

For the radio signal: Combining steps to calculate the frequency,

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{325 \text{ cm} \times \frac{10^{-2} \text{ m}}{1 \text{ cm}}} = 9.23 \times 10^7 \text{ s}^{-1}$$

For the blue sky: Combining steps to calculate the frequency,

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{473 \text{ nm} \times \frac{10^{-9} \text{ m}}{1 \text{ nm}}} = 6.34 \times 10^{14} \text{ s}^{-1}$$

Check The orders of magnitude are correct for the regions of the electromagnetic spectrum (see Figure 7.3): x-rays (10^{19} to 10^{16} s^{-1}), radio waves (10^9 to 10^4 s^{-1}), and visible light (7.5×10^{14} to $4.0 \times 10^{14} \text{ s}^{-1}$).

Comment The radio station here is broadcasting at $92.3 \times 10^6 \text{ s}^{-1}$, or 92.3 million Hz (92.3 MHz), about midway in the FM range.

FOLLOW-UP PROBLEM 7.1 Some diamonds appear yellow because they contain nitrogen compounds that absorb purple light of frequency $7.23 \times 10^{14} \text{ Hz}$. Calculate the wavelength (in nm and Å) of the absorbed light.

The Classical Distinction Between Energy and Matter In our everyday world, matter and energy behave very differently. Let's examine some distinctions between the behavior of waves of energy and particles of matter.

1. *Refraction and dispersion.* Light of a given wavelength travels at different speeds through various transparent media—vacuum, air, water, quartz, and so forth. Therefore, when a light wave passes from one medium into another, the speed of the wave changes. Figure 7.4A shows the phenomenon known as **refraction**. If the wave strikes the boundary between media, say, between air and water, at an angle other than 90° , the change in speed causes a change in direction, and the wave continues at a different angle. The angle of refraction depends on the two media and the wavelength of the light. In the related process of *dispersion*, white light separates (disperses) into its component colors when it passes through a prism (or other refracting object) because

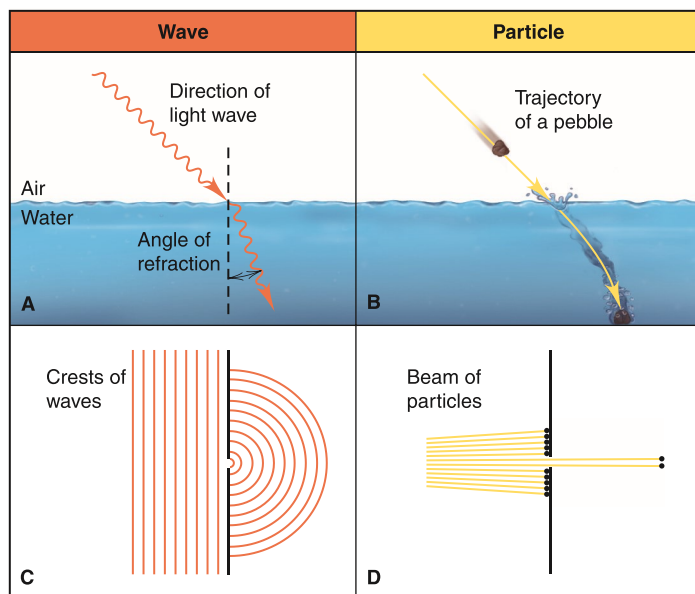


Figure 7.4 Different behaviors of waves and particles. **A**, Refraction: The speed of a light wave passing between media changes immediately, which bends its path. **B**, The speed of a particle continues changing gradually. **C**, Diffraction: A wave bends around both edges of a small opening, forming a semicircular wave. **D**, Particles either enter a small opening or not.

each incoming wave is refracted at a slightly different angle. In fact, rainbows appear when sunlight is dispersed through water droplets.

In contrast to a wave of light, a particle of matter, like a pebble, does not undergo refraction. If you throw a pebble through the air into a pond, it continues to slow down gradually along a curved path after entering the water (Figure 7.4B).

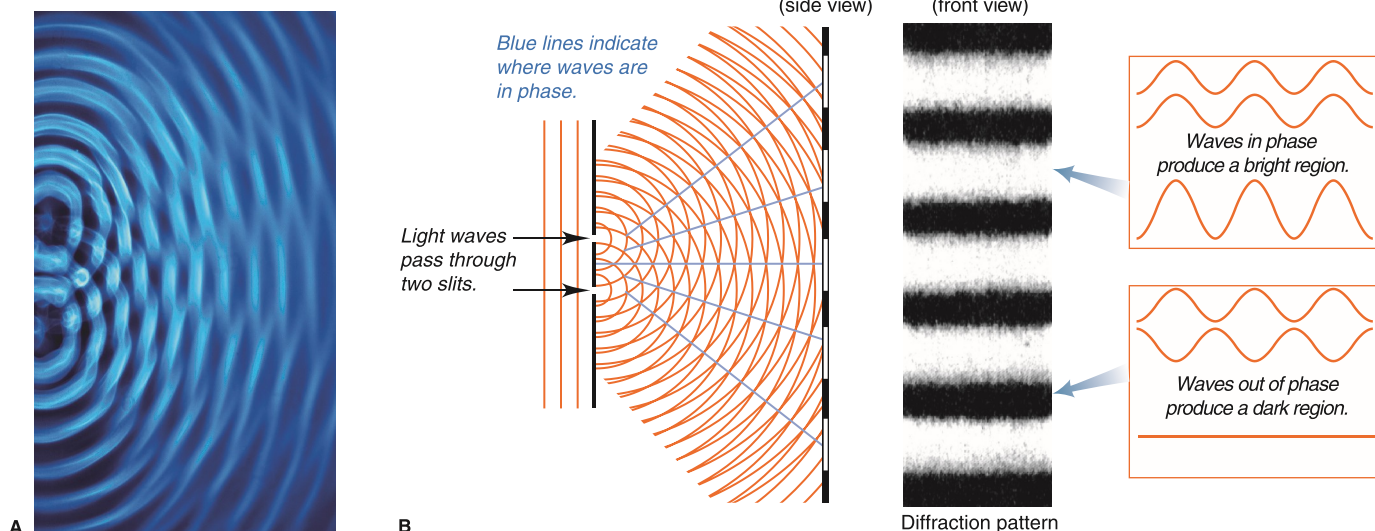
2. *Diffraction and interference.* When a wave strikes the edge of an object, it bends around it in a phenomenon called **diffraction**. If the wave passes through a slit about as wide as its wavelength, it bends around both edges of the slit and forms a semicircular wave on the other side of the opening (Figure 7.4C).

In contrast, when you throw a collection of particles, like a handful of sand, at a small opening, some particles hit the edge, while others go through the opening and continue in a narrower group (Figure 7.4D).

When waves of light pass through two adjacent slits, the nearby emerging circular waves interact through the process of *interference*. If the crests of the waves coincide (*in phase*), they interfere *constructively*—the amplitudes add together to form a brighter region. If crests coincide with troughs (*out of phase*), they interfere *destructively*—the amplitudes cancel to form a darker region. The result is a *diffraction pattern* (Figure 7.5).

In contrast, particles passing through adjacent openings continue in straight paths, some colliding and moving at different angles.

Figure 7.5 Formation of a diffraction pattern. **A**, Constructive interference and destructive interference occur as water waves pass through two adjacent slits. **B**, Light waves passing through two slits also emerge as circular waves and create a diffraction pattern.



The Particle Nature of Light

Three observations involving matter and light confounded physicists at the turn of the 20th century: blackbody radiation, the photoelectric effect, and atomic spectra. Explaining these phenomena required a radically new picture of energy. We discuss the first two of them here and the third in Section 7.2.

Blackbody Radiation and the Quantum Theory of Energy The first of the puzzling observations involved the light given off by an object being heated.

- *Observation: blackbody radiation.* When a solid object is heated to about 1000 K, it begins to emit visible light, as you can see in the red glow of smoldering coal. At about 1500 K, the light is brighter and more orange, like that from an electric heating coil. At temperatures greater than 2000 K, the light is still brighter and whiter, like that emitted by the filament of a lightbulb. These changes in intensity

and wavelength of emitted light as an object is heated are characteristic of *blackbody radiation*, light given off by a hot *blackbody*.^{*} All attempts to account for these changes by applying classical electromagnetic theory failed.

- *Explanation: the quantum theory.* In 1900, the German physicist Max Planck (1858–1947) made a radical assumption that eventually led to an entirely new view of energy. He proposed that a hot, glowing object could emit (or absorb) only *certain* quantities of energy:

$$E = nh\nu$$

where E is the energy of the radiation, ν is its frequency, n is a positive integer (1, 2, 3, and so on) called a **quantum number**, and h is **Planck's constant**. With energy in joules (J) and frequency in s^{-1} , h has units of $\text{J}\cdot\text{s}$:

$$h = 6.62606876 \times 10^{-34} \text{ J}\cdot\text{s} = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} \quad (4 \text{ sf})$$

A hot object's radiation must be emitted by its atoms. If each atom can *emit* only certain quantities of energy, it follows that each atom *has* only certain quantities of energy. Thus, the energy of an atom is *quantized*: it occurs in fixed quantities, rather than being continuous. Each change in an atom's energy occurs when the atom absorbs or emits one or more “packets,” or definite amounts, of energy. Each energy packet is called a **quantum** (“fixed quantity”; plural, *quanta*). A quantum of energy is equal to $h\nu$. Thus, *an atom changes its energy state by emitting (or absorbing) one or more quanta*, and the energy of the emitted (or absorbed) radiation is equal to the *difference in the atom's energy states*:

$$\Delta E_{\text{atom}} = E_{\text{emitted (or absorbed) radiation}} = \Delta nh\nu$$

Because the atom can change its energy only by integer multiples of $h\nu$, the smallest change occurs when an atom in a given energy state changes to an adjacent state, that is, when $\Delta n = 1$:

$$\Delta E = h\nu \quad (7.2)$$

The Photoelectric Effect and the Photon Theory of Light Despite the idea of quantization, physicists still pictured energy as traveling in waves. But, the wave model could not explain the second confusing observation, the flow of current when light strikes a metal.

- *Observation: the photoelectric effect.* When monochromatic light of sufficient frequency shines on a metal plate, a current flows (Figure 7.6). It was thought that the current arises because light transfers energy that frees electrons from the metal surface. However, the effect had two confusing features, the presence of a threshold frequency and the absence of a time lag:
 1. *Presence of a threshold frequency.* For current to flow, the light shining on the metal must have a minimum, or threshold, *frequency*, and different metals have different minimum frequencies. But the wave theory associates the energy of light with its *amplitude* (intensity), not its frequency (color). Thus, the theory predicts that an electron would break free when it absorbed enough energy from light of *any* color.
 2. *Absence of a time lag.* Current flows the moment light of the minimum frequency shines on the metal, regardless of the light's intensity. But the wave theory predicts that with dim light there would be a time lag before the current flows, because the electrons would have to absorb enough energy to break free.
- *Explanation: the photon theory.* Building on Planck's ideas, Albert Einstein proposed in 1905 that light itself is particulate, quantized into tiny “bundles” of energy, later called **photons**. Each atom changes its energy, ΔE_{atom} , when it absorbs or emits one photon, one “particle” of light, whose energy is related to its *frequency*, not its amplitude:

$$E_{\text{photon}} = h\nu = \Delta E_{\text{atom}}$$

^{*}A blackbody is an idealized object that absorbs all the radiation incident on it. A hollow cube with a small hole in one wall approximates a blackbody.

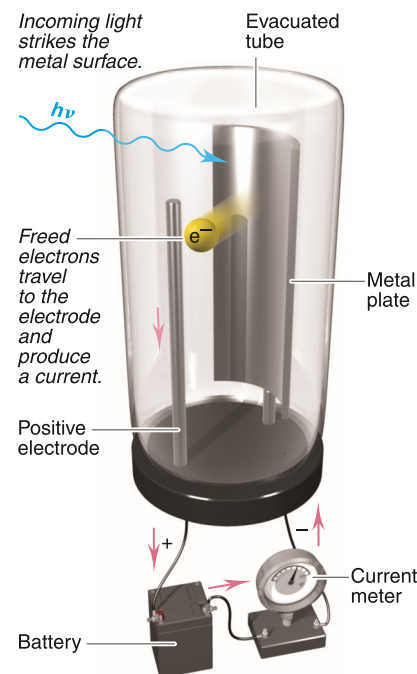


Figure 7.6 The photoelectric effect.

Let's see how the photon theory explains the two features of the photoelectric effect:

1. *Why there is a threshold frequency.* A beam of light consists of an enormous number of photons. The intensity (brightness) is related to the *number* of photons, but *not* to the energy of each. Therefore, a photon of a certain *minimum* energy must be absorbed to free an electron from the surface (see Figure 7.6). Since energy depends on frequency ($h\nu$), the theory predicts a threshold frequency.
2. *Why there is no time lag.* An electron breaks free when it absorbs a photon of *enough* energy; it cannot break free by “saving up” energy from several photons, each having less than the minimum energy. The current is weak in dim light because fewer photons of enough energy can free fewer electrons per unit time, but some current flows *as soon as* light of sufficient energy (frequency) strikes the metal.

