The Quantum-Mechanical Model of the Atom

Anyone who is not shocked by quantum mechanics has not understood it.
—Neils Bohr (1885–1962)

7.1 Schrödinger’s Cat 253
7.2 The Nature of Light 254
7.3 Atomic Spectroscopy and the Bohr Model 262
7.4 The Wave Nature of Matter: the de Broglie Wavelength, the Uncertainty Principle, and Indeterminacy 264
7.5 Quantum Mechanics and the Atom 269
7.6 The Shapes of Atomic Orbitals 276

Key Learning Objectives 282

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

The early part of the twentieth century brought changes that revolutionized how we think about physical reality, especially in the atomic realm. Before that time, all descriptions of the behavior of matter had been deterministic—the present set of conditions completely determining the future. Quantum mechanics changed that. This new theory 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 not necessarily follow the same course but instead will most likely land in a different place!
7.1 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. Electrons are small in the absolute sense of the word—they are among the smallest particles that make up matter. And yet, as we have seen, 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 20th 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 simultaneously be in two different states at the same time. For example, through a process called radioactive decay (see Chapter 19), 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 other.

Early 20th century physicists struggled with this idea. Austrian physicist Erwin Schrödinger, 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 cat is put into a steel chamber that contains radioactive atoms such as the one 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 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 not dead 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. We have already learned much about those properties. We know, for example, that some elements are metals and that others are nonmetals. We know
that the noble gases are chemically inert and that the alkali metals are chemically reactive. We
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.

### 7.2 The Nature of Light

Before we explore electrons and their behavior within the atom, we must understand a
few things about 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
chapter, we first explore the wave behavior of light, and then its particle behavior. We
then turn to electrons to see how they 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. Electromagnetic radiation can be described
as a wave composed of oscillating, mutually perpendicular electric and magnetic fields propa-
gating through space, as shown in Figure 7.1. In a vacuum, these waves move at a constant
speed of $3.00 \times 10^8$ m/s ($186,000$ mi/s)—fast enough to circle Earth in one-seventh of a
second. This great speed explains 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 explod-
ing 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 the
lightning immediately, but the sound of the thunder takes a few seconds to reach you.

An electromagnetic wave, like all waves, can be characterized by its amplitude and
its wavelength. In the graphical representation shown below, 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 is related to the intensity or brightness of the light—the
greater the amplitude, the greater the intensity. The wavelength ($\lambda$) of the wave is the
distance in space between adjacent crests (or any two analogous points) and is measured
in units of distance such as the meter, micrometer, or nanometer.

![The symbol $\lambda$ is the Greek letter lambda, pronounced “lamb-duh.”](image)

**FIGURE 7.1** Electromagnetic Radiation

Electromagnetic radiation can be described as a wave composed of oscillating electric and magnetic
fields. The fields oscillate in perpendicular planes.
7.2 The Nature of Light

Wavelength and amplitude are both related to the amount of energy carried by a wave. Imagine trying to swim out from a shore that is being pounded by waves. Greater amplitude (higher waves) or shorter wavelength (more closely spaced, and thus steeper, waves) make the swim more difficult. Notice also that amplitude and wavelength can vary independently of one another, as shown in Figure 7.2. A wave can have a large amplitude and a long wavelength, or a small amplitude and a short wavelength. The most energetic waves have large amplitudes and short wavelengths.

Like all waves, light is also characterized by its frequency ($\nu$), 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 more crests will pass a fixed location per unit time. Frequency is also inversely proportional to the wavelength (\(\lambda\))—the farther apart the crests, the fewer that pass a fixed location per unit time. For light, therefore, we write

\[\nu = \frac{c}{\lambda}\]

[7.1]

where the speed of light, \(c\), and the wavelength, \(\lambda\), are expressed using the same unit of distance. Therefore, wavelength and frequency represent different ways of specifying the same information—if we know one, we can readily calculate the other.

For visible light—that light that can be seen by the human eye—wavelength (or, alternatively, frequency) determines color. White light, as 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 is passed through a prism (Figure 7.3). 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 colors that we perceive. When a substance absorbs some colors while reflecting others, it appears colored. For example, a red shirt appears red because it reflects predominantly red light while absorbing most other colors (Figure 7.4). Our eyes see only the reflected light, making the shirt appear red.

The symbol $\nu$ is the Greek letter nu, pronounced “noo.”

\[\text{nano} = 10^{-9}\]

Figure 7.2 Wavelength and Amplitude

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

Figure 7.3 Components of White Light

White light can be decomposed into its constituent colors, each with a different wavelength, by passing it through a prism. The array of colors makes up the spectrum of visible light.

Figure 7.4 The Color of an Object

A red shirt is red because it reflects predominantly red light while absorbing most other colors.
**EXAMPLE 7.1 Wavelength and Frequency**

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

**SOLUTION**

You are given the frequency of the light and asked to find its wavelength. Use Equation 7.1, which relates frequency to wavelength. You can convert the wavelength from meters to nanometers by using the conversion factor between the two (1 nm = 10\(^{-9}\) m).

\[
\begin{align*}
\nu & = \frac{c}{\lambda} \\
\lambda & = \frac{c}{\nu} \\
& = \frac{3.00 \times 10^8}{4.62 \times 10^{14}} \text{ m/s} \\
& = 6.49 \times 10^{-7} \text{ m} \\
& = 6.49 \times 10^{-7} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 649 \text{ nm}
\end{align*}
\]

**FOR PRACTICE 7.1**

A laser used to dazzle the audience in a rock concert emits green light with a wavelength of 515 nm. Calculate the frequency of the light.

\[
\begin{align*}
\nu & = \frac{c}{\lambda} \\
& = \frac{3.00 \times 10^8}{515 \times 10^{-9}} \text{ s}^{-1} \\
& = 5.84 \times 10^{14} \text{ s}^{-1}
\end{align*}
\]

---

The Electromagnetic Spectrum

Visible light makes up only a tiny portion of the entire **electromagnetic spectrum**, which includes all known wavelengths of electromagnetic radiation. Figure 7.5 shows the main regions of the electromagnetic spectrum, ranging in wavelength from \(10^{-15}\) m (gamma rays) to \(10^5\) m (radio waves).

