28

Burning gunpowder transfers energy to the atoms of color-producing chemicals, exciting their electrons to higher energy states. In returning to the ground state, the electrons emit light of specific colors, resulting in spectacular fireworks displays. Strontium produces red, and sodium produces yellow/orange.

© Bob Krist/Corbis

ATOMIC PHYSICS

A hot gas emits light of certain characteristic wavelengths that can be used to identify it, much as a fingerprint can identify a person. For a given atom, these characteristic emitted wavelengths can be understood using physical quantities called quantum numbers. The simplest atom is hydrogen, and understanding it can lead to understanding the structure of other atoms and their combinations. The fact that no two electrons in an atom can have the same set of quantum numbers—the Pauli exclusion principle—is extremely important in understanding the properties of complex atoms and the arrangement of elements in the periodic table. Knowledge of atomic structure can be used to describe the mechanisms involved in the production of x-rays and the operation of a laser, among many other applications.

28.1 EARLY MODELS OF THE ATOM

The model of the atom in the days of Newton was a tiny, hard, indestructible sphere. Although this model was a good basis for the kinetic theory of gases, new models had to be devised when later experiments revealed the electronic nature of atoms. J. J. Thomson (1856–1940) suggested a model of the atom as a volume of positive charge with electrons embedded throughout the volume, much like the seeds in a watermelon (Fig. 28.1).

In 1911 Ernest Rutherford (1871–1937) and his students Hans Geiger and Ernest Marsden performed a critical experiment showing that Thomson's model couldn't be correct. In this experiment a beam of positively charged **alpha particles** was projected against a thin metal foil, as in Figure 28.2a (page 892). Most of the alpha particles passed through the foil as if it were empty space, but a few particles were scattered through large angles, some even traveling backwards.

Such large deflections weren't expected. In Thomson's model a positively charged alpha particle would never come close enough to a large positive charge to cause any large-angle deflections. Rutherford explained these results by assuming the positive charge in an atom was concentrated in a region called the **nucleus** that was small relative to the size of the atom. Any electrons belonging to the atom
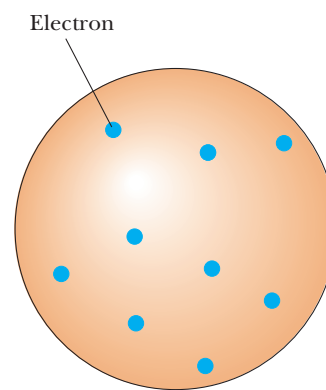
Electron

FIGURE 28.1 Thomson's model of the atom, with the electrons embedded inside the positive charge like seeds in a watermelon.

FIGURE 28.2 (a) Geiger and Marsden's technique for observing the scattering of alpha particles from a thin foil target. The source is a naturally occurring radioactive substance, such as radium. (b) Rutherford's planetary model of the atom.

(a)   (b)
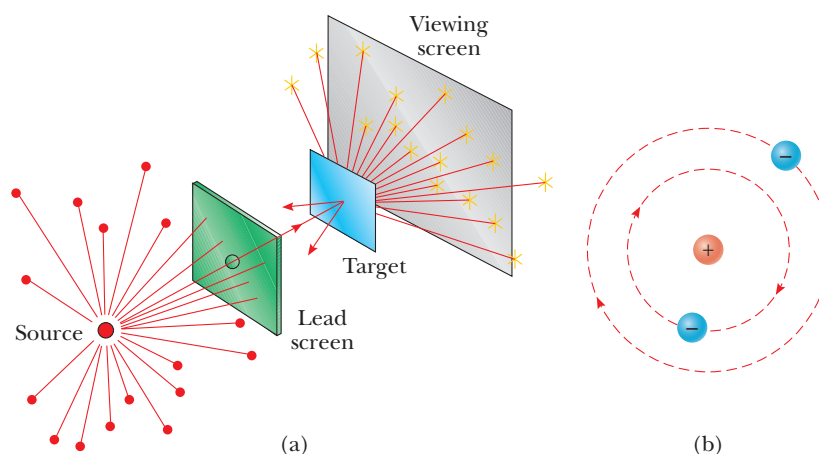
SIR JOSEPH JOHN THOMSON
English Physicist (1856–1940)

Thomson, usually considered the discoverer of the electron, opened up the field of subatomic particle physics with his extensive work on the deflection of cathode rays (electrons) in an electric field. He received the 1906 Nobel Prize in Physics for his discovery of the electron.

were visualized as orbiting the nucleus, much as planets orbit the Sun, as shown in Figure 28.2b. The alpha particles used in Rutherford's experiments were later identified as the nuclei of helium atoms.

There were two basic difficulties with Rutherford's planetary model. First, an atom emits certain discrete characteristic frequencies of electromagnetic radiation and no others; the Rutherford model was unable to explain this phenomenon. Second, the electrons in Rutherford's model undergo a centripetal acceleration. According to Maxwell's theory of electromagnetism, centripetally accelerated charges revolving with frequency f should radiate electromagnetic waves of the same frequency. As the electron radiates energy, the radius of its orbit steadily decreases and its frequency of revolution increases. This process leads to an ever-increasing frequency of emitted radiation and a rapid collapse of the atom as the electron spirals into the nucleus.

Rutherford's model of the atom gave way to that of Niels Bohr, which explained the characteristic radiation emitted from atoms. Bohr's theory, in turn, was supplanted by quantum mechanics. Both the latter theories are based on studies of atomic spectra: the special pattern in the wavelengths of emitted light that is unique for every different element.

28.2 ATOMIC SPECTRA

Suppose an evacuated glass tube is filled with hydrogen (or some other gas) at low pressure. If a voltage applied between metal electrodes in the tube is great enough to produce an electric current in the gas, the tube emits light having a color that depends on the gas inside. (That's how a neon sign works.) When the emitted light is analyzed with a spectrometer, discrete bright lines are observed, each having a different wavelength, or color. Such a series of spectral lines is called an **emission spectrum**. The wavelengths contained in such a spectrum are characteristic of the element emitting the light (Fig. 28.3). Because no two elements emit the same line spectrum, this phenomenon represents a reliable technique for identifying elements in a gaseous substance.

The emission spectrum of hydrogen shown in Figure 28.4 includes four prominent lines that occur at wavelengths of 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm. In 1885 Johann Balmer (1825–1898) found that the wavelengths of these and less prominent lines can be described by the simple empirical equation
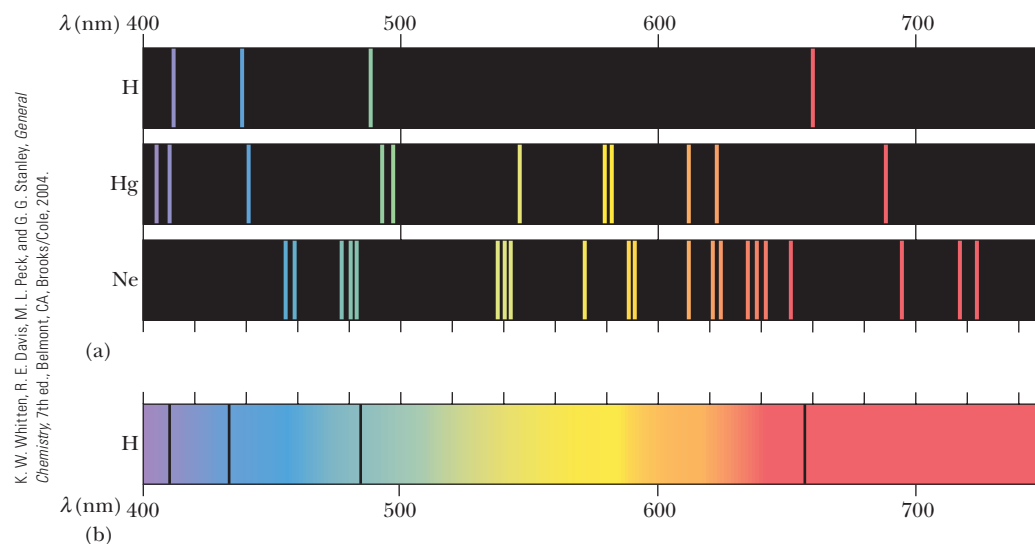
Balmer series →

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$ [28.1]

where n may have integral values of 3, 4, 5, . . . , and R_H is a constant, called the **Rydberg constant**. If the wavelength is in meters, then R_H has the value

Rydberg constant →

$$R_H = 1.097\ 373\ 2 \times 10^7\ \text{m}^{-1}$$ [28.2]

FIGURE 28.3   Visible spectra. (a) Line spectra produced by emission in the visible range for the elements hydrogen, mercury, and neon. (b) The absorption spectrum for hydrogen. The dark absorption lines occur at the same wavelengths as the emission lines for hydrogen shown in (a).
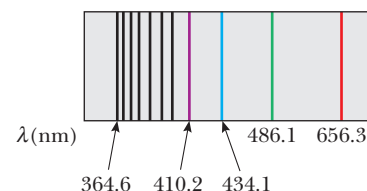
FIGURE 28.4   The Balmer series of spectral lines for atomic hydrogen, with several lines marked with the wavelength in nanometers. The line labeled 364.6 is the shortest-wavelength line and is in the ultraviolet region of the electromagnetic spectrum. The other labeled lines are in the visible region.

The first line in the Balmer series, at 656.3 nm, corresponds to $n = 3$ in Equation 28.1, the line at 486.1 nm corresponds to $n = 4$, and so on. In addition to the Balmer series of spectral lines, the Lyman series was subsequently discovered in the far ultraviolet, with the radiated wavelengths described by a similar equation, with 2^2 in Equation 28.1 replaced by 1^2 and the integer n greater than 1. The Paschen series corresponded to longer wavelengths than the Balmer series, with the 2^2 in Equation 28.1 replaced by 3^2 and $n > 3$. These models, together with many other observations, can be combined to yield the Rydberg equation,

$$\frac{1}{\lambda} = R_H\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$ **[28.3]**   ← Rydberg equation

where m and n are positive integers and $n > m$.

In addition to emitting light at specific wavelengths, an element can absorb light at specific wavelengths. The spectral lines corresponding to this process form what is known as an **absorption spectrum**. An absorption spectrum can be obtained by passing a continuous radiation spectrum (one containing all wavelengths) through a vapor of the element being analyzed. The absorption spectrum consists of a series of dark lines superimposed on the otherwise bright, continuous spectrum. Each line in the absorption spectrum of a given element coincides with a line in the emission spectrum of the element. If hydrogen is the absorbing vapor, for example, dark lines will appear at the visible wavelengths 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm, as shown in Figures 28.3b and 28.4.

The absorption spectrum of an element has many practical applications. For example, the continuous spectrum of radiation emitted by the Sun must pass through the cooler gases of the solar atmosphere before reaching Earth. The various absorption lines observed in the solar spectrum have been used to identify elements in the solar atmosphere, including helium, which was previously unknown.

APPLICATION

Discovery of Helium

APPLYING PHYSICS 28.1   THERMAL OR SPECTRAL

On observing a yellow candle flame, your laboratory partner claims that the light from the flame originates from excited sodium atoms in the flame. You disagree, stating that because the candle flame is hot, the radiation must be thermal in origin. Before the disagreement becomes more intense, how could you determine who is correct?

