detect a large number of electrons—exactly the opposite of what you would expect for particles (Figure 8.16(b)). Moving outward from this center spot, the detectors alternately detect small numbers of electrons and then large numbers again and so on, forming an interference pattern characteristic of waves.

Counter to what might be our initial intuition about electron interference, the interference pattern is *not caused by pairs of electrons interfering with each other, but rather by single electrons interfering with themselves*. If the electron source is turned down to a very low level, so that electrons come out only one at a time, *the interference pattern remains*. In other words, we can design an experiment in which electrons come out of the source singly. We can then record where each electron strikes the detector after it has passed through the slits. If we record the positions of thousands of electrons over a long period of time, we find the same interference pattern shown in Figure 8.16(a).

This observation leads us to an important conclusion: *the wave nature of the electron is an inherent property of individual electrons*. Recall from Section 8.1 that unobserved electrons can simultaneously occupy two different states. In this case, the unobserved electron goes through both slits—it exists in two states simultaneously, just like Schrödinger's cat—and interferes with itself. This wave nature explains the existence of stationary states (in the Bohr model) and prevents the electrons in an atom from crashing into the nucleus as predicted by



▲ FIGURE 8.16 **Electron Diffraction** Notice that the wave source (electrons) produces a diffraction pattern that is brightest at the center, whereas the particle beam produces two bright stripes and a central dark band.

classical physics. We now turn to three important manifestations of the electron's wave nature: the de Broglie wavelength, the uncertainty principle, and indeterminacy.

The de Broglie Wavelength

As we have seen, a single electron traveling through space has a wave nature; its wavelength is related to its kinetic energy (the energy associated with its motion). The faster the electron is moving, the higher its kinetic energy and the shorter its wavelength. The wavelength (λ) of an electron of mass m moving at velocity v is given by the **de Broglie relation**:

$$\lambda = \frac{h}{mv} \quad \text{de Broglie relation} \quad [8.4]$$

where h is Planck's constant. Notice that the velocity of a moving electron is related to its wavelength—knowing one is equivalent to knowing the other.

The mass of an object (m) times its velocity (v) is its momentum. Therefore, the wavelength of an electron is inversely proportional to its momentum.

EXAMPLE 8.4 De Broglie Wavelength

Calculate the wavelength of an electron traveling with a speed of 2.65×10^6 m/s.

SORT You are given the speed of an electron and asked to calculate its wavelength.	GIVEN: $v = 2.65 \times 10^6$ m/s FIND: λ
STRATEGIZE The conceptual plan shows how the de Broglie relation relates the wavelength of an electron to its mass and velocity.	CONCEPTUAL PLAN  $\lambda = \frac{h}{mv}$ RELATIONSHIPS USED $\lambda = h/mv$ (de Broglie relation, Equation 8.4)
SOLVE Substitute the velocity, Planck's constant, and the mass of an electron into Equation 8.4 to calculate the electron's wavelength. To correctly cancel the units, break down the J in Planck's constant into its SI base units (1 J = 1 kg · m ² /s ²).	SOLUTION $\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}}{(9.11 \times 10^{-31} \text{kg}) \left(2.65 \times 10^6 \frac{\text{m}}{\text{s}} \right)}$ $= 2.74 \times 10^{-10} \text{m}$
CHECK The units of the answer (m) are correct. The magnitude of the answer is very small, as expected for the wavelength of an electron.	FOR PRACTICE 8.4 What is the velocity of an electron that has a de Broglie wavelength approximately the length of a chemical bond? Assume the length of a chemical bond is 1.2×10^{-10} m.

THE DE BROGLIE WAVELENGTH OF MACROSCOPIC OBJECTS

Since quantum-mechanical theory is universal, it applies to all objects, regardless of size. Therefore, according to the de Broglie relation, a thrown baseball should also exhibit wave properties. Why don't we observe such properties at the ballpark?

- (a) Because of the baseball's large mass, its de Broglie wavelength is minuscule and insignificant compared to the baseball's size.
- (b) Since baseballs do not have any charge, quantum mechanics does not apply to them.
- (c) Quantum mechanics does not apply to baseballs.



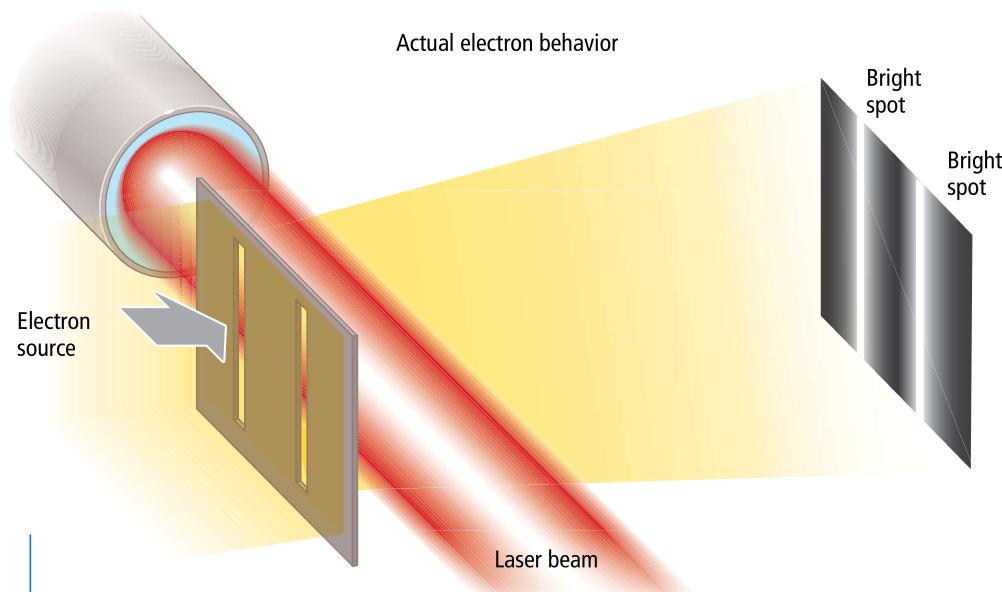
ANSWER NOW!



The Uncertainty Principle

The wave nature of the electron is difficult to reconcile with its particle nature. How can a single entity behave as both a wave and a particle? We can begin to address this question by returning to the single-electron diffraction experiment. How does a single electron aimed at a double slit produce an interference pattern? We saw previously that the electron travels through both slits and interferes with itself. This idea is testable. We simply have to observe the single electron as it travels through both of the slits. If it travels through both slits simultaneously, our hypothesis is correct. But here is where nature gets tricky.

Any experiment designed to observe the electron as it travels through the slits results in the detection of an electron “particle” traveling through a single slit and no interference pattern. Recall from Section 8.1 that an *unobserved* electron can occupy two different states; however, the act of observation forces it into one state or the other. Similarly, the act of observing the electron as it travels through both slits forces it to go through only one slit. The electron diffraction experiment illustrated here is designed to observe which slit the electron travels through by using a laser beam placed directly behind the slits:



The laser experiment described here is not an actual experiment because it would be difficult to carry out for practical reasons; however, the results are consistent with similar experiments designed to measure the same thing.

An electron that crosses the laser beam produces a tiny “flash” when a single photon is scattered at the point of crossing. If a flash shows up behind a particular slit, that indicates an electron is passing through that slit. However, as the electrons are detected, the flash always originates either from one slit *or* the other, but *never* from both at once. Furthermore, the interference pattern, which was present without the laser, is absent when the electrons are observed going through the slits. With the laser on, the electrons hit positions directly behind each slit, as if they were ordinary particles; their wavelike behavior is no longer observed.

As it turns out, no matter how hard we try or whatever method we set up, *we can never both see the interference pattern and simultaneously determine which hole the electron goes through*. It has never been done, and most scientists agree that it never will. In the words of theoretical physicist P. A. M. Dirac (1902–1984),

There is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance—a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer.

The single electron diffraction experiment demonstrates that we cannot simultaneously observe both the wave nature and the particle nature of the electron. When we try

to observe which hole the electron goes through (associated with the particle nature of the electron), we lose the interference pattern (associated with the wave nature of the electron). When we try to observe the interference pattern, we cannot determine which hole the electron goes through. The wave nature and particle nature of the electron are said to be **complementary properties**. Complementary properties exclude one another—the more we know about one, the less we know about the other. Which of two complementary properties we observe depends on the experiment we perform—in quantum mechanics, the observation of an event affects its outcome.

As we just saw in the de Broglie relation, the *velocity* of an electron is related to its *wave nature*. The *position* of an electron, however, is related to its *particle nature*. (Particles have well-defined position, but waves do not.) Consequently, our inability to observe the electron simultaneously as both a particle and a wave means that *we cannot simultaneously measure its position and its velocity*. Werner Heisenberg (1901–1976) formalized this idea with the equation:

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi} \quad \text{Heisenberg's uncertainty principle} \quad [8.5]$$

where Δx is the uncertainty in the position, Δv is the uncertainty in the velocity, m is the mass of the particle, and h is Planck's constant. **Heisenberg's uncertainty principle** states that the product of Δx and $m\Delta v$ must be greater than or equal to a finite number ($h/4\pi$). In other words, the more accurately we know the position of an electron (the smaller Δx), the less accurately we can know its velocity (the bigger Δv) and vice versa. The complementarity of the wave nature and particle nature of the electron results in the complementarity of velocity and position.

Although Heisenberg's uncertainty principle may seem puzzling, it actually solves a great puzzle. Without the uncertainty principle, we are left with a paradox: how can something be *both* a particle and a wave? Saying that an object is both a particle and a wave is like saying that an object is both a circle and a square, a contradiction. Heisenberg solved the contradiction by introducing complementarity—an electron is observed as *either* a particle or a wave but never both at once. This idea was captured by Schrödinger's thought experiment about the cat, which we discussed in Section 8.1: when observed, the cat is either dead or alive, not both.



▲ Werner Heisenberg, a pioneer of quantum mechanics

THE UNCERTAINTY PRINCIPLE

Which statement best summarizes the uncertainty principle?

- (a) Both the position and the velocity of an electron can be accurately known at the same instant.
- (b) Either the position or the velocity of an electron can be accurately known at the same instant.
- (c) Neither the position nor the velocity of an electron can be accurately known at the same instant.



ANSWER NOW!

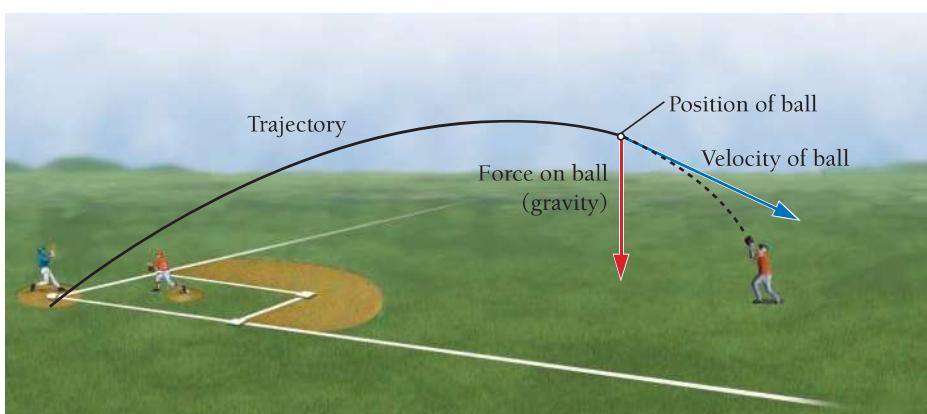


Indeterminacy and Probability Distribution Maps

According to classical physics, and in particular Newton's laws of motion, particles move in a *trajectory* (or path) that is determined by the particle's velocity (the speed and direction of travel), its position, and the forces acting on it. Even if you are not familiar with Newton's laws, you probably have an intuitive sense of them. For example, when you chase a baseball in the outfield, you visually predict where the ball will land by observing its path. You do this by noting its initial position and velocity, watching how these are affected by the forces acting on it (gravity, air resistance, wind), and then inferring its trajectory, as shown in Figure 8.17▶. If you knew only the ball's velocity, or only its position (imagine a still photo of the baseball in the air), you could not predict its landing spot. In classical mechanics, both position and velocity are required to predict a trajectory.