THINK OF IT THIS WAY

Ping-Pong Photons

This analogy helps explain why light of *insufficient* energy *cannot* free an electron from the metal surface. If one Ping-Pong ball doesn't have enough energy to knock a book off a shelf, neither does a series of Ping-Pong balls, because the book can't save up the energy from the individual impacts. But one baseball traveling at the same speed *does* have enough energy to move the book. Whereas the energy of a baseball is related to its mass and velocity, the energy of a photon is related to its frequency.

Sample Problem 7.2 Calculating the Energy of Radiation from Its Wavelength

Problem A student uses a microwave oven to heat a meal. The wavelength of the radiation is 1.20 cm. What is the energy of one photon of this microwave radiation?

Plan We know λ in centimeters (1.20 cm) so we convert to meters, find the frequency with Equation 7.1, and then find the energy of one photon with Equation 7.2.

Solution Combining steps to find the energy of a photon:

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(1.20 \text{ cm})\left(\frac{10^{-2} \text{ m}}{1 \text{ cm}}\right)} = 1.66 \times 10^{-23} \text{ J}$$

Check Checking the order of magnitude gives

$$\frac{10^{-33} \text{ J}\cdot\text{s} \times 10^8 \text{ m/s}}{10^{-2} \text{ m}} = 10^{-23} \text{ J}$$

FOLLOW-UP PROBLEM 7.2 Calculate the energy of one photon of (a) ultraviolet light ($\lambda = 1 \times 10^{-8} \text{ m}$); (b) visible light ($\lambda = 5 \times 10^{-7} \text{ m}$); and (c) infrared light ($\lambda = 1 \times 10^{-4} \text{ m}$). What do the answers indicate about the relationship between the wavelength and energy of light?

Summary of Section 7.1

- Electromagnetic radiation travels in waves characterized by a given wavelength (λ) and frequency (ν).
- Electromagnetic waves travel through a vacuum at the speed of light, c ($3.00 \times 10^8 \text{ m/s}$), which equals $\nu \times \lambda$. Therefore, wavelength and frequency have a reciprocal relationship.
- The intensity (brightness) of light is related to the amplitude of its waves.
- The electromagnetic spectrum ranges from very long radio waves to very short gamma rays and includes the visible region between wavelengths 750 nm (red) and 400 nm (violet).
- Refraction (change in a wave's speed when entering a different medium) and diffraction (bend of a wave around an edge of an object) indicate that energy is wavelike, with properties distinct from those of particles of matter.
- Blackbody radiation and the photoelectric effect, however, are consistent with energy occurring in discrete packets, like particles.

- Light exists as photons (quanta) whose energy is proportional to their frequency.
- According to quantum theory, an atom has only certain quantities of energy ($E = nh\nu$), and it can change its energy only by absorbing or emitting a photon whose energy equals the change in the atom's energy.

7.2 • ATOMIC SPECTRA

The third confusing observation about matter and energy involved the light emitted when an element is vaporized and then excited electrically, as occurs in a neon sign. In this section, we discuss the nature of that light, why it created a problem for the existing atomic model, and how a new model solved the problem.

Line Spectra and the Rydberg Equation

When light from electrically excited gaseous atoms passes through a slit and is refracted by a prism, it does not create a *continuous spectrum*, or rainbow, as sunlight does. Instead, it creates a **line spectrum**, a series of fine lines at specific frequencies separated by black spaces. Figure 7.7A shows the apparatus and the line spectrum of atomic hydrogen. Figure 7.7B shows that each spectrum is *characteristic* of the element producing it.

Spectroscopists studying atomic hydrogen identified several series of spectral lines in different regions of the electromagnetic spectrum. Figure 7.8 on the next page shows three of them. Using data, not theory, the Swedish physicist Johannes Rydberg (1854–1919) developed a relationship, called the *Rydberg equation*, that predicted the position and wavelength of any line in a given series:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (7.3)$$

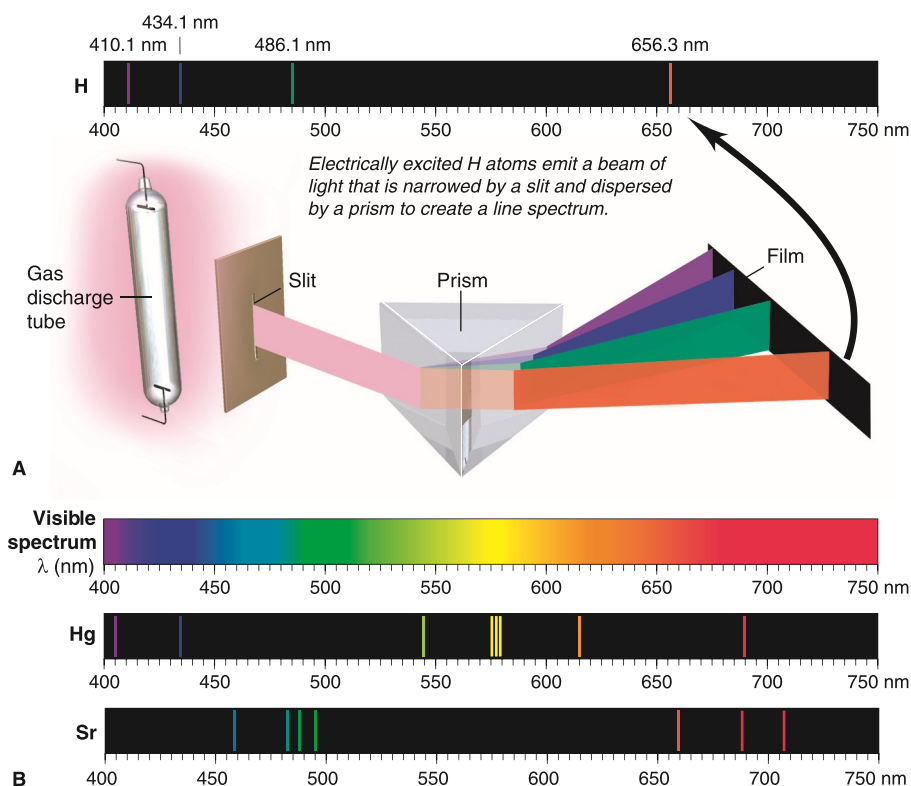
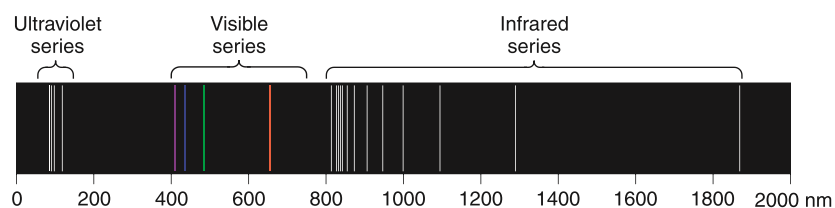


Figure 7.7 The line spectra of several elements. **A**, The line spectrum of atomic hydrogen. **B**, Unlike the continuous spectrum of white light, emission spectra of elements, such as mercury and strontium, appear as characteristic series of colored lines.

Figure 7.8 Three series of spectral lines of atomic hydrogen.



where λ is the wavelength of the line, n_1 and n_2 are positive integers with $n_2 > n_1$, and R is the Rydberg constant ($1.096776 \times 10^7 \text{ m}^{-1}$). For the visible series, $n_1 = 2$:

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n_2^2} \right), \quad \text{with } n_2 = 3, 4, 5, \dots$$

(Problems 7.19 and 7.20 are two of several at the end of the chapter that apply the Rydberg equation.)

The occurrence of line spectra did not correlate with classical theory. If an electron spiraled closer to the nucleus, the frequency of the radiation it emitted should be related to the time of revolution. That time changes smoothly on a spiral path, so the frequency of the radiation should change smoothly and, thus, create a continuous spectrum. Rutherford's model of a nuclear atom did not predict line spectra!

The Bohr Model of the Hydrogen Atom

Two years after the nuclear model was proposed, Niels Bohr (1885–1962), a young Danish physicist working in Rutherford's laboratory, suggested a model for the H atom that *did* predict the existence of line spectra.

Postulates of the Model In his model, Bohr used Planck's and Einstein's ideas about quantized energy and proposed three postulates:

1. *The H atom has only certain energy levels, which Bohr called **stationary states**. Each state is associated with a fixed circular orbit of the electron around the nucleus. The higher the energy level, the farther the orbit is from the nucleus.*
2. *The atom does **not** radiate energy while in one of its stationary states. Even though it violates principles of classical physics, the atom does not change energy while the electron moves *within* an orbit.*
3. *The atom changes to another stationary state (the electron moves to another orbit) only by absorbing or emitting a photon. The energy of the photon ($h\nu$) equals the difference in the energies of the two states:*

$$E_{\text{photon}} = \Delta E_{\text{atom}} = E_{\text{final}} - E_{\text{initial}} = h\nu$$

Features of the Model The model has several key features:

- *Quantum numbers and electron orbit.* The quantum number n is a positive integer (1, 2, 3, ...) associated with the radius of an electron orbit, which is directly related to the electron's energy: *the lower the n value, the smaller the radius of the orbit, and the lower the energy level.*
- *Ground state.* When the electron is in the first orbit ($n = 1$), it is closest to the nucleus, and the H atom is in its lowest (first) energy level, called the **ground state**.
- *Excited states.* If the electron is in any orbit farther from the nucleus, the atom is in an **excited state**. When the electron is in the second orbit ($n = 2$), the atom is in the first excited state; when it's in the third orbit ($n = 3$), the atom is in the second excited state, and so forth.
- *Absorption.* If an H atom *absorbs* a photon whose energy equals the *difference* between lower and higher energy levels, the electron moves to the outer (higher energy) orbit.
- *Emission.* If an H atom in a higher energy level (electron in farther orbit) returns to a lower energy level (electron in closer orbit), the atom *emits* a photon whose energy equals the difference between the two levels. Figure 7.9 shows an analogy that illustrates absorption and emission.

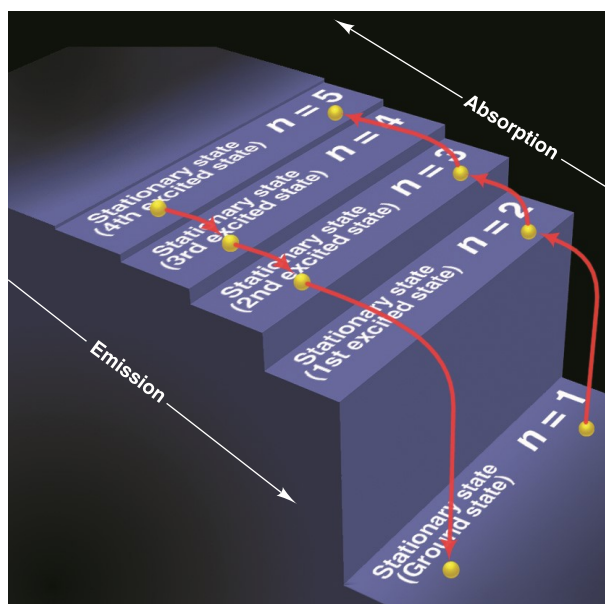


Figure 7.9 A quantum “staircase” as an analogy for atomic energy levels. Note that the electron can move up or down one or more steps at a time but cannot lie *between* steps.

How the Model Explains Line Spectra A spectral line results when a photon of specific energy (and thus frequency) is *emitted*. The emission occurs when the electron moves to an orbit closer to the nucleus as the atom’s energy changes from a higher state to a lower one. Therefore, *an atomic spectrum is not continuous because the atom’s energy is not continuous, but rather has only certain states.*

Figure 7.10A shows how Bohr’s model accounts for three series of spectral lines of hydrogen. When a sample of gaseous H atoms is excited, different atoms absorb different quantities of energy. Each atom has one electron, but there are so many

