chapter 42

Atomic Physics

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This street in the Ginza district in Tokyo displays many signs formed from neon lamps of varying bright colors. The light from these lamps has its origin in transitions between quantized energy states in the atoms contained in the lamps. In this chapter, we investigate those transitions. *(© Ken Straiton/Corbis)*

In Chapter 41, we introduced some basic concepts and techniques used in quantum mechanics along with their applications to various one-dimensional systems. In this chapter, we apply quantum mechanics to atomic systems. A large portion of the chapter is focused on the application of quantum mechanics to the study of the hydrogen atom. Understanding the hydrogen atom, the simplest atomic system, is important for several reasons:

- The hydrogen atom is the only atomic system that can be solved exactly.
- Much of what was learned in the 20th century about the hydrogen atom, with its single electron, can be extended to such single-electron ions as He^+ and Li^{2+}.
- The hydrogen atom is an ideal system for performing precise tests of theory against experiment and for improving our overall understanding of atomic structure.
- The quantum numbers that are used to characterize the allowed states of hydrogen can also be used to investigate more complex atoms, and such a description

enables us to understand the periodic table of the elements. This understanding is one of the greatest triumphs of quantum mechanics.

- The basic ideas about atomic structure must be well understood before we attempt to deal with the complexities of molecular structures and the electronic structure of solids.

The full mathematical solution of the Schrödinger equation applied to the hydrogen atom gives a complete and beautiful description of the atom's properties. Because the mathematical procedures involved are beyond the scope of this text, however, many details are omitted. The solutions for some states of hydrogen are discussed, together with the quantum numbers used to characterize various allowed states. We also discuss the physical significance of the quantum numbers and the effect of a magnetic field on certain quantum states.

A new physical idea, the *exclusion principle,* is presented in this chapter. This principle is extremely important for understanding the properties of multielectron atoms and the arrangement of elements in the periodic table.

Finally, we apply our knowledge of atomic structure to describe the mechanisms involved in the production of x-rays and in the operation of a laser.

42.1 Atomic Spectra of Gases

As pointed out in Section 40.1, all objects emit thermal radiation characterized by a *continuous* distribution of wavelengths. In sharp contrast to this continuous-distribution spectrum is the *discrete* **line spectrum** observed when a low-pressure gas undergoes an electric discharge. (Electric discharge occurs when the gas is subject to a potential difference that creates an electric field greater than the dielectric strength of the gas.) Observation and analysis of these spectral lines is called **emission spectroscopy.**

Pitfall Prevention 42.1

Why Lines?

The phrase "spectral lines" is often used when discussing the radiation from atoms. Lines are seen because the light passes through a long and very narrow slit before being separated by wavelength. You will see many references to these "lines" in both physics and chemistry.

When the light from a gas discharge is examined using a spectrometer (see Active Fig. 38.15), it is found to consist of a few bright lines of color on a generally dark background. This discrete line spectrum contrasts sharply with the continuous rainbow of colors seen when a glowing solid is viewed through the same instrument. Figure 42.1a shows that the wavelengths contained in a given line spectrum are characteristic of the element emitting the light. The simplest line spectrum is that for atomic hydrogen, and we describe this spectrum in detail. Because no two elements have the same line spectrum, this phenomenon represents a practical and sensitive technique for identifying the elements present in unknown samples.

Another form of spectroscopy very useful in analyzing substances is **absorption spectroscopy.** An absorption spectrum is obtained by passing white light from a continuous source through a gas or a dilute solution of the element being analyzed. The absorption spectrum consists of a series of dark lines superimposed on the continuous spectrum of the light source as shown in Figure 42.1b for atomic hydrogen.

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. The various absorption lines observed in the solar spectrum have been used to identify elements in the solar atmosphere. In early studies of the solar spectrum, experimenters found some lines

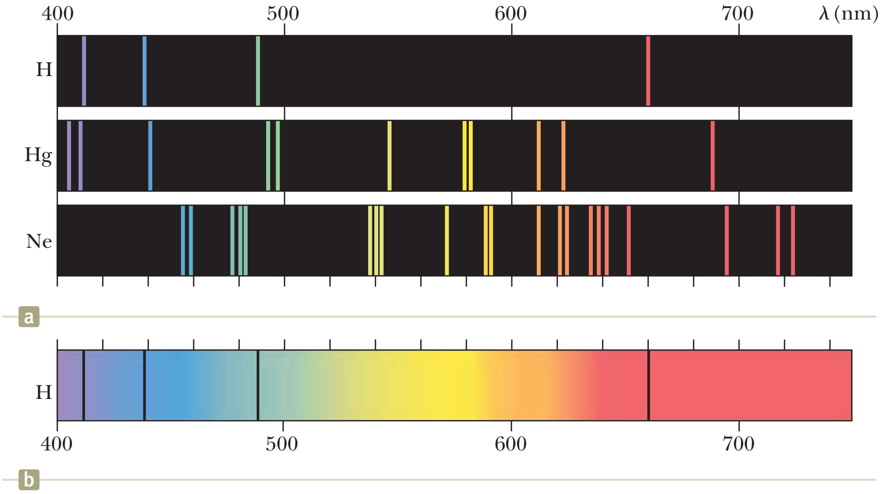


Figure 42.1 (a) Emission line spectra for hydrogen, mercury, and neon. (b) The absorption spectrum for hydrogen. Notice that the dark absorption lines occur at the same wavelengths as the hydrogen emission lines in (a). (K. W. Whitten, R. E. Davis, M. L. Peck, and G. G. Stanley, *General Chemistry,* 7th ed., Belmont, CA, Brooks/Cole, 2004.)

that did not correspond to any known element. A new element had been discovered! The new element was named helium, after the Greek word for Sun, *helios.* Helium was subsequently isolated from subterranean gas on the Earth.

Using this technique, scientists have examined the light from stars other than our Sun and have never detected elements other than those present on the Earth. Absorption spectroscopy has also been useful in analyzing heavy-metal contamination of the food chain. For example, the first determination of high levels of mercury in tuna was made with the use of atomic absorption spectroscopy.

The discrete emissions of light from gas discharges are used in "neon" signs such as those in the opening photograph of this chapter. Neon, the first gas used in these types of signs and the gas after which these signs are named, emits strongly in the red region. As a result, a glass tube filled with neon gas emits bright red light when an applied voltage causes a continuous discharge. Early signs used different gases to provide different colors, although the brightness of these signs was generally very low. Many present-day "neon" signs contain mercury vapor, which emits strongly in the ultraviolet range of the electromagnetic spectrum. The inside of a present-day sign's glass tube is coated with a material that emits a particular color when it absorbs ultraviolet radiation from the mercury. The color of the light from the tube results from the particular material chosen. A household fluorescent light operates in the same manner, with a white-emitting material coating the inside of the glass tube.