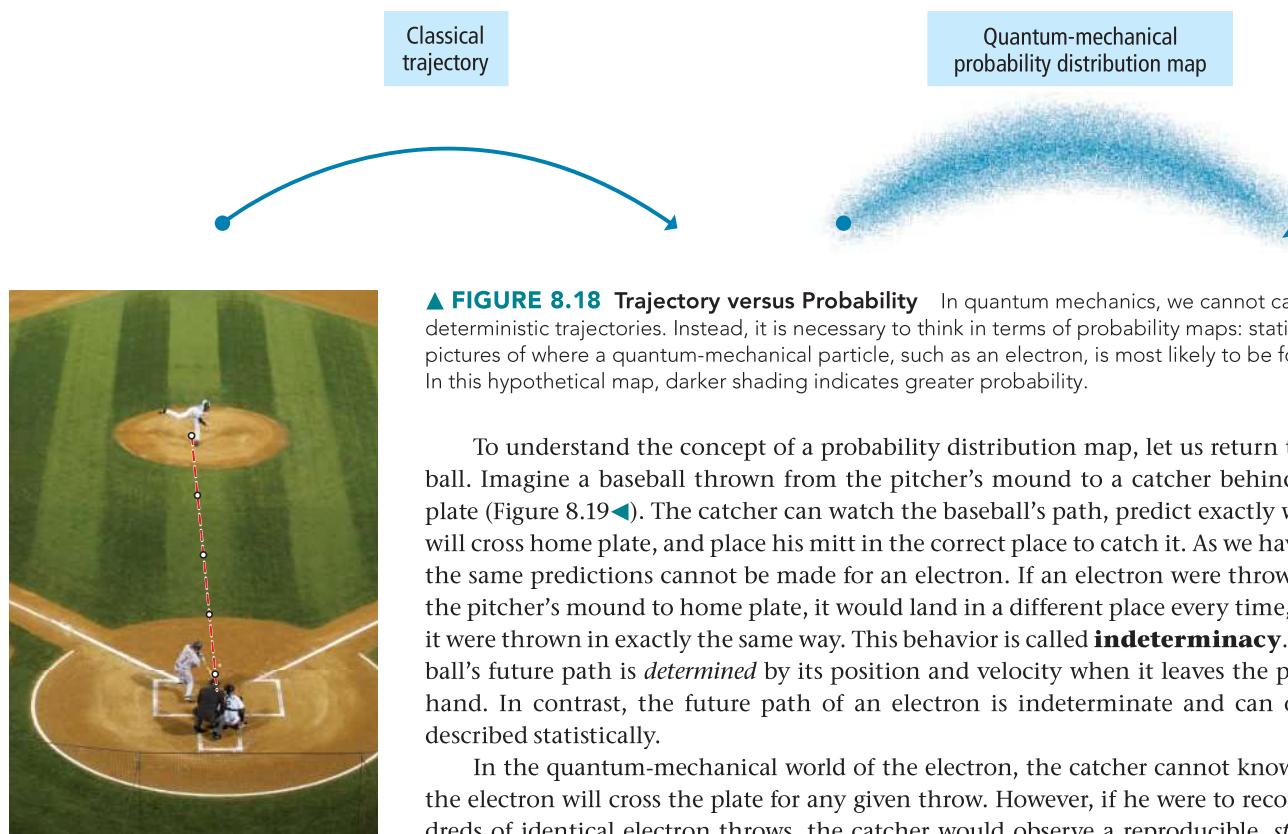
► FIGURE 8.17 The Concept of Trajectory In classical mechanics, the position and velocity of a particle determine its future trajectory, or path. Thus, an outfielder can catch a baseball by observing its position and velocity, allowing for the effects of forces acting on it, such as gravity, and estimating its trajectory. (For simplicity, air resistance and wind are not shown.)

The Classical Concept of Trajectory



Remember that velocity includes speed as well as direction of travel.

Newton's laws of motion are **deterministic**—the present *determines* the future. This means that if two baseballs are hit consecutively with the same velocity from the same position under identical conditions, they will land in exactly the same place. The same is not true of electrons. We have just seen that we cannot simultaneously know the position and velocity of an electron; therefore, we cannot know its trajectory. In quantum mechanics, trajectories are replaced with *probability distribution maps* (Figure 8.18▼). A probability distribution map is a statistical map that shows where an electron is likely to be found under a given set of conditions.

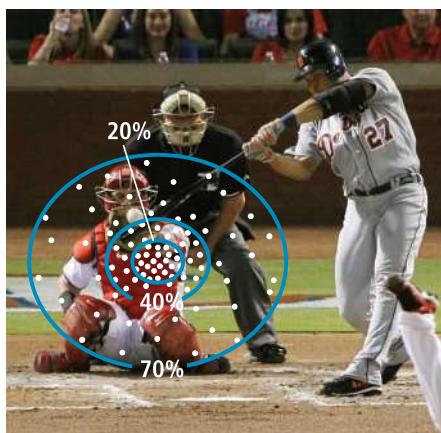


▲ FIGURE 8.19 Trajectory of a Macroscopic Object A baseball follows a well-defined trajectory from the hand of the pitcher to the mitt of the catcher.

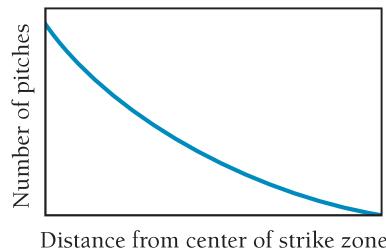
▲ FIGURE 8.18 Trajectory versus Probability In quantum mechanics, we cannot calculate deterministic trajectories. Instead, it is necessary to think in terms of probability maps: statistical pictures of where a quantum-mechanical particle, such as an electron, is most likely to be found. In this hypothetical map, darker shading indicates greater probability.

To understand the concept of a probability distribution map, let us return to baseball. Imagine a baseball thrown from the pitcher's mound to a catcher behind home plate (Figure 8.19◀). The catcher can watch the baseball's path, predict exactly where it will cross home plate, and place his mitt in the correct place to catch it. As we have seen, the same predictions cannot be made for an electron. If an electron were thrown from the pitcher's mound to home plate, it would land in a different place every time, even if it were thrown in exactly the same way. This behavior is called **indeterminacy**. A baseball's future path is *determined* by its position and velocity when it leaves the pitcher's hand. In contrast, the future path of an electron is indeterminate and can only be described statistically.

In the quantum-mechanical world of the electron, the catcher cannot know where the electron will cross the plate for any given throw. However, if he were to record hundreds of identical electron throws, the catcher would observe a reproducible, *statistical pattern* of where the electron crosses the plate. He could even draw a map of the strike zone showing the probability of an electron crossing a certain area, as shown in Figure 8.20▶. This is a probability distribution map. In the sections that follow, we discuss quantum-mechanical electron *orbitals*, which are essentially probability distribution maps for electrons as they exist within atoms.



The Quantum-Mechanical Strike Zone



◀ FIGURE 8.20 The Quantum-Mechanical Strike Zone An electron does not have a well-defined trajectory. However, we can construct a probability distribution map to show the relative probability of it crossing home plate at different points.

8.5

Quantum Mechanics and the Atom

As we have seen, the position and velocity of the electron are complementary properties—if we know one accurately, the other becomes indeterminate. Since velocity is directly related to energy (recall that kinetic energy equals $\frac{1}{2}mv^2$), position and *energy* are also complementary properties—the more we know about one, the less we know about the other. Many of the properties of an element, however, depend on the energies of its electrons. For example, whether an electron is transferred from one atom to another to form an ionic bond depends in part on the relative energies of the electron in the two atoms.

In the following paragraphs, we describe the probability distribution maps for electron states in which the electron has well-defined energy but not well-defined position. In other words, for each of these states, we can specify the *energy* of the electron precisely, but not its location at a given instant. Instead, the electron's position is described in terms of an **orbital**, a probability distribution map showing where the electron is likely to be found. Since chemical bonding often involves the sharing of electrons between atoms to form covalent bonds, the spatial distribution of atomic electrons is important to bonding.

The mathematical derivation of energies and orbitals for electrons in atoms comes from solving the Schrödinger equation for the atom of interest. The general form of the Schrödinger equation is:

$$\mathcal{H}\psi = E\psi \quad [8.6]$$

The symbol \mathcal{H} is the Hamiltonian operator, a set of mathematical operations that represents the total energy (kinetic and potential) of the electron within the atom. The symbol E is the actual energy of the electron. The symbol ψ is the **wave function**, a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared (ψ^2) represents an orbital, a position probability distribution map of the electron.

WATCH NOW!

KEY CONCEPT VIDEO 8.5A

Quantum Mechanics and the Atom: Orbitals and Quantum Numbers

These states are known as energy eigenstates.

An operator is different from a normal algebraic entity. In general, an operator transforms a mathematical function into another mathematical function. For example, d/dx is an operator that means "take the derivative of." When d/dx operates on a function (such as x^2), it returns another function ($2x$).

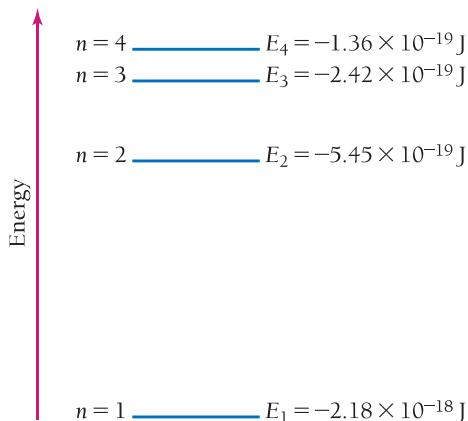
The symbol ψ is the Greek letter psi, pronounced "sigh."

Solutions to the Schrödinger Equation for the Hydrogen Atom

When the Schrödinger equation is solved, it yields many solutions—many possible wave functions. The wave functions themselves are fairly complicated mathematical functions, and we do not examine them in detail in this book. Instead, we introduce graphical representations (or plots) of the orbitals that correspond to the wave functions. Each orbital is specified by three interrelated **quantum numbers**:

- **n , the principal quantum number**
- **l , the angular momentum quantum number** (sometimes called the *azimuthal quantum number*)
- **m_l , the magnetic quantum number**

These quantum numbers all have integer values, as had been hinted at by both the Rydberg equation and Bohr's model. A fourth quantum number, **m_s , the spin quantum number**,



specifies the orientation of the spin of the electron. We examine each of these quantum numbers individually.

The Principal Quantum Number (n)

The principal quantum number is an integer that determines the overall size and energy of an orbital. Its possible values are $n = 1, 2, 3, \dots$ and so on. For the hydrogen atom, the energy of an electron in an orbital with quantum number n is given by the equation:

$$E_n = -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right) \quad (n = 1, 2, 3, \dots) \quad [8.7]$$

The energy is negative because the electron's energy is lowered (made more negative) by its interaction with the nucleus (see the description of Coulomb's law in Section 9.3). The constant, 2.18×10^{-18} J, is known as the Rydberg constant for hydrogen (R_H). Notice that orbitals with higher values of n have greater (less negative) energies, as shown in the energy-level diagram at left. Notice also that, as n increases, the spacing between the energy levels decreases.

The Angular Momentum Quantum Number (I)

The angular momentum quantum number is an integer that determines the shape of the orbital. We will consider these shapes in Section 8.6. The possible values of l are $0, 1, 2, \dots, (n - 1)$. In other words, for a given value of n , l can be any integer (including 0) up to $n - 1$. For example, if $n = 1$, then the only possible value of l is 0; if $n = 2$, the possible values of l are 0 and 1. To avoid confusion between n and l , values of l are often assigned letters as follows:

The values of l beyond 3 are designated with letters in alphabetical order so that $l = 4$ is designated g , $l = 5$ is designated h , and so on.

Value of l	Letter Designation
$l = 0$	s
$l = 1$	p
$l = 2$	d
$l = 3$	f

ANSWER NOW!



THE RELATIONSHIP BETWEEN n AND l

What values of l are possible for $n = 3$?

- (a)** 0 (or s) **(b)** 0 and 1 (or s and p)
(c) 0, 1, and 2 (or s, p , and d) **(d)** 0, 1, 2, and 3 (or s, p, d , and f)

ANSWER NOW!