Explanation   A simple determination could be made by observing the light from the candle flame through

a spectrometer, which is a slit and diffraction grating combination discussed in Chapter 25. If the spectrum of the light is continuous, it's probably thermal in origin. If the spectrum shows discrete lines, it's atomic in origin. The results of the experiment show that the light is indeed thermal in origin and originates from random molecular motion in the candle flame.

APPLYING PHYSICS 28.2   AURORAS

At extreme northern latitudes, the aurora borealis provides a beautiful and colorful display in the night sky. A similar display, called the aurora australis, occurs near the southern polar region. What is the origin of the various colors seen in the auroras?

Explanation   The aurora results from high-speed particles interacting with Earth's magnetic field and entering the atmosphere. When these particles col-

lide with molecules in the atmosphere, they excite the molecules just as does the voltage in the spectrum tubes discussed earlier in this section. In response the molecules emit colors of light according to the characteristic spectra of their atomic constituents. For our atmosphere, the primary constituents are nitrogen and oxygen, which provide the red, blue, and green colors of the aurora.
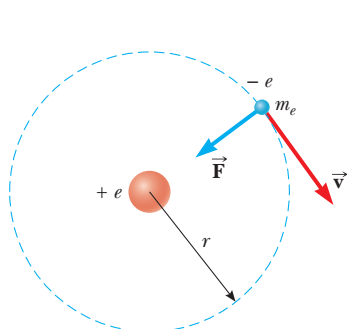
FIGURE 28.5   Diagram representing Bohr's model of the hydrogen atom. The orbiting electron is allowed only in specific orbits of discrete radii.

28.3   THE BOHR MODEL   **Read All**

At the beginning of the 20th century, it wasn't understood why atoms of a given element emitted and absorbed only certain wavelengths. In 1913 Bohr provided an explanation of the spectra of hydrogen that includes some features of the currently accepted theory. His model of the hydrogen atom included the following basic assumptions:

1. The electron moves in circular orbits about the proton under the influence of the Coulomb force of attraction, as in Figure 28.5. The Coulomb force produces the electron's centripetal acceleration.
2. Only certain electron orbits are stable and allowed. In these orbits no energy in the form of electromagnetic radiation is emitted, so the total energy of the atom remains constant.
3. Radiation is emitted by the hydrogen atom when the electron "jumps" from a more energetic initial state to a less energetic state. The "jump" can't be visualized or treated classically. The frequency f of the radiation emitted in the jump is related to the change in the atom's energy, given by

$$E_i - E_f = hf \qquad \textbf{[28.4]}$$

where E_i is the energy of the initial state, E_f is the energy of the final state, h is Planck's constant, and $E_i > E_f$. The frequency of the radiation is *independent of the frequency of the electron's orbital motion.*
4. The circumference of an electron's orbit must contain an integral number of de Broglie wavelengths,

$$2\pi r = n\lambda \qquad n = 1, 2, 3, \ldots$$

(See Fig. 28.6.) Because the de Broglie wavelength of an electron is $\lambda = h/m_e v$, we can write the preceding equation as

$$m_e vr = n\hbar \qquad n = 1, 2, 3, \ldots \qquad \textbf{[28.5]}$$

where $\hbar = h/2\pi$.

With these four assumptions, we can calculate the allowed energies and emission wavelengths of the hydrogen atom using the model pictured in Figure 28.5, in which the electron travels in a circular orbit of radius r with an orbital speed v. The electrical potential energy of the atom is

$$PE = k_e \frac{q_1 q_2}{r} = k_e \frac{(-e)(e)}{r} = -k_e \frac{e^2}{r}$$
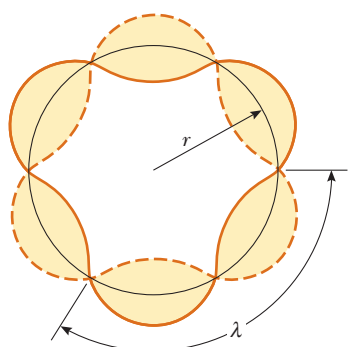
FIGURE 28.6   Standing-wave pattern for an electron wave in a stable orbit of hydrogen. There are three full wavelengths in this orbit.

where k_e is the Coulomb constant. Assuming the nucleus is at rest, the total energy E of the atom is the sum of the kinetic and potential energy:

$$E = KE + PE = \tfrac{1}{2}m_e v^2 - k_e \frac{e^2}{r} \qquad \textbf{[28.6]}$$

By Newton's second law, the electric force of attraction on the electron, $k_e e^2/r^2$, must equal $m_e a_r$, where $a_r = v^2/r$ is the centripetal acceleration of the electron, so

$$m_e \frac{v^2}{r} = k_e \frac{e^2}{r^2} \qquad \textbf{[28.7]}$$

Multiply both sides of this equation by $r/2$ to get an expression for the kinetic energy:

$$\tfrac{1}{2}m_e v^2 = \frac{k_e e^2}{2r} \qquad \textbf{[28.8]}$$

Combining this result with Equation 28.6 gives an expression for the energy of the atom,

$$E = -\frac{k_e e^2}{2r} \qquad \textbf{[28.9]}$$

where the negative value of the energy indicates that the electron is bound to the proton.

An expression for r can be obtained by solving Equations 28.5 and 28.7 for v^2 and equating the results:

$$v^2 = \frac{n^2 \hbar}{m_e^2 r^2} = \frac{k_e e^2}{m_e r}$$

$$r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \qquad n = 1, 2, 3, \ldots \qquad \textbf{[28.10]}$$

This equation is based on the assumption that the **electron can exist only in certain allowed orbits determined by the integer n**.

The orbit with the smallest radius, called the **Bohr radius**, a_0, corresponds to $n = 1$ and has the value

$$a_0 = \frac{\hbar^2}{m k_e e^2} = 0.052\ 9 \text{ nm} \qquad \textbf{[28.11]}$$

A general expression for the radius of any orbit in the hydrogen atom is obtained by substituting Equation 28.11 into Equation 28.10:

$$r_n = n^2 a_0 = n^2 (0.052\ 9 \text{ nm}) \qquad \textbf{[28.12]}$$

The first three Bohr orbits for hydrogen are shown in Active Figure 28.7.

Equation 28.10 can then be substituted into Equation 28.9 to give the following expression for the energies of the quantum states:

$$E_n = -\frac{m_e k_e^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots \qquad \textbf{[28.13]}$$

← The energy levels of hydrogen

If we substitute numerical values into Equation 28.13, we obtain

$$E_n = -\frac{13.6}{n^2} \text{ eV} \qquad \textbf{[28.14]}$$

The lowest-energy state, or **ground state**, corresponds to $n = 1$ and has an energy $E_1 = -m_e k_e^2 e^4/2\hbar^2 = -13.6$ eV. The next state, corresponding to $n = 2$, has an energy $E_2 = E_1/4 = -3.40$ eV, and so on. An energy level diagram showing the
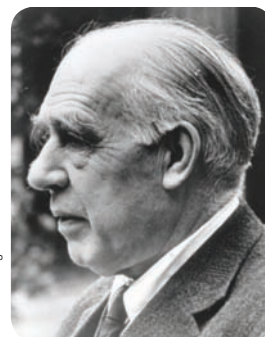
NIELS BOHR
Danish Physicist (1885–1962)

Bohr was an active participant in the early development of quantum mechanics and provided much of its philosophical framework. During the 1920s and 1930s he headed the Institute for Advanced Studies in Copenhagen, where many of the world's best physicists came to exchange ideas. Bohr was awarded the 1922 Nobel Prize in Physics for his investigation of the structure of atoms and of the radiation emanating from them.


$9a_0$

$4a_0$

$-e$

a_0

$+e$
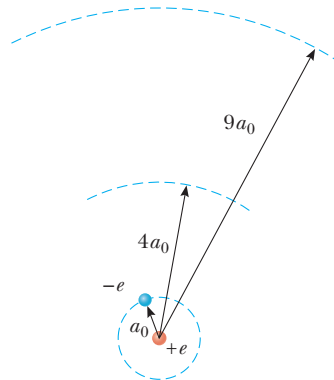
ACTIVE FIGURE 28.7
The first three circular orbits predicted by the Bohr model of the hydrogen atom.

ACTIVE FIGURE 28.8
An energy level diagram for hydrogen. Quantum numbers are given on the left, and energies (in electron volts) are given on the right. Vertical arrows represent the four lowest-energy transitions for each of the spectral series shown. The colored arrows for the Balmer series indicate that this series results in visible light.
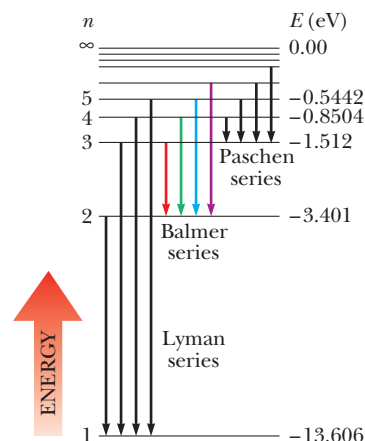
energies of these stationary states and the corresponding quantum numbers is given in Active Figure 28.8. The uppermost level shown, corresponding to $E = 0$ and $n \rightarrow \infty$, represents the state for which the electron is completely removed from the atom. In this state the electron's *KE* and *PE* are both zero, which means that the electron is at rest infinitely far away from the proton. The minimum energy required to ionize the atom—that is, to completely remove the electron—is called the **ionization energy**. The ionization energy for hydrogen is 13.6 eV.

Equations 28.4 and 28.13 and the third Bohr postulate show that if the electron jumps from one orbit with quantum number n_i to a second orbit with quantum number n_f, it emits a photon of frequency f given by

$$f = \frac{E_i - E_f}{\hbar} = \frac{m_e k_e^2 e^4}{4\pi\,\hbar^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$ **[28.15]**

where $n_f < n_i$.

To convert this equation into one analogous to the Rydberg equation, substitute $f = c/\lambda$ and divide both sides by c, obtaining

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$ **[28.16]**

where

$$R_H = \frac{m_e k_e^2 e^4}{4\pi\,c\hbar^3}$$ **[28.17]**

Substituting the known values of m_e, k_e, e, c, and $\hbar$ verifies that this theoretical value for the Rydberg constant is in excellent agreement with the experimentally derived value in Equations 12.1 through 12.3. When Bohr demonstrated this agreement, it was recognized as a major accomplishment of his theory.

We can use Equation 28.16 to evaluate the wavelengths for the various series in the hydrogen spectrum. For example, in the Balmer series, $n_f = 2$ and $n_i = 3$, 4, 5, . . . (Eq. 28.1). The energy level diagram for hydrogen shown in Active Figure 28.8 indicates the origin of the spectral lines. The transitions between levels are represented by vertical arrows. Note that whenever a transition occurs between a state designated by n_i to one designated by n_f (where $n_i > n_f$), a photon with a frequency $(E_i - E_f)/h$ is emitted. This process can be interpreted as follows: the lines in the visible part of the hydrogen spectrum arise when the electron jumps from the third, fourth, or even higher orbit to the second orbit. The Bohr theory successfully predicts the wavelengths of all the observed spectral lines of hydrogen.