From 1860 to 1885, scientists accumulated a great deal of data on atomic emissions using spectroscopic measurements. In 1885, a Swiss schoolteacher, Johann Jacob Balmer (1825–1898), found an empirical equation that correctly predicted the wavelengths of four visible emission lines of hydrogen: H_α (red), H_β (blue-green), H_γ (blue-violet), and H_δ (violet). Figure 42.2 shows these and other lines (in the ultraviolet) in the emission spectrum of hydrogen. The four visible lines occur at the wavelengths 656.3 nm, 486.1 nm, 434.1 nm, and 410.2 nm. The complete set of lines is called the **Balmer series.** The wavelengths of these lines can be described by the following equation, which is a modification made by Johannes Rydberg (1854–1919) of Balmer's original equation:

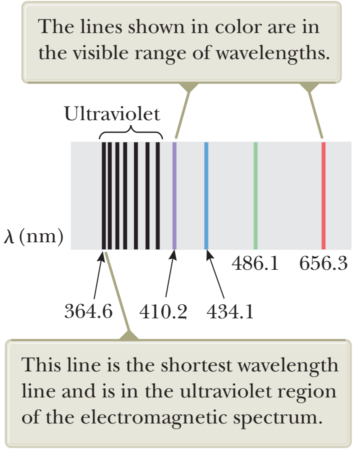


Figure 42.2 The Balmer series of spectral lines for atomic hydrogen, with several lines marked with the wavelength in nanometers. (The horizontal wavelength axis is not to scale.)

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, \ldots \tag{42.1}$$

◀ **Balmer series**

where R_{H} is a constant now called the **Rydberg constant** with a value of $1.097\,373\,2 \times 10^7\ \mathrm{m}^{-1}$. The integer values of n from 3 to 6 give the four visible lines from 656.3 nm (red) down to 410.2 nm (violet). Equation 42.1 also describes the ultraviolet spectral lines in the Balmer series if n is carried out beyond $n = 6$. The **series limit** is the shortest wavelength in the series and corresponds to $n \to \infty$, with a wavelength of 364.6 nm as in Figure 42.2. The measured spectral lines agree with the empirical equation, Equation 42.1, to within 0.1%.

Other lines in the spectrum of hydrogen were found following Balmer's discovery. These spectra are called the Lyman, Paschen, and Brackett series after their discoverers. The wavelengths of the lines in these series can be calculated through the use of the following empirical equations:

Lyman series ▶

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(1 - \frac{1}{n^2}\right) \qquad n = 2, 3, 4, \ldots \tag{42.2}$$

Paschen series ▶

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \qquad n = 4, 5, 6, \ldots \tag{42.3}$$

Brackett series ▶

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{4^2} - \frac{1}{n^2}\right) \qquad n = 5, 6, 7, \ldots \tag{42.4}$$

No theoretical basis existed for these equations; they simply worked. The same constant R_{H} appears in each equation, and all equations involve small integers. In Section 42.3, we shall discuss the remarkable achievement of a theory for the hydrogen atom that provided an explanation for these equations.


Stock Montage, Inc.

Joseph John Thomson
English physicist (1856–1940)
The recipient of a Nobel Prize in Physics in 1906, Thomson is usually considered the discoverer of the electron. He opened up the field of subatomic particle physics with his extensive work on the deflection of cathode rays (electrons) in an electric field.

42.2 Early Models of the Atom

The model of the atom in the days of Newton was a tiny, hard, indestructible sphere. Although this model provided a good basis for the kinetic theory of gases (Chapter 21), new models had to be devised when experiments revealed the electrical nature of atoms. In 1897, J. J. Thomson established the charge-to-mass ratio for electrons. (See Fig. 29.15 in Section 29.3.) The following year, he suggested a model that describes the atom as a region in which positive charge is spread out in space with electrons embedded throughout the region, much like the seeds in a watermelon or raisins in thick pudding (Fig. 42.3). The atom as a whole would then be electrically neutral.

In 1911, Ernest Rutherford (1871–1937) and his students Hans Geiger and Ernest Marsden performed a critical experiment that showed that Thomson's model could not be correct. In this experiment, a beam of positively charged alpha particles (helium nuclei) was projected into a thin metallic foil such as the target in Figure 42.4a. Most of the particles passed through the foil as if it were empty space, but some of the results of the experiment were astounding. Many of the particles deflected from their original direction of travel were scattered through *large* angles. Some particles were even deflected backward, completely reversing their direction of travel! When Geiger informed Rutherford that some alpha particles were scattered backward, Rutherford wrote, "It was quite the most incredible event that has

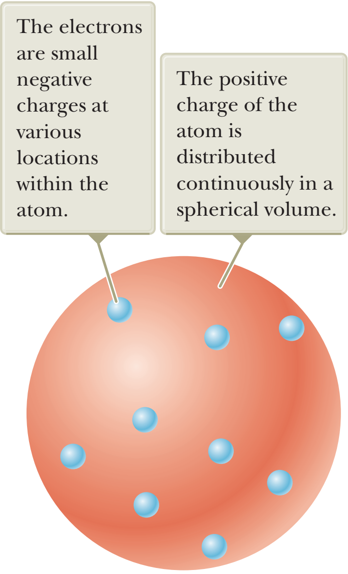


Figure 42.3 Thomson's model of the atom.

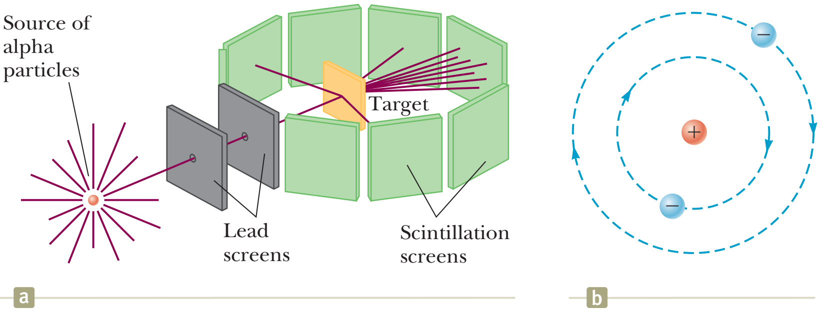


Figure 42.4 (a) Rutherford's technique for observing the scattering of alpha particles from a thin foil target. The source is a naturally occurring radioactive substance, such as radium. (b) Rutherford's planetary model of the atom.

ever happened to me in my life. It was almost as incredible as if you fired a 15-inch [artillery] shell at a piece of tissue paper and it came back and hit you."

Such large deflections were not expected on the basis of Thomson's model. According to that model, the positive charge of an atom in the foil is spread out over such a great volume (the entire atom) that there is no concentration of positive charge strong enough to cause any large-angle deflections of the positively charged alpha particles. Furthermore, the electrons are so much less massive than the alpha particles that they would not cause large-angle scattering either. Rutherford explained his astonishing results by developing a new atomic model, one that assumed the positive charge in the atom was concentrated in a region that was small relative to the size of the atom. He called this concentration of positive charge the **nucleus** of the atom. Any electrons belonging to the atom were assumed to be in the relatively large volume outside the nucleus. To explain why these electrons were not pulled into the nucleus by the attractive electric force, Rutherford modeled them as moving in orbits around the nucleus in the same manner as the planets orbit the Sun (Fig. 42.4b). For this reason, this model is often referred to as the planetary model of the atom.