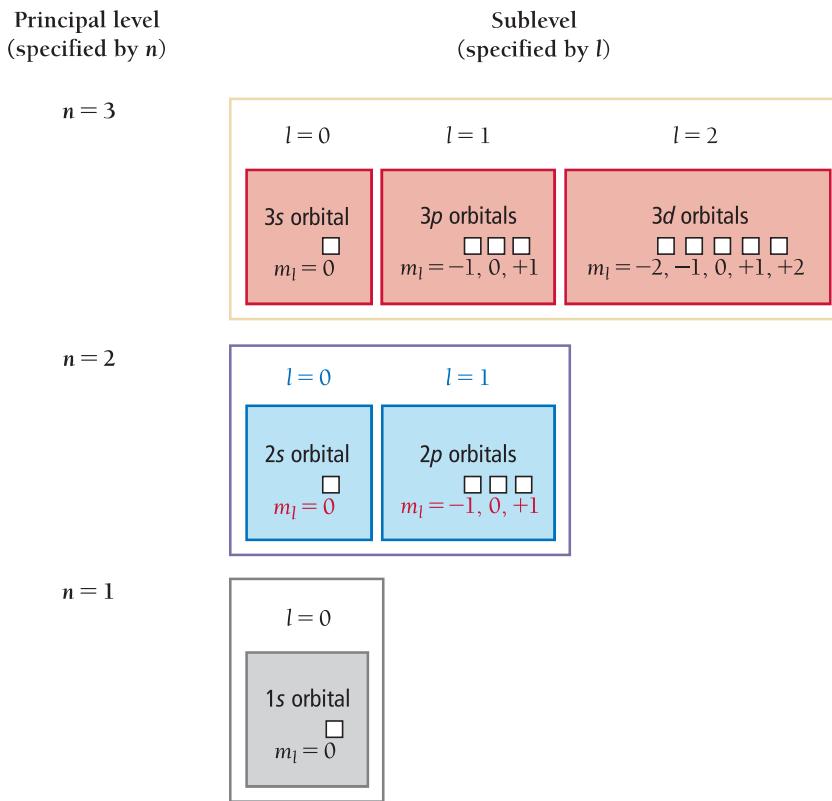


THE RELATIONSHIP BETWEEN l AND m_l What values of m_l are possible for $l = 2$?

The Spin Quantum Number (m_s)

The spin quantum number specifies the orientation of the *spin* of the electron. Electron spin is a fundamental property of an electron (like its negative charge). One electron does not have more or less spin than another—all electrons have the same amount of spin. The orientation of the electron's spin is quantized, with only two possibilities: that we can call spin up ($m_s = +1/2$) and spin down ($m_s = -1/2$). The spin quantum number becomes important in Section 9.3 when we begin to consider how electrons occupy orbitals. Here, we focus only on the first three quantum numbers.

Each specific combination of the first three quantum numbers (n , l , and m_l) specifies one atomic orbital. For example, the orbital with $n = 1$, $l = 0$, and $m_l = 0$ is known as the $1s$ orbital. The 1 in $1s$ is the value of n , and the s specifies that $l = 0$. There is only one $1s$ orbital in an atom, and its m_l value is zero. Orbitals with the same value of n are said to be in the same **principal level (or principal shell)**. Orbitals with the same value of n and l are said to be in the same **sublevel (or subshell)**. The following diagram shows all of the orbitals (each represented by a small square) in the first three principal levels:



For example, the $n = 2$ level contains the $l = 0$ and $l = 1$ sublevels. Within the $n = 2$ level, the $l = 0$ sublevel—called the $2s$ sublevel—contains only one orbital (the $2s$ orbital), with $m_l = 0$. The $l = 1$ sublevel—called the $2p$ sublevel—contains three $2p$ orbitals, with $m_l = -1, 0, +1$.

Summarizing Orbitals

- The number of sublevels in any level is equal to n , the principal quantum number. Therefore, the $n = 1$ level has one sublevel, the $n = 2$ level has two sublevels, and so on.
- The number of orbitals in any sublevel is equal to $2l + 1$. Therefore, the s sublevel ($l = 0$) has one orbital, the p sublevel ($l = 1$) has three orbitals, the d sublevel ($l = 2$) has five orbitals, and so on.
- The number of orbitals in a level is equal to n^2 . Therefore, the $n = 1$ level has one orbital, the $n = 2$ level has four orbitals, the $n = 3$ level has nine orbitals, and so on.

The idea of a “spinning” electron is something of a metaphor. A more correct way to express the same idea is to say that an electron has inherent angular momentum.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 8.5

EXAMPLE 8.5 Quantum Numbers I

What are the quantum numbers and names (for example, $2s$, $2p$) of the orbitals in the $n = 4$ principal level?

How many $n = 4$ orbitals exist?

SOLUTION

First, determine the possible values of l (from the given value of n). For a given value of n , the possible values of l are $0, 1, 2, \dots, (n - 1)$.

Next, determine the possible values of m_l for each value of l . For a given value of l , the possible values of m_l are the integer values, including zero, ranging from $-l$ to $+l$. The name of an orbital is its principal quantum number (n) followed by the letter corresponding to the value l . The total number of orbitals is given by n^2 .

$n = 4$; therefore, $l = 0, 1, 2$, and 3

l	Possible m_l Values	Orbital Name
0	0	$4s$ (1 orbital)
1	$-1, 0, +1$	$4p$ (3 orbitals)
2	$-2, -1, 0, +1, +2$	$4d$ (5 orbitals)
3	$-3, -2, -1, 0, +1, +2, +3$	$4f$ (7 orbitals)

Total number of orbitals = $4^2 = 16$

FOR PRACTICE 8.5 List the quantum numbers associated with all of the $5d$ orbitals. How many $5d$ orbitals exist?

EXAMPLE 8.6 Quantum Numbers II

These sets of quantum numbers are each supposed to specify an orbital. One set, however, is erroneous. Which one and why?

- (a) $n = 3; l = 0; m_l = 0$ (b) $n = 2; l = 1; m_l = -1$
 (c) $n = 1; l = 0; m_l = 0$ (d) $n = 4; l = 1; m_l = -2$

SOLUTION

Choice (d) is erroneous because for $l = 1$, the possible values of m_l are only $-1, 0$, and $+1$.

FOR PRACTICE 8.6 Each set of quantum numbers is supposed to specify an orbital. However, each set contains one quantum number that is not allowed. Replace the quantum number that is not allowed with one that is allowed.

- (a) $n = 3; l = 3; m_l = +2$ (b) $n = 2; l = 1; m_l = -2$ (c) $n = 1; l = 1; m_l = 0$

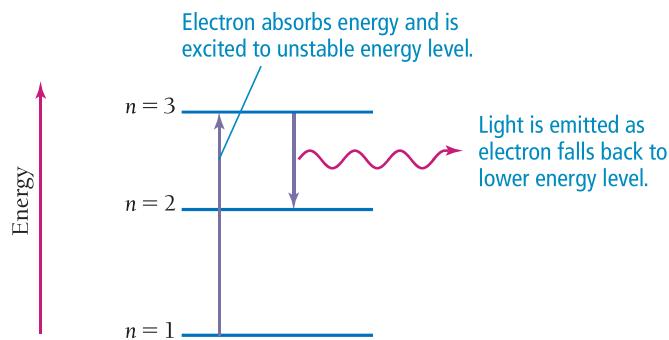
WATCH NOW!

KEY CONCEPT VIDEO 8.5B

Atomic Spectroscopy

Atomic Spectroscopy Explained

Quantum theory explains the atomic spectra of atoms we discussed in Section 8.3. Each wavelength in the emission spectrum of an atom corresponds to an electron *transition* between quantum-mechanical orbitals. When an atom absorbs energy, an electron in a lower-energy orbital is *excited* or promoted to a higher-energy orbital, as shown in Figure 8.21▼. In this new configuration, however, the atom is unstable, and the

Excitation and Radiation

► FIGURE 8.21 Excitation and Radiation When an atom absorbs energy, an electron can be excited from an orbital in a lower-energy level to an orbital in a higher-energy level. The electron in this “excited state” is unstable, however, and relaxes to a lower-energy level, releasing energy in the form of electromagnetic radiation.

electron quickly falls back or *relaxes* to a lower-energy orbital. As it does so, it releases a photon of light containing an amount of energy precisely equal to the energy difference between the two energy levels. We saw previously (see Equation 8.7) that the energy of an orbital in a hydrogen atom with principal quantum number n is given by $E_n = -2.18 \times 10^{-18} \text{ J}(1/n^2)$, where $n = 1, 2, 3, \dots$. The *difference* in energy between two levels n_{initial} and n_{final} is given by $\Delta E = E_{\text{final}} - E_{\text{initial}}$. If we substitute the expression for E_n into the expression for ΔE , we get the following important expression for the change in energy that occurs in a hydrogen atom when an electron changes energy levels:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}} \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{f}}^2} \right) - \left[-2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{i}}^2} \right) \right] \\ \Delta E &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{f}}^2} - \frac{1}{n_{\text{i}}^2} \right)\end{aligned}\quad [8.8]$$

For example, suppose that an electron in a hydrogen atom relaxes from an orbital in the $n = 3$ level to an orbital in the $n = 2$ level. We determine ΔE , the energy difference corresponding to the transition from $n = 3$ to $n = 2$, as follows:

$$\begin{aligned}\Delta E_{\text{atom}} &= E_2 - E_3 \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} \right) - \left[-2.18 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} \right) \right] \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= -3.03 \times 10^{-19} \text{ J}\end{aligned}$$

The energy carries a negative sign because the atom *emits* the energy as it relaxes from $n = 3$ to $n = 2$. Since energy must be conserved, the exact amount of energy emitted by the atom is carried away by the photon:

$$\Delta E_{\text{atom}} = -E_{\text{photon}}$$

This energy determines the frequency and wavelength of the photon. Since the wavelength of the photon is related to its energy as $E = hc/\lambda$, we calculate the wavelength of the photon as:

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{3.03 \times 10^{-19} \text{ J}} \\ &= 6.56 \times 10^{-7} \text{ m or } 656 \text{ nm}\end{aligned}$$

Consequently, the light emitted by an excited hydrogen atom as it relaxes from an orbital in the $n = 3$ level to an orbital in the $n = 2$ level has a wavelength of 656 nm (red). Similarly, we can calculate the light emitted due to a transition from $n = 4$ to $n = 2$, which is 486 nm (green). Notice that transitions between orbitals that are further apart in energy produce light that is higher in energy, and therefore shorter in wavelength, than transitions between orbitals that are closer together. Figure 8.22▶ shows several of the transitions in the hydrogen atom and their corresponding wavelengths.

The Rydberg equation, $1/\lambda = R(1/m^2 - 1/n^2)$, can be derived from the relationships just covered. We leave this derivation to an exercise (see Problem 8.98).

The energy of a photon is always positive.

EMISSION SPECTRA Which transition emits light with the shortest wavelength?

- (a) $n = 5 \longrightarrow n = 4$
- (b) $n = 4 \longrightarrow n = 3$
- (c) $n = 3 \longrightarrow n = 2$

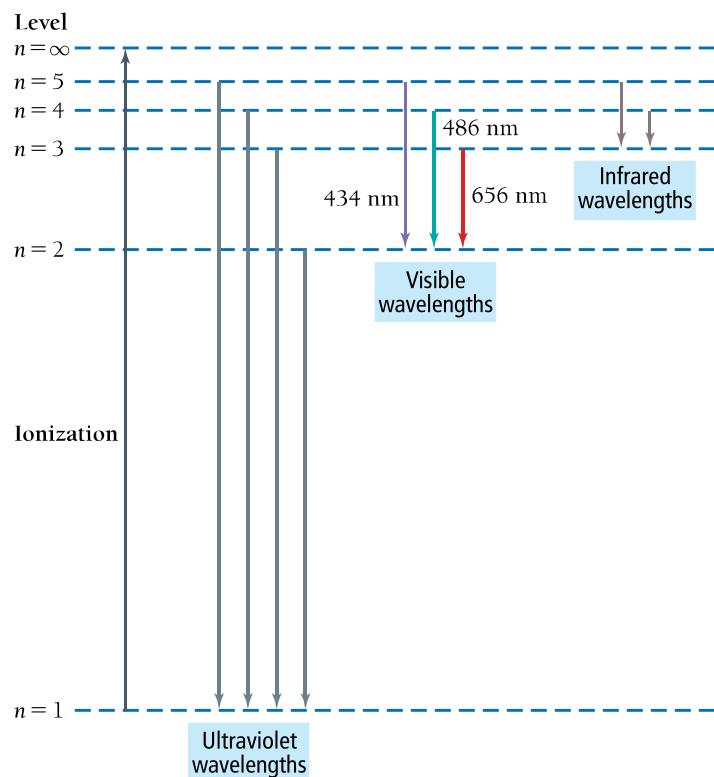


ANSWER NOW!



► FIGURE 8.22 Hydrogen

Energy Transitions and Radiation An atomic energy level diagram for hydrogen, showing some possible electron transitions between levels and the corresponding wavelengths of emitted light.

Hydrogen Energy Transitions and Radiation**WATCH NOW!****INTERACTIVE WORKED EXAMPLE 8.7****EXAMPLE 8.7** Wavelength of Light for a Transition in the Hydrogen Atom

Determine the wavelength of light emitted when an electron in a hydrogen atom makes a transition from an orbital in $n = 6$ to an orbital in $n = 5$.

SORT You are given the energy levels of an atomic transition and asked to find the wavelength of emitted light.

STRATEGIZE In the first part of the conceptual plan, calculate the energy of the electron in the $n = 6$ and $n = 5$ orbitals using Equation 8.7 and subtract to find ΔE_{atom} .