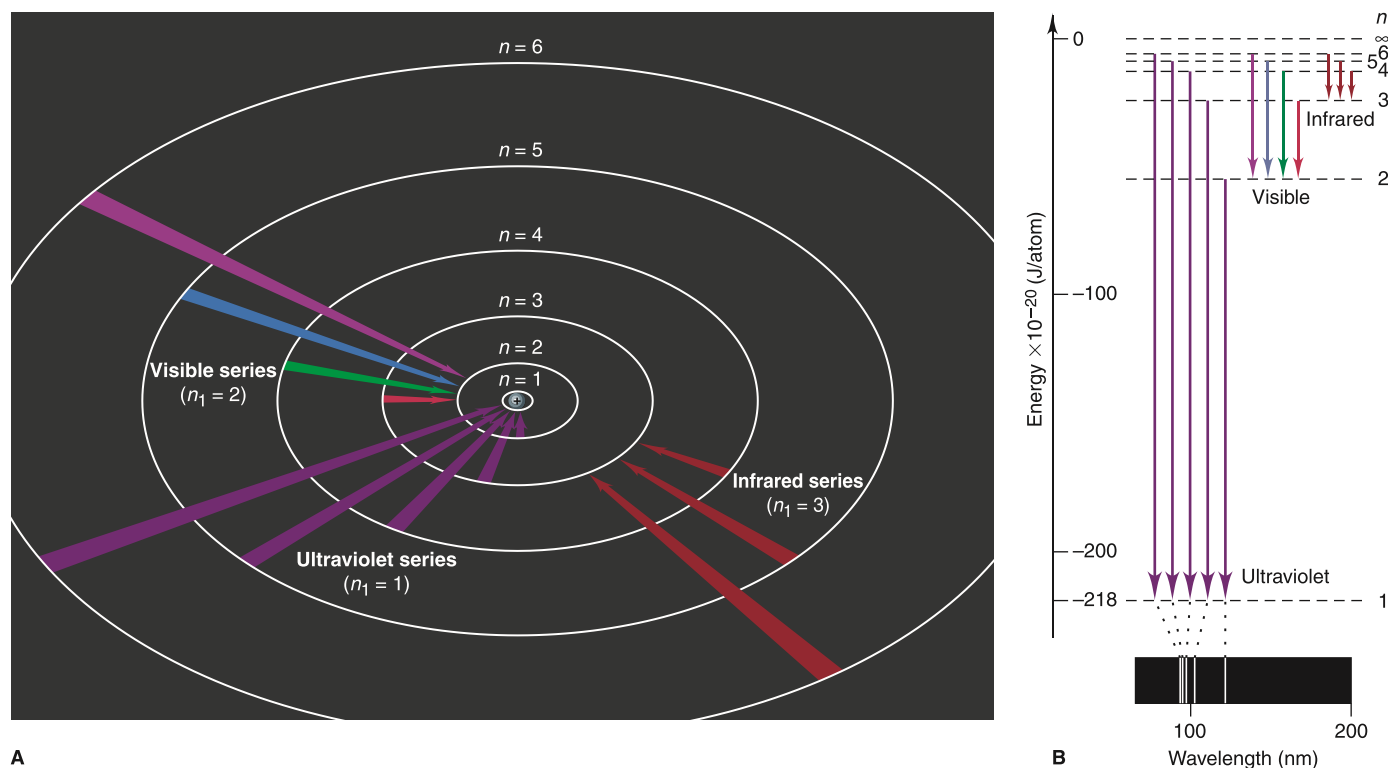


Figure 7.10 The Bohr explanation of three series of spectral lines emitted by the H atom. **A**, In a given series, the outer electron drops to the

same inner orbit (the same value of n_1 in the Rydberg equation). **B**, An energy diagram shows how the ultraviolet series arises.

atoms in the sample that all the energy levels (orbits) have electrons. When electrons drop from outer orbits to the $n = 3$ orbit (second excited state), the emitted photons create the *infrared* series of lines. The *visible* series arises when electrons drop to the $n = 2$ orbit (first excited state), and the *ultraviolet* series arises when electrons drop to the $n = 1$ orbit (ground state). Figure 7.10B shows how the specific lines in the ultraviolet series appear.

Limitations of the Model Despite its great success in predicting the spectral lines of H, the Bohr model failed with every other atom. The reason is that it is a *one-electron model*: it works beautifully for the H atom and for one-electron ions, such as He^+ ($Z = 2$), Li^{2+} ($Z = 3$), and Be^{3+} ($Z = 4$). But it fails completely for species with more than one electron because electron-electron repulsions and additional nucleus-electron attractions create much more complex interactions. Even more fundamentally, as we'll see in Section 7.4, *electrons do not move in fixed, defined orbits*. As a picture of the atom, the Bohr model is incorrect, but we still retain the terms “ground state” and “excited state” and the model’s central idea: *the energy of an atom occurs in discrete levels, and an atom changes energy by absorbing or emitting a photon of specific energy*.

The Energy Levels of the Hydrogen Atom

Bohr’s work leads to an equation for calculating the energy levels of an atom:

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

where Z is the charge of the nucleus. For the H atom, $Z = 1$, so we have

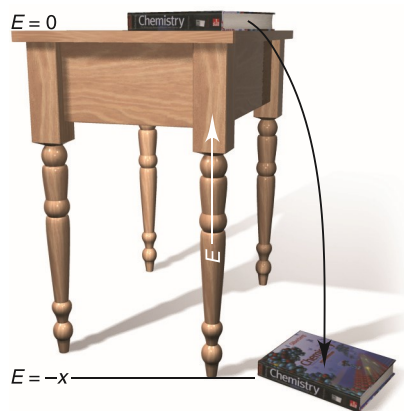
$$E = -2.18 \times 10^{-18} \text{ J} \left(\frac{1^2}{n^2} \right) = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n^2} \right)$$

Therefore, the energy of the ground state ($n = 1$) of the H atom is

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

The negative sign for the energy (also used for the axis values in Figure 7.10B) appears because we *define* the zero point of the atom’s energy when *the electron is completely removed from the nucleus*. Thus, $E = 0$ when $n = \infty$, so $E < 0$ for any smaller n .

THINK OF IT THIS WAY A Book on a Desk and the H Atom’s Energy



If you *define* the potential energy of a book-desk system as zero when the book rests on the desk, the system has negative energy when the book lies on the floor. Similarly, the nucleus-electron system of the H atom is defined as having zero energy when the electron is completely separated from the nucleus. Thus, this system’s energy is negative when the electron is close enough to the nucleus to be attracted by it.

Applying Bohr’s Equation for the Energy Levels of an Atom We can use the equation for the energy levels in several ways:

1. *Finding the difference in energy between two levels.* By subtracting the initial energy level of the atom from its final energy level, we find the change in energy when the electron moves between the two levels:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \quad (7.4)$$

Note that, since n is in the denominator,

- When the atom emits energy, the electron moves closer to the nucleus ($n_{\text{final}} < n_{\text{initial}}$), so the atom’s final energy is a *larger* negative number and ΔE is negative.
- When the atom absorbs energy, the electron moves away from the nucleus ($n_{\text{final}} > n_{\text{initial}}$), so the atom’s final energy is a *smaller* negative number and ΔE is positive. (Analogously, in Chapter 6, you saw that, when the system releases heat, ΔH is negative, and when it absorbs heat, ΔH is positive.)

2. *Finding the energy needed to ionize the H atom.* We can also find the energy needed to remove the electron completely, that is, find ΔE for the following change:



We substitute $n_{\text{final}} = \infty$ and $n_{\text{initial}} = 1$ into Equation 7.4 and obtain

$$\begin{aligned}\Delta E = E_{\text{final}} - E_{\text{initial}} &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{\infty^2} - \frac{1}{1^2} \right) \\ &= -2.18 \times 10^{-18} \text{ J} (0 - 1) = 2.18 \times 10^{-18} \text{ J}\end{aligned}$$

Energy must be *absorbed* to remove the electron from the nucleus, so ΔE is positive.

The *ionization energy* of hydrogen is the energy required to form 1 mol of gaseous H^+ ions from 1 mol of gaseous H atoms. Thus, for 1 mol of H atoms,

$$\Delta E = \left(2.18 \times 10^{-18} \frac{\text{J}}{\text{atom}} \right) \left(6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}} \right) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) = 1.31 \times 10^3 \text{ kJ/mol}$$

Ionization energy is a key atomic property, and we'll return to it in Chapter 8.

3. *Finding the wavelength of a spectral line.* Once we know ΔE from Equation 7.4, we find the wavelengths of the spectral lines of the H atom by combining the relation between frequency and wavelength (Equation 7.1) with Planck's expression for the change in energy of an atom (Equation 7.2) and solving for λ :

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{\Delta E}$$

In Sample Problem 7.3, we find the energy change when an H atom absorbs a photon.

Sample Problem 7.3 Determining ΔE and λ of an Electron Transition

Problem A hydrogen atom absorbs a photon of UV light (see Figure 7.10), and its electron enters the $n = 4$ energy level. Calculate (a) the change in energy of the atom and (b) the wavelength (in nm) of the photon.

Plan (a) The H atom absorbs energy, so $E_{\text{final}} > E_{\text{initial}}$. We are given $n_{\text{final}} = 4$, and Figure 7.10 shows that $n_{\text{initial}} = 1$ because a UV photon is absorbed. We apply Equation 7.4 to find ΔE . (b) Once we know ΔE , we find the frequency with Equation 7.2 and the wavelength (in m) with Equation 7.1. Then we convert from meters to nanometers.

Solution (a) Substituting the known values into Equation 7.4:

$$\begin{aligned}\Delta E &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) = -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{4^2} - \frac{1}{1^2} \right) \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{16} - \frac{1}{1} \right) = 2.04 \times 10^{-18} \text{ J}\end{aligned}$$

(b) Using Equations 7.2 and 7.1 to solve for λ :

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

therefore,

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{2.04 \times 10^{-18} \text{ J}} = 9.74 \times 10^{-8} \text{ m}$$

Converting m to nm:

$$\lambda = 9.74 \times 10^{-8} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 97.4 \text{ nm}$$

Check (a) The energy change is positive, which is consistent with absorption.

(b) The wavelength is within the UV region (about 10–380 nm).

Comment In the follow-up problem, note that if ΔE is negative (the atom loses energy), we use its absolute value, $|\Delta E|$, because λ must have a positive value.

FOLLOW-UP PROBLEM 7.3 A hydrogen atom with its electron in the $n = 6$ energy level emits a photon of IR light. Calculate (a) the change in energy of the atom and (b) the wavelength (in Å) of the photon.

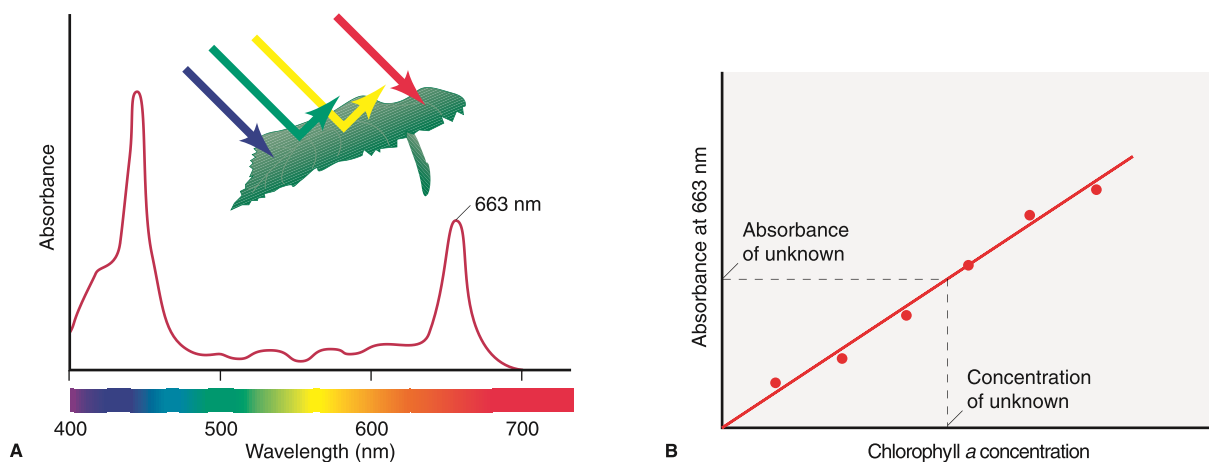


Figure 7.11 Measuring chlorophyll *a* concentration in leaf extract. Chlorophyll *a*, one of several leaf pigments, absorbs red and blue wavelengths strongly. Thus, leaves containing large amounts of chlorophyll *a* appear green. We can use the strong absorption at

663 nm in the spectrum (A) to quantify the amount of chlorophyll *a* present in a plant extract by comparing that absorbance to a series of known standards (B).

Spectral Analysis in the Laboratory

Analysis of the spectrum of the H atom led to the Bohr model, the first step toward our current model of the atom. From its use by 19th-century chemists as a means of identifying elements and compounds, spectrometry has developed into a major tool of modern chemistry. The terms *spectroscopy*, *spectrophotometry*, and **spectrometry** refer to a large group of instrumental techniques that obtain spectra that correspond to a substance's atomic or molecular energy levels. (Elements produce lines, but complex molecules produce spectral peaks.) The two types of spectra most often obtained are emission and absorption spectra:

- An **emission spectrum** is produced when atoms in an excited state emit photons characteristic of the element as they return to lower energy states. The characteristic colors of fireworks and sodium-vapor streetlights are due to one or a few prominent lines in the emission spectra of the atoms present.
- An **absorption spectrum** is produced when atoms absorb photons of certain wavelengths and become excited from lower to higher energy states. Therefore, the absorption spectrum of an element appears as dark lines against a bright background.

A spectrometer can also be used to measure the concentration of a substance in a solution because *the absorbance, the amount of light of a given wavelength absorbed by a substance, is proportional to the number of molecules*. Suppose, for example, you want to determine the concentration of chlorophyll in an ether solution of leaf extract. You select a strongly absorbed wavelength in a peak of the chlorophyll spectrum (such as 663 nm in Figure 7.11A), measure the absorbance of the leaf-extract solution, and compare it with the absorbances of a series of ether solutions with known chlorophyll concentrations (Figure 7.11B).

Summary of Section 7.2

- Unlike sunlight, light emitted by electrically excited atoms of an element appears as separate spectral lines.
- Spectroscopists use an empirical formula (the Rydberg equation) to determine the wavelength of a spectral line. Atomic hydrogen displays several series of lines.
- To explain the existence of line spectra, Bohr proposed that an electron moves in fixed orbits. It moves from one orbit to another when the atom absorbs or emits a photon whose energy equals the difference in energy levels (orbits).
- Bohr's model predicts only the spectrum of the H atom and other one-electron species. Despite this, Bohr was correct that an atom's energy is quantized.
- Spectrometry is an instrumental technique that obtains emission and absorption spectra used to identify substances and measure their concentrations.