Two basic difficulties exist with Rutherford's planetary model. As we saw in Section 42.1, an atom emits (and absorbs) certain characteristic frequencies of electromagnetic radiation and no others, but the Rutherford model cannot explain this phenomenon. A second difficulty is that Rutherford's electrons are undergoing a centripetal acceleration. According to Maxwell's theory of electromagnetism, centripetally accelerated charges revolving with frequency f should radiate electromagnetic waves of frequency f. Unfortunately, this classical model leads to a prediction of self-destruction when applied to the atom. As the electron radiates, energy is carried away from the atom, the radius of the electron's orbit steadily decreases, and its frequency of revolution increases. This process would lead to an ever-increasing frequency of emitted radiation and an ultimate collapse of the atom as the electron plunges into the nucleus (Fig. 42.5).

Because the accelerating electron radiates energy, the size of the orbit decreases until the electron falls into the nucleus.

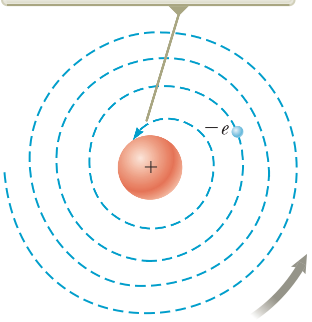


Figure 42.5 The classical model of the nuclear atom predicts that the atom decays.

42.3 Bohr's Model of the Hydrogen Atom

Given the situation described at the end of Section 42.2, the stage was set for Niels Bohr in 1913 when he presented a new model of the hydrogen atom that circumvented the difficulties of Rutherford's planetary model. Bohr applied Planck's ideas of quantized energy levels (Section 40.1) to Rutherford's orbiting atomic electrons. Bohr's theory was historically important to the development of quantum physics, and it appeared to explain the spectral line series described by Equations 42.1 through 42.4. Although Bohr's model is now considered obsolete and has been completely replaced by a probabilistic quantum-mechanical theory, we can use the Bohr model to develop the notions of energy quantization and angular momentum quantization as applied to atomic-sized systems.

Bohr combined ideas from Planck's original quantum theory, Einstein's concept of the photon, Rutherford's planetary model of the atom, and Newtonian mechanics to arrive at a semiclassical model based on some revolutionary ideas. The postulates of the Bohr theory as it applies to the hydrogen atom are as follows:

1. The electron moves in circular orbits around the proton under the influence of the electric force of attraction as shown in Figure 42.6.
2. Only certain electron orbits are stable. When in one of these **stationary states,** as Bohr called them, the electron does not emit energy in the form of radiation, even though it is accelerating. Hence, the total energy of the atom remains constant and classical mechanics can be used to describe the electron's motion. Bohr's model claims that the centripetally accelerated electron does not continuously emit radiation, losing energy and eventually spiraling into the nucleus, as predicted by classical physics in the form of Rutherford's planetary model.

The orbiting electron is allowed to be only in specific orbits of discrete radii.

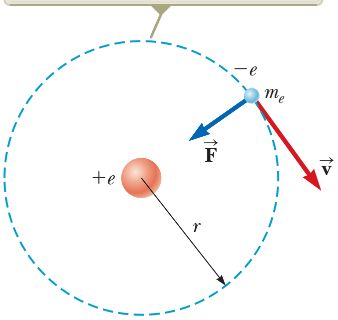
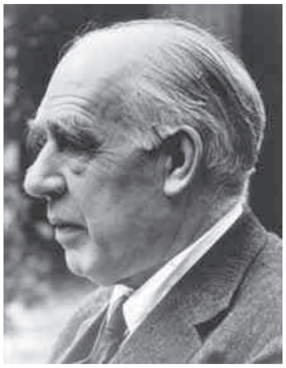


Figure 42.6 Diagram representing Bohr's model of the hydrogen atom.



Princeton University, Courtesy of AIP Emilio Segrè Visual Archives

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. The institute was a magnet for many of the world's best physicists and provided a forum for the exchange of ideas. When Bohr visited the United States in 1939 to attend a scientific conference, he brought news that the fission of uranium had been observed by Hahn and Strassman in Berlin. The results were the foundations of the nuclear weapon developed in the United States during World War II. Bohr was awarded the 1922 Nobel Prize in Physics for his investigation of the structure of atoms and the radiation emanating from them.

3. The atom emits radiation when the electron makes a transition from a more energetic initial stationary state to a lower-energy stationary state. This transition cannot be visualized or treated classically. In particular, the frequency f of the photon emitted in the transition is related to the change in the atom's energy and is not equal to the frequency of the electron's orbital motion. The frequency of the emitted radiation is found from the energy-conservation expression

$$E_i - E_f = hf \qquad \textbf{(42.5)}$$

where E_i is the energy of the initial state, E_f is the energy of the final state, and $E_i > E_f$. In addition, energy of an incident photon can be absorbed by the atom, but only if the photon has an energy that exactly matches the difference in energy between an allowed state of the atom and a higher-energy state. Upon absorption, the photon disappears and the atom makes a transition to the higher-energy state.

4. The size of an allowed electron orbit is determined by a condition imposed on the electron's orbital angular momentum: the allowed orbits are those for which the electron's orbital angular momentum about the nucleus is quantized and equal to an integral multiple of $\hbar = h/2\pi$,

$$m_e v r = n\hbar \quad n = 1, 2, 3, \ldots \qquad \textbf{(42.6)}$$

where m_e is the electron mass, v is the electron's speed in its orbit, and r is the orbital radius.

These postulates are a mixture of established principles and completely new and untested ideas at the time. Postulate 1, from classical mechanics, treats the electron in orbit around the nucleus in the same way we treat a planet in orbit around a star. Postulate 2 was a radical new idea in 1913 that was completely at odds with the understanding of electromagnetism at the time. Postulate 3 represents the principle of conservation of energy. Postulate 4 is another new idea that had no basis in classical physics.

Postulate 3 implies qualitatively the existence of a characteristic discrete emission line spectrum *and also* a corresponding absorption line spectrum of the kind shown in Figure 42.1 for hydrogen. Using these four postulates, let's calculate the allowed energy levels and find quantitative values of the emission wavelengths of the hydrogen atom.

The electric potential energy of the system shown in Figure 42.6 is given by Equation 25.13, $U = k_e q_1 q_2/r = -k_e e^2/r$, where k_e is the Coulomb constant and the negative sign arises from the charge $-e$ on the electron. Therefore, the *total* energy of the atom, which consists of the electron's kinetic energy and the system's potential energy, is

$$E = K + U = \tfrac{1}{2} m_e v^2 - k_e \frac{e^2}{r} \qquad \textbf{(42.7)}$$

The electron is modeled as a particle in uniform circular motion, so the electric force $k_e e^2/r^2$ exerted on the electron must equal the product of its mass and its centripetal acceleration ($a_c = v^2/r$):

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

$$v^2 = \frac{k_e e^2}{m_e r} \qquad \textbf{(42.8)}$$

From Equation 42.8, we find that the kinetic energy of the electron is

$$K = \tfrac{1}{2} m_e v^2 = \frac{k_e e^2}{2r}$$

Substituting this value of K into Equation 42.7 gives the following expression for the total energy of the atom:[1]

$$E = -\frac{k_e e^2}{2r} \tag{42.9}$$

Because the total energy is *negative,* which indicates a bound electron–proton system, energy in the amount of $k_e e^2/2r$ must be added to the atom to remove the electron and make the total energy of the system zero.