In the second part, find E_{photon} by taking the negative of ΔE_{atom} and then calculate the wavelength corresponding to a photon of this energy using Equation 8.3. (The difference in sign between E_{photon} and ΔE_{atom} applies only to emission. *The energy of a photon must always be positive.*)

SOLVE Follow the conceptual plan. Begin by calculating ΔE_{atom} .

GIVEN: $n = 6 \longrightarrow n = 5$

FIND: λ

CONCEPTUAL PLAN

$$n = 5, n = 6 \rightarrow \Delta E_{\text{atom}}$$

$$\Delta E_{\text{atom}} = E_5 - E_6$$

$$\Delta E_{\text{atom}} \rightarrow E_{\text{photon}} \rightarrow \lambda$$

$$\Delta E_{\text{atom}} = -E_{\text{photon}}$$

$$E = \frac{hc}{\lambda}$$

RELATIONSHIPS USED

$$E_n = -2.18 \times 10^{-18} \text{ J} (1/n^2)$$

$$E = hc/\lambda$$

SOLUTION

$$\begin{aligned} \Delta E_{\text{atom}} &= E_5 - E_6 \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} \right) - \left[-2.18 \times 10^{-18} \text{ J} \left(\frac{1}{6^2} \right) \right] \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{6^2} \right) \\ &= -2.6644 \times 10^{-20} \text{ J} \end{aligned}$$

Calculate E_{photon} by changing the sign of ΔE_{atom} .

$$E_{\text{photon}} = -\Delta E_{\text{atom}} = +2.6644 \times 10^{-20} \text{ J}$$

Solve the equation relating the energy of a photon to its wavelength for λ . Substitute the energy of the photon and calculate λ .

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ \lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{2.6644 \times 10^{-20} \text{ J}} \\ &= 7.46 \times 10^{-6} \text{ m or } 7460 \text{ nm} \end{aligned}$$

CHECK The units of the answer (m) are correct for wavelength. The magnitude is reasonable because 10^{-6} m is in the infrared region of the electromagnetic spectrum. You know that transitions from $n = 3$ or $n = 4$ to $n = 2$ lie in the visible region, so it makes sense that a transition between levels of higher n value (which are energetically closer to one another) results in light of longer wavelength.

FOR PRACTICE 8.7 Determine the wavelength of the light absorbed when an electron in a hydrogen atom makes a transition from an orbital in the $n = 2$ level to an orbital in the $n = 7$ level.

FOR MORE PRACTICE 8.7 An electron in the $n = 6$ level of the hydrogen atom relaxes to a lower energy level, emitting light of $\lambda = 93.8$ nm. Find the principal level to which the electron relaxed.

8.6

The Shapes of Atomic Orbitals

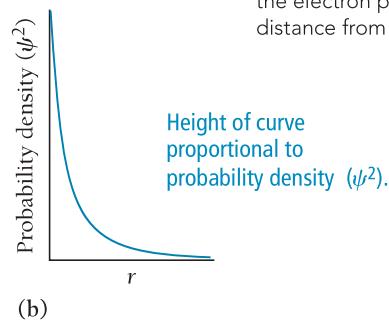
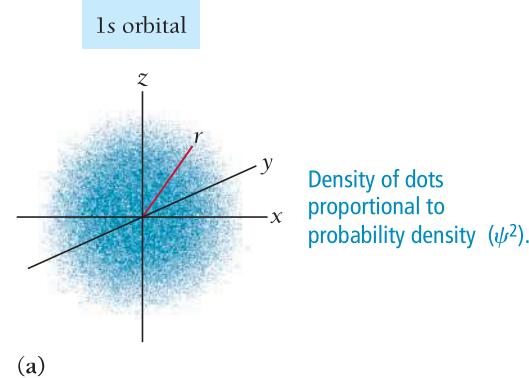
As we noted previously, the shapes of atomic orbitals are important because covalent chemical bonds depend on the sharing of the electrons that occupy these orbitals. In one model of chemical bonding, for example, a bond consists of the overlap of atomic orbitals on adjacent atoms. The shapes of the overlapping orbitals determine the shape of the molecule. Although we limit ourselves in this chapter to the orbitals of the hydrogen atom, we will see in Chapter 9 that the orbitals of all atoms can be approximated as being hydrogen-like and therefore having very similar shapes to those of hydrogen.

The shape of an atomic orbital is determined primarily by l , the angular momentum quantum number. Recall that each value of l is assigned a letter that corresponds to particular orbitals. For example, the orbitals with $l = 0$ are called s orbitals; those with $l = 1$, p orbitals; those with $l = 2$, d orbitals, and so on. We now examine the shape of each of these orbitals.

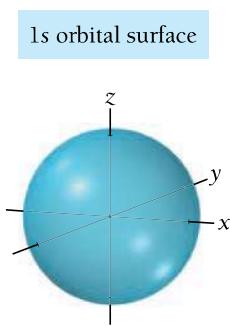
s Orbitals ($l = 0$)

The lowest energy orbital is the spherically symmetrical $1s$ orbital shown in Figure 8.23(a). This image is actually a three-dimensional plot of the wave function squared (ψ^2), which represents **probability density**, the probability (per unit volume) of finding the electron at a point in space.

$$\psi^2 = \text{probability density} = \frac{\text{probability}}{\text{unit volume}}$$



◀ FIGURE 8.23 The $1s$ Orbital: Two Representations In (a) the dot density is proportional to the electron probability density. In (b), the height of the curve is proportional to the electron probability density. The x -axis is r , the distance from the nucleus.

**▲ FIGURE 8.24** The 1s Orbital Surface

1s Orbital Surface In this representation, the surface of the sphere encompasses the volume where the electron is found 90% of the time when the electron is in the 1s orbital.

The magnitude of ψ^2 in this plot is proportional to the density of the dots shown in the image. The high dot density near the nucleus (at the very center of the plot) indicates a higher probability density for the electron. As you move away from the nucleus, the probability density decreases. Figure 8.23(b) shows a plot of probability density (ψ^2) versus r , the distance from the nucleus. The plot represents a slice through the three-dimensional plot of ψ^2 and illustrates how the probability density decreases as r increases.

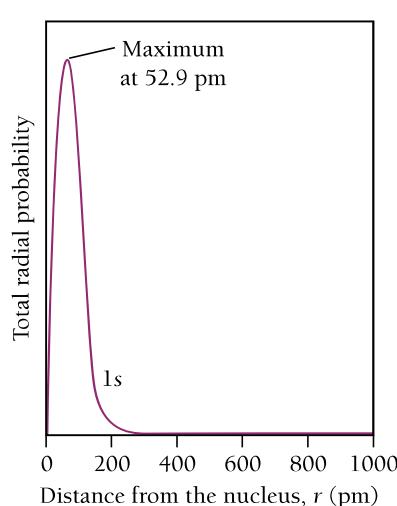
We can better understand probability density with the help of a thought experiment. Imagine an electron in the 1s orbital located within the volume surrounding the nucleus. Imagine also taking a photograph of the electron every second for 10 or 15 minutes. In one photograph, the electron is very close to the nucleus, in another it is farther away, and so on. Each photo has a dot showing the electron's position relative to the nucleus when the photo was taken. Remember that we can never predict where the electron will be for any one photo. However, if we took hundreds of photos and superimposed all of them, we would have a plot similar to Figure 8.23(a)—a statistical representation of how likely the electron is to be found at each point.

This thought experiment can result in a possible misunderstanding: that the electron is moving around (like a moth near a flame) between photographs. However, in the quantum-mechanical model, that is not the case. Between photographs, the location of the electron is uncertain—in a sense its location is spread out over the entire volume of the orbital. Only when the photograph is taken (that is, when a measurement of the electron's location is made) does the location of the electron become localized to one spot. Between measurements, the electron has no single location. Recall from Section 8.1 that the measurement affects the outcome of any quantum system.

We can also represent an atomic orbital as a geometrical shape that encompasses the volume where the electron is likely to be found most frequently—typically, 90% of the time. For example, we represent the 1s orbital as the three-dimensional sphere shown in Figure 8.24◀. If we were to superimpose the dot-density representation of the 1s orbital on the shape representation, 90% of the dots would be within the sphere, meaning that when the electron is in the 1s orbital it has a 90% chance of being found within the sphere.

The plots we have just seen in Figures 8.23 and 8.24 represent probability *density*. However, they are a bit misleading because they seem to imply that the electron is most likely to be found *at the nucleus*. To get a better idea of where the electron is most likely to be found, we use a plot called the **radial distribution function**, shown in Figure 8.25◀ for the 1s orbital. The radial distribution function represents the *total probability of finding the electron within a thin spherical shell at a distance r from the nucleus*:

$$\text{Total radial probability (at a given } r) = \frac{\text{probability}}{\text{unit volume}} \times \text{volume of shell at } r$$

**▲ FIGURE 8.25** The Radial Distribution Function for the 1s Orbital

The curve shows the total probability of finding the electron within a thin shell at a distance r from the nucleus.

The radial distribution function represents, not probability density *at a point r* , but total probability *at a radius r* . In contrast to probability density, which has a maximum at the nucleus, the radial distribution function has a value of zero at the nucleus. It increases to a maximum at 52.9 pm and then decreases again with increasing r .

The shape of the radial distribution function is the result of multiplying together two functions with opposite trends in r . The two functions are:

1. the probability density function (ψ^2), which is the probability per unit volume, has a maximum at the nucleus, and decreases with increasing r ; and
2. the volume of the thin shell, which is zero at the nucleus and increases with increasing r .

At the nucleus ($r = 0$), for example, the probability *density* is at a maximum; however, the volume of a thin spherical shell is zero, so the radial distribution function is zero. As r increases, the volume of the thin spherical shell increases. We can understand this by making an analogy to an onion. A spherical shell at a distance r from the nucleus is like a layer in an onion at a distance r from its center. If the layers of the onion all have the same thickness, then the volume of any one layer—think of this as the total amount of onion in the layer—is greater as r increases. Similarly, the volume of any one spherical shell in the radial distribution function increases with increasing distance from the

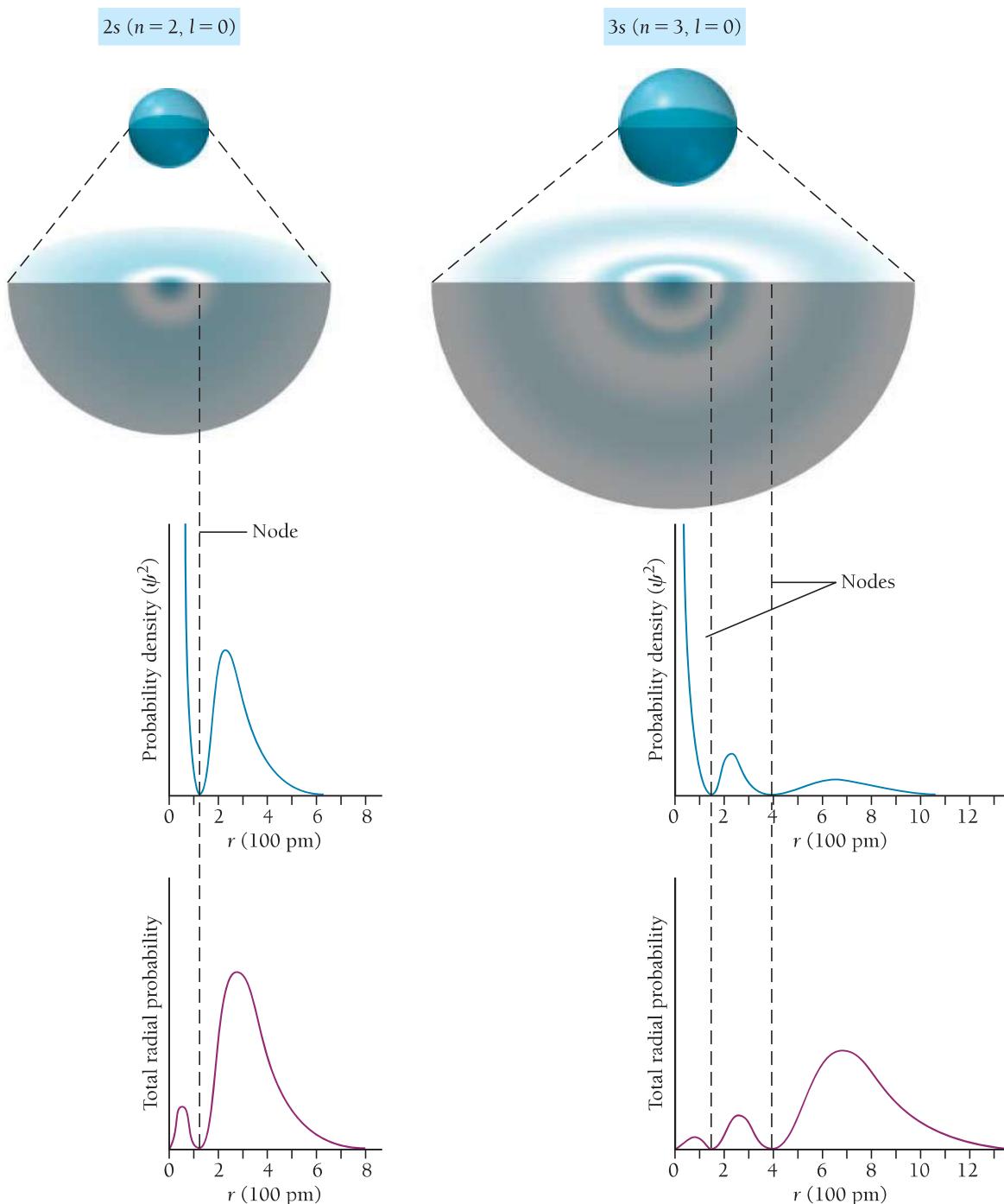
nucleus, resulting in a greater total probability of finding the electron within that shell. Close to the nucleus, this increase in volume with increasing r outpaces the decrease in probability density, reaching a maximum at 52.9 pm. Farther out, however, the density tapers off faster than the volume increases.