As we noted previously, short-wavelength light inherently has greater energy than long-wavelength light. Therefore, 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. Human exposure to gamma rays is dangerous 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. While several yearly exposures to X-rays are relatively harmless, excessive 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. While 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—as long as the intensity is not too high—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 vision. 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 used in night vision technology to “see” in the dark.

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 are those of radio waves, which are used to transmit the signals responsible for AM and FM radio, cellular telephones, television, and other forms of communication.

Interference and Diffraction

Waves, including electromagnetic waves, interact with each other in a characteristic way called interference: they can cancel each other out or build each other up, depending on their alignment upon interaction. For example, if waves of equal amplitude from two sources 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.

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

When a wave encounters an obstacle or a slit that is comparable in size to its wavelength, it bends around it—a phenomenon called diffraction (Figure 7.6). The diffraction of light through two slits separated by a distance comparable to the wavelength of the light results in an interference pattern, as shown in Figure 7.7. Each slit acts as a new wave source, and the two new waves interfere with each other. The resulting pattern consists of a series of bright and dark lines that can be viewed on a screen (or recorded on a film) placed at 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. However, a small distance away from the center in either direction, the two waves travel slightly different distances, so that they are out of phase. At the point where the difference in distance is one-half of a wavelength, the interference is destructive and a dark line appears on the screen. Moving a bit further away from the center produces constructive interference again because the difference between the paths is one whole wavelength. The end result is the interference pattern shown. Notice that interference results from the ability of a wave to diffract through the two slits—this is an inherent property of waves.
The term classical, as in classical electromagnetic theory or classical mechanics, refers to descriptions of matter and energy before the advent of quantum mechanics.

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 those for light was the photoelectric effect.

The photoelectric effect was the observation that many metals eject electrons when light shines upon them, as shown in Figure 7.8. The light dislodges an electron from the metal when it shines on the metal, much like an ocean wave might dislodge a rock from a cliff when it breaks on a cliff. Classical electromagnetic theory attributed this effect to the...
7.2 The Nature of Light

Transfer of energy from the light to the electron in the metal, dislodging the electron. In this description, changing either the wavelength (color) or the amplitude (intensity) of the light should affect the ejection of electrons (just as changing the wavelength or intensity of the ocean wave would affect the dislodging of rocks from the cliff). In other words, according to the classical description, the rate at which electrons were ejected from a metal due to the photoelectric effect could be increased by using either light of shorter wavelength or light of higher intensity (brighter light). If a dim light were used, the classical description predicted that there would be a lag time between the initial shining of the light and the subsequent ejection of an electron. The lag time was the minimum amount of time required for the dim light to transfer sufficient energy to the electron to dislodge it (much as there would be a lag time for small waves to finally dislodge a rock from a cliff).

However, when observed in the laboratory, it was found that high-frequency, low-intensity light produced electrons without the predicted lag time. Furthermore, experiments showed that the light used to eject electrons in the photoelectric effect had a threshold frequency, below which no electrons were ejected from the metal, no matter how long or how brightly the light shone on the metal. In other words, low-frequency (long-wavelength) light would not eject electrons from a metal regardless of its intensity or its duration. But high-frequency (short-wavelength) light would eject electrons, even if its intensity were low. This is like observing that long wavelength waves crashing on a cliff would not dislodge rocks even if their amplitude (wave height) was large, but that short wavelength waves crashing on the same cliff would dislodge rocks even if their amplitude was small. Figure 7.9 is a graph of the

**Figure 7.8** The Photoelectric Effect  
(a) When sufficiently energetic light shines on a metal surface, electrons are emitted. (b) The emitted electrons can be measured as an electrical current.

**Figure 7.9** The Photoelectric Effect  
A plot of the electron ejection rate versus frequency of light for the photoelectric effect. Electrons are only ejected when the energy of a photon exceeds the energy with which an electron is held to the metal. The frequency at which this occurs is called the threshold frequency.
Einstein was not the first to suggest that energy was quantized. Max Planck used the idea in 1900 to account for certain characteristics of radiation from hot bodies. However, he did not suggest that light actually traveled in discrete packets.

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

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

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. What could explain this odd behavior?

In 1905, Albert Einstein proposed a bold explanation of this observation: light energy must come in packets. In other words, light was not like ocean waves, but more like particles. According to Einstein, the amount of energy \( (E) \) in a light packet depends on its frequency \( (\nu) \) according to the equation:

\[
E = h\nu \tag{7.2}
\]

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:

\[
E = \frac{hc}{\lambda} \tag{7.3}
\]

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, each with energy \( h\nu \).

### Example 7.2 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.

**GIVEN**

\[ E_{\text{pulse}} = 3.83 \text{ mJ} \]

\[ \lambda = 337 \text{ nm} \]

**FIND** number of photons

**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.

**CONCEPTUAL PLAN**

\[
E_{\text{pulse}} = \text{number of photons}
\]

RELATIONSHIPS USED

\[ E = \frac{hc}{\lambda} \] (Equation 7.3)

**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.

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.