We can obtain an expression for r, the radius of the allowed orbits, by solving Equation 42.6 for v^2 and equating it to Equation 42.8:

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

$$r_n = \frac{n^2\hbar^2}{m_e k_e e^2} \qquad n = 1, 2, 3, \ldots \tag{42.10}$$

Equation 42.10 shows that the radii of the allowed orbits have discrete values: they are quantized. The result is based on the *assumption* that the electron can exist only in certain allowed orbits determined by the integer n (Bohr's postulate 4).

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

$$a_0 = \frac{\hbar^2}{m_e k_e e^2} = 0.052\ 9 \text{ nm} \tag{42.11}$$

◀ **Bohr radius**

Substituting Equation 42.11 into Equation 42.10 gives a general expression for the radius of any orbit in the hydrogen atom:

$$r_n = n^2 a_0 = n^2(0.052\ 9 \text{ nm}) \qquad n = 1, 2, 3, \ldots \tag{42.12}$$

◀ **Radii of Bohr orbits in hydrogen**

Bohr's theory predicts a value for the radius of a hydrogen atom on the right order of magnitude, based on experimental measurements. This result was a striking triumph for Bohr's theory. The first three Bohr orbits are shown to scale in Active Figure 42.7.

The quantization of orbit radii leads to energy quantization. Substituting $r_n = n^2 a_0$ into Equation 42.9 gives

$$\boxed{E_n = -\frac{k_e e^2}{2a_0}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots} \tag{42.13}$$

Inserting numerical values into this expression, we find that

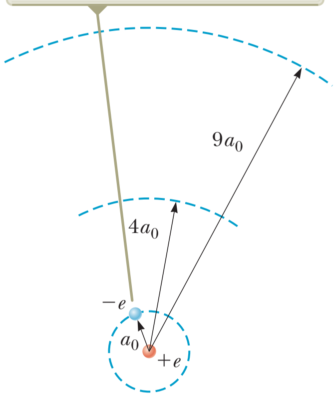
$$\boxed{E_n = -\frac{13.606 \text{ eV}}{n^2} \qquad n = 1, 2, 3, \ldots} \tag{42.14}$$

Only energies satisfying this equation are permitted. The lowest allowed energy level, the ground state, has $n = 1$ and energy $E_1 = -13.606$ eV. The next energy level, the first excited state, has $n = 2$ and energy $E_2 = E_1/2^2 = -3.401$ eV. Active Figure 42.8 on page 1258 is an energy-level diagram showing the energies of these discrete energy states and the corresponding quantum numbers n. The uppermost level corresponds to $n = \infty$ (or $r = \infty$) and $E = 0$.

Notice how the allowed energies of the hydrogen atom differ from those of the particle in a box. The particle-in-a-box energies (Eq. 41.14) increase as n^2, so they become farther apart in energy as n increases. On the other hand, the energies of the hydrogen atom (Eq. 42.14) vary inversely with n^2, so their separation in energy becomes smaller as n increases. The separation between energy levels approaches zero as n approaches infinity and the energy approaches zero.

Zero energy represents the boundary between a bound system of an electron and a proton and an unbound system. If the energy of the atom is raised from that

The electron is shown in the lowest-energy orbit, but it could be in any of the allowed orbits.



ACTIVE FIGURE 42.7

The first three circular orbits predicted by the Bohr model of the hydrogen atom.

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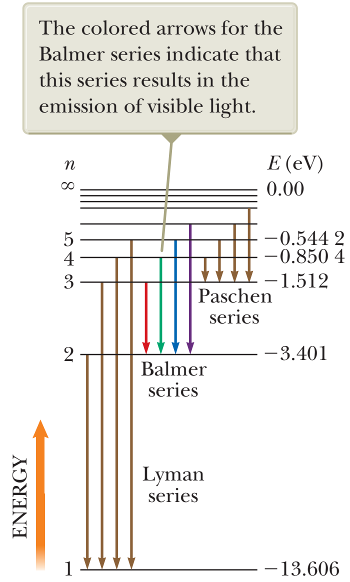
[1] Compare Equation 42.9 with its gravitational counterpart, Equation 13.18.



The colored arrows for the Balmer series indicate that this series results in the emission of visible light.

ACTIVE FIGURE 42.8

An energy-level diagram for the hydrogen atom. 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.

of the ground state to any energy larger than zero, the atom is **ionized.** The minimum energy required to ionize the atom in its ground state is called the **ionization energy.** As can be seen from Active Figure 42.8, the ionization energy for hydrogen in the ground state, based on Bohr's calculation, is 13.6 eV. This finding constituted another major achievement for the Bohr theory because the ionization energy for hydrogen had already been measured to be 13.6 eV.

Equations 42.5 and 42.13 can be used to calculate the frequency of the photon emitted when the electron makes a transition from an outer orbit to an inner orbit:

$$f = \frac{E_i - E_f}{h} = \frac{k_e e^2}{2a_0 h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad (42.15)$$

Because the quantity measured experimentally is wavelength, it is convenient to use $c = f\lambda$ to express Equation 42.15 in terms of wavelength:

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{k_e e^2}{2a_0 hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad (42.16)$$

Remarkably, this expression, which is purely theoretical, is *identical* to the general form of the empirical relationships discovered by Balmer and Rydberg and given by Equations 42.1 to 42.4:

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad (42.17)$$

provided the constant $k_e e^2/2a_0 hc$ is equal to the experimentally determined Rydberg constant. Soon after Bohr demonstrated that these two quantities agree to within approximately 1%, this work was recognized as the crowning achievement of his new quantum theory of the hydrogen atom. Furthermore, Bohr showed that all the spectral series for hydrogen have a natural interpretation in his theory. The different series correspond to transitions to different final states characterized by the quantum number n_f. Active Figure 42.8 shows the origin of these spectral series as transitions between energy levels.

Bohr extended his model for hydrogen to other elements in which all but one electron had been removed. These systems have the same structure as the hydrogen atom except that the nuclear charge is larger. Ionized elements such as He^+, Li^{2+}, and Be^{3+} were suspected to exist in hot stellar atmospheres, where atomic collisions frequently have enough energy to completely remove one or more atomic electrons. Bohr showed that many mysterious lines observed in the spectra of the Sun and several other stars could not be due to hydrogen but were correctly predicted by his theory if attributed to singly ionized helium. In general, the number of protons in the nucleus of an atom is called the **atomic number** of the element and is given the symbol Z. To describe a single electron orbiting a fixed nucleus of charge $+Ze$, Bohr's theory gives

$$r_n = (n^2)\frac{a_0}{Z} \qquad (42.18)$$

$$E_n = -\frac{k_e e^2}{2a_0}\left(\frac{Z^2}{n^2}\right) \quad n = 1, 2, 3, \ldots \qquad (42.19)$$

Although the Bohr theory was triumphant in its agreement with some experimental results on the hydrogen atom, it suffered from some difficulties. One of the first indications that the Bohr theory needed to be modified arose when improved spectroscopic techniques were used to examine the spectral lines of hydrogen. It was found that many of the lines in the Balmer and other series were not single lines at all. Instead, each was a group of lines spaced very close together. An additional difficulty arose when it was observed that in some situations certain single spectral lines were split into three closely spaced lines when the atoms were placed

Pitfall Prevention 42.2

The Bohr Model Is Great, but . . .
The Bohr model correctly predicts the ionization energy and general features of the spectrum for hydrogen, but it cannot account for the spectra of more complex atoms and is unable to predict many subtle spectral details of hydrogen and other simple atoms. Scattering experiments show that the electron in a hydrogen atom does not move in a flat circle around the nucleus. Instead, the atom is spherical. The ground-state angular momentum of the atom is zero and not $\hbar$.

in a strong magnetic field. Efforts to explain these and other deviations from the Bohr model led to modifications in the theory and ultimately to a replacement theory that will be discussed in Section 42.4.