TIP 28.1 Energy Depends on n Only for Hydrogen

Because all other quantities in Equation 28.13 are constant, the energy levels of a hydrogen atom depend only on the quantum number n. For more complicated atoms, the energy levels depend on other quantum numbers as well.

EXAMPLE 28.1 The Balmer Series for Hydrogen

Goal Calculate the wavelength, frequency, and energy of a photon emitted during an electron transition in an atom.

Problem The Balmer series for the hydrogen atom corresponds to electronic transitions that terminate in the state with quantum number $n = 2$, as shown in Figure 28.9. **(a)** Find the longest-wavelength photon emitted in the Balmer series and determine its frequency and energy. **(b)** Find the shortest-wavelength photon emitted in the same series.

Strategy This problem is a matter of substituting values into Equation 28.16. The frequency can then be obtained from $c = f\lambda$ and the energy from $E = hf$. The longest-wavelength photon corresponds to the one that is emitted when the electron jumps from the $n_i = 3$ state to the $n_f = 2$ state. The shortest-wavelength photon corresponds to the one that is emitted when the electron jumps from $n_i = \infty$ to the $n_f = 2$ state.
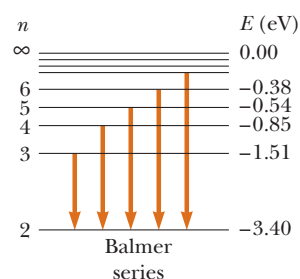
FIGURE 28.9 (Example 28.1) Transitions responsible for the Balmer series for the hydrogen atom. All transitions terminate at the $n = 2$ level.

Solution

(a) Find the longest-wavelength photon emitted in the Balmer series and determine its frequency and energy.

Substitute into Equation 28.16, with $n_i = 3$ and $n_f = 2$:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_H\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5R_H}{36}$$

Take the reciprocal and substitute, finding the wavelength:

$$\lambda = \frac{36}{5R_H} = \frac{36}{5(1.097 \times 10^7 \text{ m}^{-1})} = 6.563 \times 10^{-7} \text{ m}$$

$$= \boxed{656.3 \text{ nm}}$$

Now use $c = f\lambda$ to obtain the frequency:

$$f = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{6.563 \times 10^{-7} \text{ m}} = \boxed{4.568 \times 10^{14} \text{ Hz}}$$

Calculate the photon's energy by substituting into Equation 27.5:

$$E = hf = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(4.568 \times 10^{14} \text{ Hz})$$

$$= 3.027 \times 10^{-19} \text{ J} = \boxed{1.892 \text{ eV}}$$

(b) Find the shortest-wavelength photon emitted in the Balmer series.

Substitute into Equation 28.16, with $1/n_i \to 0$ as $n_i \to \infty$ and $n_f = 2$:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = R_H\left(\frac{1}{2^2} - 0\right) = \frac{R_H}{4}$$

Take the reciprocal and substitute, finding the wavelength:

$$\lambda = \frac{4}{R_H} = \frac{4}{(1.097 \times 10^7 \text{ m}^{-1})} = 3.646 \times 10^{-7} \text{ m}$$

$$= \boxed{364.6 \text{ nm}}$$

Remarks The first wavelength is in the red region of the visible spectrum. We could also obtain the energy of the photon by using Equation 28.4 in the form $hf = E_3 - E_2$, where E_2 and E_3 are the energy levels of the hydrogen atom, calculated from Equation 28.14. Note that this photon is the lowest-energy photon in the Balmer series because it involves the smallest energy change. The second photon, the most energetic, is in the ultraviolet region.

QUESTION 28.1

What is the upper-limit energy of a photon that can be emitted from hydrogen due to the transition of an electron between energy levels? Explain.

EXERCISE 28.1
(a) Calculate the energy of the shortest-wavelength photon emitted in the Balmer series for hydrogen. (b) Calculate the wavelength of the photon emitted when an electron transits from $n = 4$ to $n = 2$.

Answers   (a) 3.40 eV (b) 486 nm

Bohr's Correspondence Principle

In our study of relativity in Chapter 26, we found that Newtonian mechanics can't be used to describe phenomena that occur at speeds approaching the speed of light. Newtonian mechanics is a special case of relativistic mechanics and applies only when v is much smaller than c. Similarly, **quantum mechanics is in agreement with classical physics when the energy differences between quantized levels are very small**. This principle, first set forth by Bohr, is called the **correspondence principle**.

Hydrogen-like Atoms

The analysis used in the Bohr theory is also successful when applied to *hydrogen-like* atoms. An atom is said to be hydrogen-like when it contains only one electron. Examples are singly ionized helium, doubly ionized lithium, and triply ionized beryllium. The results of the Bohr theory for hydrogen can be extended to hydrogen-like atoms by substituting Ze^2 for e^2 in the hydrogen equations, where Z is the atomic number of the element. For example, Equations 28.13 and 28.16 through 28.17 become

$$E_n = -\frac{m_e k_e^{\,2} Z^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots \qquad \text{[28.18]}$$

and

$$\frac{1}{\lambda} = \frac{m_e k_e^{\,2} Z^2 e^4}{4\pi c\hbar^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad \text{[28.19]}$$

Although many attempts were made to extend the Bohr theory to more complex, multi-electron atoms, the results were unsuccessful. Even today, only approximate methods are available for treating multi-electron atoms.

> **QUICK QUIZ 28.1**   Consider a hydrogen atom and a singly ionized helium atom. Which atom has the lower ground state energy? (a) Hydrogen (b) Helium (c) The ground state energy is the same for both.

EXAMPLE 28.2   Singly Ionized Helium

Goal   Apply the modified Bohr theory to a hydrogen-like atom.

Problem   Singly ionized helium, He$^+$, a hydrogen-like system, has one electron in the 1s orbit when the atom is in its ground state. Find **(a)** the energy of the system in the ground state in electron volts and **(b)** the radius of the ground-state orbit.

Strategy   Part (a) requires substitution into the modified Bohr model, Equation 28.18. In part (b) modify Equation 28.10 for the radius of the Bohr orbits by replacing e^2 by Ze^2, where Z is the number of protons in the nucleus.

Solution
(a) Find the energy of the system in the ground state.

Write Equation 28.18 for the energies of a hydrogen-like system:

$$E_n = -\frac{m_e k_e^{\,2} Z^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right)$$

Substitute the constants and convert to electron volts:

$$E_n = -\frac{Z^2(13.6\ \text{eV})}{n^2}$$

Substitute $Z = 2$ (the atomic number of helium) and $n = 1$ to obtain the ground state energy:

$$E_1 = -4(13.6\ \text{eV}) = \boxed{-54.4\ \text{eV}}$$

(b) Find the radius of the ground state.

Generalize Equation 28.10 to a hydrogen-like atom by substituting Ze^2 for e^2:

$$r_n = \frac{n^2\hbar^2}{m_e k_e Z e^2} = \frac{n^2}{Z}(a_0) = \frac{n^2}{Z}(0.052\ 9\ \text{nm})$$

For our case, $n = 1$ and $Z = 2$:

$$r_1 = \boxed{0.026\ 5\ \text{nm}}$$

Remarks   Notice that for higher Z, the energy of a hydrogen-like atom is lower, which means that the electron is more tightly bound than in hydrogen. The result is a smaller atom, as seen in part (b).

QUESTION 28.2

When an electron undergoes a transition from a higher to lower state in singly ionized helium, how will the energy of the emitted photon compare with the analogous transition in hydrogen? Explain.

EXERCISE 28.2

Repeat the problem for the first excited state of doubly ionized lithium ($Z = 3$, $n = 2$).

Answers   (a) $E_2 = -30.6\ \text{eV}$ (b) $r_2 = 0.070\ 5\ \text{nm}$

Bohr's theory was extended in an ad hoc manner so as to include further details of atomic spectra. All these modifications were replaced with the theory of quantum mechanics, developed independently by Werner Heisenberg and Erwin Schrödinger.

28.4   QUANTUM MECHANICS AND THE HYDROGEN ATOM

One of the first great achievements of quantum mechanics was the solution of the wave equation for the hydrogen atom. Although the details of the solution are beyond the level of this book, the solution and its implications for atomic structure can be described.

According to quantum mechanics, the energies of the allowed states are in exact agreement with the values obtained by the Bohr theory (Eq. 28.13) when the allowed energies depend only on the principal quantum number n.

In addition to the principal quantum number, two other quantum numbers emerged from the solution of the Schrödinger wave equation: the **orbital quantum number**, ℓ, and the **orbital magnetic quantum number**, m_ℓ.

The effect of the magnetic quantum number m_ℓ can be observed in spectra when magnetic fields are present, which results in a splitting of individual spectral lines into several lines. This splitting is called the *Zeeman effect*. Figure 28.10 shows a single spectral line being split into three closely spaced lines. This indicates that the energy of an electron is slightly modified when the atom is immersed in a magnetic field.

The allowed ranges of the values of these quantum numbers are as follows:

- The value of n can range from 1 to ∞ in integer steps.
- The value of ℓ can range from 0 to $n - 1$ in integer steps.
- The value of m_ℓ can range from $-\ell$ to ℓ in integer steps.

From these rules, it can be seen that for a given value of n, there are n possible values of ℓ, whereas for a given value of ℓ, there are $2\ell + 1$ possible values of m_ℓ.
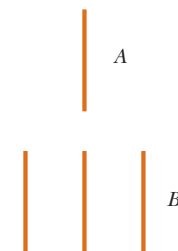
FIGURE 28.10   A single line (A) can split into three separate lines (B) in a magnetic field.

TABLE 28.1

Three Quantum Numbers for the Hydrogen Atom

Quantum Number	Name	Allowed Values	Number of Allowed States
n	Principal quantum number	$1, 2, 3, \ldots$	Any number
ℓ	Orbital quantum number	$0, 1, 2, \ldots, n-1$	n
m_ℓ	Orbital magnetic quantum number	$-\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell$	$2\ell + 1$

TABLE 28.2

Shell and Subshell Notation

n	Shell Symbol	ℓ	Subshell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

For example, if $n = 1$, there is only 1 value of ℓ, $\ell = 0$. Because $2\ell + 1 = 2 \cdot 0 + 1 = 1$, there is only one value of m_ℓ, which is $m_\ell = 0$. If $n = 2$, the value of ℓ may be 0 or 1; if $\ell = 0$, then $m_\ell = 0$; but if $\ell = 1$, then m_ℓ may be 1, 0, or −1. Table 28.1 summarizes the rules for determining the allowed values of ℓ and m_ℓ for a given value of n.
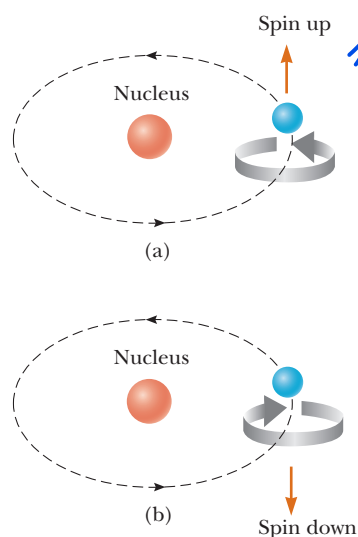
For historical reasons, **all states with the same principal quantum number n are said to form a shell**. Shells are identified by the letters K, L, M, . . . , which designate the states for which $n = 1, 2, 3$, and so forth. **The states with given values of n and ℓ are said to form a subshell**. The letters $s, p, d, f, g, \ldots$ are used to designate the states for which $\ell = 0, 1, 2, 3, 4, \ldots$. These notations are summarized in Table 28.2.