7.3 • THE WAVE-PARTICLE DUALITY OF MATTER AND ENERGY

The early proponents of quantum theory demonstrated that *energy is particle-like*. Physicists who further developed the theory turned this proposition upside down and showed that *matter is wavelike*. The sharp divisions we perceive in everyday life between matter and energy have been completely blurred. Strange as this idea may seem, it is the key to our modern atomic model.

The Wave Nature of Electrons and the Particle Nature of Photons

Bohr's model was a perfect case of fitting theory to data: he *assumed* that an atom has only certain energy levels in order to *explain* line spectra. However, Bohr had no theoretical basis for the assumption. Several breakthroughs in the early 1920s provided that basis and blurred the distinction between matter (chunky and massive) and energy (diffuse and massless).

The Wave Nature of Electrons Attempting to explain why an atom has fixed energy levels, a French physics student, Louis de Broglie, considered other systems that display only certain allowed motions, such as the vibrations of a plucked guitar string. Figure 7.12 shows that, because the end of the string is fixed, only certain vibrational frequencies (and wavelengths) can occur. De Broglie proposed that *if energy is particle-like, perhaps matter is wavelike*. He reasoned that *if electrons have wavelike motion* in orbits of fixed radii, they would have only certain allowable frequencies and energies.

Combining Einstein's famous equation for mass-energy equivalence ($E = mc^2$) with the equation for the energy of a photon ($E = h\nu = hc/\lambda$), de Broglie derived an equation for the wavelength of any particle of mass m —whether planet, baseball, or electron—moving at speed u :

$$\lambda = \frac{h}{mu} \quad (7.5)$$

According to this equation for the **de Broglie wavelength**, *matter behaves as though it moves in a wave*. An object's wavelength is *inversely* proportional to its mass, so heavy objects such as planets and baseballs have wavelengths *many* orders of magnitude smaller than the object itself (Table 7.1, *next page*).

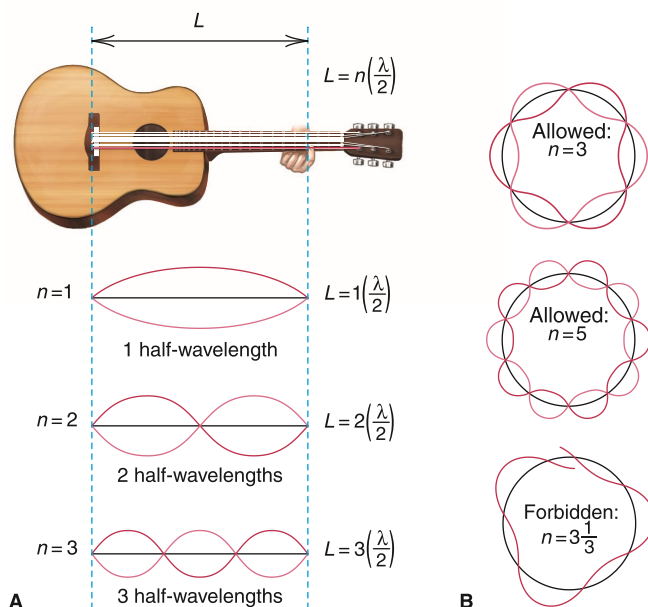


Figure 7.12 Wave motion in restricted systems. **A**, One half-wavelength ($\lambda/2$) is the “quantum” of the guitar string’s vibration. With string length L fixed by a finger on the fret, allowed vibrations occur when L is a whole-number multiple (n) of $\lambda/2$. **B**, In a circular electron orbit, only whole numbers of wavelengths are allowed ($n = 3$ and $n = 5$ are shown). A wave with a fractional number of wavelengths (such as $n = 3\frac{1}{3}$) is “forbidden” because it will die out through overlap of crests and troughs.

Table 7.1 The de Broglie Wavelengths of Several Objects

Substance	Mass (g)	Speed (m/s)	λ (m)
Slow electron	9×10^{-28}	1.0	7×10^{-4}
Fast electron	9×10^{-28}	5.9×10^6	1×10^{-10}
Alpha particle	6.6×10^{-24}	1.5×10^7	7×10^{-15}
1-gram mass	1.0	0.01	7×10^{-29}
Baseball	142	40.0	1×10^{-34}
Earth	6.0×10^{27}	3.0×10^4	4×10^{-63}

Sample Problem 7.4 Calculating the de Broglie Wavelength of an Electron

Problem Find the de Broglie wavelength of an electron with a speed of 1.00×10^6 m/s (electron mass = 9.11×10^{-31} kg; $h = 6.626 \times 10^{-34}$ kg·m²/s).

Plan We know the speed (1.00×10^6 m/s) and mass (9.11×10^{-31} kg) of the electron, so we substitute these into Equation 7.5 to find λ .

Solution

$$\lambda = \frac{h}{mu} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}}{(9.11 \times 10^{-31} \text{ kg})(1.00 \times 10^6 \text{ m/s})} = 7.27 \times 10^{-10} \text{ m}$$

Check The order of magnitude and units seem correct:

$$\lambda \approx \frac{10^{-33} \text{ kg} \cdot \text{m}^2/\text{s}}{(10^{-30} \text{ kg})(10^6 \text{ m/s})} = 10^{-9} \text{ m}$$

FOLLOW-UP PROBLEM 7.4 What is the speed of an electron that has a de Broglie wavelength of 100. nm?

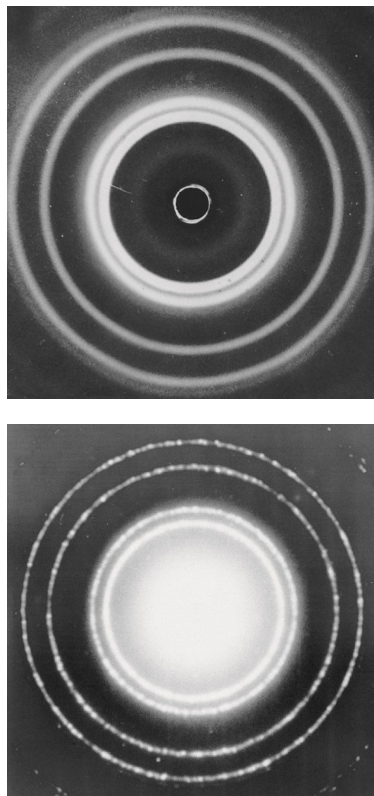


Figure 7.13 Diffraction patterns of aluminum with x-rays (top) and electrons (bottom).

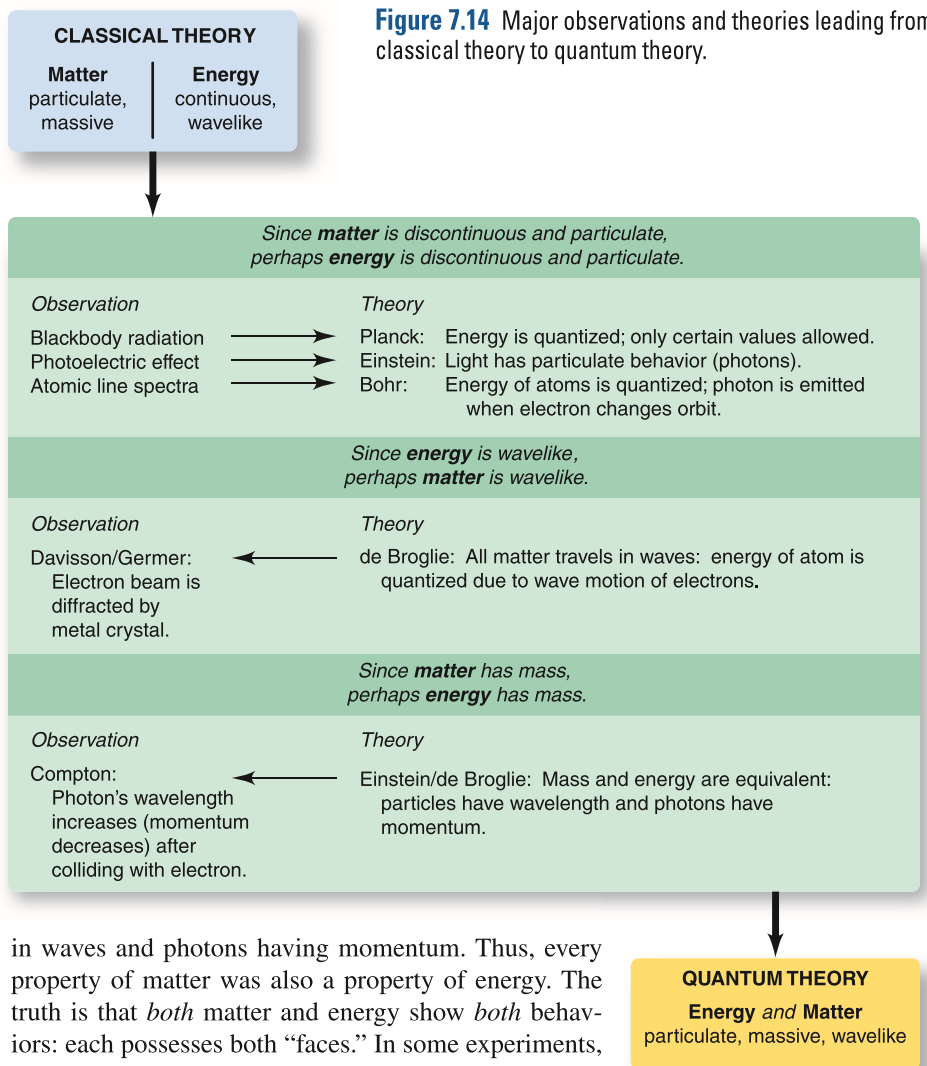
If electrons travel in waves, they should exhibit diffraction and interference. A fast-moving electron has a wavelength of about 10^{-10} m, so a beam of such electrons should be diffracted by the spaces between atoms in a crystal—about 10^{-10} m. In 1927, C. Davisson and L. Germer guided a beam of x-rays and then a beam of electrons at a nickel crystal and obtained two diffraction patterns; Figure 7.13 shows the patterns for aluminum. Thus, electrons—particles with mass and charge—create diffraction patterns, just as electromagnetic waves do. (Indeed, the electron microscope has had a revolutionary impact on modern biology due to its ability to magnify objects up to 200,000 times, which depends on the wavelike behavior of electrons.) Even though electrons do not have orbits of fixed radius, as de Broglie thought, the energy levels of the atom *are* related to the wave nature of the electron.

The Particle Nature of Photons If electrons have properties of energy, do photons have properties of matter? The de Broglie equation suggests that we can calculate the momentum (p), the product of mass and speed, for a photon. Substituting the speed of light (c) for speed u in Equation 7.5 and solving for p gives

$$\lambda = \frac{h}{mc} = \frac{h}{p} \quad \text{and} \quad p = \frac{h}{\lambda}$$

The inverse relationship between p and λ in this equation means that shorter wavelength (higher energy) photons have greater momentum. Thus, a decrease in a photon's momentum should appear as an increase in its wavelength. In 1923, Arthur Compton directed a beam of x-ray photons at graphite and observed an increase in the wavelength of the reflected photons. Thus, just as billiard balls transfer momentum when they collide, the photons transferred momentum to the electrons in the carbon atoms of the graphite. In this experiment, photons behaved as particles.

Wave-Particle Duality Classical experiments had shown matter to be particle-like and energy to be wavelike. But results on the atomic scale show electrons moving



in waves and photons having momentum. Thus, every property of matter was also a property of energy. The truth is that *both* matter and energy show *both* behaviors: each possesses both “faces.” In some experiments, we observe one face; in other experiments, we observe the other face. Our everyday distinction between matter and energy is meaningful in the macroscopic world, *not* in the atomic world. The distinction is in our minds and the limited definitions we have created, not inherent in nature. This dual character of matter and energy is known as the **wave-particle duality**. Figure 7.14 summarizes the theories and observations that led to this new understanding.

Heisenberg's Uncertainty Principle

In classical physics, a moving particle has a definite location at any instant, whereas a wave is spread out in space. If an electron has the properties of *both* a particle and a wave, can we determine its position in the atom? In 1927, the German physicist Werner Heisenberg postulated the **uncertainty principle**, which states that it is impossible to know simultaneously the position *and* momentum (mass times speed) of a particle. For a particle with constant mass m , the principle is expressed mathematically as

$$\Delta x \cdot m \Delta u \geq \frac{h}{4\pi} \quad (7.6)$$

where Δx is the uncertainty in position, Δu is the uncertainty in speed, and h is Planck's constant. The more accurately we know the position of the particle (smaller Δx), the less accurately we know its speed (larger Δu), and vice versa.

For a macroscopic object like a baseball, Δx and Δu are insignificant because the mass is enormous compared with $h/4\pi$. Thus, by knowing the position and speed of a pitched baseball, we can use the laws of motion to predict its trajectory

and whether it will be a ball or a strike. However, using the position and speed of an electron to predict its trajectory is a very different proposition. For example, if we take an electron's speed as $6 \times 10^6 \text{ m/s} \pm 1\%$, then Δu in Equation 7.6 is $6 \times 10^4 \text{ m/s}$, and the uncertainty in the electron's position (Δx) is 10^{-9} m , which is about 10 times greater than the diameter of the entire atom (10^{-10} m). Therefore, we have no idea where in the atom the electron is located!