Bohr's Correspondence Principle

In our study of relativity, we found that Newtonian mechanics is a special case of relativistic mechanics and is usable only for speeds much less than c. Similarly,

> quantum physics agrees with classical physics when the difference between quantized levels becomes vanishingly small.

This principle, first set forth by Bohr, is called the **correspondence principle.**[2]

For example, consider an electron orbiting the hydrogen atom with $n > 10\ 000$. For such large values of n, the energy differences between adjacent levels approach zero; therefore, the levels are nearly continuous. Consequently, the classical model is reasonably accurate in describing the system for large values of n. According to the classical picture, the frequency of the light emitted by the atom is equal to the frequency of revolution of the electron in its orbit about the nucleus. Calculations show that for $n > 10\ 000$, this frequency is different from that predicted by quantum mechanics by less than 0.015%.

***Quick Quiz* 42.1** A hydrogen atom is in its ground state. Incident on the atom is a photon having an energy of 10.5 eV. What is the result? **(a)** The atom is excited to a higher allowed state. **(b)** The atom is ionized. **(c)** The photon passes by the atom without interaction.

***Quick Quiz* 42.2** A hydrogen atom makes a transition from the $n = 3$ level to the $n = 2$ level. It then makes a transition from the $n = 2$ level to the $n = 1$ level. Which transition results in emission of the longest-wavelength photon? **(a)** the first transition **(b)** the second transition **(c)** neither transition because the wavelengths are the same for both

Example 42.1 Electronic Transitions in Hydrogen

(A) The electron in a hydrogen atom makes a transition from the $n = 2$ energy level to the ground level ($n = 1$). Find the wavelength and frequency of the emitted photon.

SOLUTION

Conceptualize Imagine the electron in a circular orbit about the nucleus as in the Bohr model in Figure 42.6. When the electron makes a transition to a lower stationary state, it emits a photon with a given frequency.

Categorize We evaluate the results using equations developed in this section, so we categorize this example as a substitution problem.

Use Equation 42.17 to obtain λ, with $n_i = 2$ and $n_f = 1$:

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

$$\lambda = \frac{4}{3R_H} = \frac{4}{3(1.097 \times 10^7\ \text{m}^{-1})} = 1.22 \times 10^{-7}\ \text{m} = \boxed{122\ \text{nm}}$$

continued

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[2] In reality, the correspondence principle is the starting point for Bohr's postulate 4 on angular momentum quantization. To see how postulate 4 arises from the correspondence principle, see J. W. Jewett Jr., *Physics Begins with Another M . . . Mysteries, Magic, Myth, and Modern Physics* (Boston: Allyn & Bacon, 1996), pp. 353–356.

42.1 *cont.*

Use Equation 34.20 to find the frequency of the photon:

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^{8}\ \text{m/s}}{1.22 \times 10^{-7}\ \text{m}} = \boxed{2.47 \times 10^{15}\ \text{Hz}}$$

(B) In interstellar space, highly excited hydrogen atoms called Rydberg atoms have been observed. Find the wavelength to which radio astronomers must tune to detect signals from electrons dropping from the $n = 273$ level to the $n = 272$ level.

SOLUTION

Use Equation 42.17, this time with $n_i = 273$ and $n_f = 272$:

$$\frac{1}{\lambda} = R_{\text{H}}\left(\frac{1}{n_f^{2}} - \frac{1}{n_i^{2}}\right) = R_{\text{H}}\left(\frac{1}{(272)^2} - \frac{1}{(273)^2}\right) = 9.88 \times 10^{-8}\ R_{\text{H}}$$

Solve for λ:

$$\lambda = \frac{1}{9.88 \times 10^{-8} R_{\text{H}}} = \frac{1}{(9.88 \times 10^{-8})(1.097 \times 10^{7}\ \text{m}^{-1})} = \boxed{0.922\ \text{m}}$$

(C) What is the radius of the electron orbit for a Rydberg atom for which $n = 273$?

SOLUTION

Use Equation 42.12 to find the radius of the orbit:

$$r_{273} = (273)^2\ (0.052\,9\ \text{nm}) = \boxed{3.94\ \mu\text{m}}$$

This radius is large enough that the atom is on the verge of becoming macroscopic!

(D) How fast is the electron moving in a Rydberg atom for which $n = 273$?

SOLUTION

Solve Equation 42.8 for the electron's speed:

$$v = \sqrt{\frac{k_e e^2}{m_e r}} = \sqrt{\frac{(8.99 \times 10^{9}\ \text{N} \cdot \text{m}^2/\text{C}^2)(1.60 \times 10^{-19}\ \text{C})^2}{(9.11 \times 10^{-31}\ \text{kg})(3.94 \times 10^{-6}\ \text{m})}}$$

$$= \boxed{8.01 \times 10^{3}\ \text{m/s}}$$

WHAT IF? What if radiation from the Rydberg atom in part (B) is treated classically? What is the wavelength of radiation emitted by the atom in the $n = 273$ level?

Answer Classically, the frequency of the emitted radiation is that of the rotation of the electron around the nucleus.

Calculate this frequency using the period defined in Equation 4.15:

$$f = \frac{1}{T} = \frac{v}{2\pi r}$$

Substitute the radius and speed from parts (C) and (D):

$$f = \frac{v}{2\pi r} = \frac{8.02 \times 10^{3}\ \text{m/s}}{2\pi(3.94 \times 10^{-6}\ \text{m})} = 3.24 \times 10^{8}\ \text{Hz}$$

Find the wavelength of the radiation from Equation 34.20:

$$\lambda = \frac{c}{f} = \frac{3.00 \times 10^{8}\ \text{m/s}}{3.24 \times 10^{8}\ \text{Hz}} = 0.927\ \text{m}$$

This value is less than 0.5% different from the wavelength calculated in part (B). As indicated in the discussion of Bohr's correspondence principle, this difference becomes even smaller for higher values of n.

42.4 The Quantum Model of the Hydrogen Atom

In the preceding section, we described how the Bohr model views the electron as a particle orbiting the nucleus in nonradiating, quantized energy levels. This model combines both classical and quantum concepts. Although the model demonstrates excellent agreement with some experimental results, it cannot explain others. These difficulties are removed when a full quantum model involving the Schrödinger equation is used to describe the hydrogen atom.

The formal procedure for solving the problem of the hydrogen atom is to substitute the appropriate potential energy function into the Schrödinger equation, find solutions to the equation, and apply boundary conditions as we did for the particle in a box in Chapter 41. The potential energy function for the hydrogen atom is that due to the electrical interaction between the electron and the proton (see Section 25.3):

$$U(r) = -k_e \frac{e^2}{r} \tag{42.20}$$

where $k_e = 8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2$ is the Coulomb constant and r is the radial distance from the proton (situated at $r = 0$) to the electron.