The maximum in the radial distribution function, 52.9 pm, turns out to be the very same radius that Bohr had predicted for the innermost orbit of the hydrogen atom. However, there is a significant conceptual difference between the two radii. In the Bohr model, every time you probe the atom (in its lowest energy state), you would find the electron at a radius of 52.9 pm. In the quantum-mechanical model, you would generally find the electron at various radii, with 52.9 pm having the greatest probability.

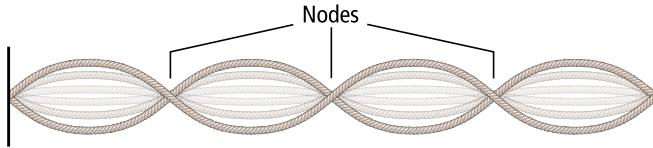
The probability densities and radial distribution functions for the 2s and 3s orbitals are shown in Figure 8.26▼. Like the 1s orbital, these orbitals are spherically symmetric.

▼ FIGURE 8.26 Probability Densities and Radial Distribution Functions for the 2s and 3s Orbitals

The 2s and 3s Orbitals



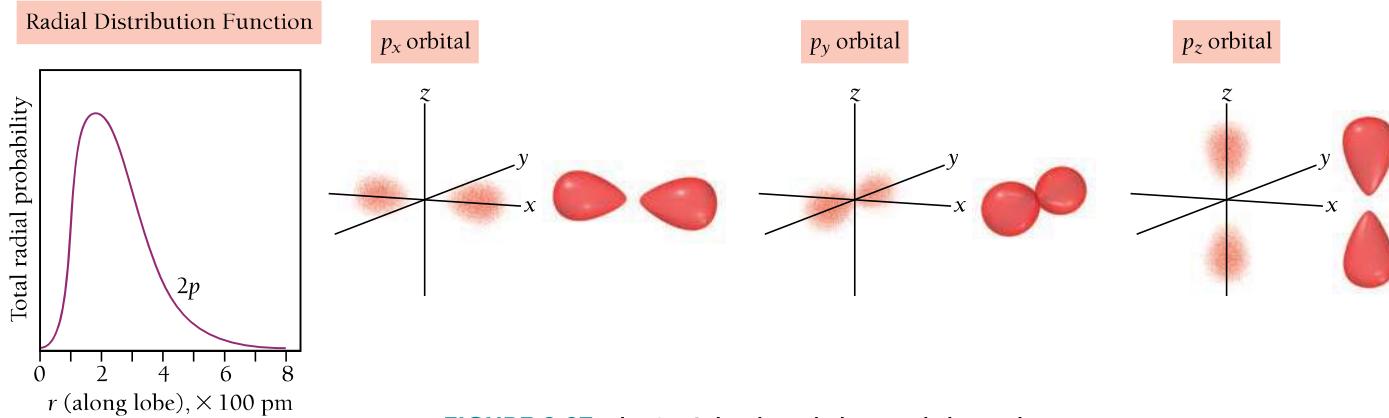
These orbitals are larger in size than the 1s orbital, and, unlike the 1s orbital, they contain at least one *node*. A **node** is a point where the wave function (ψ), and therefore the probability density (ψ^2) and radial distribution function, all pass through zero. A node in a wave function is much like a node in a standing wave on a vibrating string. We can see nodes in an orbital most clearly by looking at a slice through the orbital. Plots of probability density and the radial distribution function as a function of r both reveal the presence of nodes. The probability of finding the electron at a node is zero.



▲ The nodes in quantum-mechanical atomic orbitals are three-dimensional analogs of the nodes on a vibrating string.

p Orbitals ($l = 1$)

Each principal level with $n = 2$ or greater contains three p orbitals ($m_l = -1, 0, +1$). The three $2p$ orbitals and their radial distribution functions are shown in Figure 8.27▼. The p orbitals are not spherically symmetric like the s orbitals, but they have two *lobes* of electron density on either side of the nucleus and a node located at the nucleus. The three p orbitals differ only in their orientation and are orthogonal (mutually perpendicular) to one another. It is convenient to define an x -, y -, and z -axis system and then label each p orbital as p_x , p_y , and p_z . The $3p$, $4p$, $5p$, and higher p orbitals are all similar in shape to the $2p$ orbitals, but they contain additional nodes (like the higher s orbitals) and are progressively larger in size.



▲ FIGURE 8.27 The 2p Orbitals and Their Radial Distribution Function The radial distribution function is the same for each of the three 2p orbitals when the x-axis of the graph is taken as the axis containing the lobes of the orbital.

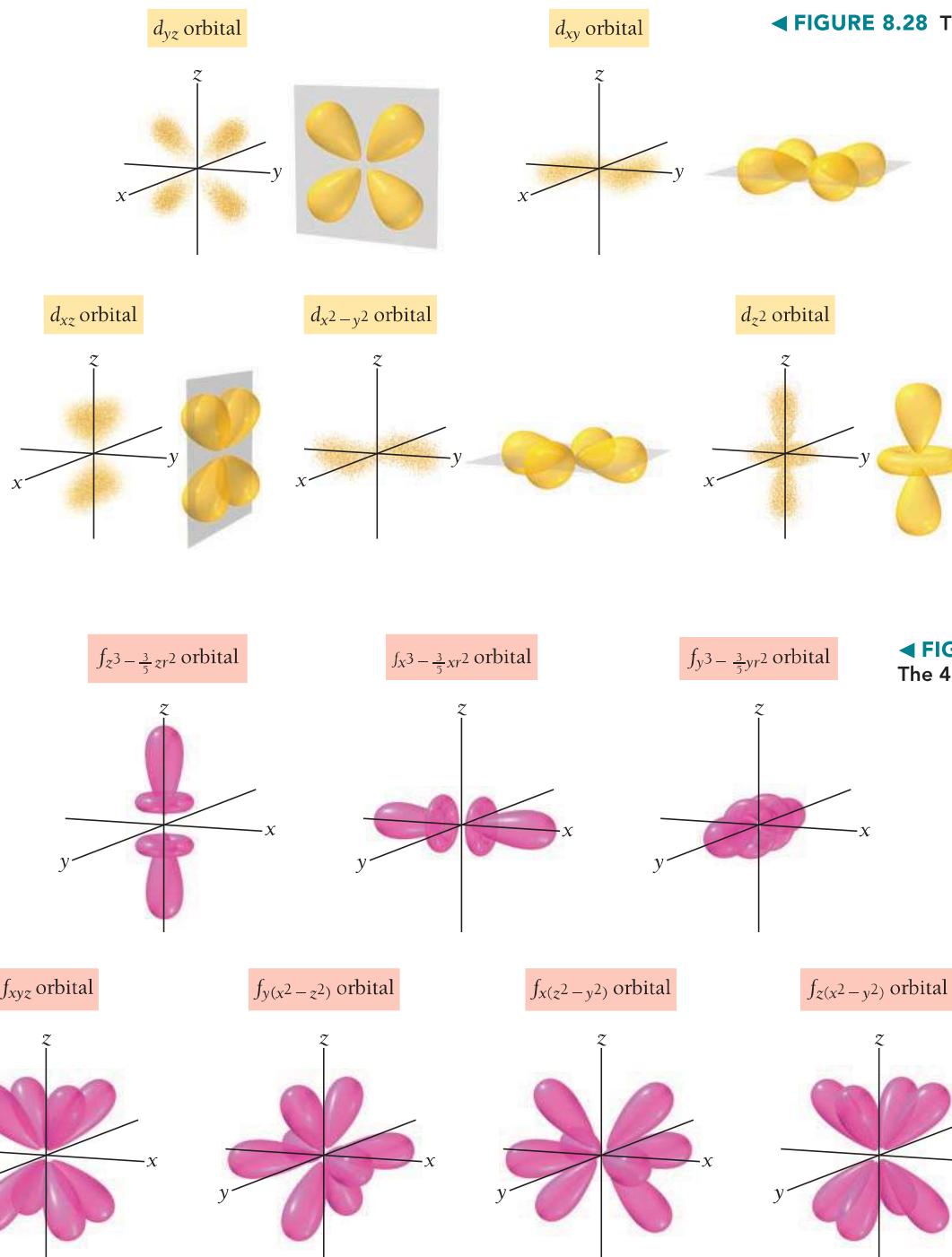
d Orbitals ($l = 2$)

Each principal level with $n = 3$ or greater contains five d orbitals ($m_l = -2, -1, 0, +1, +2$). The five $3d$ orbitals are shown in Figure 8.28►. Four of these orbitals have a cloverleaf shape, with four lobes of electron density around the nucleus and two perpendicular nodal planes. The d_{xy} , d_{xz} , and d_{yz} orbitals are oriented along the xy , xz , and yz planes, respectively, and their lobes are oriented *between* the corresponding axes. The four lobes of the $d_{x^2-y^2}$ orbital are oriented along the x - and y -axes. The d_{z^2} orbital is different in shape from the other four, having two lobes oriented along the z -axis and a donut-shaped ring along the xy plane. The $4d$, $5d$, $6d$,..., orbitals are all similar in shape to the $3d$ orbitals, but they contain additional nodes and are progressively larger in size.

A nodal plane is a plane where the electron probability density is zero. For example, in the d_{xy} orbitals, the nodal planes lie in the xz and yz planes.

f Orbitals ($l = 3$)

Each principal level with $n = 4$ or greater contains seven f orbitals ($m_l = -3, -2, -1, 0, +1, +2, +3$), as shown in Figure 8.29►. These f orbitals have more lobes and nodes than d orbitals.



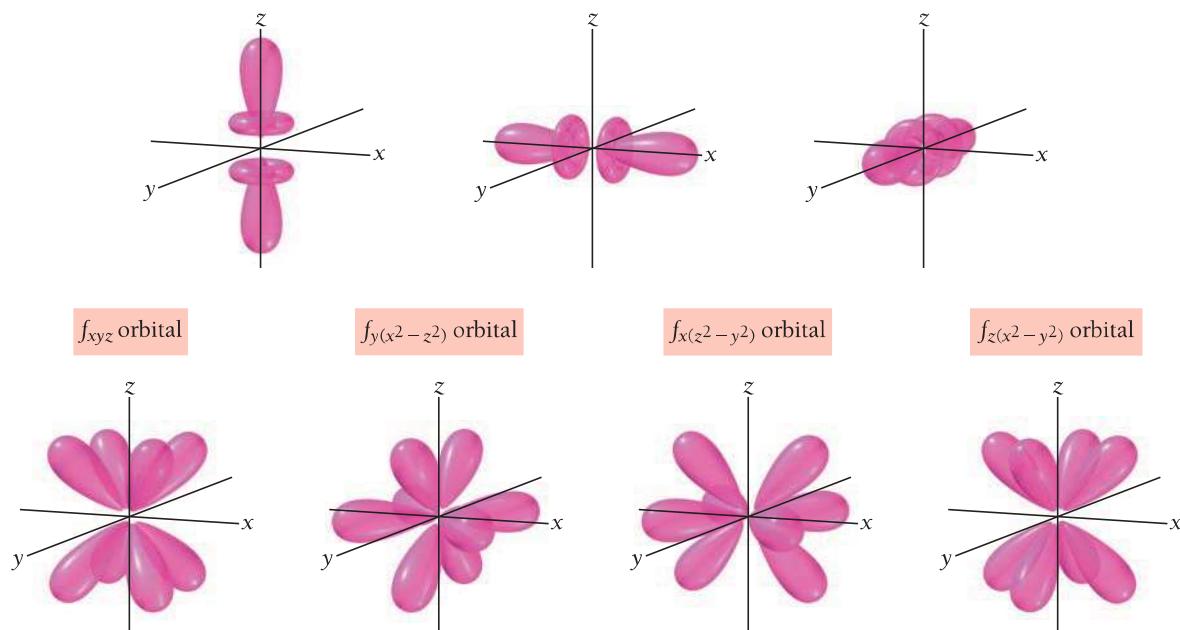
The Phase of Orbitals

The orbitals we have just shown are three-dimensional waves. We can understand an important property of these orbitals by analogy to one-dimensional waves. Consider the following one-dimensional waves:



The wave on the left has a positive amplitude over its entire length, whereas the wave on the right has a positive amplitude over half of its length and a negative amplitude over the other half. The sign of the amplitude of a wave—positive or negative—is known as its **phase**. In these images, blue indicates positive phase and red indicates negative phase. The phase of a wave determines how it interferes with another wave as we saw in Section 8.2.