**SOLUTION**

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

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

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

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

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

\[ = \frac{3.83 \times 10^{-3} \text{ J}}{5.8985 \times 10^{-19} \text{ J}} \]

\[ = 6.49 \times 10^{15} \text{ photons} \]

**FOR PRACTICE 7.2**

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 7.2**

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?
EXAMPLE 7.3  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 7.5 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 order 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 7.3

Arrange these 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 was 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 $\phi$, the threshold frequency is reached when the energy of the photon is equal to $\phi$.

\[
\text{Threshold frequency condition}
\]

\[
\nu = \frac{\text{hv}}{\phi}
\]

Energy of photon  Binding energy of emitted electron

Low-frequency light will not eject electrons because no single photon has the minimum energy necessary to dislodge the electron. Increasing the intensity of low-frequency light simply increases the number of low-energy photons, but does not produce any single photon with greater energy. In contrast, increasing the frequency of the light, even at low intensity, increases the energy of each photon, allowing the photons to dislodge electrons with no lag time.

As the frequency of the light is increased past the threshold frequency, the excess energy of the photon (beyond what is needed to dislodge the electron) is transferred 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 ($hv$) and the binding energy of the electron, as given by the equation

\[
\text{KE} = hv - \phi
\]

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 you observe depends on the particular experiment performed.
Chapter 7  The Quantum-Mechanical Model of the Atom

Conceptual Connection 7.1  The Photoelectric Effect

Light of three different wavelengths—325 nm, 455 nm, and 632 nm—was shone on a metal surface. The observations for each wavelength, labeled A, B, and C, were as follows:

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 which wavelength of light?

7.3 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 (see Section 7.4). Just as the photoelectric effect suggested the particle nature of light, so certain observations of atoms began to suggest a wave nature for particles. The most important of these 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 not neon atoms but those of a different gas, the emitted light is a different color. 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 7.10). Closer investigation of the light emitted by atoms reveals that it contains several distinct wavelengths. Just as the white light from a lightbulb can be separated into its constituent wavelengths by passing it through a prism, so can the light emitted by an element when it is heated, as shown in Figure 7.11. 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—and can be used 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. The white light spectrum is continuous; there are no sudden interruptions in the intensity of the light as a function of wavelength—it 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 spiral into the nucleus.

Johannes Rydberg, a Swedish mathematician, analyzed many atomic spectra and developed an equation (shown in the margin) that predicted the wavelengths of the hydrogen emission spectrum. However, his equation gave little insight into why atomic spectra were discrete, why atoms were stable, or why his equation worked.

The Danish physicist Niels Bohr (1885–1962) attempted to develop a model for the atom that explained atomic spectra. In his model, electrons travel around the nucleus in circular orbits (similar to those of the planets around the sun). However, in
contrast to planetary orbits—which can theoretically exist at any distance from the sun—Bohr’s orbits could exist only at specific, fixed distances from the nucleus. The energy of each Bohr orbit was also fixed, or quantized. Bohr called these orbits stationary states and suggested that, although they obeyed the laws of classical mechanics, they also possessed “a peculiar, mechanically unexplainable, stability.” We now know that the stationary states were really manifestations of the wave nature of the electron, which we expand upon shortly. Bohr further proposed that, in contradiction to classical electromagnetic theory, no radiation was emitted by an electron orbiting the nucleus in a stationary state. It was only when an electron jumped, or made a transition, from one stationary state to another that radiation was emitted or absorbed (Figure 7.12).

The transitions between stationary states in a hydrogen atom are quite unlike any transitions that you might imagine in the macroscopic world. The electron is never observed between states, only in one state or the next—the transition between states is instantaneous. The emission spectrum of an atom consists of discrete lines because the states exist only at specific, fixed energies. The energy of the photon created 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.

In spite of its initial success in explaining the line spectrum of hydrogen (including the correct wavelengths), the Bohr model left many unanswered questions. It did,
The Quantum-Mechanical Model of the Atom

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.

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

The heart of the quantum-mechanical theory that replaced Bohr’s model 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 thought of 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 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 is recorded behind the slits (Figure 7.13a). 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 7.13b). 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.

It is critical to understand that the interference pattern described here 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 7.13(a). This leads us to an important conclusion: The wave nature of the electron is an inherent property of individual electrons. Recall from Section 7.1 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. As it turns out, this wave nature is what explains the existence of stationary states (in the Bohr model).
The Wave Nature of Matter: 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 ($\lambda$) of an electron of mass $m$ moving at velocity $v$ is given by the de Broglie relation:

$$\lambda = \frac{h}{mv} \quad \text{de Broglie relation}$$  \[7.4\]

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.
EXAMPLE 7.4 De Broglie Wavelength

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

**SORT** You are given the speed of an electron and asked to calculate its wavelength.

**GIVEN** $\nu = 2.65 \times 10^6$ m/s

**FIND** $\lambda$

**CONCEPTUAL PLAN**

The conceptual plan shows how the de Broglie relation relates the wavelength of an electron to its mass and velocity.

**RELATIONSHIPS USED**

$\lambda = \frac{h}{mv}$ (de Broglie relation, Equation 7.4)

**SOLVE** Substitute the velocity, Planck’s constant, and the mass of an electron to calculate the electron’s wavelength. To correctly cancel the units, break down the J in Planck’s constant into its SI base units ($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$).

**SOLUTION**

$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}^2}{(9.11 \times 10^{-31} \text{ kg}) \left(2.65 \times 10^6 \text{ m/s}\right)}$

$= 2.74 \times 10^{-10}$ 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 7.4**

What is the velocity of an electron having a de Broglie wavelength that is approximately the length of a chemical bond? Assume this length to be $1.2 \times 10^{-10}$ m.

Conceptual Connection 7.2 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 do we not observe such properties at the ballpark?

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 answer this question by returning to the single-electron diffraction experiment. Specifically, we can ask the question: 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 7.1 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 following electron diffraction experiment is designed to “watch” which slit the electron travels through by using a laser beam placed directly behind the slits.