The mathematics for the hydrogen atom is more complicated than that for the particle in a box because the atom is three-dimensional and U depends on the radial coordinate r. If the time-independent Schrödinger equation (Eq. 41.15) is extended to three-dimensional rectangular coordinates, the result is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + U\psi = E\psi$$

It is easier to solve this equation for the hydrogen atom if rectangular coordinates are converted to spherical polar coordinates, an extension of the plane polar coordinates introduced in Section 3.1. In spherical polar coordinates, a point in space is represented by the three variables r, θ, and ϕ, where r is the radial distance from the origin, $r = \sqrt{x^2 + y^2 + z^2}$. With the point represented at the end of a position vector $\vec{\mathbf{r}}$ as shown in Figure 42.9, the angular coordinate θ specifies its angular position relative to the z axis. Once that position vector is projected onto the xy plane, the angular coordinate ϕ specifies the projection's (and therefore the point's) angular position relative to the x axis.

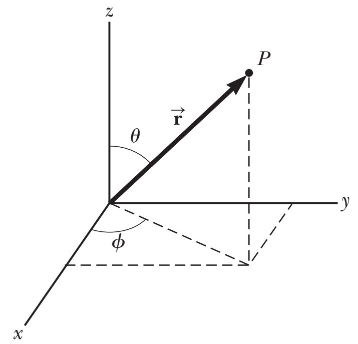

Figure 42.9 A point P in space is located by means of a position vector $\vec{\mathbf{r}}$. In Cartesian coordinates, the components of this vector are x, y, and z. In spherical polar coordinates, the point is described by r, the distance from the origin; θ, the angle between $\vec{\mathbf{r}}$ and the z axis; and ϕ, the angle between the x axis and a projection of $\vec{\mathbf{r}}$ onto the xy plane.

The conversion of the three-dimensional time-independent Schrödinger equation for $\psi(x, y, z)$ to the equivalent form for $\psi(r, \theta, \phi)$ is straightforward but very tedious, so we omit the details.[3] In Chapter 41, we separated the time dependence from the space dependence in the general wave function Ψ. In this case of the hydrogen atom, the three space variables in $\psi(r, \theta, \phi)$ can be similarly separated by writing the wave function as a product of functions of each single variable:

$$\psi(r, \theta, \phi) = R(r)f(\theta)g(\phi)$$

In this way, Schrödinger's equation, which is a three-dimensional partial differential equation, can be transformed into three separate ordinary differential equations: one for $R(r)$, one for $f(\theta)$, and one for $g(\phi)$. Each of these functions is subject to boundary conditions. For example, $R(r)$ must remain finite as $r \to 0$ and $r \to \infty$; furthermore, $g(\phi)$ must have the same value as $g(\phi + 2\pi)$.

The potential energy function given in Equation 42.20 depends *only* on the radial coordinate r and not on either of the angular coordinates; therefore, it appears only in the equation for $R(r)$. As a result, the equations for θ and ϕ are independent of the particular system and their solutions are valid for *any* system exhibiting rotation.

When the full set of boundary conditions is applied to all three functions, three different quantum numbers are found for each allowed state of the hydrogen atom, one for each of the separate differential equations. These quantum numbers are restricted to integer values and correspond to the three independent degrees of freedom (three space dimensions).

The first quantum number, associated with the radial function $R(r)$ of the full wave function, is called the **principal quantum number** and is assigned the symbol n. The differential equation for $R(r)$ leads to functions giving the probability of finding the electron at a certain radial distance from the nucleus. In Section 42.5,

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[3] Descriptions of the solutions to the Schrödinger equation for the hydrogen atom are available in modern physics textbooks such as R. A. Serway, C. Moses, and C. A. Moyer, *Modern Physics,* 3rd ed. (Belmont, CA: Brooks/Cole, 2005).

we will describe two of these radial wave functions. The energies of the allowed states for the hydrogen atom are found to be related to n as follows:

Allowed energies of the quantum hydrogen atom

$$E_n = -\left(\frac{k_e e^2}{2a_0}\right)\frac{1}{n^2} = -\frac{13.606\text{ eV}}{n^2} \qquad n = 1, 2, 3, \ldots \tag{42.21}$$

This result is in exact agreement with that obtained in the Bohr theory (Eqs. 42.13 and 42.14)! This agreement is *remarkable* because the Bohr theory and the full quantum theory arrive at the result from completely different starting points.

Pitfall Prevention 42.3

Energy Depends on *n* Only for Hydrogen

The implication in Equation 42.21 that the energy depends only on the quantum number n is true only for the hydrogen atom. For more complicated atoms, we will use the same quantum numbers developed here for hydrogen. The energy levels for these atoms depend primarily on n, but they also depend to a lesser degree on other quantum numbers.

The **orbital quantum number,** symbolized ℓ, comes from the differential equation for $f(\theta)$ and is associated with the orbital angular momentum of the electron. The **orbital magnetic quantum number** m_ℓ arises from the differential equation for $g(\phi)$. Both ℓ and m_ℓ are integers. We will expand our discussion of these two quantum numbers in Section 42.6, where we also introduce a fourth (nonintegral) quantum number, resulting from a relativistic treatment of the hydrogen atom.

The application of boundary conditions on the three parts of the full wave function leads to important relationships among the three quantum numbers as well as certain restrictions on their values:

Restrictions on the values of hydrogen-atom quantum numbers

The values of n are integers that can range from 1 to ∞.

The values of ℓ are integers that can range from 0 to $n - 1$.

The values of m_ℓ are integers that can range from $-\ell$ to ℓ.

For example, if $n = 1$, only $\ell = 0$ and $m_\ell = 0$ are permitted. If $n = 2$, then 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 42.1 summarizes the rules for determining the allowed values of ℓ and m_ℓ for a given n.

Pitfall Prevention 42.4

Quantum Numbers Describe a System

It is common to assign the quantum numbers to an electron. Remember, however, that these quantum numbers arise from the Schrödinger equation, which involves a potential energy function for the *system* of the electron and the nucleus. Therefore, it is more *proper* to assign the quantum numbers to the atom, but it is more *popular* to assign them to an electron. We follow this latter usage because it is so common.

For historical reasons, all states having the same principal quantum number are said to form a **shell.** Shells are identified by the letters K, L, M, . . . , which designate the states for which $n = 1, 2, 3, \ldots$. Likewise, all states having the same values of n and ℓ are said to form a **subshell.** The letters[4] *s, p, d, f, g, h,* . . . are used to designate the subshells for which $\ell = 0, 1, 2, 3, \ldots$. The state designated by 3*p*, for example, has the quantum numbers $n = 3$ and $\ell = 1$; the 2*s* state has the quantum numbers $n = 2$ and $\ell = 0$. These notations are summarized in Tables 42.2 and 42.3.