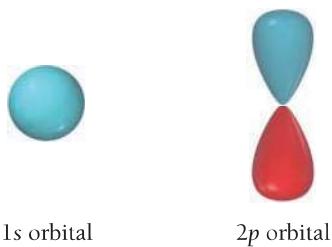
FIGURE 8.29
The 4f Orbitals





▲ FIGURE 8.30 Why Atoms Are Spherical Atoms are depicted as roughly spherical because all the orbitals together make up a roughly spherical shape.

Just as a one-dimensional wave has a phase, so does a three-dimensional wave. We often represent the phase of a quantum-mechanical orbital with color. For example, the phases of a 1s and 2p orbital are represented as follows:



In these depictions, blue represents positive phase and red represents negative phase. The 1s orbital is all one phase, whereas the 2p orbital exhibits two different phases. The phase of quantum-mechanical orbitals is important in bonding, as we shall see in Chapter 11.

The Shape of Atoms

If some orbitals are shaped like dumbbells and three-dimensional cloverleafs, and if most of the volume of an atom is empty space diffusely occupied by electrons in these orbitals, then why do we often depict atoms as spheres? Atoms are drawn as spheres because most atoms contain many electrons occupying a number of different orbitals. Therefore, the shape of an atom is obtained by superimposing all of its orbitals. If we superimpose the s, p, and d orbitals, we get a roughly spherical shape, as shown in Figure 8.30 ▲.

QUIZ YOURSELF NOW!

Self-Assessment Quiz



- Q1.** Which wavelength of light has the highest frequency?
MISSED THIS? Read Section 8.2; Watch KCV 8.2, IWE 8.3

- a) 10 nm b) 10 mm c) 1 nm d) 1 mm

- Q2.** Which kind of electromagnetic radiation contains the greatest energy per photon?

- MISSED THIS?** Read Section 8.2; Watch KCV 8.2, IWE 8.3

- a) microwaves b) gamma rays
c) X-rays d) visible light

- Q3.** How much energy (in J) is contained in 1.00 mole of 552-nm photons?

- MISSED THIS?** Read Section 8.2; Watch KCV 8.2, IWE 8.2

- a) 3.60×10^{-19} J b) 2.17×10^5 J
c) 3.60×10^{-28} J d) 5.98×10^{-43} J

- Q4.** Light from three different lasers (A, B, and C), each with a different wavelength, was shined onto the same metal surface. Laser A produced no photoelectrons. Lasers B and C both produced photoelectrons, but the photoelectrons produced by laser B had a greater velocity than those produced by laser C. Arrange the lasers in order of increasing wavelength.

- MISSED THIS?** Read Section 8.2

- a) A < B < C b) B < C < A
c) C < B < A d) A < C < B

- Q5.** Calculate the wavelength of an electron traveling at 1.85×10^7 m/s.

- MISSED THIS?** Read Section 8.4; Watch KCV 8.4

- a) 2.54×10^{13} m b) 3.93×10^{-14} m
c) 2.54×10^{10} m d) 3.93×10^{-11} m

- Q6.** Which set of three quantum numbers *does not* specify an orbital in the hydrogen atom?

- MISSED THIS?** Read Section 8.5; Watch KCV 8.5A, IWE 8.5

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

- Q7.** Calculate the wavelength of light emitted when an electron in the hydrogen atom makes a transition from an orbital with $n = 5$ to an orbital with $n = 3$.

- MISSED THIS?** Read Section 8.5; Watch KCV 8.5B, IWE 8.7

- a) 1.28×10^{-6} m b) 6.04×10^{-7} m
c) 2.28×10^{-6} m d) 1.55×10^{-19} m

- Q8.** Which electron transition produces light of the highest frequency in the hydrogen atom?

- MISSED THIS?** Read Section 8.5; Watch KCV 8.5B, IWE 8.7

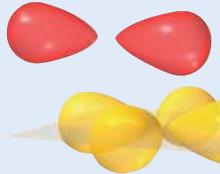
- a) $5p \rightarrow 1s$ b) $4p \rightarrow 1s$
c) $3p \rightarrow 1s$ d) $2p \rightarrow 1s$

- Q9.** How much time (in seconds) does it take light in a vacuum to travel 1.00 billion km? **MISSED THIS?** Read Section 8.2

- a) 3.00×10^{17} s b) 3.33 s
c) 3.33×10^3 s d) 3.00×10^{20} s

- Q10.** Which orbital is a d orbital?

- MISSED THIS?** Read Section 8.6

- a) 
b) 
c) 
d) None of the above

CHAPTER 8 IN REVIEW

TERMS

Section 8.1

quantum-mechanical model (312)

Section 8.2

electromagnetic radiation (313)
amplitude (314)
wavelength (λ) (314)
frequency (ν) (314)
electromagnetic spectrum (315)
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Section 8.3

emission spectrum (323)

Section 8.4

de Broglie relation (327)
complementary properties (329)
Heisenberg's uncertainty principle (329)
deterministic (330)
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Section 8.5

orbital (331)
wave function (331)
quantum number (331)
principal quantum number (n) (331)

angular momentum quantum number (l) (331)
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Section 8.6

probability density (337)
radial distribution function (338)
node (340)
phase (341)

CONCEPTS

The Realm of Quantum Mechanics (8.1)

- The theory of quantum mechanics explains the behavior of particles, such as photons (particles of light) and electrons, in the atomic and subatomic realms.
- Since the electrons of an atom determine many of its chemical and physical properties, quantum mechanics is foundational to understanding chemistry.

The Nature of Light (8.2)

- Light is a type of electromagnetic radiation—a form of energy embodied in oscillating electric and magnetic fields that travels through space at 3.00×10^8 m/s.
- The wave nature of light is characterized by its wavelength—the distance between wave crests—and its ability to experience interference (constructive or destructive) and diffraction.
- The particle nature of light is characterized by the specific quantity of energy carried in each photon.
- The electromagnetic spectrum includes all wavelengths of electromagnetic radiation from gamma rays (high energy per photon, short wavelength) to radio waves (low energy per photon, long wavelength). Visible light is a tiny sliver in the middle of the electromagnetic spectrum.

Atomic Spectroscopy (8.3)

- Atomic spectroscopy is study of the light absorbed and emitted by atoms when an electron makes a transition from one energy level to another.
- The wavelengths absorbed or emitted in atomic spectra depend on the energy differences between the levels involved in the transition; large energy differences result in short wavelengths, and small energy differences result in long wavelengths.

The Wave Nature of Matter (8.4)

- Electrons have a wave nature with an associated wavelength; the de Broglie relation quantifies the wavelength of an electron.

- The wave nature and particle nature of matter are complementary—the more we know of one, the less we know of the other.
- The wave-particle duality of electrons is quantified in Heisenberg's uncertainty principle, which states that there is a limit to how well we can know both the position of an electron (associated with the electron's particle nature) and the velocity times the mass of an electron (associated with the electron's wave nature)—the more accurately one is measured, the greater the uncertainty in measurement of the other.
- The inability to simultaneously know both the position and velocity of an electron results in indeterminacy, the inability to predict a trajectory for an electron. Consequently, electron behavior is described differently than the behavior of everyday-sized particles.
- The trajectory we normally associate with macroscopic objects is replaced, for electrons, with statistical descriptions that show not the electron's path, but the region where it is most likely to be found.

The Quantum-Mechanical Model of the Atom (8.5, 8.6)

- The most common way to describe electrons in atoms according to quantum mechanics is to solve the Schrödinger equation for the energy states of the electrons within the atom. When the electron is in these states, its energy is well defined but its position is not. The position of an electron is described by a probability distribution map called an orbital.
- The solutions to the Schrödinger equation (including the energies and orbitals) are characterized by four quantum numbers: n , l , m_l , and m_s .
- The principal quantum number (n) determines the energy of the electron and the size of the orbital; the angular momentum quantum number (l) determines the shape of the orbital; the magnetic quantum number (m_l) determines the orientation of the orbital; and the spin quantum number (m_s) specifies the orientation of the spin of the electron.

EQUATIONS AND RELATIONSHIPS

Relationship between Frequency (ν), Wavelength (λ), and the Speed of Light (c) (8.2)

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

Relationship between Energy (E), Frequency (ν), Wavelength (λ), and Planck's Constant (h) (8.2)

$$E = h\nu$$

$$E = \frac{hc}{\lambda}$$

De Broglie Relation: Relationship between Wavelength (λ), Mass (m), and Velocity (v) of a Particle (8.4)

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

Heisenberg's Uncertainty Principle: Relationship between a Particle's Uncertainty in Position (Δx) and Uncertainty in Velocity (Δv) (8.4)

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

Energy of an Electron in an Orbital with Quantum Number n in a Hydrogen Atom (8.5)

$$E_n = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} \right) \quad (n = 1, 2, 3, \dots)$$

Change in Energy That Occurs in an Atom When It Undergoes a Transition between Levels n_{initial} and n_{final} (8.5)

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

LEARNING OUTCOMES

Chapter Objectives	Assessment
Analyze the wave properties and wave behaviors associated with light (8.2)	Example 8.1 For Practice 8.1 Exercises 35–36, 39–40
Analyze the particle properties and particle behaviors associated with light (8.2)	Examples 8.2, 8.3 For Practice 8.2, 8.3 For More Practice 8.2 Exercises 37–38, 41–46
Analyze the wave properties of matter (8.4)	Example 8.4 For Practice 8.4 Exercises 47–56
Describe orbitals using quantum numbers (8.5)	Examples 8.5, 8.6 For Practice 8.5, 8.6 Exercises 57–64
Calculate the energy change of an electron transition according to the Bohr model (8.5)	Example 8.7 For Practice 8.7 For More Practice 8.7 Exercises 65–72

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- Why is the quantum-mechanical model of the atom important for understanding chemistry?
- What is light? How fast does it travel in a vacuum?
- Define the wavelength and amplitude of a wave. How are these related to the energy of the wave?
- Define the frequency of electromagnetic radiation. How is frequency related to wavelength?
- What determines the color of light? Describe the difference between red light and blue light.
- What determines the color of a colored object? Explain why grass appears green.
- Give an approximate range of wavelengths for each type of electromagnetic radiation and summarize the characteristics and/or the uses of each.
 - gamma rays
 - X-rays
 - ultraviolet radiation
 - visible light
 - infrared radiation
 - microwave radiation
 - radio waves
- Explain the wave behavior known as interference. Explain the difference between constructive and destructive interference.
- Explain the wave behavior known as diffraction. Draw the diffraction pattern that occurs when light travels through two slits comparable in size and separation to the light's wavelength.
- Describe the photoelectric effect. How did experimental observations of this phenomenon differ from the predictions of classical electromagnetic theory?
- How did the photoelectric effect lead Einstein to propose that light is quantized?
- What is a photon? How is the energy of a photon related to its wavelength? Its frequency?
- What is an emission spectrum? How does an emission spectrum of a gas in a discharge tube differ from a white light spectrum?
- Describe the Bohr model for the atom. How did the Bohr model account for the emission spectra of atoms?
- Explain electron diffraction.
- What is the de Broglie wavelength of an electron? What determines the value of the de Broglie wavelength for an electron?