States that violate the rules given in Table 28.1 can't exist. One state that cannot exist, for example, is the $2d$ state, which would have $n = 2$ and $\ell = 2$. This state is not allowed because the highest allowed value of ℓ is $n - 1$, or 1 in this case. So for $n = 2$, $2s$ and $2p$ are allowed states, but $2d, 2f, \ldots$ are not. For $n = 3$, the allowed states are $3s$, $3p$, and $3d$.

In general, for a given value of n, there are n^2 states with distinct pairs of values of ℓ and m_ℓ.

QUICK QUIZ 28.2   When the principal quantum number is $n = 5$, how many different values of (a) ℓ and (b) m_ℓ are possible? (c) How many states have distinct pairs of values of ℓ and m_ℓ?

Spin

In high-resolution spectrometers, close examination of one of the prominent lines of sodium vapor shows that it is, in fact, two very closely spaced lines. The wavelengths of these lines occur in the yellow region of the spectrum, at 589.0 nm and 589.6 nm. This kind of splitting is referred to as **fine structure**. In 1925, when this doublet was first noticed, atomic theory couldn't explain it, so Samuel Goudsmit and George Uhlenbeck, following a suggestion by Austrian physicist Wolfgang Pauli, proposed the introduction of a fourth quantum number to describe atomic energy levels, m_s, called the **spin magnetic quantum number**. Spin isn't found in the solutions of Schrödinger's equations; rather, it naturally arises in the Dirac equation, derived in 1927 by Paul Dirac. This equation is important in relativistic quantum theory.

In describing the spin quantum number, it's convenient (but technically incorrect) to think of the electron as spinning on its axis as it orbits the nucleus, just as Earth spins on its axis as it orbits the Sun. Unlike the spin of a world, however, there are only two ways in which the electron can spin as it orbits the nucleus, as shown in Figure 28.11. If the direction of spin is as shown in Figure 28.11a, the electron is said to have "spin up." If the direction of spin is reversed as in Figure 28.11b, the electron is said to have "spin down." The energy of the electron is slightly different for the two spin directions, and this energy difference accounts for the sodium doublet. The quantum numbers associated with electron spin are

FIGURE 28.11   As an electron moves in its orbit about the nucleus, its spin can be either (a) up or (b) down.

$m_s = \frac{1}{2}$ for the spin-up state and $m_s = -\frac{1}{2}$ for the spin-down state. As we see in Example 28.3, this new quantum number doubles the number of allowed states specified by the quantum numbers n, ℓ, and m_ℓ.

For each electron, there are two spin states. A subshell corresponding to a given factor of ℓ can contain no more than $2(2\ell + 1)$ electrons. This number is used because electrons in a subshell must have unique pairs of the quantum numbers (m_ℓ, m_s). There are $2\ell + 1$ different magnetic quantum numbers m_ℓ and two different spin quantum numbers m_s, making $2(2\ell + 1)$ unique pairs (m_ℓ, m_s). For example, the p subshell ($\ell = 1$) is filled when it contains $2(2 \cdot 1 + 1) = 6$ electrons. This fact can be extended to include all four quantum numbers, as will be important to us later when we discuss the *Pauli exclusion principle*.

> **TIP 28.2 The Electron Isn't Actually Spinning**
>
> The electron is *not* physically spinning. Electron spin is a purely quantum effect that gives the electron an angular momentum *as if* it were physically spinning.

EXAMPLE 28.3   The $n = 2$ Level of Hydrogen

Goal   Count and tabulate distinct quantum states and determine their energy based on atomic energy level.

Problem   (a) Determine the number of states with a unique set of values for ℓ, m_ℓ, and m_s in the hydrogen atom for $n = 2$. (b) Tabulate the distinct possible quantum states, including spin. (c) Calculate the energies of these states in the absence of a magnetic field, disregarding small differences caused by spin.

Strategy   This problem is a matter of counting, following the quantum rules for n, ℓ, m_ℓ, and m_s. "Unique" means that no other quantum state has the same set of numbers. The energies—disregarding spin or Zeeman splitting in magnetic fields—are all the same because all states have the same principal quantum number, $n = 2$.

Solution

(a) Determine the number of states with a unique set of values for ℓ and m_ℓ in the hydrogen atom for $n = 2$.

Determine the different possible values of ℓ for $n = 2$:

$0 \le \ell \le n - 1$, so for $n = 2$, $0 \le \ell \le 1$ and $\ell = 0$ or 1

Find the different possible values of m_ℓ for $\ell = 0$:

$-\ell \le m_\ell \le \ell$, so $-0 \le m_\ell \le 0$ implies that $m_\ell = 0$

List the distinct pairs of (ℓ, m_ℓ) for $\ell = 0$:

There is only one: $(\ell, m_\ell) = (0, 0)$.

Find the different possible values of m_ℓ for $\ell = 1$:

$-\ell \le m_\ell \le \ell$, so $-1 \le m_\ell \le 1$ implies that $m_\ell = -1, 0,$ or 1

List the distinct pairs of (ℓ, m_ℓ) for $\ell = 1$:

There are three: $(\ell, m_\ell) = (1, -1), (1, 0),$ and $(1, 1)$.

Sum the results for $\ell = 0$ and $\ell = 1$ and multiply by 2 to account for the two possible spins of each state:

Number of states $= 2(1 + 3) =$ **8**

(b) Tabulate the different possible sets of quantum numbers.

Use the results of part (a) and recall that the spin quantum number is always $+\frac{1}{2}$ or $-\frac{1}{2}$.

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

(c) Calculate the energies of these states.

The common energy of all the states, disregarding Zeeman splitting and spin, can be found with Equation 28.14:

$$E_n = -\frac{13.6 \text{ eV}}{n^2} \quad \rightarrow \quad E_2 = -\frac{13.6 \text{ eV}}{2^2} = -3.40 \text{ eV}$$

Remarks   Although these states normally have the same energy, the application of a magnetic field causes them to take slightly different energies centered around the energy corresponding to $n = 2$. In addition, the slight difference in energy due to spin state was neglected.
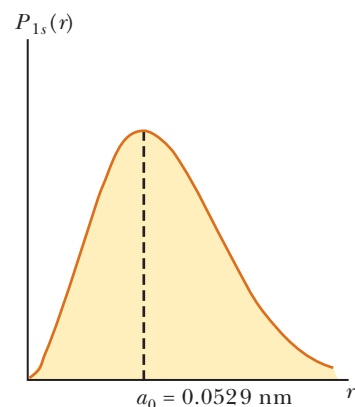
QUESTION 28.3
Which of the four quantum numbers are never negative?

EXERCISE 28.3
(a) Determine the number of states with a unique pair of values for ℓ, m_ℓ, and m_s in the $n = 3$ level of hydrogen.
(b) Determine the energies of those states, disregarding any splitting effects.

Answers   (a) 18   (b) $E_3 = -1.51$ eV

$P_{1s}(r)$

$a_0 = 0.0529$ nm r

FIGURE 28.12   The probability per unit length of finding the electron versus distance from the nucleus for the hydrogen atom in the $1s$ (ground) state. Note that the graph has its maximum value when r equals the first Bohr radius, a_0.
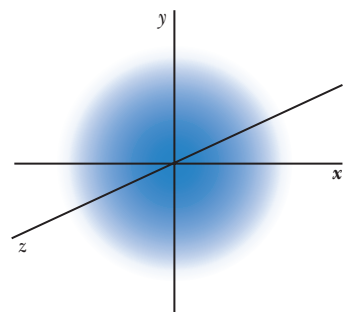
FIGURE 28.13   The spherical electron cloud for the hydrogen atom in its $1s$ state.

Electron Clouds

The solution of the wave equation, as discussed in Section 27.7, yields a wave function Ψ that depends on the quantum numbers n, ℓ, and m_ℓ. Recall that if p is a point and V_p a very small volume containing that point, then $\Psi^2 V_p$ is approximately the probability of finding the electron inside the volume V_p. Figure 28.12 gives the probability per unit length of finding the electron at various distances from the nucleus in the $1s$ state of hydrogen ($n = 1$, $\ell = 0$, and $m_\ell = 0$). Note that the curve peaks at a value of $r = 0.052\ 9$ nm, the Bohr radius for the first ($n = 1$) electron orbit in hydrogen. This peak means that there is a maximum probability of finding the electron in a small interval of a given, fixed length centered at that distance from the nucleus. As the curve indicates, however, there is also a probability of finding the electron in such a small interval centered at any other distance from the nucleus. In quantum mechanics the electron is not confined to a particular orbital distance from the nucleus, as assumed in the Bohr model. The electron may be found at various distances from the nucleus, but finding it in a small interval centered on the Bohr radius has the greatest probability. Quantum mechanics also predicts that the wave function for the hydrogen atom in the ground state is spherically symmetric; hence, the electron can be found in a spherical region surrounding the nucleus. This is in contrast to the Bohr theory, which confines the position of the electron to points in a plane. The quantum mechanical result is often interpreted by viewing the electron as a cloud surrounding the nucleus. An attempt at picturing this cloud-like behavior is shown in Figure 28.13. The densest regions of the cloud represent those locations where the electron is most likely to be found.

If a similar analysis is carried out for the $n = 2$, $\ell = 0$ state of hydrogen, a peak of the probability curve is found at $4a_0$, whereas for the $n = 3$, $\ell = 0$ state, the curve peaks at $9a_0$. In general, quantum mechanics predicts a most probable electron distance to the nucleus that is in agreement with the location predicted by the Bohr theory.

28.5   THE EXCLUSION PRINCIPLE AND THE PERIODIC TABLE

Sir said short question from here.

The state of an electron in a hydrogen atom is specified by four quantum numbers: n, ℓ, m_ℓ, and m_s. As it turns out, the state of any electron in any other atom can also be specified by this same set of quantum numbers.

How many electrons in an atom can have a particular set of quantum numbers? This important question was answered by Pauli in 1925 in a powerful statement known as the **Pauli exclusion principle**:

No two electrons in an atom can ever have the same set of values for the set of quantum numbers n, ℓ, m_ℓ, and m_s.

← The Pauli exclusion principle

The Pauli exclusion principle explains the electronic structure of complex atoms as a succession of filled levels with different quantum numbers increasing in energy, where the outermost electrons are primarily responsible for the chemical properties of the element. If this principle weren't valid, every electron would end up in the lowest energy state of the atom and the chemical behavior of the elements would be grossly different. Nature as we know it would not exist, and *we* would not exist to wonder about it!