An electron that crosses a laser beam produces a tiny “flash”—a single photon is scattered at the point of crossing. A flash behind a particular slit indicates an electron...
The Wave Nature of Matter: the de Broglie Wavelength, the Uncertainty Principle, and Indeterminacy

passing through that slit. However, when the experiment is performed, 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 now absent. With the laser on, the electrons hit positions directly behind each slit, as if they were ordinary particles.

As it turns out, no matter how hard we try, or whatever method we set up, we can never 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 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 you cannot simultaneously observe both the wave nature and the particle nature of the electron. When you try to observe which hole the electron goes through (associated with the particle nature of the electron) you lose the interference pattern (associated with the wave nature of the electron). When you try to observe the interference pattern, you 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 you know about one, the less you know about the other. Which of two complementary properties you observe depends on the experiment you 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 positions, 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 formalized this idea with the equation:

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

Heisenberg’s uncertainty principle

where \( \Delta x \) is the uncertainty in the position, \( \Delta v \) 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 $\Delta x$ and $m\Delta v$ must be greater than or equal to a finite number ($\hbar/4\pi$). In other words, the more accurately you know the position of an electron (the smaller $\Delta x$) the less accurately you can know its velocity (the bigger $\Delta v$) 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 the question: 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.

**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 7.14▼. 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.

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, as shown in Figure 7.15▼.

**FIGURE 7.14 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.)

**FIGURE 7.15 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.
A probability distribution map is a statistical map that shows where an electron is likely to be found under a given set of conditions.

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 7.16). 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, this would be impossible for an electron. If an electron were thrown from the pitcher’s mound to home plate, it would generally land in a different place every time, even if it were thrown in exactly the same way. This behavior is called indeterminacy. Unlike a baseball, whose future path is determined by its position and velocity when it leaves the pitcher’s hand, the future path of an electron is indeterminate, and can only be described statistically.

In the quantum-mechanical world of the electron, the catcher could not know exactly where the electron will cross the plate for any given throw. However, if he kept track of hundreds of identical electron throws, the catcher could 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 7.17. This would be 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.

7.5 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 (we have seen that kinetic energy equals \( \frac{1}{2}mv^2 \)), position and energy are also complementary properties—the more you know about one, the less you 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 state, 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:

\[
H\psi = E\psi
\]  

[7.6]
The symbol \( H \) stands for the Hamiltonian operator, a set of mathematical operations that represent the total energy (kinetic and potential) of the electron within the atom. The symbol \( E \) is the actual energy of the electron. The symbol \( \psi \) is the wave function, a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared \((\psi^2)\) represents an orbital, a position probability distribution map of the electron.

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); and \( m \), 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 \( n = 1, 2, 3, \ldots \) and so on. For the hydrogen atom, the energy of an electron in an orbital with quantum number \( n \) is given by

\[
E_n = -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{n^2} \right) \quad (n = 1, 2, 3, \ldots) \tag{7.7}
\]

The energy is negative because the energy of the electron in the atom is less than the energy of the electron when it is very far away from the atom (which is taken to be zero). Notice that orbitals with higher values of \( n \) have greater (less negative) energies, as shown in the energy level diagram below. Notice also that, as \( n \) increases, the spacing between the energy levels becomes smaller.

\[
\begin{align*}
E_1 &= -2.18 \times 10^{-18} \text{ J} \\
E_2 &= -5.45 \times 10^{-19} \text{ J} \\
E_3 &= -2.42 \times 10^{-19} \text{ J} \\
E_4 &= -1.36 \times 10^{-19} \text{ J}
\end{align*}
\]

The Angular Momentum Quantum Number \((l)\)

The angular momentum quantum number is an integer that determines the shape of the orbital. We consider these shapes in Section 7.6. The possible values of \( l \) are \( 0, 1, 2, \ldots, (n - 1) \). 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. In order to avoid confusion between \( n \) and \( l \), values of \( l \) are often assigned letters as follows:

<table>
<thead>
<tr>
<th>Value of ( l )</th>
<th>Letter Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l = 0 )</td>
<td>( s )</td>
</tr>
<tr>
<td>( l = 1 )</td>
<td>( p )</td>
</tr>
<tr>
<td>( l = 2 )</td>
<td>( d )</td>
</tr>
<tr>
<td>( l = 3 )</td>
<td>( f )</td>
</tr>
</tbody>
</table>

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.
We consider these orientations in Section 7.6. The possible values of the magnetic quantum number is an integer that specifies the orientation of the orbital. Orbitals with the same value of \( n, l, \) and \( m_l \) 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 \( m_l = -1, 0, +1 \).

In general, notice the following:

- 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, etc.
- 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, etc.
- 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, etc.
EXAMPLE 7.5 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

You first determine the possible values of \( l \) (from the given value of \( n \)). You then determine the possible values of \( m_l \) for each possible value of \( l \). For a given value of \( n \), the possible values of \( l \) are 0, 1, 2, \ldots, \((n - 1)\).

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 \( n^2 \).

<table>
<thead>
<tr>
<th>( l )</th>
<th>Possible ( m_l ) Values</th>
<th>Orbital Name(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>4s (1 orbital)</td>
</tr>
<tr>
<td>1</td>
<td>(-1, 0, +1)</td>
<td>4p (3 orbitals)</td>
</tr>
<tr>
<td>2</td>
<td>(-2, -1, 0, +1, +2)</td>
<td>4d (5 orbitals)</td>
</tr>
<tr>
<td>3</td>
<td>(-3, -2, -1, 0, +1, +2, +3)</td>
<td>4f (7 orbitals)</td>
</tr>
</tbody>
</table>

Total number of orbitals = \( 4^2 = 16 \)

FOR PRACTICE 7.5

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

EXAMPLE 7.6 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 \(-1, 0, +1\).