The uncertainty principle has profound implications for an atomic model. It means that *we cannot assign fixed paths for electrons*, such as the circular orbits of Bohr's model. As you'll see in the next section, the most we can know is the *probability*—the odds—of finding an electron in a given region of space; but we are not *sure* it is there any more than a gambler is sure about the next roll of the dice.

Summary of Section 7.3

- As a result of work based on Planck's quantum theory and Einstein's photon theory, we no longer view matter and energy as distinct entities.
- The de Broglie wavelength is based on the idea that an electron (or any object) has wavelike motion. Allowed atomic energy levels are related to allowed wavelengths of the electron's motion.
- Electrons exhibit diffraction, just as light waves do, and photons exhibit transfer of momentum, just as objects do. This wave-particle duality of matter and energy is observable only on the atomic scale.
- According to the uncertainty principle, we can never know the position and speed of an electron simultaneously.

7.4 • THE QUANTUM-MECHANICAL MODEL OF THE ATOM

Acceptance of the dual nature of matter and energy and of the uncertainty principle culminated in the field of **quantum mechanics**, which examines the wave nature of objects on the atomic scale. In 1926, Erwin Schrödinger derived an equation that is the basis for the *quantum-mechanical model* of the H atom. The model describes an atom with specific quantities of energy that result from allowed frequencies of its electron's wavelike motion. The electron's position can only be known within a certain probability. Key features of the model are described in the following subsections.

The Atomic Orbital and the Probable Location of the Electron

Two central aspects of the quantum-mechanical model concern the atomic orbital and the electron's probable location.

The Schrödinger Equation and the Atomic Orbital The electron's matter-wave occupies the space near the nucleus and is continuously influenced by it. The **Schrödinger equation** is quite complex but can be represented in simpler form as

$$\mathcal{H}\psi = E\psi$$

where E is the energy of the atom. The symbol ψ (Greek *psi*, pronounced “sigh”) is called a **wave function**, or **atomic orbital**, a mathematical description of the electron's matter-wave in three dimensions. The symbol $\mathcal{H}$, called the Hamiltonian operator, represents a set of mathematical operations that, when carried out with a particular ψ , yields one of the allowed energy states of the atom.* Thus, *each solution of the equation gives an energy state associated with a given atomic orbital*.

*The complete form of the Schrödinger equation in terms of the three linear axes is

$$\left[-\frac{\hbar^2}{8\pi^2 m_e} \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) + V(x, y, z) \right] \psi(x, y, z) = E\psi(x, y, z)$$

where ψ is the wave function; m_e is the electron's mass; E is the total quantized energy of the atomic system; and V is the potential energy at point (x, y, z) .

An important point to keep in mind throughout this discussion is that an “orbital” in the quantum-mechanical model *bears no resemblance* to an “orbit” in the Bohr model: an *orbit* is an electron’s actual path around the nucleus, whereas an *orbital* is a mathematical function that describes the electron’s matter-wave but has no physical meaning.

The Probable Location of the Electron While we cannot know *exactly* where the electron is at any moment, we can know where it *probably* is, that is, where it spends most of its time. We get this information by squaring the wave function. Thus, even though ψ has no physical meaning, ψ^2 does and is called the *probability density*, a measure of the probability of finding the electron in some tiny volume of the atom. We depict the electron’s probable location in several ways, which we’ll look at first for the H atom’s *ground state*:

1. *Probability of the electron being in some tiny volume of the atom.* For each energy level, we can create an *electron probability density diagram*, or more simply, an **electron density diagram**. The value of ψ^2 for a given volume is shown with dots: the greater the density of dots, the higher the probability of finding the electron in that volume. Note, that for the ground state of the H atom, *the electron probability density decreases with distance from the nucleus along a line, r* (Figure 7.15A).

These diagrams are also called **electron cloud depictions** because, if we *could* take a time-exposure photograph of the electron in wavelike motion around the nucleus, it would appear as a “cloud” of positions. The electron cloud is an *imaginary* picture of the electron changing its position rapidly over time; it does *not* mean that an electron is a diffuse cloud of charge.

Figure 7.15B shows a plot of ψ^2 vs. r . Due to the thickness of the printed line, the curve appears to touch the axis; however, in the blow-up circle, we see that *the probability of the electron being far from the nucleus is very small, but not zero*.

2. *Total probability density at some distance from the nucleus.* To find *radial probability distribution*, that is, the *total* probability of finding the electron at some distance r from the nucleus, we first mentally divide the volume around the nucleus into thin, concentric, spherical layers, like the layers of an onion (shown in cross section in Figure 7.15C). Then, we find the *sum of ψ^2 values* in each layer to see which is most likely to contain the electron.

The falloff in probability density with distance has an important effect. Near the nucleus, *the volume of each layer increases faster than its density of dots decreases*. The result of these opposing effects is that the *total* probability peaks in a layer *near*,

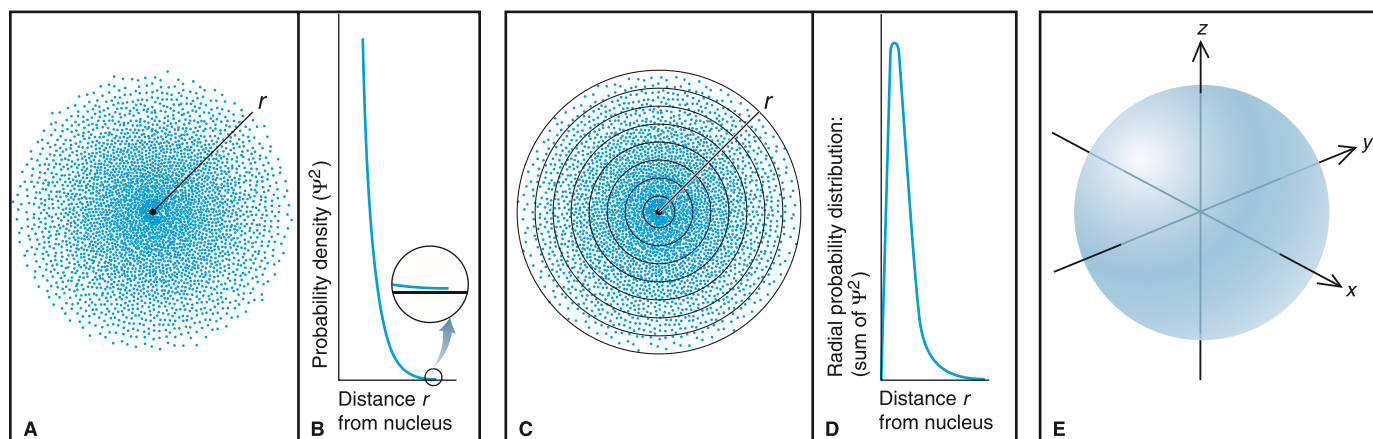


Figure 7.15 Electron probability density in the ground-state H atom.

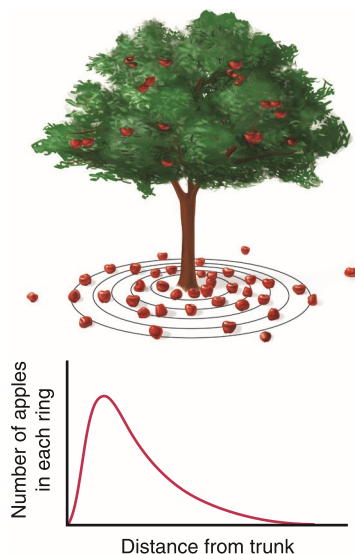
A, In the electron density diagram, the density of dots represents the probability of the electron within a tiny volume and decreases with distance, r , from the nucleus. **B**, The probability density (ψ^2) decreases with r but does not reach zero (*blow-up circle*). **C**, Count-

ing dots within each layer gives the total probability of the electron being in that layer. **D**, A radial probability distribution plot shows that total electron density peaks *near*, but not *at*, the nucleus. **E**, A 90% probability contour for the ground state of the H atom.

but not *at*, the nucleus. For example, the total probability in the second layer is higher than in the first, but this result disappears with greater distance. Figure 7.15D shows this result as a **radial probability distribution plot**.

THINK OF IT THIS WAY

A Radial Probability Distribution of Apples



An analogy might clarify why the curve in the radial probability distribution plot peaks and then falls off. Picture fallen apples around the base of an apple tree: the density of apples is greatest near the trunk and decreases with distance. Divide the ground under the tree into foot-wide concentric rings and collect the apples within each ring. Apple density is greatest in the first ring, but the area of the second ring is larger, and so it contains a greater *total* number of apples. Farther out near the edge of the tree, rings have more area but lower apple “density,” so the total number of apples decreases. A plot of “number of apples in each ring” vs. “distance from trunk” shows a peak at some distance close to the trunk.

3. *Probability contour and the size of the atom.* How far away from the nucleus can we find the electron? This is the same as asking “How big is the H atom?” Recall from Figure 7.15B that the probability of finding the electron far from the nucleus is not zero. Therefore, we *cannot* assign a definite volume to an atom. However, we can visualize an atom with a 90% **probability contour**: the electron is somewhere within that volume 90% of the time (Figure 7.15E).

As you’ll see later in this section, each atomic orbital has a distinctive radial probability distribution and 90% probability contour.

Quantum Numbers of an Atomic Orbital

An *atomic orbital* is specified by three quantum numbers (Table 7.2) that are part of the solution of the Schrödinger equation and indicate the size, shape, and orientation in space of the orbital.*

1. The **principal quantum number (n)** is a positive integer (1, 2, 3, and so forth). It indicates the relative *size* of the orbital and therefore the relative *distance from the nucleus* of the peak in the radial probability distribution plot. The principal quantum number specifies the *energy level* of the H atom: *the higher the n value, the higher the energy level*. When the electron occupies an orbital with $n = 1$, the H atom is in its ground state and has its lowest energy. When the electron occupies an orbital with $n = 2$ (first excited state), the atom has more energy.

*For ease in discussion, chemists often refer to the size, shape, and orientation of an “atomic orbital,” although we really mean the size, shape, and orientation of an “atomic orbital’s radial probability distribution.”

Table 7.2 The Hierarchy of Quantum Numbers for Atomic Orbitals

Name, Symbol (Property)	Allowed Values	Quantum Numbers
Principal, n (size, energy)	Positive integer (1, 2, 3, . . .)	1 2 3
Angular momentum, l (shape)	Integers from 0 to $n - 1$	0 0 1 0 -1 0 $+1$
Magnetic, m_l (orientation)	Integers from $-l$ to 0 to $+l$	0 0 -1 0 $+1$ -2 -1 0 $+1$ $+2$

2. The **angular momentum quantum number (l)** is an integer from 0 to $n - 1$. It is related to the *shape* of the orbital. Note that the principal quantum number sets a limit on the angular momentum quantum number: n limits l . For an orbital with $n = 1$, l can have only one value, 0. For orbitals with $n = 2$, l can have two values, 0 or 1. For orbitals with $n = 3$, l can have three values, 0, 1, or 2; and so forth. Thus, the number of possible l values equals the value of n .

3. The **magnetic quantum number (m_l)** is an integer from $-l$ through 0 to $+l$. It prescribes the three-dimensional *orientation* of the orbital in the space around the nucleus. The angular momentum quantum number sets a limit on the magnetic quantum number: l limits m_l . An orbital with $l = 0$ can have only $m_l = 0$. However, an orbital with $l = 1$ can have one of three m_l values, -1 , 0, or $+1$; that is, there are three possible orbitals with $l = 1$, each with its own orientation. Note that the number of m_l values equals $2l + 1$, which is the number of orbitals for a given l . The total number of m_l values, that is, the total number of orbitals, for a given n value is n^2 .

Sample Problem 7.5 Determining Quantum Numbers for an Energy Level

Problem What values of the angular momentum (l) and magnetic (m_l) quantum numbers are allowed for a principal quantum number (n) of 3? How many orbitals are allowed?

Plan We determine allowable quantum numbers with the rules from the text: l values are integers from 0 to $n - 1$, and m_l values are integers from $-l$ to 0 to $+l$. One m_l value is assigned to each orbital, so the number of m_l values gives the number of orbitals.

Solution Determining l values: for $n = 3$, $l = 0, 1, 2$.

Determining m_l for each l value:

For $l = 0$, $m_l = 0$

For $l = 1$, $m_l = -1, 0, +1$

For $l = 2$, $m_l = -2, -1, 0, +1, +2$

There are nine m_l values, so there are nine orbitals with $n = 3$.

Check Table 7.2 shows that we are correct. As we saw, the total number of orbitals for a given n value is n^2 , and for $n = 3$, $n^2 = 9$.

FOLLOW-UP PROBLEM 7.5 What are the possible l and m_l values for $n = 4$?

Quantum Numbers and Energy Levels

The energy states and orbitals of the atom are described with specific terms and are associated with one or more quantum numbers:

1. **Level.** The atom's energy **levels**, or **shells**, are given by the n value: the smaller the n value, the lower the energy level and the greater the probability that the electron is closer to the nucleus.

2. **Sublevel.** The atom's levels are divided into **sublevels**, or **subshells**, that are given by the l value. Each designates the orbital shape with a letter:

$l = 0$ is an *s* sublevel.

$l = 1$ is a *p* sublevel.