- 17.** What are complementary properties? How does electron diffraction demonstrate the complementarity of the wave nature and particle nature of the electron?
- 18.** Explain Heisenberg's uncertainty principle. What paradox is at least partially solved by the uncertainty principle?
- 19.** What is a trajectory? What kind of information do you need to predict the trajectory of a particle?
- 20.** Why does the uncertainty principle make it impossible to predict a trajectory for the electron?
- 21.** Newton's laws of motion are *deterministic*. Explain this statement.
- 22.** An electron behaves in ways that are at least partially indeterminate. Explain this statement.
- 23.** What is a probability distribution map?
- 24.** For each solution to the Schrödinger equation, what can be precisely specified: the electron's energy or its position? Explain.
- 25.** What is a quantum-mechanical orbital?
- 26.** What is the Schrödinger equation? What is a wave function? How is a wave function related to an orbital?
- 27.** What are the possible values of the principal quantum number n ? What does the principal quantum number determine?
- 28.** What are the possible values of the angular momentum quantum number l ? What does the angular momentum quantum number determine?
- 29.** What are the possible values of the magnetic quantum number m_l ? What does the magnetic quantum number determine?
- 30.** List all the orbitals in each principal level. Specify the three quantum numbers for each orbital.
- a. $n = 1$ b. $n = 2$ c. $n = 3$ d. $n = 4$
- 31.** Explain the difference between a plot showing the probability density for an orbital and one showing the radial distribution function.
- 32.** Make sketches of the general shapes of the s , p , and d orbitals.
- 33.** List the four different sublevels associated with $n = 4$. Given that only a maximum of two electrons can occupy an orbital, determine the maximum number of electrons that can exist in each sublevel.
- 34.** Why are atoms usually portrayed as spheres when most orbitals are not spherically shaped?

PROBLEMS BY TOPIC

Electromagnetic Radiation

- 35.** The distance from the sun to Earth is 1.496×10^8 km. How long does it take light to travel from the sun to Earth?
MISSED THIS? Read Section 8.2
- 36.** The nearest star to our sun is Proxima Centauri, at a distance of 4.3 light-years from the sun. A light-year is the distance that light travels in one year (365 days). How far away, in km, is Proxima Centauri from the sun?
- 37.** List these types of electromagnetic radiation in order of (i) increasing wavelength and (ii) increasing energy per photon.
MISSED THIS? Read Section 8.2; Watch KCV 8.2, IWE 8.3
- a. radio waves b. microwaves
c. infrared radiation d. ultraviolet radiation
- 38.** List these types of electromagnetic radiation in order of (i) increasing frequency and (ii) decreasing energy per photon.
- a. gamma rays b. radio waves
c. microwaves d. visible light
- 39.** Calculate the frequency of each wavelength of electromagnetic radiation. **MISSED THIS? Read Section 8.2**
- a. 632.8 nm (wavelength of red light from helium–neon laser)
b. 503 nm (wavelength of maximum solar radiation)
c. 0.052 nm (a wavelength contained in medical X-rays)
- 40.** Calculate the wavelength of each frequency of electromagnetic radiation.
- a. 100.2 MHz (typical frequency for FM radio broadcasting)
b. 1070 kHz (typical frequency for AM radio broadcasting) (assume four significant figures)
c. 835.6 MHz (common frequency used for cell phone communication)

- 41.** Calculate the energy of a photon of electromagnetic radiation at each of the wavelengths indicated in Problem 39.
MISSED THIS? Read Section 8.2; Watch KCV 8.2, IWE 8.2
- 42.** Calculate the energy of a photon of electromagnetic radiation at each of the frequencies indicated in Problem 40.
- 43.** A laser pulse with wavelength 532 nm contains 3.85 mJ of energy. How many photons are in the laser pulse?
MISSED THIS? Read Section 8.2; Watch KCV 8.2, IWE 8.2
- 44.** A heat lamp produces 32.8 watts of power at a wavelength of $6.5 \mu\text{m}$. How many photons are emitted per second? (1 watt = 1 J/s)
- 45.** Determine the energy of 1 mol of photons for each kind of light. (Assume three significant figures.)
MISSED THIS? Read Section 8.2; Watch KCV 8.2, IWE 8.2
- a. infrared radiation (1500 nm)
b. visible light (500 nm)
c. ultraviolet radiation (150 nm)
- 46.** How much energy is contained in 1 mol of each?
- a. X-ray photons with a wavelength of 0.135 nm
b. γ -ray photons with a wavelength of 2.15×10^{-5} nm

The Wave Nature of Matter and the Uncertainty Principle

- 47.** Sketch the interference pattern that results from the diffraction of electrons passing through two closely spaced slits.
MISSED THIS? Read Section 8.4; Watch KCV 8.4
- 48.** What happens to the interference pattern described in Problem 47 if the rate of electrons going through the slits is decreased to one electron per hour? What happens to the pattern if we try to determine which slit the electron goes through by using a laser placed directly behind the slits?

49. The resolution limit of a microscope is roughly equal to the wavelength of light used in producing the image. Electron microscopes use an electron beam (in place of photons) to produce much higher resolution images, about 0.20 nm in modern instruments. Assuming that the resolution of an electron microscope is equal to the de Broglie wavelength of the electrons used, to what speed must the electrons be accelerated to obtain a resolution of 0.20 nm?

MISSED THIS? Read Section 8.4; Watch KCV 8.4

50. The smallest atoms can themselves exhibit quantum-mechanical behavior. Calculate the de Broglie wavelength (in pm) of a hydrogen atom traveling at 475 m/s.

51. What is the de Broglie wavelength of an electron traveling at 1.35×10^5 m/s? **MISSED THIS? Read Section 8.4; Watch KCV 8.4**

52. A proton in a linear accelerator has a de Broglie wavelength of 122 pm. What is the speed of the proton?

53. Calculate the de Broglie wavelength of a 143-g baseball traveling at 95 mph. Why is the wave nature of matter not important for a baseball? **MISSED THIS? Read Section 8.4; Watch KCV 8.4**

54. A 0.22-caliber handgun fires a 1.9-g bullet at a velocity of 765 m/s. Calculate the de Broglie wavelength of the bullet. Is the wave nature of matter significant for bullets?

55. An electron has an uncertainty in its position of 552 pm. What is the minimum uncertainty in its velocity?

MISSED THIS? Read Section 8.4

56. An electron traveling at 3.7×10^5 m/s has an uncertainty in its velocity of 1.88×10^5 m/s. What is the minimum uncertainty in its position?

Orbitals and Quantum Numbers

57. Which electron is, on average, closer to the nucleus: an electron in a 2s orbital or an electron in a 3s orbital?

MISSED THIS? Read Sections 8.5, 8.6; Watch KCV 8.5A

58. Which electron is, on average, farther from the nucleus: an electron in a 3p orbital or an electron in a 4p orbital?

59. What are the possible values of l for each value of n ?

MISSED THIS? Read Section 8.5; Watch KCV 8.5A

- a. 1 b. 2 c. 3 d. 4

60. What are the possible values of m_l for each value of l ?

- a. 0 b. 1 c. 2 d. 3

61. Which set of quantum numbers *cannot* specify an orbital?

MISSED THIS? Read Section 8.5; Watch KCV 8.5A, IWE 8.5

- a. $n = 2, l = 1, m_l = -1$ b. $n = 3, l = 2, m_l = 0$

- c. $n = 3, l = 3, m_l = 2$ d. $n = 4, l = 3, m_l = 0$

62. Which combinations of n and l represent real orbitals, and which do not exist?

- a. 1s b. 2p c. 4s d. 2d

63. Sketch the 1s and 2p orbitals. How do the 2s and 3p orbitals differ from the 1s and 2p orbitals? **MISSED THIS? Read Section 8.6**

64. Sketch the 3d orbitals. How do the 4d orbitals differ from the 3d orbitals?

Atomic Spectroscopy

65. An electron in a hydrogen atom is excited with electrical energy to an excited state with $n = 2$. The atom then emits a photon. What is the value of n for the electron following the emission?

MISSED THIS? Read Section 8.5; Watch KCV 8.5B

66. Determine whether each transition in the hydrogen atom corresponds to absorption or emission of energy.

- a. $n = 3 \longrightarrow n = 1$
b. $n = 2 \longrightarrow n = 4$
c. $n = 4 \longrightarrow n = 3$

67. According to the quantum-mechanical model for the hydrogen atom, which electron transition produces light with the longer wavelength: $2p \longrightarrow 1s$ or $3p \longrightarrow 1s$?

MISSED THIS? Read Section 8.5; Watch KCV 8.5B

68. According to the quantum-mechanical model for the hydrogen atom, which electron transition produces light with the longer wavelength: $3p \longrightarrow 2s$ or $4p \longrightarrow 3p$?

69. Calculate the wavelength of the light emitted when an electron in a hydrogen atom makes each transition and indicate the region of the electromagnetic spectrum (infrared, visible, ultraviolet, etc.) where the light is found.

MISSED THIS? Read Section 8.5; Watch KCV 8.5B, IWE 8.7

- a. $n = 2 \longrightarrow n = 1$ b. $n = 3 \longrightarrow n = 1$
c. $n = 4 \longrightarrow n = 2$ d. $n = 5 \longrightarrow n = 2$

70. Calculate the frequency of the light emitted when an electron in a hydrogen atom makes each transition.

- a. $n = 4 \longrightarrow n = 3$ b. $n = 5 \longrightarrow n = 1$
c. $n = 5 \longrightarrow n = 4$ d. $n = 6 \longrightarrow n = 5$

71. An electron in the $n = 7$ level of the hydrogen atom relaxes to a lower energy level, emitting light of 397 nm. What is the value of n for the level to which the electron relaxed?

MISSED THIS? Read Section 8.5; Watch KCV 8.5B, IWE 8.7

72. An electron in a hydrogen atom relaxes to the $n = 4$ level, emitting light of 114 THz. What is the value of n for the level in which the electron originated?

CUMULATIVE PROBLEMS

73. Ultraviolet radiation and radiation of shorter wavelengths can damage biological molecules because these kinds of radiation carry enough energy to break bonds within the molecules. A typical carbon–carbon bond requires 348 kJ/mol to break. What is the longest wavelength of radiation with enough energy to break carbon–carbon bonds?

74. The human eye contains a molecule called 11-cis-retinal that changes shape when struck with light of sufficient energy. The change in shape triggers a series of events that result in an electrical signal being sent to the brain that results in vision. The minimum energy required to change the conformation of

11-cis-retinal within the eye is about 164 kJ/mol. Calculate the longest wavelength visible to the human eye.

75. An argon ion laser puts out 5.0 W of continuous power at a wavelength of 532 nm. The diameter of the laser beam is 5.5 mm. If the laser is pointed toward a pinhole with a diameter of 1.2 mm, how many photons travel through the pinhole per second? Assume that the light intensity is equally distributed throughout the entire cross-sectional area of the beam. ($1\text{ W} = 1\text{ J/s}$)

76. A green leaf has a surface area of 2.50 cm^2 . If solar radiation is 1000 W/m^2 , how many photons strike the leaf every second? Assume three significant figures and an average wavelength of 504 nm for solar radiation.

- 77.** In a technique used for surface analysis called Auger electron spectroscopy (AES), electrons are accelerated toward a metal surface. These electrons cause the emissions of secondary electrons—called Auger electrons—from the metal surface. The kinetic energy of the Auger electrons depends on the composition of the surface. The presence of oxygen atoms on the surface results in Auger electrons with a kinetic energy of approximately 506 eV. What is the de Broglie wavelength of one of these electrons?

$$[KE = \frac{1}{2}mv^2; 1 \text{ electron volt (eV)} = 1.602 \times 10^{-19} \text{ J}]$$

- 78.** An X-ray photon of wavelength 0.989 nm strikes a surface. The emitted electron has a kinetic energy of 969 eV. What is the binding energy of the electron in kJ/mol?

$$[1 \text{ electron volt (eV)} = 1.602 \times 10^{-19} \text{ J}]$$

- 79.** Ionization involves completely removing an electron from an atom. How much energy is required to ionize a hydrogen atom in its ground (or lowest energy) state? What wavelength of light contains enough energy in a single photon to ionize a hydrogen atom?

- 80.** The energy required to ionize sodium is 496 kJ/mol. What minimum frequency of light is required to ionize sodium?

- 81.** Suppose that in an alternate universe, the possible values of l are the integer values from 0 to n (instead of 0 to $n - 1$). Assuming no other differences between this imaginary universe and ours, how many orbitals exist in each level in the alternate universe?

a. $n = 1$ b. $n = 2$ c. $n = 3$

- 82.** Suppose that, in an alternate universe, the possible values of m_l are the integer values including 0 ranging from $-l - 1$ to $l + 1$ (instead of simply $-l$ to $+l$). How many orbitals exist in each sublevel in the alternate universe?

a. s sublevel b. p sublevel c. d sublevel

- 83.** An atomic emission spectrum of hydrogen shows three wavelengths: 1875 nm, 1282 nm, and 1093 nm. Assign these wavelengths to transitions in the hydrogen atom.