As a general rule, the order that electrons fill an atom's subshell is as follows. Once one subshell is filled, the next electron goes into the vacant subshell that is lowest in energy. If the atom were not in the lowest energy state available to it, it would radiate energy until it reached that state. A subshell is filled when it contains $2(2\ell + 1)$ electrons. This rule is based on the analysis of quantum numbers to be described later. Following the rule, shells and subshells can contain numbers of electrons according to the pattern given in Table 28.3.

The exclusion principle can be illustrated by examining the electronic arrangement in a few of the lighter atoms. *Hydrogen* has only one electron, which, in its ground state, can be described by either of two sets of quantum numbers: $1, 0, 0, \frac{1}{2}$ or $1, 0, 0, -\frac{1}{2}$. The electronic configuration of this atom is often designated as $1s^1$. The notation $1s$ refers to a state for which $n = 1$ and $\ell = 0$, and the superscript indicates that one electron is present in this level.

Neutral *helium* has two electrons. In the ground state, the quantum numbers for these two electrons are $1, 0, 0, \frac{1}{2}$ and $1, 0, 0, -\frac{1}{2}$. No other possible combinations of quantum numbers exist for this level, and we say that the K shell is filled. The helium electronic configuration is designated as $1s^2$.

Neutral *lithium* has three electrons. In the ground state, two of them are in the $1s$ subshell and the third is in the $2s$ subshell because the latter subshell is lower in energy than the $2p$ subshell. Hence, the electronic configuration for lithium is $1s^2 2s^1$.

A list of electronic ground-state configurations for a number of atoms is provided in Table 28.4 (page 904). In 1871 Dmitry Mendeleyev (1834–1907), a Russian chemist, arranged the elements known at that time into a table according to their atomic masses and chemical similarities. The first table Mendeleyev proposed

TIP 28.3 The Exclusion Principle Is More General

The exclusion principle stated here is a limited form of the more general exclusion principle, which states that no two *fermions* (particles with spin $\frac{1}{2}$, $\frac{3}{2}$ . . .) can be in the same quantum state.

TABLE 28.3

Number of Electrons in Filled Subshells and Shells

Shell	Subshell	Number of Electrons in Filled Subshell	Number of Electrons in Filled Shell
K ($n = 1$)	$s(\ell = 0)$	2	2
L ($n = 2$)	$s(\ell = 0)$	2	8
	$p(\ell = 1)$	6	
M ($n = 3$)	$s(\ell = 0)$	2	18
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
N ($n = 4$)	$s(\ell = 0)$	2	32
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
	$f(\ell = 3)$	14	

CERN/Courtesy of AIP Emilio Segre Visual Archives

WOLFGANG PAULI
Austrian Theoretical Physicist
(1900–1958)

The extremely talented Pauli first gained public recognition at the age of 21 with a masterful review article on relativity. In 1945 he received the Nobel Prize in Physics for his discovery of the exclusion principle. Among his other major contributions were the explanation of the connection between particle spin and statistics, the theory of relativistic quantum electrodynamics, the neutrino hypothesis, and the hypothesis of nuclear spin.

TABLE 28.4

Electronic Configurations of Some Elements

Z	Symbol	Ground-State Configuration		Ionization Energy (eV)	Z	Symbol	Ground-State Configuration		Ionization Energy (eV)
1	H		$1s^1$	13.595	19	K	[Ar]	$4s^1$	4.339
2	He		$1s^2$	24.581	20	Ca		$4s^2$	6.111
					21	Sc		$3d4s^2$	6.54
3	Li	[He]	$2s^1$	5.390	22	Ti		$3d^24s^2$	6.83
4	Be		$2s^2$	9.320	23	V		$3d^34s^2$	6.74
5	B		$2s^22p^1$	8.296	24	Cr		$3d^54s^1$	6.76
6	C		$2s^22p^2$	11.256	25	Mn		$3d^54s^2$	7.432
7	N		$2s^22p^3$	14.545	26	Fe		$3d^64s^2$	7.87
8	O		$2s^22p^4$	13.614	27	Co		$3d^74s^2$	7.86
9	F		$2s^22p^5$	17.418	28	Ni		$3d^84s^2$	7.633
10	Ne		$2s^22p^6$	21.559	29	Cu		$3d^{10}4s^1$	7.724
					30	Zn		$3d^{10}4s^2$	9.391
11	Na	[Ne]	$3s^1$	5.138	31	Ga		$3d^{10}4s^24p^1$	6.00
12	Mg		$3s^2$	7.644	32	Ge		$3d^{10}4s^24p^2$	7.88
13	Al		$3s^23p^1$	5.984	33	As		$3d^{10}4s^24p^3$	9.81
14	Si		$3s^23p^2$	8.149	34	Se		$3d^{10}4s^24p^4$	9.75
15	P		$3s^23p^3$	10.484	35	Br		$3d^{10}4s^24p^5$	11.84
16	S		$3s^23p^4$	10.357	36	Kr		$3d^{10}4s^24p^6$	13.996
17	Cl		$3s^23p^5$	13.01					
18	Ar		$3s^23p^6$	15.755					

Note: The bracket notation is used as a shorthand method to avoid repetition in indicating inner-shell electrons. Thus, [He] represents $1s^2$, [Ne] represents $1s^22s^22p^6$, [Ar] represents $1s^22s^22p^63s^23p^6$, and so on.

contained many blank spaces, and he boldly stated that the gaps were there only because those elements had not yet been discovered. By noting the column in which these missing elements should be located, he was able to make rough predictions about their chemical properties. Within 20 years of this announcement, those elements were indeed discovered.

The elements in our current version of the periodic table are still arranged so that all those in a vertical column have similar chemical properties. For example, consider the elements in the last column: He (helium), Ne (neon), Ar (argon), Kr (krypton), Xe (xenon), and Rn (radon). The outstanding characteristic of these elements is that they don't normally take part in chemical reactions, joining with other atoms to form molecules, and are therefore classified as inert. They are called the *noble gases*. We can partially understand their behavior by looking at the electronic configurations shown in Table 28.4. The element helium has the electronic configuration $1s^2$. In other words, one shell is filled. The electrons in this filled shell are considerably separated in energy from the next available level, the $2s$ level.

The electronic configuration for neon is $1s^22s^22p^6$. Again, the outer shell is filled and there is a large difference in energy between the $2p$ level and the $3s$ level. Argon has the configuration $1s^22s^22p^63s^23p^6$. Here, the $3p$ subshell is filled and there is a wide gap in energy between the $3p$ subshell and the $3d$ subshell. Through all the noble gases, the pattern remains the same: a noble gas is formed when either a shell or a subshell is filled, and there is a large gap in energy before the next possible level is encountered.

The elements in the first column of the periodic table are called the *alkali metals* and are highly active chemically. Referring to Table 28.4, we can understand why these elements interact so strongly with other elements. These alkali metals all have a single outer electron in an *s* subshell. This electron is shielded from the nucleus by all the electrons in the inner shells. Consequently, it's only loosely

bound to the atom and can readily be accepted by other atoms that bind it more tightly to form molecules.

The elements in the seventh column of the periodic table are called the *halogens* and are also highly active chemically. All these elements are lacking one electron in a subshell, so they readily accept electrons from other atoms to form molecules.

QUICK QUIZ 28.3   Krypton (atomic number 36) has how many electrons in its next-to-outer shell ($n = 3$)? (a) 2 (b) 4 (c) 8 (d) 18

28.6   CHARACTERISTIC X-RAYS

X-rays are emitted when a metal target is bombarded with high-energy electrons. The x-ray spectrum typically consists of a broad continuous band and a series of intense sharp lines that are dependent on the type of metal used for the target, as shown in Figure 28.14. These discrete lines, called **characteristic x-rays**, were discovered in 1908, but their origin remained unexplained until the details of atomic structure were developed.

The first step in the production of characteristic x-rays occurs when a bombarding electron collides with an electron in an inner shell of a target atom with sufficient energy to remove the electron from the atom. The vacancy created in the shell is filled when an electron in a higher level drops down into the lower-energy level containing the vacancy. The time it takes for that to happen is very short, less than 10^{-9} s. The transition is accompanied by the emission of a photon with energy equaling the difference in energy between the two levels. Typically, the energy of such transitions is greater than 1 000 eV, and the emitted x-ray photons have wavelengths in the range of 0.01 nm to 1 nm.

We assume the incoming electron has dislodged an atomic electron from the innermost shell, the K shell. If the vacancy is filled by an electron dropping from the next-higher shell, the L shell, the photon emitted in the process is referred to as the K_α line on the curve of Figure 28.14. If the vacancy is filled by an electron dropping from the M shell, the line produced is called the K_β line.

Other characteristic x-ray lines are formed when electrons drop from upper levels to vacancies other than those in the K shell. For example, L lines are produced when vacancies in the L shell are filled by electrons dropping from higher shells. An L_α line is produced as an electron drops from the M shell to the L shell, and an L_β line is produced by a transition from the N shell to the L shell.

We can estimate the energy of the emitted x-rays as follows. Consider two electrons in the K shell of an atom whose atomic number is Z. Each electron partially shields the other from the charge of the nucleus, Ze, so each is subject to an effective nuclear charge $Z_{eff} = (Z - 1)e$. We can now use a modified form of Equation 28.18 to estimate the energy of either electron in the K shell (with $n = 1$). We have

$$E_K = -m_e Z_{eff}^2 \frac{k_e^2 e^4}{2\hbar^2} = -Z_{eff}^2 E_0$$

where E_0 is the ground-state energy. Substituting $Z_{eff} = Z - 1$ gives

$$E_K = -(Z - 1)^2 (13.6 \text{ eV}) \qquad \text{[28.20]}$$

As Example 28.4 shows, we can estimate the energy of an electron in an L or an M shell in a similar fashion. Taking the energy difference between these two levels, we can then calculate the energy and wavelength of the emitted photon.

In 1914 Henry G. J. Moseley plotted the Z values for a number of elements against $\sqrt{1/\lambda}$, where λ is the wavelength of the K_α line for each element. He found that such a plot produced a straight line, as in Figure 28.15, which is consistent with our rough calculations of the energy levels based on Equation 28.20. From his plot, Moseley was able to determine the Z values of other elements, providing a periodic chart in excellent agreement with the known chemical properties of the elements.
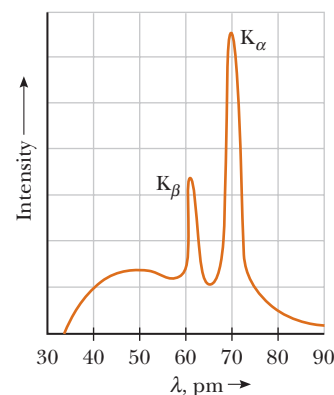
FIGURE 28.14   The x-ray spectrum of a metal target consists of a broad continuous spectrum (bremsstrahlung) plus a number of sharp lines that are due to *characteristic x-rays*. The data shown were obtained when 35-keV electrons bombarded a molybdenum target. Note that 1 pm = 10^{-12} m = 0.001 nm.
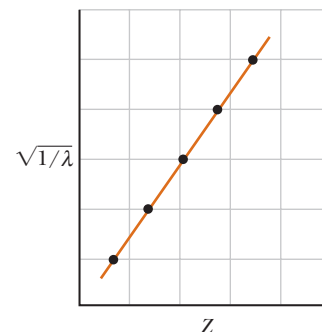
FIGURE 28.15   A Moseley plot of $\sqrt{1/\lambda}$ versus Z, where λ is the wavelength of the K_α x-ray line of the element of atomic number Z.