States that violate the rules given in Table 42.1 do not exist. (They do not satisfy the boundary conditions on the wave function.) For instance, the 2*d* state, which would have $n = 2$ and $\ell = 2$, cannot exist because the highest allowed value of ℓ is $n - 1$, which in this case is 1. Therefore, for $n = 2$, the 2*s* and 2*p* states are allowed but 2*d*, 2*f*, . . . are not. For $n = 3$, the allowed subshells are 3*s*, 3*p*, and 3*d*.

***Quick Quiz* 42.3** How many possible subshells are there for the $n = 4$ level of hydrogen? **(a)** 5 **(b)** 4 **(c)** 3 **(d)** 2 **(e)** 1

***Quick Quiz* 42.4** When the principal quantum number is $n = 5$, how many different values of **(a)** ℓ and **(b)** m_ℓ are possible?

TABLE 42.1 *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	$-\ell, -\ell + 1, \ldots, 0, \ldots, \ell - 1, \ell$	$2\ell + 1$

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[4] The first four of these letters come from early classifications of spectral lines: sharp, principal, diffuse, and fundamental. The remaining letters are in alphabetical order.

TABLE 42.2

Atomic Shell Notations

n	Shell Symbol
1	K
2	L
3	M
4	N
5	O
6	P

TABLE 42.3

Atomic Subshell Notations

ℓ	Subshell Symbol
0	s
1	p
2	d
3	f
4	g
5	h

Example 42.2 The $n = 2$ Level of Hydrogen

For a hydrogen atom, determine the allowed states corresponding to the principal quantum number $n = 2$ and calculate the energies of these states.

SOLUTION

Conceptualize Think about the atom in the $n = 2$ quantum state. There is only one such state in the Bohr theory, but our discussion of the quantum theory allows for more states because of the possible values of ℓ and m_ℓ.

Categorize We evaluate the results using rules discussed in this section, so we categorize this example as a substitution problem.

From Table 42.1, we find that when $n = 2$, ℓ can be 0 or 1. Find the possible values of m_ℓ from Table 42.1:

$$\ell = 0 \quad \rightarrow \quad m_\ell = 0$$

$$\ell = 1 \quad \rightarrow \quad m_\ell = -1, 0, \text{ or } 1$$

Hence, we have one state, designated as the $2s$ state, that is associated with the quantum numbers $n = 2$, $\ell = 0$, and $m_\ell = 0$, and we have three states, designated as $2p$ states, for which the quantum numbers are $n = 2$, $\ell = 1$, and $m_\ell = -1$; $n = 2$, $\ell = 1$, and $m_\ell = 0$; and $n = 2$, $\ell = 1$, and $m_\ell = 1$.

Find the energy for all four of these states with $n = 2$ from Equation 42.21:

$$E_2 = -\frac{13.606 \text{ eV}}{2^2} = \boxed{-3.401 \text{ eV}}$$

42.5 The Wave Functions for Hydrogen

Because the potential energy of the hydrogen atom depends only on the radial distance r between nucleus and electron, some of the allowed states for this atom can be represented by wave functions that depend only on r. For these states, $f(\theta)$ and $g(\phi)$ are constants. The simplest wave function for hydrogen is the one that describes the $1s$ state and is designated $\psi_{1s}(r)$:

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0{}^3}} e^{-r/a_0} \qquad (42.22)$$

◀ **Wave function for hydrogen in its ground state**

where a_0 is the Bohr radius. (In Problem 24, you can verify that this function satisfies the Schrödinger equation.) Note that ψ_{1s} approaches zero as r approaches ∞ and is normalized as presented (see Eq. 41.7). Furthermore, because ψ_{1s} depends only on r, it is *spherically symmetric*. This symmetry exists for all s states.

Recall that the probability of finding a particle in any region is equal to an integral of the probability density $|\psi|^2$ for the particle over the region. The probability density for the $1s$ state is

$$|\psi_{1s}|^2 = \left(\frac{1}{\pi a_0{}^3}\right) e^{-2r/a_0} \qquad (42.23)$$

Because we imagine the nucleus to be fixed in space at $r = 0$, we can assign this probability density to the question of locating the electron. According to Equation

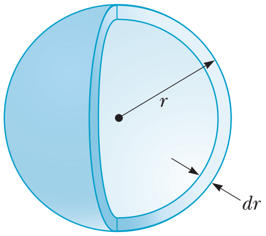


Figure 42.10 A spherical shell of radius r and thickness dr has a volume equal to $4\pi r^2\ dr$.

41.3, the probability of finding the electron in a volume element dV is $|\psi|^2\ dV$. It is convenient to define the *radial probability density function* $P(r)$ as the probability per unit radial length of finding the electron in a spherical shell of radius r and thickness dr. Therefore, $P(r)\ dr$ is the probability of finding the electron in this shell. The volume dV of such an infinitesimally thin shell equals its surface area $4\pi r^2$ multiplied by the shell thickness dr (Fig. 42.10), so we can write this probability as

$$P(r)\ dr = |\psi|^2\ dV = |\psi|^2 4\pi r^2\ dr$$

Therefore, the radial probability density function is

$$P(r) = 4\pi r^2 |\psi|^2 \qquad \textbf{(42.24)}$$

Substituting Equation 42.23 into Equation 42.24 gives the radial probability density function for the hydrogen atom in its ground state:

Radial probability density for the 1*s* state of hydrogen

$$P_{1s}(r) = \left(\frac{4r^2}{a_0{}^3}\right) e^{-2r/a_0} \qquad \textbf{(42.25)}$$

A plot of the function $P_{1s}(r)$ versus r is presented in Figure 42.11a. The peak of the curve corresponds to the most probable value of r for this particular state. We show in Example 42.3 that this peak occurs at the Bohr radius, the radial position of the electron when the hydrogen atom is in its ground state in the Bohr theory, another remarkable agreement between the Bohr theory and the quantum theory.

According to quantum mechanics, the atom has no sharply defined boundary as suggested by the Bohr theory. The probability distribution in Figure 42.11a suggests that the charge of the electron can be modeled as being extended throughout a region of space, commonly referred to as an *electron cloud*. Figure 42.11b shows the probability density of the electron in a hydrogen atom in the 1*s* state as a function of position in the *xy* plane. The darkness of the blue color corresponds to the value of the probability density. The darkest portion of the distribution appears at $r = a_0$, corresponding to the most probable value of r for the electron.

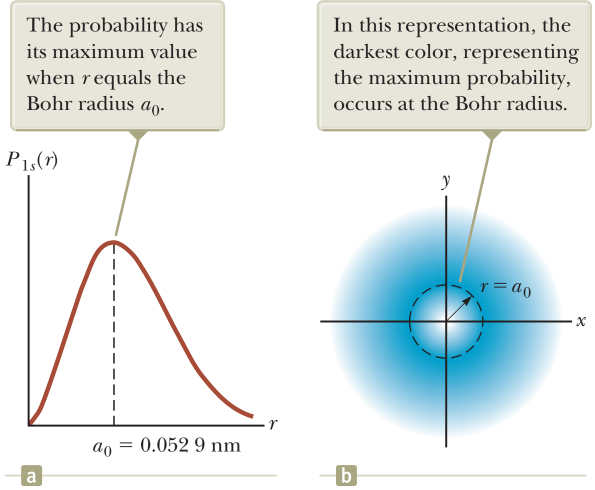


Figure 42.11 (a) The probability of finding the electron as a function of distance from the nucleus for the hydrogen atom in the 1*s* (ground) state. (b) The cross section in the *xy* plane of the spherical electronic charge distribution for the hydrogen atom in its 1*s* state.