- 84.** An atomic emission spectrum of hydrogen shows three wavelengths: 121.5 nm, 102.6 nm, and 97.23 nm. Assign these wavelengths to transitions in the hydrogen atom.

- 85.** The binding energy of electrons in a metal is 193 kJ/mol. Find the threshold frequency of the metal.

- 86.** In order for a thermonuclear fusion reaction of two deuterons (${}^2\text{H}^+$) to take place, the deuterons must collide and each must

have a velocity of about $1 \times 10^6 \text{ m/s}$. Find the wavelength of such a deuteron.

- 87.** The speed of sound in air is 344 m/s at room temperature. The lowest frequency of a large organ pipe is 30 s^{-1} and the highest frequency of a piccolo is $1.5 \times 10^4 \text{ s}^{-1}$. Find the difference in wavelength between these two sounds.

- 88.** The distance from Earth to the sun is $1.5 \times 10^8 \text{ km}$. Find the number of crests in a light wave of frequency $1.0 \times 10^{14} \text{ s}^{-1}$ traveling from the sun to Earth.

- 89.** The iodine molecule can be photodissociated (broken apart with light) into iodine atoms in the gas phase with light of wavelengths shorter than about 792 nm. A 100.0-mL glass tube contains 55.7 mtorr of gaseous iodine at 25.0°C . What minimum amount of light energy must be absorbed by the iodine in the tube to dissociate 15.0% of the molecules?

- 90.** A 5.00-mL ampule of a 0.100-M solution of naphthalene in hexane is excited with a flash of light. The naphthalene emits 15.5 J of energy at an average wavelength of 349 nm. What percentage of the naphthalene molecules emitted a photon?

- 91.** A laser produces 20.0 mW of red light. In 1.00 hr, the laser emits 2.29×10^{20} photons. What is the wavelength of the laser?

- 92.** A particular laser consumes 150.0 watts of electrical power and produces a stream of 1.33×10^{19} 1064-nm photons per second. What is the percent efficiency of the laser in converting electrical power to light?

- 93.** The quantum yield of light-induced chemical reactions (called photochemical reactions) measures the efficiency of the process. The quantum yield, ϕ , is defined as:

$$\phi = \frac{\text{number of reaction events}}{\text{number of photons absorbed}}$$

Suppose the quantum yield for the reaction $\text{CH}_3\text{X} \longrightarrow \text{CH}_3 + \text{X}$ is $\phi = 0.24$. A cuvette containing a solution of CH_3X is irradiated with 280-nm light with a power of 885 mW for 10.0 minutes. Assuming total absorption of the light by the sample, what is the maximum amount (in moles) of CH_3X that breaks apart?

- 94.** A student is studying the photodissociation (dissociation with light) of $\text{I}_2 \longrightarrow 2\text{I}$. When a sample of I_2 is irradiated with a power of 255 mW at 590 nm for 35 seconds, 0.0256 mmol of I forms. Assuming complete absorption of the incident radiation, what is the quantum yield, ϕ , of the reaction? (See Problem 93 for definition of quantum yield.)

CHALLENGE PROBLEMS

- 95.** An electron confined to a one-dimensional box has energy levels given by the equation:

$$E_n = n^2 h^2 / 8 mL^2$$

where n is a quantum number with possible values of 1, 2, 3, ..., m is the mass of the particle, and L is the length of the box.

- a. Calculate the energies of the $n = 1$, $n = 2$, and $n = 3$ levels for an electron in a box with a length of 155 pm.
 b. Calculate the wavelength of light required to make a transition from $n = 1 \longrightarrow n = 2$ from $n = 2 \longrightarrow n = 3$. In what region of the electromagnetic spectrum do these wavelengths lie?
 c. The energy of a vibrating molecule is quantized much like the energy of an electron in the hydrogen atom. The energy levels of a vibrating molecule are given by the equation:

$$E_n = \left(n + \frac{1}{2}\right)hv$$

where n is a quantum number with possible values of 1, 2, ..., and ν is the frequency of vibration. The vibration frequency of HCl is approximately $8.85 \times 10^{13} \text{ s}^{-1}$. What minimum energy is required to excite a vibration in HCl? What wavelength of light is required to excite this vibration?

- 97.** The wave functions for the 1s and 2s orbitals are as follows:

$$1s \quad \psi = (1/\pi)^{1/2}(1/a_0^{3/2})\exp(-r/a_0)$$

$$2s \quad \psi = (1/32\pi)^{1/2}(1/a_0^{3/2})(2 - r/a_0)\exp(-r/2a_0)$$

where a_0 is a constant ($a_0 = 53 \text{ pm}$) and r is the distance from the nucleus. Use a spreadsheet to make a plot of each of these wave functions for values of r ranging from 0 pm to 200 pm. Describe the differences in the plots and identify the node in the 2s wave function.

- 98.** Before quantum mechanics was developed, Johannes Rydberg developed an equation that predicted the wavelengths (λ) in the atomic spectrum of hydrogen:

$$1/\lambda = R(1/m^2 - 1/n^2)$$

In this equation, R is a constant and m and n are integers. Use the quantum-mechanical model for the hydrogen atom to derive the Rydberg equation.

- 99.** Find the velocity of an electron emitted by a metal with a threshold frequency of $2.25 \times 10^{14} \text{ s}^{-1}$ when it is exposed to visible light of wavelength $5.00 \times 10^{-7} \text{ m}$.
- 100.** Water is exposed to infrared radiation of wavelength $2.8 \times 10^{-4} \text{ cm}$. Assume that all the radiation is absorbed and converted to heat. How many photons are required to raise the temperature of 2.0 g of water by 2.0 K ?
- 101.** The 2005 Nobel Prize in Physics was given, in part, to scientists who had made ultrashort pulses of light. These pulses are important in making measurements involving very short time

periods. One challenge in making such pulses is the uncertainty principle, which can be stated with respect to energy and time as $\Delta E \cdot \Delta t \geq h/4\pi$. What is the energy uncertainty (ΔE) associated with a short pulse of laser light that lasts for only 5.0 femtoseconds (fs)? Suppose the low-energy end of the pulse had a wavelength of 722 nm . What is the wavelength of the high-energy end of the pulse that is limited only by the uncertainty principle?

- 102.** A metal with a threshold frequency of $6.71 \times 10^{14} \text{ s}^{-1}$ emits an electron with a velocity of $6.95 \times 10^5 \text{ m/s}$ when radiation of $1.01 \times 10^{15} \text{ s}^{-1}$ strikes the metal. Calculate the mass of the electron.
- 103.** Find the longest wavelength of a wave that can travel around in a circular orbit of radius 1.8 m .
- 104.** The heat of fusion of ice is 6.00 kJ/mol . Find the number of photons of wavelength $= 6.42 \times 10^{-6} \text{ m}$ that must be absorbed to melt 1.00 g of ice.

CONCEPTUAL PROBLEMS

- 105.** Explain the difference between the Bohr model for the hydrogen atom and the quantum-mechanical model. Is the Bohr model consistent with Heisenberg's uncertainty principle?
- 106.** The light emitted from one of the following electronic transitions ($n = 4 \longrightarrow n = 3$ or $n = 3 \longrightarrow n = 2$) in the hydrogen atom causes the photoelectric effect in a particular metal, while light from the other transition does not. Which transition causes the photoelectric effect and why?
- 107.** Determine whether an interference pattern is observed on the other side of the slits in each experiment.
- An electron beam is aimed at two closely spaced slits. The beam produces only one electron per minute.
 - An electron beam is aimed at two closely spaced slits. A light beam is placed at each slit to determine when an electron goes through the slit.

- A high-intensity light beam is aimed at two closely spaced slits.
 - A gun is fired at a solid wall containing two closely spaced slits. (Will the bullets that pass through the slits form an interference pattern on the other side of the solid wall?)
- 108.** Which transition in the hydrogen atom produces emitted light with the longest wavelength?
- $n = 4 \longrightarrow n = 3$
 - $n = 2 \longrightarrow n = 1$
 - $n = 3 \longrightarrow n = 2$

QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 109.** Discuss the nature of light with your group. Ask each member of your group to transcribe one complete sentence about the physical nature of light.
- 110.** How are electrons like baseballs? How are they unlike baseballs?
- 111.** What are all the possible values of m_l if $l = 0$ (an s orbital)? If $l = 1$ (a p orbital)? If $l = 2$ (a d orbital)? How many possible values of m_l would there be if $l = 20$? Write an equation to determine the number of possible values of m_l from the value of l .

Active Classroom Learning

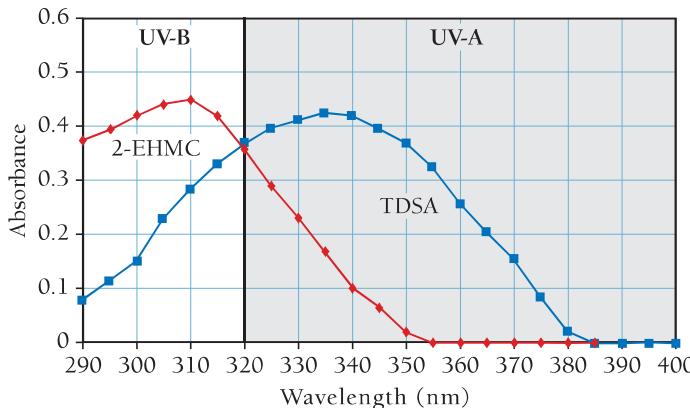
- 112.** Have each group member choose a set of quantum numbers for an electron in a hydrogen atom. Calculate the wavelength of light produced if an electron moves from your state to each state of the other group members. Make a table comparing all possible combinations, and list all wavelengths in order of increasing energy.
- 113.** How many nodes are there in the $1s$, $2p$, and $3d$ orbitals? How many nodes are in a $4f$ orbital?



DATA INTERPRETATION AND ANALYSIS

UV Radiation and Sunscreen

- 114.** Sunscreen contains compounds that absorb ultraviolet light. When sunscreen is applied to skin, it prevents ultraviolet light from reaching the skin. The graph that follows shows the absorbance of light as a function of wavelength for two different compounds (2-EHMC and TDSA) common in sunscreen. Absorbance is a measure of the amount of light absorbed by the compound—the higher the absorbance, the more light is absorbed. Study the graph and answer the questions.



<http://mycpss.com/critical-wavelength-broad-spectrum-uv-protection/>



ANSWERS TO CONCEPTUAL CONNECTIONS

Wave Nature of Light

- 8.1 (c)** Since the light emitted from the lasers have different colors, they must also have different frequencies. The brighter the light, the greater its amplitude, so the bright green laser emits light with a greater amplitude than the dim red one.

Frequency of Light

- 8.2 (a)** As you can see in the electromagnetic spectrum, infrared has the longest wavelength of the three types of electromagnetic radiation listed and X-rays have the shortest.

The Photoelectric Effect

- 8.3 (b)** The 325-nm light has the shortest wavelength of light (highest energy per photon) and corresponds to the photoelectrons with the greatest kinetic energy.

The de Broglie Wavelength of Macroscopic Objects

- 8.4 (a)** Because of the baseball's large mass, its de Broglie wavelength is minuscule. (For a 150-g baseball, λ is on the order of 10^{-34} m.) This minuscule wavelength is insignificant compared to the size of the baseball itself, and therefore its effects are not observable.

- a.** Calculate the energy of a photon at the maximum absorption of TDSA.

- b.** Calculate the energy of a photon at the maximum absorption of 2-EHMC.

- c.** Which compound absorbs more energy at its maximum absorption?

- d.** Why do you think sunscreens commonly contain both of these compounds and not just one of them?

- e.** Assuming that sunlight produces $3.066 \times 10^{22} \frac{\text{uv photons}}{\text{m}^2 \cdot \text{s}}$, and that the skin absorbs one-half of these photons (and reflects the other half) calculate the total uv energy absorbed over 0.42 m^2 of skin that is exposed to sunlight for one hour. Assume that the average wavelength of the uv photons is 330 nm.

The Uncertainty Principle

- 8.5 (b)** The uncertainty principle states that the position and velocity of an electron cannot be simultaneously known. Position and velocity are complementary: the more precisely you know one quantity, the less precisely you know the other.

The Relationship between n and l

- 8.6 (c)** Since l can have a maximum value of $n - 1$ and since $n = 3$, l can have a maximum value of 2.

The Relationship between l and m_l

- 8.7 (d)** Since m_l can have the integer values (including 0) between $-l$ and $+l$ and since $l = 2$, the possible values of m_l are $-2, -1, 0, +1$, and $+2$.

Emission Spectra

- 8.8 (c)** The energy difference between $n = 3$ and $n = 2$ is greatest because the energy differences become closer together with increasing n . The greater energy difference results in an emitted photon of greater energy and therefore shorter wavelength.