$l = 2$ is a *d* sublevel.

$l = 3$ is an *f* sublevel.

(The letters derive from names of spectroscopic lines: sharp, principal, diffuse, and fundamental.) Sublevels with l values greater than 3 are designated by consecutive letters after *f*: *g* sublevel, *h* sublevel, and so on. A sublevel is named with its n value and letter designation; for example, the sublevel (subshell) with $n = 2$ and $l = 0$ is called 2*s*. (We discuss orbital shapes in the next subsection and in Chapter 8.)

3. *Orbital.* Each combination of n , l , and m_l specifies the size (energy), shape, and spatial orientation of one of the atom's orbitals. We know the quantum numbers of the orbitals in a sublevel from the sublevel name and the quantum-number hierarchy. For example, any orbital in the $2s$ sublevel has $n = 2$ and $l = 0$, and given that l value, it can have only $m_l = 0$; thus, the $2s$ sublevel has only one orbital. Any orbital in the $3p$ sublevel has $n = 3$ and $l = 1$, and given that l value, one orbital has $m_l = -1$, another has $m_l = 0$, and a third has $m_l = +1$; thus, the $3p$ sublevel has three orbitals.

Sample Problem 7.6

Determining Sublevel Names and Orbital Quantum Numbers

Problem Give the name, magnetic quantum numbers, and number of orbitals for each sublevel with the given n and l quantum numbers:

(a) $n = 3, l = 2$ (b) $n = 2, l = 0$ (c) $n = 5, l = 1$ (d) $n = 4, l = 3$

Plan We name the sublevel (subshell) with the n value and the letter designation of the l value. From the l value, we find the number of possible m_l values, which equals the number of orbitals in that sublevel.

Solution

n	l	Sublevel Name	Possible m_l Values	No. of Orbitals
(a) 3	2	$3d$	$-2, -1, 0, +1, +2$	5
(b) 2	0	$2s$	0	1
(c) 5	1	$5p$	$-1, 0, +1$	3
(d) 4	3	$4f$	$-3, -2, -1, 0, +1, +2, +3$	7

Check Check the number of orbitals in each sublevel using

$$\text{No. of orbitals} = \text{no. of } m_l \text{ values} = 2l + 1$$

FOLLOW-UP PROBLEM 7.6 What are the n , l , and possible m_l values for the $2p$ and $5f$ sublevels?

Sample Problem 7.7

Identifying Incorrect Quantum Numbers

Problem What is wrong with each of the following quantum number designations and/or sublevel names?

n	l	m_l	Name
(a) 1	1	0	$1p$
(b) 4	3	+1	$4d$
(c) 3	1	-2	$3p$

Solution (a) A sublevel with $n = 1$ can have only $l = 0$, not $l = 1$. The only possible sublevel name is $1s$.

(b) A sublevel with $l = 3$ is an f sublevel, not a d sublevel. The name should be $4f$.

(c) A sublevel with $l = 1$ can have only $-1, 0$, or $+1$ for m_l , not -2 .

Check Check that l is always less than n and that m_l is always $\geq -l$ and $\leq +l$.

FOLLOW-UP PROBLEM 7.7 Supply the missing quantum numbers and sublevel names.

n	l	m_l	Name
(a) ?	?	0	$4p$
(b) 2	1	0	?
(c) 3	2	-2	?
(d) ?	?	?	$2s$

Shapes of Atomic Orbitals

Each sublevel of the H atom consists of a set of orbitals with characteristic shapes. As you'll see in Chapter 8, orbitals for the other atoms have similar shapes.

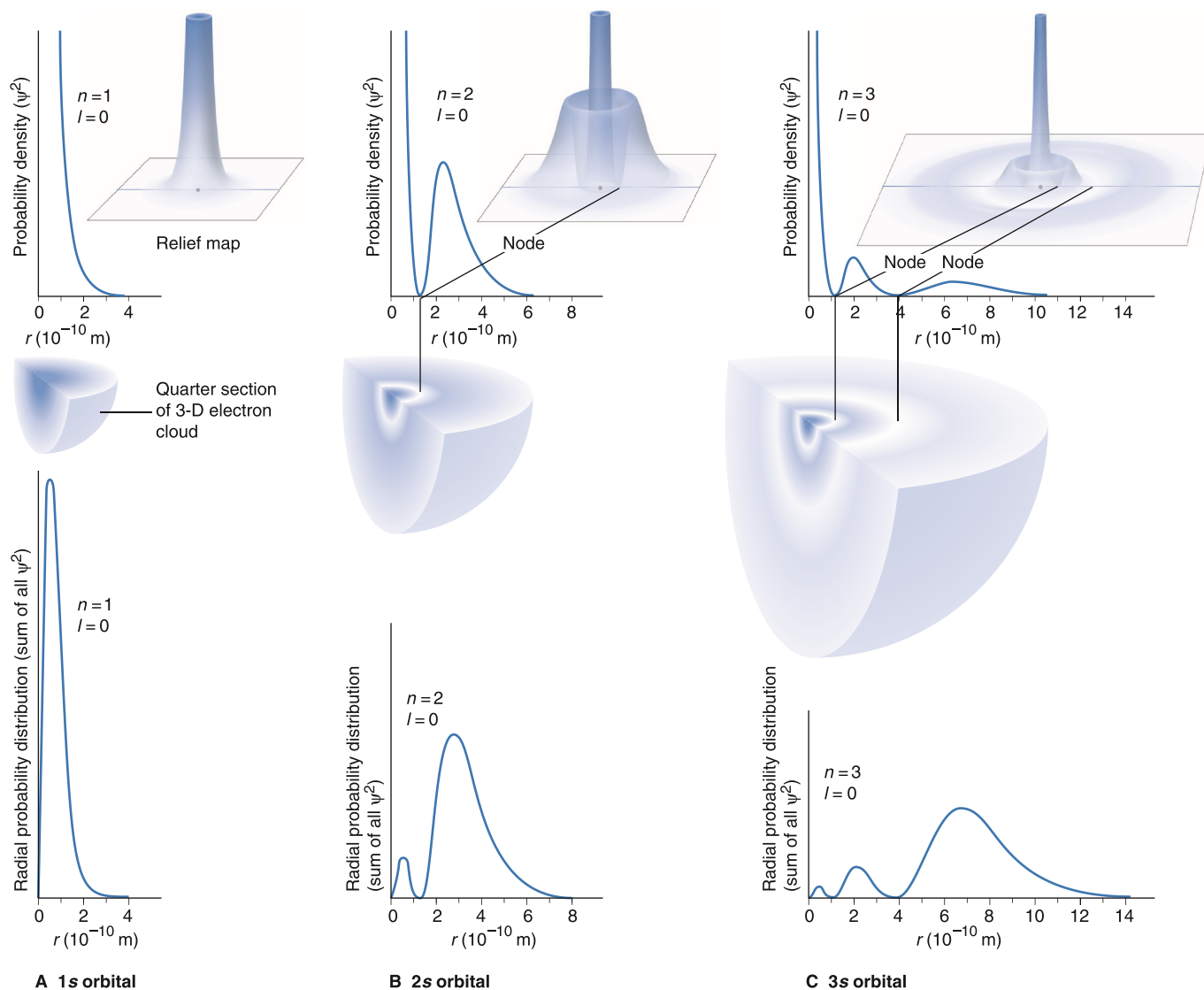
The *s* Orbital An orbital with $l = 0$ has a *spherical* shape with the nucleus at its center and is called an *s orbital*. Because a sphere has only one orientation, an *s* orbital has only one m_l value: for any *s* orbital, $m_l = 0$.

1. The *1s orbital* holds the electron in the H atom's ground state. The *electron probability density is highest at the nucleus*. Figure 7.16A shows this graphically (*top*), and an electron density *relief map* (*inset*) depicts the graph's curve in three dimensions. Note the quarter-section of a three-dimensional electron cloud depiction (*middle*) has the darkest shading at the nucleus. For reasons discussed earlier (see Figure 7.16D), the radial probability distribution plot (*bottom*) has its peak slightly out from the nucleus. Both plots fall off smoothly with distance.

2. The *2s orbital* (Figure 7.16B) has two regions of higher electron density. The radial probability distribution (Figure 7.16B, *bottom*) of the more distant region is *higher* than that of the closer one because the sum of ψ^2 for it is taken over a much larger volume. Between the two regions is a spherical **node**, where the probability of finding the electron drops to zero ($\psi^2 = 0$ at the node, analogous to zero amplitude

Figure 7.16 The 1s, 2s, and 3s orbitals.

For each of the *s* orbitals, a plot of probability density vs. distance (*top*, with the relief map, *inset*, showing the plot in three dimensions) lies above a quarter section of an electron cloud depiction of the 90% probability contour (*middle*), which lies above a radial probability distribution plot (*bottom*). **A**, The 1s orbital. **B**, The 2s orbital. **C**, The 3s orbital.



of a wave exactly between the peak and trough). Because the $2s$ orbital is larger than the $1s$, an electron in the $2s$ spends more time farther from the nucleus (in the larger of the two regions) than it does when it occupies the $1s$.

3. The $3s$ orbital (Figure 7.16C) has three regions of high electron density and two nodes. Here again, the highest radial probability is at the greatest distance from the nucleus. This pattern of more nodes and higher probability with distance from the nucleus continues with the $4s$, $5s$, and so forth.

The p Orbital An orbital with $l = 1$ is called a **p orbital** and has two regions (lobes) of high probability, one on *either side* of the nucleus (Figure 7.17). The *nucleus lies at the nodal plane* of this dumbbell-shaped orbital. Since the maximum value of l is $n - 1$, only levels with $n = 2$ or higher have a p orbital: the lowest energy p orbital (the one closest to the nucleus) is the $2p$. *One p orbital consists of two lobes*, and the electron spends *equal* time in both. Similar to the pattern for s orbitals, a $3p$ orbital is larger than a $2p$, a $4p$ is larger than a $3p$, and so forth.

Unlike s orbitals, p orbitals *have* different spatial orientations. The three possible m_l values of -1 , 0 , and $+1$ refer to three *mutually perpendicular* orientations; that is, while identical in size, shape, and energy, the three p orbitals differ in orientation. We associate p orbitals with the x , y , and z axes: the p_x orbital lies along the x axis, the p_y along the y axis, and the p_z along the z axis. (There is no relationship between a particular axis and a given m_l value.)

The d Orbital An orbital with $l = 2$ is called a **d orbital**. There are five possible m_l values for $l = 2$: -2 , -1 , 0 , $+1$, and $+2$. Thus, a d orbital has any one of five orientations (Figure 7.18). Four of the five d orbitals have four lobes (a cloverleaf shape) with two mutually perpendicular nodal planes between them and the nucleus at the junction of the lobes (Figure 7.18C). (The orientation of the nodal planes always lies between the orbital lobes.) Three of these orbitals lie in the xy , xz , and yz planes, with their lobes *between* the axes, and are called the d_{xy} , d_{xz} , and d_{yz} orbitals. A fourth, the $d_{x^2-y^2}$ orbital, also lies in the xy plane, but its lobes are *along* the axes. The fifth d orbital, the d_{z^2} , has two major lobes *along* the z axis, and a donut-shaped region girdles the center. An electron in a d orbital spends equal time in all of its lobes.

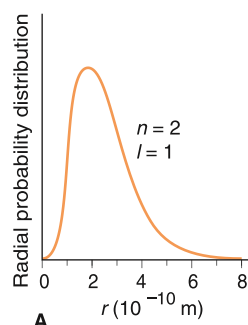
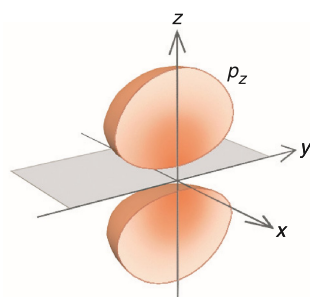
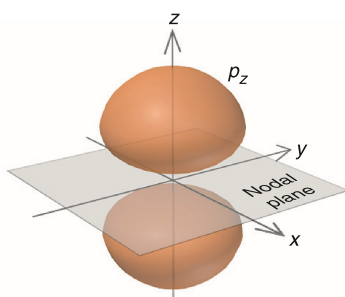


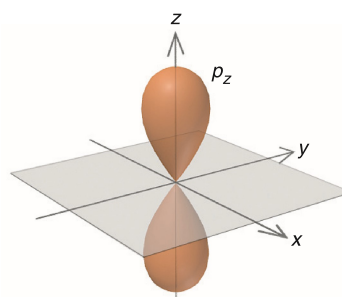
Figure 7.17 The $2p$ orbitals. **A**, A radial probability distribution plot of the $2p$ orbital shows a peak much farther from the nucleus than for the $1s$. **B**, Cross section of an electron cloud depiction of the 90% probability contour of the $2p_z$ orbital shows a nodal plane. **C**, An accurate representation of the $2p_z$ probability contour. **D**, The stylized depiction of the $2p$ probability contour used in the text. **E**, The three (stylized) $2p$ orbitals occupy mutually perpendicular regions of space, contributing to the atom's overall spherical shape.