EXAMPLE 28.4   Characteristic X-Rays

Goal   Calculate the energy and wavelength of characteristic x-rays.

Problem   Estimate the energy and wavelength of the characteristic x-ray emitted from a tungsten target when an electron drops from an M shell ($n = 3$ state) to a vacancy in the K shell ($n = 1$ state).

Strategy   Develop two estimates, one for the electron in the K shell ($n = 1$) and one for the electron in the M shell ($n = 3$). For the K-shell estimate, we can use Equa-tion 28.20. For the M-shell estimate, we need a new equation. There is 1 electron in the K shell (because one is missing) and there are 8 in the L shell, making 9 electrons shielding the nuclear charge. Therefore $Z_{eff} = 74 - 9$ and $E_M = -Z_{eff}^2 E_3$, where E_3 is the energy of the $n = 3$ level in hydrogen. The difference $E_M - E_K$ is the energy of the photon.

Solution

Use Equation 28.20 to estimate the energy of an electron in the K shell of tungsten, atomic number $Z = 74$:

$$E_K = -(74 - 1)^2 (13.6 \text{ eV}) = -72\,500 \text{ eV}$$

Estimate the energy of an electron in the M shell in the same way:

$$E_M = -Z_{eff}^2 E_3 = -(Z - 9)^2 \frac{E_0}{3^2} = -(74 - 9)^2 \frac{(13.6 \text{ eV})}{9}$$

$$= -6\,380 \text{ eV}$$

Calculate the difference in energy between the M and K shells:

$$E_M - E_K = -6\,380 \text{ eV} - (-72\,500 \text{ eV}) = \boxed{66\,100 \text{ eV}}$$

Find the wavelength of the emitted x-ray:

$$\Delta E = hf = h\frac{c}{\lambda} \quad \rightarrow \quad \lambda = \frac{hc}{\Delta E}$$

$$\lambda = \frac{(6.63 \times 10^{-34} \text{ J·s})(3.00 \times 10^8 \text{ m/s})}{(6.61 \times 10^4 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})}$$

$$= 1.88 \times 10^{-11} \text{ m} = \boxed{0.018\,8 \text{ nm}}$$

Remarks   These estimates depend on the amount of shielding of the nuclear charge, which can be difficult to determine.

QUESTION 28.4

Could a transition from the L shell to the K shell ever result in a more energetic photon than a transition from the M to the K shell? Discuss.

EXERCISE 28.4

Repeat the problem for a $2p$ electron transiting from the L shell to the K shell. (For technical reasons, the L shell electron must have $\ell = 1$, so a single $1s$ electron and two $2s$ electrons shield the nucleus.)

Answers   (a) 5.54×10^4 eV   (b) $0.022\,4$ nm
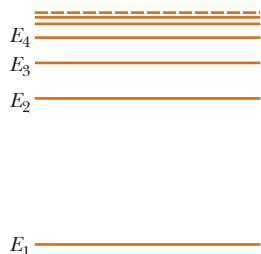
FIGURE 28.16   Energy level diagram of an atom with various allowed states. The lowest-energy state, E_1, is the ground state. All others are excited states.

28.7   ATOMIC TRANSITIONS AND LASERS

We have seen that an atom will emit radiation only at certain frequencies that correspond to the energy separation between the various allowed states. Consider an atom with many allowed energy states, labeled E_1, E_2, E_3, . . . , as in Figure 28.16. When light is incident on the atom, only those photons with energy hf matching the energy separation ΔE between two levels can be absorbed by the atom. A schematic diagram representing this **stimulated absorption process** is shown in Active Figure 28.17. At ordinary temperatures, most of the atoms in a sample are in the ground state. If a vessel containing many atoms of a gas is illuminated with a light beam containing all possible photon frequencies (that is, a continuous spec-
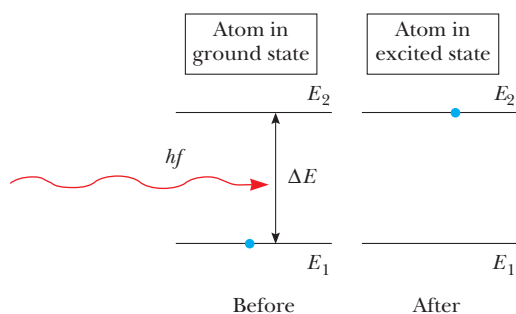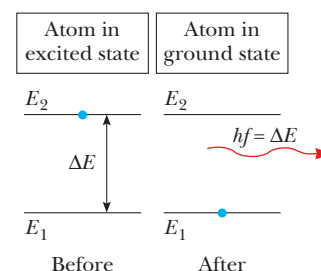
ACTIVE FIGURE 28.17 Diagram representing the process of *stimulated absorption* of a photon by an atom. The blue dot represents an electron. The electron is transferred from the ground state to the excited state when the atom absorbs a photon of energy $hf = E_2 - E_1$.

FIGURE 28.18 Diagram representing the process of *spontaneous emission* of a photon by an atom that is initially in the excited state E_2. When the electron falls to the ground state, the atom emits a photon of energy $hf = E_2 - E_1$.
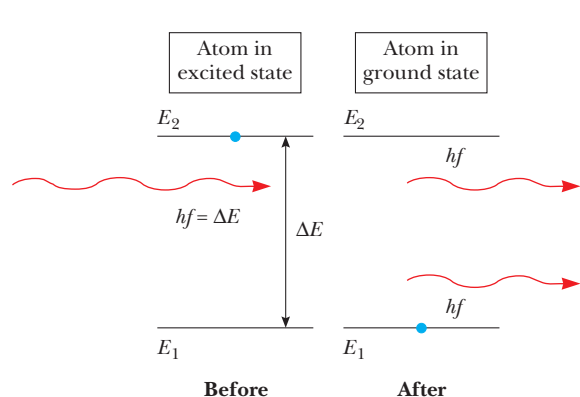
trum), only those photons of energies $E_2 - E_1$, $E_3 - E_1$, $E_4 - E_1$, and so on can be absorbed. As a result of this absorption, some atoms are raised to various allowed higher-energy levels, called **excited states**.

Once an atom is in an excited state, there is a constant probability that it will jump back to a lower level by emitting a photon, as shown in Figure 28.18. This process is known as **spontaneous emission**. Typically, an atom will remain in an excited state for only about 10^{-8} s.

A third process that is important in lasers, **stimulated emission**, was predicted by Einstein in 1917. Suppose an atom is in the excited state E_2, as in Figure 28.19, and a photon with energy $hf = E_2 - E_1$ is incident on it. The incoming photon increases the probability that the excited atom will return to the ground state and thereby emit a second photon having the same energy hf. Note that two identical photons result from stimulated emission: the incident photon and the emitted photon. *The emitted photon is exactly in phase with the incident photon*. These photons can stimulate other atoms to emit photons in a chain of similar processes.

The intense, coherent (in-phase) light in a laser (*l*ight *a*mplification by *s*timulated *e*mission of *r*adiation) is a result of stimulated emission. In a laser, voltages can be used to put more electrons in excited states than in the ground state. This process is called **population inversion**. The excited state of the system must be a *metastable state*, which means that its lifetime must be relatively long. When that is the case, stimulated emission will occur before spontaneous emission. Finally, the photons produced must be retained in the system for a while so that they can stimulate the production of still more photons. This step can be done with mirrors, one of which is partly transparent.
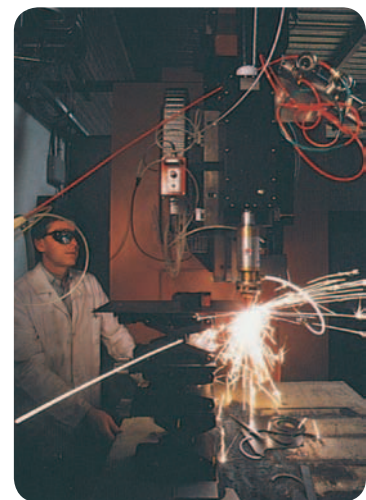
Figure 28.20 is an energy level diagram for the neon atom in a helium–neon gas laser. The mixture of helium and neon is confined to a glass tube sealed at

Scientist checking the performance of an experimental laser-cutting device mounted on a robot arm. The laser is being used to cut through a metal plate.

FIGURE 28.19 Diagram representing the process of *stimulated emission* of a photon by an incoming photon of energy hf. Initially, the atom is in the excited state. The incoming photon stimulates the atom to emit a second photon of energy $hf = E_2 - E_1$.
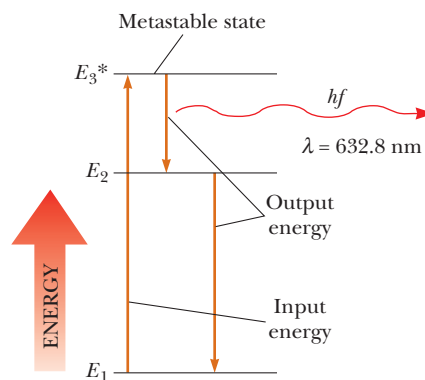
FIGURE 28.20 Energy level diagram for the neon atom in a helium–neon laser. The atom emits 632.8-nm photons through stimulated emission in the transition $E_3^* \rightarrow E_2$. This transition is the source of coherent light in the laser.

the ends by mirrors. A high voltage applied to the tube causes electrons to sweep through it, colliding with the atoms of the gas and raising them into excited states. Neon atoms are excited to state $E_3{}^*$ through this process and also as a result of collisions with excited helium atoms. When a neon atom makes a transition to state E_2, it stimulates emission by neighboring excited atoms. The result is the production of coherent light at a wavelength of 632.8 nm. Figure 28.21 summarizes the steps in the production of a laser beam.

Lasers that cover wavelengths in the infrared, visible, and ultraviolet regions of the spectrum are now available. Applications include the surgical "welding" of detached retinas, "lasik" surgery, precision surveying and length measurement, a potential source for inducing nuclear fusion reactions, precision cutting of metals and other materials, and telephone communication along optical fibers.