FOR PRACTICE 7.6

Each of the following sets 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) \( n = 1; l = 1; m_l = 0 \)
Atomic Spectroscopy Explained

Quantum theory explains the atomic spectra of atoms discussed in Section 7.3. 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 level orbital is excited or promoted to a higher energy level orbital, as shown in Figure 7.18. In this new configuration, however, the atom is unstable, and the 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 7.7) that the energy of an orbital with principal quantum number \( n \) is given by

\[
E_n = -\frac{2.18 \times 10^{-18}}{n^2} \text{ J},
\]

where \( n = 1, 2, 3, \ldots \). Therefore, the difference in energy between two levels \( n_{\text{initial}} \) and \( n_{\text{final}} \) is given by \( \Delta E = E_{n_{\text{final}}} - E_{n_{\text{initial}}} \). If we substitute the expression for \( E_n \) into the expression for \( \Delta E \), we get the following important expression for the change in energy that occurs in an atom when an electron changes energy levels:

\[
\Delta E = E_{n_{\text{final}}} - E_{n_{\text{initial}}}
= -2.18 \times 10^{-18} \left( \frac{1}{n_f^2} \right) - \left[ -2.18 \times 10^{-18} \left( \frac{1}{n_i^2} \right) \right]
\]

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

[7.8]

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. Recall that the energy of an orbital in the hydrogen atom depends only on \( n \) and is given by \( E_n = -2.18 \times 10^{-18} \frac{1}{n^2} \text{ J}, \) where \( n = 1, 2, 3, \ldots \). Therefore, \( \Delta E \), the energy difference corresponding to the transition from \( n = 3 \) to \( n = 2 \), is determined as follows:

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

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:

\[
\Delta E_{\text{atom}} = -E_{\text{photon}}
\]

**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.
This energy then determines the frequency and wavelength of the photon. Since the wavelength of the photon is related to its energy as \( E = \frac{hc}{\lambda} \), we calculate the wavelength of the photon as follows:

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

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). We can similarly calculate the light emitted due to a transition from \( n = 4 \) to \( n = 2 \) to be 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 7.19 shows several of the transitions in the hydrogen atom and their corresponding wavelengths.

<table>
<thead>
<tr>
<th>Level</th>
<th>( n = \infty )</th>
<th>( n = 5 )</th>
<th>( n = 4 )</th>
<th>( n = 3 )</th>
<th>( n = 2 )</th>
<th>( n = 1 )</th>
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<td>Ionization</td>
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<td>656 nm</td>
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EXAMPLE 7.7  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 7.7 and subtract to find \( \Delta E_\text{atom} \).

In the second part, find \( E_\text{photon} \) by taking the negative of \( \Delta E_\text{atom} \), and then calculate the wavelength corresponding to a photon of this energy using Equation 7.3. (The difference in sign between \( E_\text{photon} \) and \( \Delta E_\text{atom} \) applies only to emission. The energy of a photon must always be positive.)

**CONCEPTUAL PLAN**

\[
\begin{align*}
\Delta E_\text{atom} & = E_5 - E_6 \\
E &= \frac{hc}{\lambda}
\end{align*}
\]

**RELATIONSHIPS USED**

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

**SOLVE** Follow the conceptual plan. Begin by calculating \( \Delta E_\text{atom} \).

Calculate \( E_\text{photon} \) by changing the sign of \( \Delta E_\text{atom} \).

Solve the equation relating the energy of a photon to its wavelength for \( \lambda \). Substitute the energy of the photon and calculate \( \lambda \).

**SOLUTION**

\[
\begin{align*}
\Delta E_\text{atom} &= E_5 - E_6 \\
&= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} \right) - \left[ -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{6^2} \right) \right] \\
&= -2.18 \times 10^{-18} \text{ J} \left( \frac{1}{5^2} - \frac{1}{6^2} \right) \\
&= -2.6644 \times 10^{-20} \text{ J} \\
E_\text{photon} &= -\Delta E_\text{atom} = +2.6644 \times 10^{-20} \text{ J} \\
E &= \frac{hc}{\lambda} \\
\lambda &= \frac{hc}{E} \\
&= \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{2.6644 \times 10^{-20} \text{ J}} \\
&= 7.46 \times 10^{-6} \text{ m}
\end{align*}
\]

**CHECK** The units of the answer (m) are correct for wavelength. The magnitude seems reasonable because \( 10^{-6} \text{ m} \) is in the infrared region of the electromagnetic spectrum. We 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) would result in light of longer wavelength.

**FOR PRACTICE 7.7**

Determine the wavelength of the light absorbed when an electron in a hydrogen atom makes a transition from an orbital in \( n = 2 \) to an orbital in \( n = 7 \).

**FOR MORE PRACTICE 7.7**

An electron in the \( n = 6 \) level of the hydrogen atom relaxes to a lower energy level, emitting light of \( \lambda = 93.8 \text{ nm} \). Find the principal level to which the electron relaxed.
7.6 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. Therefore 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 8 that the orbitals of all atoms can be approximated as being hydrogen-like and therefore have 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 therefore corresponds to particular orbitals. For example, the orbitals with \( l = 0 \) are \( s \) orbitals; those with \( l = 1 \), \( p \) orbitals; those with \( l = 2 \), \( d \) orbitals, etc. 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 7.20a. This image is actually a three-dimensional plot of the wave function squared (\( \psi^2 \)), which represents probability density, the probability (per unit volume) of finding the electron at a point in space.

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

The magnitude of \( \psi^2 \) in this plot is proportional to the density of the dots shown in the image. The high dot density near the nucleus indicates a higher probability density for the electron there. As you move away from the nucleus, the probability density decreases. Figure 7.20(b) shows a plot of probability density (\( \psi^2 \)) versus \( r \), the distance from the nucleus. This is essentially a slice through the three-dimensional plot of \( \psi^2 \) and shows how the probability density decreases as \( r \) increases.