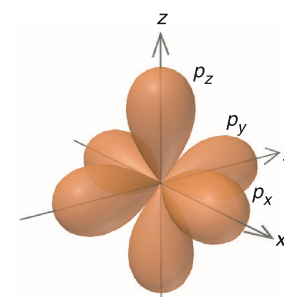
B Cross section of electron cloud depiction



C Accurate probability contour



D Stylized probability contour



E The three p orbitals

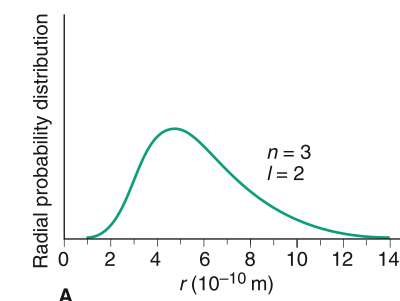
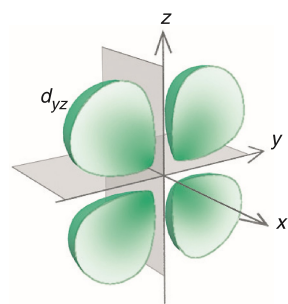
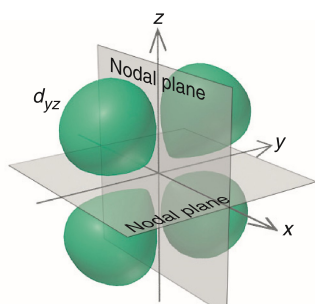
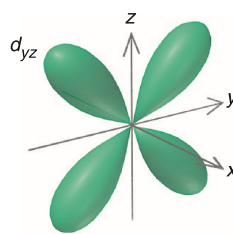
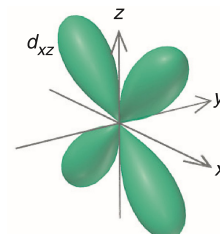
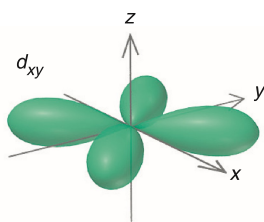
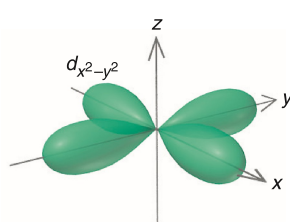
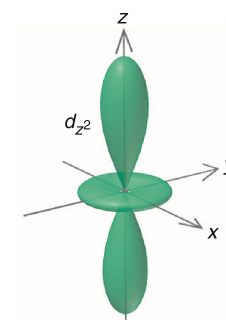
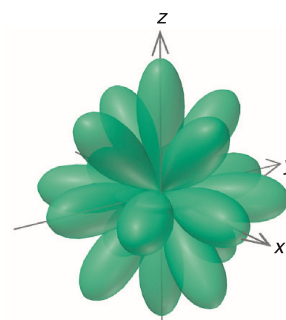
**A**

Figure 7.18 The $3d$ orbitals. **A**, A radial probability distribution plot. **B**, Cross section of an electron cloud depiction of the $3d_{yz}$ orbital probability contour shows two mutually perpendicular nodal planes and lobes lying *between* the axes. **C**, An accurate representation of the $3d_{yz}$ orbital probability contour. **D**, The stylized depiction of the $3d_{yz}$ orbital used in the text. **E**, The $3d_{xz}$ orbital. **F**, The $3d_{xy}$ orbital. **G**, The lobes of the $d_{x^2-y^2}$ orbital lie *along* the x and y axes. **H**, The d_{z^2} orbital has two lobes and a central, donut-shaped region. **I**, A composite of the five $3d$ (stylized) orbitals shows how they contribute to the atom's spherical shape.

**B** Cross section of electron cloud depiction**C** Accurate probability contour**D** Stylized probability contour**E****F****G****H****I** The five d orbitals

In keeping with the quantum-number hierarchy, a d orbital ($l = 2$) must have a principal quantum number of $n = 3$ or higher, so $3d$ is the lowest energy d sublevel. Orbitals in the $4d$ sublevel are larger (extend farther from the nucleus) than the $3d$, and the $5d$ are larger still.

Orbitals with Higher l Values Orbitals with $l = 3$ are f orbitals and have a principal quantum number of at least $n = 4$. Figure 7.19 shows one of the seven f orbitals ($2l + 1 = 7$); each f orbital has a complex, multilobed shape with several nodal planes. Orbitals with $l = 4$ are g orbitals, but they play no known role in chemical bonding.

The Special Case of Energy Levels in the H Atom

With regard to energy levels and sublevels, the H atom is a special case. When an H atom gains energy, its electron occupies an orbital of higher n value, which is (on average) farther from the nucleus. But, because it has just one electron, *hydrogen is the only atom whose energy state depends completely on the principal quantum number, n* . As you'll see in Chapter 8, because of additional nucleus-electron attractions and electron-electron repulsions, the energy states of all other atoms depend on the n and l values of the occupied orbitals. Thus, *for the H atom only*, all four $n = 2$ orbitals (one $2s$ and three $2p$) have the same energy, all nine $n = 3$ orbitals (one $3s$, three $3p$, and five $3d$) have the same energy (Figure 7.20, *next page*), and so forth.

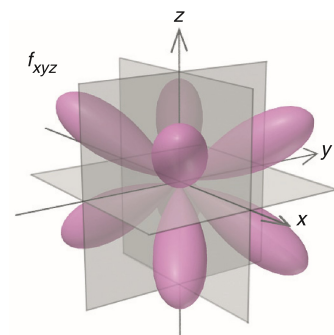
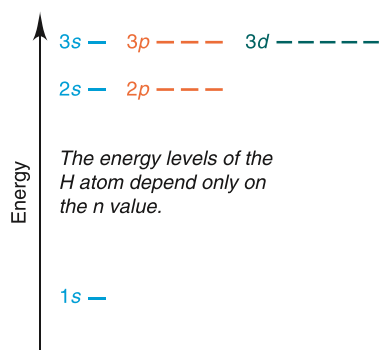


Figure 7.19 The $4f_{xyz}$ orbital, one of the seven $4f$ orbitals.



Summary of Section 7.4

- The atomic orbital (ψ , wave function) is a mathematical description of the electron's wavelike behavior in an atom. The Schrödinger equation converts each allowed wave function to one of the atom's energy states.
- The probability density of finding the electron at a particular location is represented by ψ^2 . For a given energy level, an electron density diagram and a radial probability distribution plot show how the electron occupies the space near the nucleus.
- An atomic orbital is described by three quantum numbers: size (n), shape (l), and orientation (m_l): n limits l to $n - 1$ values, and l limits m_l to $2l + 1$ values.
- An energy level has sublevels with the same n value; a sublevel has orbitals with the same n and l values but differing m_l values.
- A sublevel with $l = 0$ has a spherical (s) orbital; a sublevel with $l = 1$ has three, two-lobed (p) orbitals; and a sublevel with $l = 2$ has five multilobed (d) orbitals.
- In the special case of the H atom, the energy levels depend only on the n value.

Figure 7.20 Energy levels of the H atom.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Describe the relationships among frequency, wavelength, and energy of light, and know the meaning of amplitude; have a general understanding of the electromagnetic spectrum (§7.1) (SPs 7.1, 7.2) (EPs 7.1, 7.2, 7.5, 7.7–7.14)
2. Understand how particles and waves differ and how the work of Planck (quantization of energy) and Einstein (photon theory) changed thinking about it (§7.1) (EPs 7.3, 7.4, 7.6)
3. Explain the Bohr model and the importance of discrete atomic energy levels (§7.2) (SP 7.3) (EPs 7.15–7.28)
4. Describe the wave-particle duality of matter and energy and the theories and experiments that revealed it (particle wavelength, electron diffraction, photon momentum, uncertainty principle) (§7.3) (SP 7.4) (EPs 7.29–7.36)
5. Distinguish between ψ (wave function) and ψ^2 (probability density); understand the meaning of electron density diagrams and radial probability distribution plots; describe the hierarchy of quantum numbers, the hierarchy of levels, sublevels, and orbitals, and the shapes and nodes of s , p , and d orbitals; and determine quantum numbers and sublevel designations (§7.4) (SPs 7.5–7.7) (EPs 7.37–7.49)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 7.1

electromagnetic radiation (217)
frequency (ν) (217)
wavelength (λ) (217)
speed of light (c) (217)
amplitude (218)
electromagnetic spectrum (218)
infrared (IR) (218)
ultraviolet (UV) (218)
refraction (219)
diffraction (220)
quantum number (221)
Planck's constant (h) (221)
quantum (221)

photoelectric effect (221)
photon (221)

Section 7.2

line spectrum (223)
stationary state (224)
ground state (224)
excited state (224)
spectrometry (228)
emission spectrum (228)
absorption spectrum (228)

Section 7.3
de Broglie wavelength (229)
wave-particle duality (231)
uncertainty principle (231)

Section 7.4

quantum mechanics (232)
Schrödinger equation (232)
atomic orbital (wave function) (232)
electron density diagram (233)
electron cloud depiction (233)
radial probability distribution plot (234)
probability contour (234)
principal quantum number (n) (234)

angular momentum quantum number (l) (235)
magnetic quantum number (m_l) (235)
level (shell) (235)
sublevel (subshell) (235)
 s orbital (237)
node (237)
 p orbital (238)
 d orbital (238)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

7.1 Relating the speed of light to its frequency and wavelength (217):

$$c = \nu \times \lambda$$

7.2 Determining the smallest change in an atom's energy (221):

$$\Delta E = h\nu$$

7.3 Calculating the wavelength of any line in the H atom spectrum (Rydberg equation) (223):

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where n_1 and n_2 are positive integers and $n_2 > n_1$ **7.4** Finding the difference between two energy levels in the H atom (226):

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

7.5 Calculating the wavelength of any moving particle (de Broglie wavelength) (229):

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

7.6 Finding the uncertainty in position or speed of a particle (Heisenberg's uncertainty principle) (231):

$$\Delta x \cdot m \Delta u \geq \frac{h}{4\pi}$$

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

$$\begin{aligned} 7.1 \quad \lambda \text{ (nm)} &= \frac{3.00 \times 10^8 \text{ m/s}}{7.23 \times 10^{14} \text{ s}^{-1}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} = 415 \text{ nm} \\ \lambda \text{ (Å)} &= 415 \text{ nm} \times \frac{10 \text{ Å}}{1 \text{ nm}} = 4150 \text{ Å} \end{aligned}$$

$$\begin{aligned} 7.2 \text{ (a) UV: } E &= hc/\lambda \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1 \times 10^{-8} \text{ m}} \\ &= 2 \times 10^{-17} \text{ J} \end{aligned}$$

(b) Visible: $E = 4 \times 10^{-19} \text{ J}$; (c) IR: $E = 2 \times 10^{-21} \text{ J}$
As λ increases, E decreases.**7.3** (a) With $n_{\text{final}} = 3$ for an IR photon:

$$\begin{aligned} \Delta E &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{3^2} - \frac{1}{6^2} \right) \\ &= -2.18 \times 10^{-18} \text{ J} \left(\frac{1}{9} - \frac{1}{36} \right) = -1.82 \times 10^{-19} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{(b) } \lambda &= \frac{hc}{|\Delta E|} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.82 \times 10^{-19} \text{ J}} \times \frac{1 \text{ Å}}{10^{-10} \text{ m}} \\ &= 1.09 \times 10^4 \text{ Å} \end{aligned}$$

$$\begin{aligned} 7.4 \quad u &= \frac{h}{m\lambda} = \frac{6.626 \times 10^{-34} \text{ kg}\cdot\text{m}^2/\text{s}}{(9.11 \times 10^{-31} \text{ kg}) \left(100 \text{ nm} \times \frac{1 \text{ m}}{10^9 \text{ nm}} \right)} \\ &= 7.27 \times 10^3 \text{ m/s} \end{aligned}$$

7.5 $n = 4$, so $l = 0, 1, 2, 3$. In addition to the nine m_l values in Sample Problem 7.5 there are those for $l = 3$:

$$m_l = -3, -2, -1, 0, +1, +2, +3$$

7.6 For $2p$: $n = 2, l = 1, m_l = -1, 0, +1$
For $5f$: $n = 5, l = 3, m_l = -3, -2, -1, 0, +1, +2, +3$ **7.7** (a) $n = 4, l = 1$; (b) name is $2p$; (c) name is $3d$; (d) $n = 2, l = 0, m_l = 0$

PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

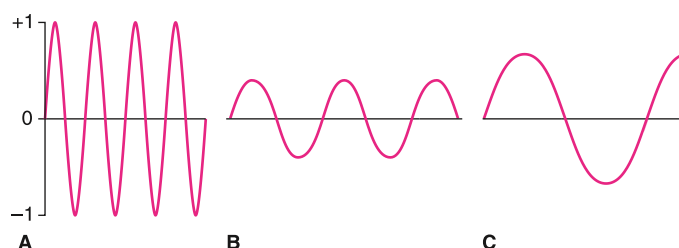
The Nature of Light

(Sample Problems 7.1 and 7.2)

7.1 In what ways are microwave and ultraviolet radiation the same? In what ways are they different?**7.2** Consider the following types of electromagnetic radiation:

- (1) Microwave (2) Ultraviolet (3) Radio waves
(4) Infrared (5) X-ray (6) Visible

- (a) Arrange them in order of increasing wavelength.
(b) Arrange them in order of increasing frequency.
(c) Arrange them in order of increasing energy.