APPLICATION

Laser Technology
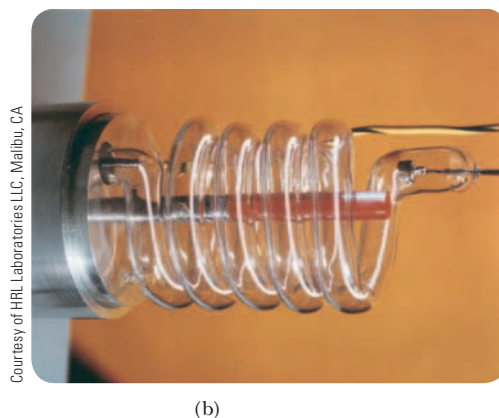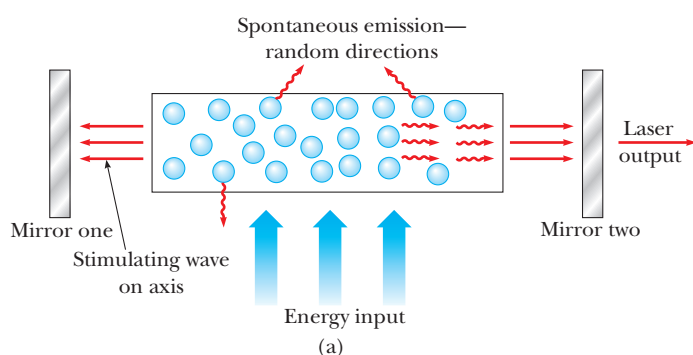
FIGURE 28.21   (a) Steps in the production of a laser beam. The tube contains atoms, which represent the active medium. An external source of energy (optical, electrical, etc.) is needed to "pump" the atoms to excited energy states. The parallel end mirrors provide the feedback of the stimulating wave. (b) Photograph of the first ruby laser, showing the flash lamp surrounding the ruby rod.

SUMMARY

28.3   The Bohr Model

The **Bohr model** of the atom is successful in describing the spectra of atomic hydrogen and hydrogen-like ions. One basic assumption of the model is that the electron can exist only in certain orbits such that its angular momentum mvr is an integral multiple of $\hbar$, where $\hbar$ is Planck's constant divided by 2π. Assuming circular orbits and a Coulomb force of attraction between electron and proton, the energies of the quantum states for hydrogen are

$$E_n = -\frac{m_e k_e{}^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots \quad [28.13]$$

where k_e is the Coulomb constant, e is the charge on the electron, and n is an integer called a **quantum number**.

If the electron in the hydrogen atom jumps from an orbit having quantum number n_i to an orbit having quantum number n_f, it emits a photon of frequency f, given by

$$f = \frac{E_i - E_f}{h} = \frac{m_e k_e{}^2 e^4}{4\pi\hbar^3}\left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right) \quad [28.15]$$

Bohr's **correspondence principle** states that quantum mechanics is in agreement with classical physics when the quantum numbers for a system are very large.

The Bohr theory can be generalized to hydrogen-like atoms, such as singly ionized helium or doubly ionized lithium. This modification consists of replacing e^2 by Ze^2 wherever it occurs.

28.4   Quantum Mechanics and the Hydrogen Atom

One of the many successes of quantum mechanics is that the quantum numbers n, ℓ, and m_ℓ associated with atomic structure arise directly from the mathematics of the theory. The quantum number n is called the **principal quantum number**, ℓ is the **orbital quantum number**, and m_ℓ is

the **orbital magnetic quantum number**. These quantum numbers can take only certain values: $1 \leq n < \infty$ in integer steps, $0 \leq \ell \leq n - 1$, and $-\ell \leq m_\ell \leq \ell$. In addition, a fourth quantum number, called the **spin magnetic quantum number** m_s, is needed to explain a fine doubling of lines in atomic spectra, with $m_s = \pm\frac{1}{2}$.

28.5 The Exclusion Principle and the Periodic Table

An understanding of the periodic table of the elements became possible when Pauli formulated the **exclusion principle**, which states that no two electrons in the same atom can have the same values for the set of quantum numbers n, ℓ, m_ℓ, and m_s. A particular set of these quantum numbers is called a quantum state. The exclusion principle explains how different energy levels in atoms are populated. Once one subshell is filled, the next electron goes into the vacant subshell that is lowest in energy. Atoms with similar configurations in their outermost shell have similar chemical properties and are found in the same column of the periodic table.

28.6 Characteristic X-Rays

Characteristic x-rays are produced when a bombarding electron collides with an electron in an inner shell of an atom with sufficient energy to remove the electron from the atom. The vacancy is filled when an electron from a higher level drops down into the level containing the vacancy, emitting a photon in the x-ray part of the spectrum in the process.

28.7 Atomic Transitions and Lasers

When an atom is irradiated by light of all different wavelengths, it will only absorb only wavelengths equal to the difference in energy of two of its energy levels. This phenomenon, called **stimulated absorption**, places an atom's electrons into **excited states**. Atoms in an excited state have a probability of returning to a lower level of excitation by **spontaneous emission**. The wavelengths that can be emitted are the same as the wavelengths that can be absorbed. If an atom is in an excited state and a photon with energy $hf = E_2 - E_1$ is incident on it, the probability of emission of a second photon of this energy is greatly enhanced. The emitted photon is exactly in phase with the incident photon. This process is called **stimulated emission**. The emitted and original photon can then stimulate more emission, creating an amplifying effect.

  Lasers are monochromatic, coherent light sources that work on the principle of **stimulated emission** of radiation from a system of atoms.

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MULTIPLE-CHOICE QUESTIONS

1. An electron in the $n = 5$ energy level of hydrogen undergoes a transition to the $n = 3$ energy level. What wavelength photon does the atom emit in this process? (a) 1.28×10^{-6} m (b) 2.37×10^{-6} m (c) 4.22×10^{-7} m (d) 3.04×10^{-6} m (e) 5.92×10^{-5} m

2. A beryllium atom is stripped of all but one of its electrons. What is the energy of the ground state? (a) -13.6 eV (b) -218 eV (c) -122 eV (d) -40.8 eV (e) 0

3. An electron in a hydrogen atom is in the $n = 3$ energy level. How many different quantum states are available to it? (a) 1 (b) 2 (c) 8 (d) 9 (e) 18

4. Consider an atom having four distinct energy levels. If an electron is able to make transitions between any two levels, how many different wavelengths of radiation could the atom emit? (a) 2 (b) 3 (c) 4 (d) 5 (e) 6

5. The periodic table is based mainly on which of the following principles? (a) It is based on the uncertainty principle. (b) All electrons in an atom must have the same set of quantum numbers. (c) No two electrons in an atom can have the same set of quantum numbers. (d) All electrons in an atom are in orbitals having the same energy. (e) Energy is conserved in all interactions.

6. If an electron in an atom has the quantum numbers $n = 3$, $\ell = 2$, $m_\ell = 1$, and $m_s = \frac{1}{2}$, what state is it in? (a) $3s$ (b) $3p$ (c) $3d$ (d) $4d$ (e) $3f$

7. Which of the following electronic configurations are not allowed? (a) $2s^2 2p^6$ (b) $3s^2 3p^7$ (c) $3d^7 4s^2$ (d) $3d^{10} 4s^2 4p^6$ (e) $1s^2 2s^2 2d^1$

8. What can be concluded about a hydrogen atom with an electron in the d state? (a) The atom is ionized. (b) The orbital angular momentum of the atom is zero. (c) The orbital angular momentum of the atom is not zero. (d) The atom is in its ground state. (e) The principal quantum number is $n = 2$.

9. If an electron had a spin of $\frac{3}{2}$, its spin quantum number could have the following four values: $m_s = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}$, and $-\frac{3}{2}$. If that were true, which one of the following elements with a filled shell would become the first of the noble gases? (a) He with 2 electrons (b) Li with 3 electrons (c) Be with 4 electrons (d) B with 5 electrons (e) C with 6 electrons

10. In relating Bohr's theory to the de Broglie wavelength of electrons, why does the circumference of an electron's orbit become nine times greater when the electron moves from the $n = 1$ level to the $n = 3$ level? (a) There are nine times as many wavelengths in the new orbit. (b) The wavelength of the electron becomes nine times as long. (c) There are three times as many wavelengths, and each wavelength is three times as long. (d) The electron is moving nine times faster. (e) The atom is partly ionized.

CONCEPTUAL QUESTIONS

1. In the hydrogen atom, the quantum number n can increase without limit. Because of this fact, does the frequency of possible spectral lines from hydrogen also increase without limit?

2. Does the light emitted by a neon sign constitute a continuous spectrum or only a few colors? Defend your answer.

3. In an x-ray tube, if the energy with which the electrons strike the metal target is increased, the wavelengths of the characteristic x-rays do not change. Why not?

4. Must an atom first be ionized before it can emit light? Discuss.

5. Is it possible for a spectrum from an x-ray tube to show the continuous spectrum of x-rays without the presence of the characteristic x-rays?

6. Suppose the electron in the hydrogen atom obeyed classical mechanics rather than quantum mechanics. Why should such a hypothetical atom emit a continuous spectrum rather than the observed line spectrum?

7. When a hologram is produced, the system (including light source, object, beam splitter, and so on) must be held motionless within a quarter of the light's wavelength. Why?

8. If matter has a wave nature, why is that not observable in our daily experience?

9. Discuss some consequences of the exclusion principle.

10. Can the electron in the ground state of hydrogen absorb a photon of energy less than 13.6 eV? Can it absorb a photon of energy greater than 13.6 eV? Explain.

11. Why do lithium, potassium, and sodium exhibit similar chemical properties?

12. List some ways in which quantum mechanics altered our view of the atom pictured by the Bohr theory.

13. It is easy to understand how two electrons (one with spin up, one with spin down) can fill the $1s$ shell for a helium atom. How is it possible that eight more electrons can fit into the $2s$, $2p$ level to complete the $1s2s^22p^6$ shell for a neon atom?

14. The ionization energies for Li, Na, K, Rb, and Cs are 5.390, 5.138, 4.339, 4.176, and 3.893 eV, respectively. Explain why these values are to be expected in terms of the atomic structures.

15. Why is stimulated emission so important in the operation of a laser?

PROBLEMS

1, 2, 3 = straightforward, intermediate, challenging

GP = denotes guided problem

ecp = denotes enhanced content problem

🔬 = biomedical application

☐ = denotes full solution available in *Student Solutions Manual/Study Guide*

SECTION 28.1 EARLY MODELS OF THE ATOM

SECTION 28.2 ATOMIC SPECTRA

1. **ecp** The wavelengths of the Lyman series for hydrogen are given by

$$\frac{1}{\lambda} = R_H\left(1 - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, \ldots$$

(a) Calculate the wavelengths of the first three lines in this series. (b) Identify the region of the electromagnetic spectrum in which these lines appear.

2. The wavelengths of the Paschen series for hydrogen are given by

$$\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \qquad n = 4, 5, 6, \ldots$$

(a) Calculate the wavelengths of the first three lines in this series. (b) Identity the region of the electromagnetic spectrum in which these lines appear.

3. The "size" of the *atom* in Rutherford's model is about 1.0×10^{-10} m. (a) Determine the attractive electrostatic force between an electron and a proton separated by this distance. (b) Determine (in eV) the electrostatic potential energy of the atom.

4. The "size" of the *nucleus* in Rutherford's model of the atom is about 1.0 fm $= 1.0 \times 10^{-15}$ m. (a) Determine the repulsive electrostatic force between two protons separated by this distance. (b) Determine (in MeV) the electrostatic potential energy of the pair of protons.

5. **ecp** The "size" of the atom in Rutherford's model is about 1.0×10^{-10} m. (a) Determine the speed of an electron moving about the proton using the attractive electrostatic force between an electron and a proton separated by this distance. (b) Does this speed suggest that Einsteinian relativity must be considered in studying the atom? (c) Compute the de Broglie wavelength of the electron as it moves about the proton. (d) Does this wavelength suggest that wave effects, such as diffraction and interference, must be considered in studying the atom?