We can 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 you can never predict where the electron will be for any one photo. However, if you took hundreds of photos and superimposed all of them, you would have a plot similar to Figure 7.20(a)—a statistical representation of how likely the electron is to be found at each point.

An atomic orbital can also be represented by a geometrical shape that encompasses the volume where the electron is likely to be found most frequently—typically, 90% of

---

FIGURE 7.20 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.
the time. For example, the 1s orbital can be represented as the three-dimensional sphere shown in Figure 7.21. 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 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 can use a plot called the radial distribution function, shown in Figure 7.22 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.

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

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 \( r \):

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

At the nucleus \( (r = 0) \) 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 see this by 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, producing a maximum at 52.9 pm.

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 7.23. Like the 1s orbital, these orbitals are spherically symmetric. These orbitals are larger in size, however, than the 1s orbital, and, unlike the 1s orbital, they contain nodes. A node is a point where the wave function \( (\psi) \), and therefore the probability density \( (\psi^2) \) and radial distribution function, all go 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 actually 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.

When an orbital is represented as shown below, the surface shown is one of constant probability. The probability of finding the electron at any point on the surface is the same.

\[ \text{1s orbital surface} \]

\[ \text{1s Radial Distribution Function} \]

\[ \text{Maximum at 52.9 pm} \]

\[ \text{0} \quad 200 \quad 400 \quad 600 \quad 800 \quad 1000 \]

\[ \text{Distance from the nucleus, } r \text{ (pm)} \]

\[ \text{Total radial probability} \]

\[ \text{Nodes} \]

\[ \text{The nodes in quantum-mechanical atomic orbitals are three-dimensional analogs of the nodes we find on a vibrating string.} \]
**Chapter 7  The Quantum-Mechanical Model of the Atom**

The 2s and 3s Orbitals

\( 2s \ (n=2, l=0) \)

\( 3s \ (n=3, l=0) \)

\( p \) Orbitals \((l=1)\)

Each principal level with \( n = 2 \) or greater contains three \( p \) orbitals \((m_l = -1, 0, +1)\). The three 2\( p \) orbitals and their radial distribution functions are shown in Figure 7.24. The \( p \) orbitals are not spherically symmetric like the \( s \) orbitals, but have two lobes of electron density on
7.6 The Shapes of Atomic Orbitals

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.

$d$ 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 7.25. 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 $4d$, $5d$, $6d$, etc., orbitals are all similar in shape to the $3d$ orbitals, but they contain additional nodes and are progressively larger in size.

**Figure 7.24** The 2p Orbitals and Their Radial Distribution Function

The radial distribution function is the same for all three 2p orbitals when the $x$-axis of the graph is taken as the axis containing the lobes of the orbital.
Chapter 7  The Quantum-Mechanical Model of the Atom

\( f \) Orbitals \((l = 3)\)
Each principal level with \( n = 4 \) or greater contains seven \( f \) orbitals \((m_l = -3, -2, -1, 0, +1, +2, +3)\). These orbitals have more lobes and nodes than \( d \) orbitals.

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

The wave on the left has a positive amplitude over its entire length, while 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 7.2.

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, we can represent the phase of a 1s and 2p orbital as follows:

In these depictions, blue represents positive phase and red represents negative phase. The 1s orbital is all one phase, while the 2p orbital exhibits two different phases. The phase of quantum mechanical orbitals is important in bonding, as we shall see in Chapter 10.

The Shapes 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 usually 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 spherical shape, as shown in Figure 7.26.

CHAPTER IN REVIEW

Key Terms

**Section 7.1**
quantum-mechanical model (253)

gamma rays (256)
X-rays (256)
ultraviolet (UV) radiation (256)
visible light (257)
infrared (IR) radiation (257)
microwaves (257)
radio waves (257)
interference (257)
constructive interference (257)
destructive interference (257)
diffraction (257)
photoelectric effect (258)
photon (quantum) (260)
complementary properties (267)
Heisenberg’s uncertainty principle (267)
deterministic (268)
indeterminacy (269)

**Section 7.2**
electromagnetic radiation (254)
amplitude (254)
wavelength (\( \lambda \)) (254)
frequency (\( \nu \)) (255)
electromagnetic spectrum (256)

**Section 7.3**
emission spectrum (262)

**Section 7.4**
de Broglie relation (265)

**Section 7.5**
orbital (269)
wave function (270)
quantum number (270)
### Key Concepts

**The Realm of Quantum Mechanics (7.1)**
- The theory of quantum mechanics explains the behavior of particles in the atomic and subatomic realms. These particles include photons (particles of light) and electrons.
- Because the electrons of an atom determine many of its chemical and physical properties, quantum mechanics is foundational to understanding chemistry.

**The Nature of Light (7.2)**
- Light is a type of electromagnetic radiation—a form of energy embodied in oscillating electric and magnetic fields that travels through space at $3.00 \times 10^8$ m/s. Light has both a wave nature and a particle nature.
- The wave nature of light is characterized by its wavelength—the distance between wave crests—and the ability of light to experience interference (constructive or destructive) and diffraction. Its particle nature is characterized by the energy carried in each photon.
- The electromagnetic spectrum includes all wavelengths of electromagnetic radiation from gamma rays (high energy per photon, long 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 (7.3)**
- Atomic spectroscopy is the 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 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 (7.4)**
- Electrons have a wave nature with an associated wavelength, as quantified by the de Broglie relation.
- The wave nature and particle nature of matter are complementary, which means that the more you know of one, the less you 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 of an electron (associated with the electron’s wave nature)—the more accurately one is measured, the greater the uncertainty in the other.
- The inability to simultaneously know both the position and the 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 (7.5, 7.6)**
- 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 three quantum numbers: $n$, $l$, and $m_l$.
- 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; and the magnetic quantum number ($m_l$) determines the orientation of the orbital.