7.3 In the 17th century, Newton proposed that light was a stream of particles. The wave-particle debate continued for over 250 years until Planck and Einstein presented their ideas. Give two pieces of evidence for the wave model and two for the particle model.**7.4** What new idea about energy did Planck use to explain black-body radiation?**7.5** Portions of electromagnetic waves A, B, and C are represented below (not drawn to scale):

Rank them in order of (a) increasing frequency; (b) increasing energy; (c) increasing amplitude. (d) If wave B just barely fails to cause a current when shining on a metal, is wave A or C more likely to do so? (e) If wave B represents visible radiation, is wave A or C more likely to be IR radiation?

7.6 What new idea about light did Einstein use to explain the photoelectric effect? Why does the photoelectric effect exhibit a threshold frequency but not a time lag?

7.7 An AM station broadcasts rock music at “950 on your radio dial.” Units for AM frequencies are given in kilohertz (kHz). Find the wavelength of the station’s radio waves in meters (m), nanometers (nm), and angstroms (Å).

7.8 An FM station broadcasts music at 93.5 MHz (megahertz, or 10^6 Hz). Find the wavelength (in m, nm, and Å) of these waves.

7.9 A radio wave has a frequency of 3.8×10^{10} Hz. What is the energy (in J) of one photon of this radiation?

7.10 An x-ray has a wavelength of 1.3 Å . Calculate the energy (in J) of one photon of this radiation.

7.11 Rank these photons in terms of increasing energy: (a) blue ($\lambda = 453 \text{ nm}$); (b) red ($\lambda = 660 \text{ nm}$); (c) yellow ($\lambda = 595 \text{ nm}$).

7.12 Rank these photons in terms of decreasing energy: (a) IR ($\nu = 6.5 \times 10^{13} \text{ s}^{-1}$); (b) microwave ($\nu = 9.8 \times 10^{11} \text{ s}^{-1}$); (c) UV ($\nu = 8.0 \times 10^{15} \text{ s}^{-1}$).

7.13 Cobalt-60 is a radioactive isotope used to treat cancers. A gamma ray emitted by this isotope has an energy of 1.33 MeV (million electron volts; $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). What is the frequency (in Hz) and the wavelength (in m) of this gamma ray?

7.14 (a) Ozone formation in the upper atmosphere starts when oxygen molecules absorb UV radiation of wavelengths $\leq 242 \text{ nm}$. Find the frequency and energy of the least energetic of these photons. (b) Ozone absorbs radiation of wavelengths 2200–2900 Å, thus protecting organisms from this radiation. Find the frequency and energy of the most energetic of these photons.

Atomic Spectra

(Sample Problem 7.3)

7.15 How is n_1 in the Rydberg equation (Equation 7.3) related to the quantum number n in the Bohr model?

7.16 Distinguish between an absorption spectrum and an emission spectrum. With which did Bohr work?

7.17 Which of these electron transitions correspond to absorption of energy and which to emission?

- (a) $n = 2$ to $n = 4$ (b) $n = 3$ to $n = 1$
(c) $n = 5$ to $n = 2$ (d) $n = 3$ to $n = 4$

7.18 Why couldn’t the Bohr model predict spectra for atoms other than hydrogen?

7.19 Use the Rydberg equation to find the wavelength (in nm) of the photon emitted when an H atom undergoes a transition from $n = 5$ to $n = 2$.

7.20 Use the Rydberg equation to find the wavelength (in Å) of the photon absorbed when an H atom undergoes a transition from $n = 1$ to $n = 3$.

7.21 Calculate the energy difference (ΔE) for the transition in Problem 7.19 for 1 mol of H atoms.

7.22 Calculate the energy difference (ΔE) for the transition in Problem 7.20 for 1 mol of H atoms.

7.23 Arrange the following H atom electron transitions in order of *increasing* frequency of the photon absorbed or emitted:

- (a) $n = 2$ to $n = 4$ (b) $n = 2$ to $n = 1$
(c) $n = 2$ to $n = 5$ (d) $n = 4$ to $n = 3$

7.24 Arrange the following H atom electron transitions in order of *decreasing* wavelength of the photon absorbed or emitted:

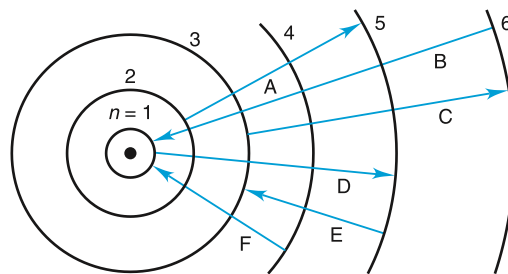
- (a) $n = 2$ to $n = \infty$ (b) $n = 4$ to $n = 20$
(c) $n = 3$ to $n = 10$ (d) $n = 2$ to $n = 1$

7.25 The electron in a ground-state H atom absorbs a photon of wavelength 97.20 nm. To what energy level does it move?

7.26 An electron in the $n = 5$ level of an H atom emits a photon of wavelength 1281 nm. To what energy level does it move?

7.27 In addition to continuous radiation, fluorescent lamps emit some visible lines from mercury. A prominent line has a wavelength of 436 nm. What is the energy (in J) of one photon of it?

7.28 A Bohr-model representation of the H atom is shown below with six electron transitions depicted by arrows:



- (a) Which transitions are absorptions and which are emissions?
(b) Rank the emissions in terms of increasing energy.
(c) Rank the absorptions in terms of increasing wavelength of light absorbed.

The Wave-Particle Duality of Matter and Energy

(Sample Problem 7.4)

7.29 If particles have wavelike motion, why don’t we observe that motion in the macroscopic world?

7.30 Why can’t we overcome the uncertainty predicted by Heisenberg’s principle by building more precise instruments to reduce the error in measurements below the $h/4\pi$ limit?

7.31 A 232-lb fullback runs 40 yd at $19.8 \pm 0.1 \text{ mi/h}$.

- (a) What is his de Broglie wavelength (in meters)?
(b) What is the uncertainty in his position?

7.32 An alpha particle (mass = $6.6 \times 10^{-24} \text{ g}$) emitted by a radium isotope travels at $3.4 \times 10^7 \pm 0.1 \times 10^7 \text{ mi/h}$.

- (a) What is its de Broglie wavelength (in meters)?
(b) What is the uncertainty in its position?

7.33 How fast must a 56.5-g tennis ball travel to have a de Broglie wavelength equal to that of a photon of green light (5400 Å)?

7.34 How fast must a 142-g baseball travel to have a de Broglie wavelength equal to that of an x-ray photon with $\lambda = 100. \text{ pm}$?

7.35 A sodium flame has a characteristic yellow color due to emissions of wavelength 589 nm. What is the mass equivalence of one photon of this wavelength ($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$)?

7.36 A lithium flame has a characteristic red color due to emissions of wavelength 671 nm. What is the mass equivalence of 1 mol of photons of this wavelength ($1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$)?

The Quantum-Mechanical Model of the Atom

(Sample Problems 7.5 to 7.7)

7.37 What physical meaning is attributed to ψ^2 ?

7.38 What does “electron density in a tiny volume of space” mean?

7.39 What feature of an orbital is related to each of the following?

- (a) Principal quantum number (n)
- (b) Angular momentum quantum number (l)
- (c) Magnetic quantum number (m_l)

7.40 How many orbitals in an atom can have each of the following designations: (a) $1s$; (b) $4d$; (c) $3p$; (d) $n = 3$?

7.41 How many orbitals in an atom can have each of the following designations: (a) $5f$; (b) $4p$; (c) $5d$; (d) $n = 2$?

7.42 Give all possible m_l values for orbitals that have each of the following: (a) $l = 2$; (b) $n = 1$; (c) $n = 4, l = 3$.

7.43 Give all possible m_l values for orbitals that have each of the following: (a) $l = 3$; (b) $n = 2$; (c) $n = 6, l = 1$.

7.44 For each of the following, give the sublevel designation, the allowable m_l values, and the number of orbitals:

- (a) $n = 4, l = 2$ (b) $n = 5, l = 1$ (c) $n = 6, l = 3$

7.45 For each of the following, give the sublevel designation, the allowable m_l values, and the number of orbitals:

- (a) $n = 2, l = 0$ (b) $n = 3, l = 2$ (c) $n = 5, l = 1$

7.46 For each of the following sublevels, give the n and l values and the number of orbitals: (a) $5s$; (b) $3p$; (c) $4f$.

7.47 For each of the following sublevels, give the n and l values and the number of orbitals: (a) $6g$; (b) $4s$; (c) $3d$.

7.48 Are the following combinations allowed? If not, show two ways to correct them:

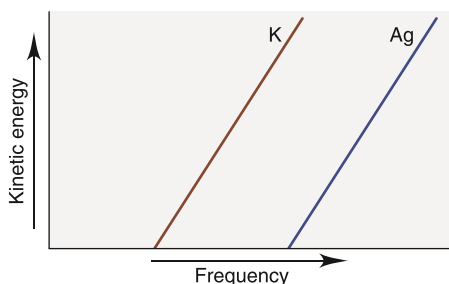
- (a) $n = 2; l = 0; m_l = -1$ (b) $n = 4; l = 3; m_l = -1$
- (c) $n = 3; l = 1; m_l = 0$ (d) $n = 5; l = 2; m_l = +3$

7.49 Are the following combinations allowed? If not, show two ways to correct them:

- (a) $n = 1; l = 0; m_l = 0$ (b) $n = 2; l = 2; m_l = +1$
- (c) $n = 7; l = 1; m_l = +2$ (d) $n = 3; l = 1; m_l = -2$

Comprehensive Problems

7.50 The photoelectric effect is illustrated in a plot of the kinetic energies of electrons ejected from the surface of potassium metal or silver metal at different frequencies of incident light.



- (a) Why don't the lines begin at the origin? (b) Why don't the lines begin at the same point? (c) From which metal will light of shorter wavelength eject an electron? (d) Why are the slopes equal?

7.51 A minimum of $2.0 \times 10^{-17} \text{ J}$ of energy is needed to trigger a series of impulses in the optic nerve that eventually reach the brain. (a) How many photons of red light (700. nm) are needed? (b) How many photons of blue light (475 nm)?

7.52 One reason carbon monoxide (CO) is toxic is that it binds to the blood protein hemoglobin more strongly than oxygen does. The bond between hemoglobin and CO absorbs radiation of 1953 cm^{-1} . (The units are the reciprocal of the wavelength in centimeters.) Calculate the wavelength (in nm and Å) and the frequency (in Hz) of the absorbed radiation.

7.53 A metal ion M^{n+} has a single electron. The highest energy line in its emission spectrum has a frequency of $2.961 \times 10^{16} \text{ Hz}$. Identify the ion.

7.54 TV and radio stations transmit in specific frequency bands of the radio region of the electromagnetic spectrum.

(a) TV channels 2 to 13 (VHF) broadcast signals between the frequencies of 59.5 and 215.8 MHz, whereas FM radio stations broadcast signals with wavelengths between 2.78 and 3.41 m. Do these bands of signals overlap?

(b) AM radio signals have frequencies between 550 and 1600 kHz. Which has a broader transmission band, AM or FM?

7.55 In his explanation of the threshold frequency in the photoelectric effect, Einstein reasoned that the absorbed photon must have a minimum energy to dislodge an electron from the metal surface. This energy is called the *work function* (ϕ) of that metal. What is the longest wavelength of radiation (in nm) that could cause the photoelectric effect in each of these metals: (a) calcium, $\phi = 4.60 \times 10^{-19} \text{ J}$; (b) titanium, $\phi = 6.94 \times 10^{-19} \text{ J}$; (c) sodium, $\phi = 4.41 \times 10^{-19} \text{ J}$?

7.56 You have three metal samples—A, B, and C—that are tantalum (Ta), barium (Ba), and tungsten (W), but you don't know which is which. Metal A emits electrons in response to visible light; metals B and C require UV light. (a) Identify metal A, and find the longest wavelength that removes an electron. (b) What range of wavelengths would distinguish B and C? [The work functions are Ta ($6.81 \times 10^{-19} \text{ J}$), Ba ($4.30 \times 10^{-19} \text{ J}$), and W ($7.16 \times 10^{-19} \text{ J}$); work function is explained in Problem 7.55.]

7.57 A laser (light amplification by stimulated emission of radiation) provides nearly monochromatic high-intensity light. Lasers are used in eye surgery, CD/DVD players, basic research, and many other areas. Some dye lasers can be “tuned” to emit a desired wavelength. Fill in the blanks in the following table of the properties of some common lasers:

Type	λ (nm)	ν (s^{-1})	E (J)	Color
He-Ne	632.8	?	?	?
Ar	?	6.148×10^{14}	?	?
Ar-Kr	?	?	3.499×10^{-19}	?
Dye	663.7	?	?	?

7.58 As space exploration increases, means of communication with humans and probes on other planets are being developed.

- (a) How much time (in s) does it take for a radio wave of frequency $8.93 \times 10^7 \text{ s}^{-1}$ to reach Mars, which is $8.1 \times 10^7 \text{ km}$ from Earth?
- (b) If it takes this radiation 1.2 s to reach the Moon, how far (in m) is the Moon from Earth?

7.59 A ground-state H atom absorbs a photon of wavelength 94.91 nm, and its electron attains a higher energy level. The atom then emits two photons: one of wavelength 1281 nm to reach an