6. In a Rutherford scattering experiment, an α-particle (charge $= +2e$) heads directly toward a gold nucleus (charge $= +79e$). The α-particle had a kinetic energy of 5.0 MeV when very far ($r \to \infty$) from the nucleus. Assuming the gold nucleus to be fixed in space, determine the distance of closest approach. Hint: Use conservation of energy with $PE = k_e q_1 q_2/r$.

SECTION 28.3 THE BOHR MODEL

7. A hydrogen atom is in its first excited state ($n = 2$). Using the Bohr theory of the atom, calculate (a) the radius

of the orbit, (b) the linear momentum of the electron, (c) the angular momentum of the electron, (d) the kinetic energy, (e) the potential energy, and (f) the total energy.

8. For a hydrogen atom in its ground state, use the Bohr model to compute (a) the orbital speed of the electron, (b) the kinetic energy of the electron, and (c) the electrical potential energy of the atom.

9. **ecp** Show that the speed of the electron in the nth Bohr orbit in hydrogen is given by

$$v_n = \frac{k_e e^2}{n\hbar}$$

10. A photon is emitted when a hydrogen atom undergoes a transition from the $n = 5$ state to the $n = 3$ state. Calculate (a) the wavelength, (b) the frequency, and (c) the energy (in electron volts) of the emitted photon.

11. A hydrogen atom emits a photon of wavelength 656 nm. From what energy orbit to what lower-energy orbit did the electron jump?

12. Following are four possible transitions for a hydrogen atom

   I. $n_i = 2$; $n_f = 5$ II. $n_i = 5$; $n_f = 3$

   III. $n_i = 7$; $n_f = 4$ IV. $n_i = 4$; $n_f = 7$

(a) Which transition will emit the shortest-wavelength photon? (b) For which transition will the atom gain the most energy? (c) For which transition(s) does the atom lose energy?

13. What is the energy of a photon that, when absorbed by a hydrogen atom, could cause an electronic transition from (a) the $n = 2$ state to the $n = 5$ state and (b) the $n = 4$ state to the $n = 6$ state?

14. A hydrogen atom initially in its ground state $(n = 1)$ absorbs a photon and ends up in the state for which $n = 3$. (a) What is the energy of the absorbed photon? (b) If the atom eventually returns to the ground state, what photon energies could the atom emit?

15. How much energy is required to ionize a hydrogen atom when it is in (a) the ground state and (b) the $n = 3$ state?

16. **ecp** A particle of charge q and mass m, moving with a constant speed v, perpendicular to a constant magnetic field B, follows a circular path. If in this case the angular momentum about the center of this circle is quantized so that $mvr = 2n\hbar$, show that the allowed radii for the particle are

$$r_n = \sqrt{\frac{2n\hbar}{qB}}$$

where $n = 1, 2, 3, \ldots$.

17. (a) If an electron makes a transition from the $n = 4$ Bohr orbit to the $n = 2$ orbit, determine the wavelength of the photon created in the process. (b) Assuming that the atom was initially at rest, determine the recoil speed of the hydrogen atom when this photon is emitted.

18. Consider a large number of hydrogen atoms, with electrons all initially in the $n = 4$ state. (a) How many different wavelengths would be observed in the emission spectrum of these atoms? (b) What is the longest wavelength that could be observed? To which series does it belong?

19. Two hydrogen atoms, both initially in the ground state, undergo a head-on collision. If both atoms are to be excited to the $n = 2$ level in this collision, what is the minimum speed each atom can have before the collision?

20. (a) Calculate the angular momentum of the Moon due to its orbital motion about Earth. In your calculation use 3.84×10^8 m as the average Earth–Moon distance and 2.36×10^6 s as the period of the Moon in its orbit. (b) If the angular momentum of the Moon obeys Bohr's quantization rule $(L = n\hbar)$, determine the value of the quantum number n. (c) By what fraction would the Earth–Moon radius have to be increased to increase the quantum number by 1?

21. An electron is in the second excited orbit of hydrogen, corresponding to $n = 3$. Find (a) the radius of the orbit and (b) the wavelength of the electron in this orbit.

22. **ecp** (a) Write an expression relating the kinetic energy KE of the electron and the potential energy PE in the Bohr model of the hydrogen atom. (b) Suppose a hydrogen atom absorbs a photon of energy E, resulting in the transfer of the electron to a higher-energy level. Express the resulting change in the potential energy of the system in terms of E. (c) What is the change in the electron's kinetic energy during this process?

23. The orbital radii of a hydrogen-like atom is given by the equation

$$r = \frac{n^2 \hbar^2}{Z m_e k_e e^2}$$

What is the radius of the first Bohr orbit in (a) He$^+$, (b) Li^{2+}, and (c) Be^{3+}?

24. **GP** Consider a Bohr model of doubly ionized lithium. (a) Write an expression similar to Equation 28.14 for the energy levels of the sole remaining electron. (b) Find the energy corresponding to $n = 4$. (c) Find the energy corresponding to $n = 2$. (d) Calculate the energy of the photon emitted when the electron transits from the fourth energy level to the second energy level. Express the answer both in electron volts and in joules. (e) Find the frequency and wavelength of the emitted photon. (f) In what part of the spectrum is the emitted light?

25. Determine the wavelength of an electron in the third excited orbit of the hydrogen atom, with $n = 4$.

26. **ecp** Using the concept of standing waves, de Broglie was able to derive Bohr's stationary orbit postulate. He assumed a confined electron could exist only in states where its de Broglie waves form standing-wave patterns, as in Figure 28.6. Consider a particle confined in a box of length L to be equivalent to a string of length L and fixed at both ends. Apply de Broglie's concept to show that (a) the linear momentum of this particle is quantized with $p = mv = nh/2L$ and (b) the allowed states correspond to particle energies of $E_n = n^2 E_0$, where $E_0 = h^2/(8mL^2)$.

SECTION 28.4 QUANTUM MECHANICS AND THE HYDROGEN ATOM

27. List the possible sets of quantum numbers for electrons in the $3d$ subshell.

28. When the principal quantum number is $n = 4$, how many different values of (a) ℓ and (b) m_ℓ are possible?

29. The ρ-meson has a charge of $-e$, a spin quantum number of 1, and a mass 1 507 times that of the electron. If the electrons in atoms were replaced by ρ-mesons, list the possible sets of quantum numbers for ρ-mesons in the $3d$ subshell.

SECTION 28.5 THE EXCLUSION PRINCIPLE AND THE PERIODIC TABLE

30. (a) Write out the electronic configuration of the ground state for nitrogen ($Z = 7$). (b) Write out the values for the possible set of quantum numbers n, ℓ, m_ℓ, and m_s for the electrons in nitrogen.

31. Two electrons in the same atom have $n = 3$ and $\ell = 1$. (a) List the quantum numbers for the possible states of the atom. (b) How many states would be possible if the exclusion principle did not apply to the atom?

32. How many different sets of quantum numbers are possible for an electron for which (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, and (e) $n = 5$? Check your results to show that they agree with the general rule that the number of different sets of quantum numbers is equal to $2n^2$.

33. Zirconium ($Z = 40$) has two electrons in an incomplete d subshell. (a) What are the values of n and ℓ for each electron? (b) What are all possible values of m_ℓ and m_s? (c) What is the electron configuration in the ground state of zirconium?

SECTION 28.6 CHARACTERISTIC X-RAYS

34. The K-shell ionization energy of copper is 8 979 eV. The L-shell ionization energy is 951 eV. Determine the wavelength of the K_α emission line of copper. What must the minimum voltage be on an x-ray tube with a copper target to see the K_α line?

35. The K_α x-ray is emitted when an electron undergoes a transition from the L shell ($n = 2$) to the K shell ($n = 1$). Use the method illustrated in Example 28.4 to calculate the wavelength of the K_α x-ray from a nickel target ($Z = 28$).

36. When an electron drops from the M shell ($n = 3$) to a vacancy in the K shell ($n = 1$), the measured wavelength of the emitted x-ray is found to be 0.101 nm. Identify the element.

37. The K series of the discrete spectrum of tungsten contains wavelengths of 0.018 5 nm, 0.020 9 nm, and 0.021 5 nm. The K-shell ionization energy is 69.5 keV. Determine the ionization energies of the L, M, and N shells.

ADDITIONAL PROBLEMS

38. In a hydrogen atom, what is the principal quantum number of the electron orbit with a radius closest to $1.0 \ \mu m$?

39. (a) How much energy is required to cause an electron in hydrogen to move from the $n = 1$ state to the $n = 2$ state? (b) If the electrons gain this energy by collision between hydrogen atoms in a high-temperature gas, find the minimum temperature of the heated hydrogen gas. The thermal energy of the heated atoms is given by $3k_B T/2$, where k_B is the Boltzmann constant.

40. A pulsed ruby laser emits light at 694.3 nm. For a 14.0-ps pulse containing 3.00 J of energy, find (a) the physical length of the pulse as it travels through space and (b) the number of photons in it. (c) If the beam has a circular cross section 0.600 cm in diameter, what is the number of photons per cubic millimeter?

41. An electron in chromium moves from the $n = 2$ state to the $n = 1$ state without emitting a photon. Instead, the excess energy is transferred to an outer electron (one in the $n = 4$ state), which is then ejected by the atom. In this Auger (pronounced "ohjay") process, the ejected electron is referred to as an Auger electron. (a) Find the change in energy associated with the transition from $n = 2$ into the vacant $n = 1$ state using Bohr theory. Assume only one electron in the K shell is shielding part of the nuclear charge. (b) Find the energy needed to ionize an $n = 4$ electron, assuming 22 electrons shield the nucleus. (c) Find the kinetic energy of the ejected (Auger) electron. (All answers should be in electron volts.)

42. (a) Construct an energy level diagram for the He^+ ion, for which $Z = 2$. (b) What is the ionization energy for He^+?

43. A laser used in eye surgery emits a 3.00-mJ pulse in 1.00 ns, focused to a spot 30.0 μm in diameter on the retina. (a) Find (in SI units) the power per unit area at the retina. (This quantity is called the *irradiance*.) (b) What energy is delivered per pulse to an area of molecular size (say, a circular area 0.600 nm in diameter)?

44. An electron has a de Broglie wavelength equal to the diameter of a hydrogen atom in its ground state. (a) What is the kinetic energy of the electron? (b) How does this energy compare with the ground-state energy of the hydrogen atom?

45. ecp Use Bohr's model of the hydrogen atom to show that when the atom makes a transition from the state n to the state $n - 1$, the frequency of the emitted light is given by

$$f = \frac{2\pi^2 m k_e^2 e^4}{h^3}\left[\frac{2n - 1}{(n-1)^2 n^2}\right]$$

46. Suppose the ionization energy of an atom is 4.100 eV. In this same atom, we observe emission lines that have wavelengths of 310.0 nm, 400.0 nm, and 1 378 nm. Use this information to construct the energy level diagram with the least number of levels. Assume that the higher energy levels are closer together.