### Key Equations and Relationships

**Relationship between Frequency ($\nu$), Wavelength ($\lambda$), and the Speed of Light ($c$) (7.2)**

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

**Relationship between Energy ($E$), Frequency ($\nu$), Wavelength ($\lambda$), and Planck’s Constant ($h$) (7.2)**

$$E = h\nu$$

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

**de Broglie Relation: Relationship between Wavelength ($\lambda$), Mass ($m$), and Velocity ($v$) of a Particle (7.4)**

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

**Heisenberg’s Uncertainty Principle: Relationship between a Particle’s Uncertainty in Position ($\Delta x$) and Uncertainty in Velocity ($\Delta v$) (7.4)**

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

**Energy of an Electron in an Orbital with Quantum Number $n$ in a Hydrogen Atom (7.5)**

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

<table>
<thead>
<tr>
<th>Chapter Objectives</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculating the Wavelength and Frequency of Light (7.2)</td>
<td>Example 7.1</td>
</tr>
<tr>
<td>Calculating the Energy of a Photon (7.2)</td>
<td>Example 7.2</td>
</tr>
<tr>
<td>Relating Wavelength, Energy, and Frequency to the Electromagnetic Spectrum (7.2)</td>
<td>Example 7.3</td>
</tr>
<tr>
<td>Using the de Broglie Relation to Calculate Wavelength (7.4)</td>
<td>Example 7.4</td>
</tr>
<tr>
<td>Relating Quantum Numbers to One Another and to Their Corresponding Orbitals (7.5)</td>
<td>Examples 7.5, 7.6</td>
</tr>
<tr>
<td>Relating the Wavelength of Light to Transitions in the Hydrogen Atom (7.5)</td>
<td>Example 7.7</td>
</tr>
</tbody>
</table>

EXERCISES

Problems by Topic

Electromagnetic Radiation

1. The distance from the sun to Earth is $1.496 \times 10^8$ km. How long does it take light to travel from the sun to Earth?

2. The star nearest 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?

3. List these types of electromagnetic radiation in order of (i) increasing wavelength and (ii) increasing energy per photon:
   - (a) radio waves
   - (b) microwaves
   - (c) infrared radiation
   - (d) ultraviolet radiation

4. 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

5. Calculate the frequency of each wavelength of electromagnetic radiation:
   - (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)

6. 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)

7. Calculate the energy of a photon of electromagnetic radiation at each of the wavelengths indicated in Problem 5.

8. Calculate the energy of a photon of electromagnetic radiation at each of the frequencies indicated in Problem 6.

9. A laser pulse with wavelength 532 nm contains 4.88 mJ of energy. How many photons are in the laser pulse?

10. A heat lamp produces 41.7 watts of power at a wavelength of 6.5 $\mu$m. How many photons are emitted per second? (1 watt = 1 J/s)

11. Determine the energy of 1 mol of photons for each kind of light. (Assume three significant figures.)
   - (a) infrared radiation (1500 nm)
   - (b) visible light (500 nm)
   - (c) ultraviolet radiation (150 nm)

12. How much energy is contained in 1 mol of each type of photon?
   - (a) X-ray photons with a wavelength of 0.155 nm
   - (b) $\gamma$-ray photons with a wavelength of $2.55 \times 10^{-5}$ nm

The Wave Nature of Matter and the Uncertainty Principle

13. Make a sketch of the interference pattern that results from the diffraction of electrons passing through two closely spaced slits.

14. What happens to the interference pattern described in Problem 13 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?

15. Calculate the wavelength of an electron traveling at $1.15 \times 10^5$ m/s.

16. An electron has a de Broglie wavelength of 225 nm. What is the speed of the electron?

17. 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?

18. A 0.22-caliber handgun fires a 2.7-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?

Orbitals and Quantum Numbers

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

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

21. What are the possible values of $l$ for each value of $n$?
   - (a) 1
   - (b) 2
   - (c) 3
   - (d) 4
22. What are the possible values of \( m_l \) for each value of \( l \)?
   a. 0  b. 1  c. 2  d. 3

23. For the \( n = 3 \) level, list all the possible values of \( l \) and \( m_l \). How many orbitals does the \( n = 3 \) level contain?

24. For the \( n = 4 \) level, list all the possible values of \( l \) and \( m_l \). How many orbitals does the \( n = 4 \) level contain?

25. What are the possible values of \( m_f \)?

26. What do each of the possible values of \( m_f \) in the previous problem specify?

27. Which set of quantum numbers cannot occur together to specify an orbital?
   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. \( n = 4, l = 3, m_l = 0 \)

28. Which combinations of \( n \) and \( l \) represent real orbitals and which are impossible?
   a. 1\( s \)  b. 2\( p \)  c. 4\( s \)  d. 2\( d \)

29. Make a sketch of the 1\( s \) and 2\( p \) orbitals. How would the 2\( s \) and 3\( p \) orbitals differ from the 1\( s \) and 2\( p \) orbitals?

30. Make a sketch of the 3\( d \) orbitals. How would the 4\( d \) orbitals differ from the 3\( d \) orbitals?

Atomic Spectroscopy

31. 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 after the emission?

Cumulative Problems

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

40. The human eye contains a molecule called 11-cis-retinal within the eye is about 164 kJ/mol. Calculate the longest wavelength visible to the human eye.

41. 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 will travel through the pinhole per second? Assume that the light intensity is equally distributed throughout the entire cross-sectional area of the beam. (1 W = 1 J/s)

42. 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.

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

44. 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? 
   \[ KE = \frac{1}{2}mv^2; \text{ 1 electron volt (eV) } = 1.602 \times 10^{-19} \text{ J} \]

45. 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?

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

47. Suppose that in an alternate universe, the possible values of \( l \) were the integer values from 0 to \( n \) (instead of 0 to \( n - 1 \)). Assuming no other differences from this universe, how many orbitals would exist in each level?
   a. \( n = 1 \)  b. \( n = 2 \)  c. \( n = 3 \)

48. Suppose that, in an alternate universe, the possible values of \( m_l \) were the integer values including 0 ranging from \( -l \) to \( +l \). How many orbitals would exist in each sublevel?
   a. \( s \) sublevel  b. \( p \) sublevel  c. \( d \) sublevel

49. 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.
50. 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.

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

52. In order for a thermonuclear fusion reaction of two deuterons (\(^\text{2H}\)) to occur, the deuterons must collide each with a velocity of about \(1 \times 10^6\) m/s. Find the wavelength of such a deuteron.

53. 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\(^4\) s\(^{-1}\). Find the difference in wavelength between these two sounds.

54. The distance from Earth to the sun is 1.5 \(\times\) 10\(^8\) km. Find the number of crests in a light wave of frequency 1.0 \(\times\) 10\(^{15}\) s\(^{-1}\) traveling from the sun to the Earth.

55. The iodine molecule can be photodissociated 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 \(^\circ\)C. What minimum amount of light energy must be absorbed by the iodine in the tube to dissociate 15.0% of the molecules?

56. 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?

57. A laser produces 20.0 mW of red light. In 1.00 hr, the laser emits 2.29 \(\times\) 10\(^{19}\) photons. What is the wavelength of the laser?

58. A 1064 nm laser consumes 150.0 watts of electrical power and produces a stream of 1.33 \(\times\) 10\(^9\) photons per second. What is the percent efficiency of the laser in converting electrical power to light?

**Challenge Problems**

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

\[ E_n = n^2 \frac{\hbar^2}{2mL^2} \]

where \( n \) is a quantum number with possible values of 1, 2, 3, \ldots, \( m \) 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 \( n = 1 \rightarrow n = 2 \) and from \( n = 2 \rightarrow n = 3 \). In what region of the electromagnetic spectrum do these wavelengths lie?

60. 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

\[ E_n = (n + \frac{1}{2}) \hbar \nu \]

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

61. The wave functions for the 1s and 2s orbitals are specified by these equations:

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

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

where \( a_0 \) is a constant (\( a_0 = 53 \) pm) and \( r \) is the distance from the nucleus. 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.

62. Before quantum mechanics was developed, Johannes Rydberg developed the following equation that predicted the wavelengths (\( \lambda \)) 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.

63. Find the velocity of an electron emitted by a metal whose threshold frequency is 2.25 \(\times\) 10\(^{14}\) s\(^{-1}\) when it is exposed to visible light of wavelength 5.00 \(\times\) 10\(^{-7}\) m.

64. Water is exposed to infrared radiation of wavelength 2.8 \(\times\) 10\(^{-4}\) cm. Assume that all the radiation is absorbed and converted to heat. How many photons will be required to raise the temperature of 2.0 g of water by 2.0 K?

65. 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 \( \Delta E \cdot \Delta t > h/4\pi \). What is the energy uncertainty (\( \Delta E \)) 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?

66. A metal whose threshold frequency is 6.71 \(\times\) 10\(^{14}\) s\(^{-1}\) emits an electron with a velocity of 6.95 \(\times\) 10\(^4\) m/s when radiation of 1.01 \(\times\) 10\(^{15}\) s\(^{-1}\) strikes the metal. Use these data to calculate the mass of the electron.

**Conceptual Problems**

67. 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?

68. The light emitted from one of these electronic transitions \((n = 4 \rightarrow n = 3 \text{ or } n = 3 \rightarrow n = 2)\) in the hydrogen atom caused the photoelectric effect in a particular metal while light from the other transition did not. Which transition was able to cause the photoelectric effect and why?

69. Which transition in the hydrogen atom will result in emitted light with the longest wavelength?

\[ \text{a. } n = 4 \rightarrow n = 3 \quad \text{b. } n = 2 \rightarrow n = 1 \quad \text{c. } n = 3 \rightarrow n = 2 \]
70. Determine whether an interference pattern is observed on the other side of the slits in each experiment.

a. An electron beam is aimed at two closely spaced slits. The beam is attenuated to produce only 1 electron per minute.

b. 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.

c. A high-intensity light beam is aimed at two closely spaced slits.

d. 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?)

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**Answers to Conceptual Connections**

**The Photoelectric Effect**

7.1 Observation A corresponds to 632 nm; observation B corresponds to 325 nm; and observation C corresponds to 455 nm. The shortest wavelength of light (highest energy per photon) must correspond to the photoelectrons with the greatest kinetic energy. The longest wavelength of light (lowest energy per photon) must correspond to the observation where no photoelectrons were observed.

**The de Broglie Wavelength of Macroscopic Objects**

7.2 Because of the baseball’s large mass, its de Broglie wavelength is minuscule. (For a 150-g baseball, \( \hbar \approx 10^{-34} \text{ m} \)) This minuscule wavelength is insignificant compared to the size of the baseball itself, and therefore its effects are not measurable.

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**The Relationship between \( n \) and \( l \)**

7.3 (c) Since \( l \) can have a maximum value of \( n - 1 \), and since \( n = 3 \), then \( l \) can have a maximum value of 2.

**The Relationship between \( l \) and \( m_l \)**

7.4 (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**

7.5 (c) The energy difference between \( n = 3 \) and \( n = 2 \) is greatest because the energy spacings get closer together with increasing \( n \). The greater energy difference results in an emitted photon of greater energy and therefore shorter wavelength.