Example 42.3 The Ground State of Hydrogen

(A) Calculate the most probable value of r for an electron in the ground state of the hydrogen atom.

SOLUTION

Conceptualize Do not imagine the electron in orbit around the proton as in the Bohr theory of the hydrogen atom. Instead, imagine the charge of the electron spread out in space around the proton in an electron cloud with spherical symmetry.

42.3 *cont.*

Categorize Because the statement of the problem asks for the "most probable value of *r*," we categorize this example as a problem in which the quantum approach is used. (In the Bohr atom, the electron moves in an orbit with an *exact* value of *r*.)

Analyze The most probable value of r corresponds to the maximum in the plot of $P_{1s}(r)$ versus r. We can evaluate the most probable value of r by setting $dP_{1s}/dr = 0$ and solving for r.

Differentiate Equation 42.25 and set the result equal to zero:

$$\frac{dP_{1s}}{dr} = \frac{d}{dr}\left[\left(\frac{4r^2}{a_0{}^3}\right)e^{-2r/a_0}\right] = 0$$

$$e^{-2r/a_0}\frac{d}{dr}(r^2) + r^2\frac{d}{dr}(e^{-2r/a_0}) = 0$$

$$2re^{-2r/a_0} + r^2(-2/a_0)e^{-2r/a_0} = 0$$

$$(1) \quad 2r[1 - (r/a_0)]e^{-2r/a_0} = 0$$

Set the bracketed expression equal to zero and solve for r:

$$1 - \frac{r}{a_0} = 0 \quad \rightarrow \quad r = \boxed{a_0}$$

Finalize The most probable value of r is the Bohr radius! Equation (1) is also satisfied at $r = 0$ and as $r \rightarrow \infty$. These points are locations of the *minimum* probability, which is equal to zero as seen in Figure 42.11a.

(B) Calculate the probability that the electron in the ground state of hydrogen will be found outside the first Bohr radius.

SOLUTION

Analyze The probability is found by integrating the radial probability density function $P_{1s}(r)$ for this state from the Bohr radius a_0 to ∞.

Set up this integral using Equation 42.25:

$$P = \int_{a_0}^{\infty} P_{1s}(r)\,dr = \frac{4}{a_0{}^3}\int_{a_0}^{\infty} r^2 e^{-2r/a_0}\,dr$$

Put the integral in dimensionless form by changing variables from r to $z = 2r/a_0$, noting that $z = 2$ when $r = a_0$ and that $dr = (a_0/2)\ dz$:

$$P = \frac{4}{a_0{}^3}\int_2^{\infty}\left(\frac{za_0}{2}\right)^2 e^{-z}\left(\frac{a_0}{2}\right)dz = \tfrac{1}{2}\int_2^{\infty} z^2e^{-z}\,dz$$

Evaluate the integral using partial integration (see Appendix B.7):

$$P = -\tfrac{1}{2}(z^2 + 2z + 2)e^{-z}\Big|_2^{\infty}$$

Evaluate between the limits:

$$P = 0 - [-\tfrac{1}{2}(4 + 4 + 2)e^{-2}] = 5e^{-2} = \boxed{0.677 \text{ or } 67.7\ \%}$$

Finalize This probability is larger than 50%. The reason for this value is the asymmetry in the radial probability density function (Fig. 42.11a), which has more area to the right of the peak than to the left.

WHAT IF? What if you were asked for the *average* value of r for the electron in the ground state rather than the most probable value?

Answer The average value of r is the same as the expectation value for r.

Use Equation 42.25 to evaluate the average value of r:

$$r_{\text{avg}} = \langle r\rangle = \int_0^{\infty} rP(r)\,dr = \int_0^{\infty} r\left(\frac{4r^2}{a_0{}^3}\right)e^{-2r/a_0}\,dr$$

$$= \left(\frac{4}{a_0{}^3}\right)\int_0^{\infty} r^3e^{-2r/a_0}\,dr$$

Evaluate the integral with the help of the first integral listed in Table B.6 in Appendix B:

$$r_{\text{avg}} = \left(\frac{4}{a_0{}^3}\right)\left(\frac{3!}{(2/a_0)^4}\right) = \tfrac{3}{2}a_0$$

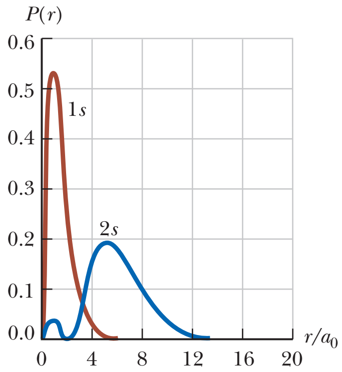
Again, the average value is larger than the most probable value because of the asymmetry in the wave function as seen in Figure 42.11a.

The next-simplest wave function for the hydrogen atom is the one corresponding to the 2s state ($n = 2$, $\ell = 0$). The normalized wave function for this state is

Wave function for hydrogen in the 2s state ▶

$$\psi_{2s}(r) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0} \tag{42.26}$$

Again notice that ψ_{2s} depends only on r and is spherically symmetric. The energy corresponding to this state is $E_2 = -(13.606/4)$ eV $= -3.401$ eV. This energy level represents the first excited state of hydrogen. A plot of the radial probability density function for this state in comparison to the 1s state is shown in Active Figure 42.12. The plot for the 2s state has two peaks. In this case, the most probable value corresponds to that value of r that has the highest value of P ($\approx 5a_0$). An electron in the 2s state would be much farther from the nucleus (on the average) than an electron in the 1s state.



ACTIVE FIGURE 42.12

The radial probability density function versus r/a_0 for the 1s and 2s states of the hydrogen atom.

42.6 Physical Interpretation of the Quantum Numbers

The principal quantum number n of a particular state in the hydrogen atom determines the energy of the atom according to Equation 42.21. Now let's see what the other quantum numbers in our atomic model correspond to physically.

The Orbital Quantum Number ℓ

We begin this discussion by returning briefly to the Bohr model of the atom. If the electron moves in a circle of radius r, the magnitude of its angular momentum relative to the center of the circle is $L = m_e vr$. The direction of $\vec{\mathbf{L}}$ is perpendicular to the plane of the circle and is given by a right-hand rule. According to classical physics, the magnitude L of the orbital angular momentum can have any value. The Bohr model of hydrogen, however, postulates that the magnitude of the angular momentum of the electron is restricted to multiples of $\hbar$; that is, $L = n\hbar$. This model must be modified because it predicts (incorrectly) that the ground state of hydrogen has one unit of angular momentum. Furthermore, if L is taken to be zero in the Bohr model, the electron must be pictured as a particle oscillating along a straight line through the nucleus, which is a physically unacceptable situation.

These difficulties are resolved with the quantum-mechanical model of the atom, although we must give up the convenient mental representation of an electron orbiting in a well-defined circular path. Despite the absence of this representation, the atom does indeed possess an angular momentum and it is still called orbital angular momentum. According to quantum mechanics, an atom in a state whose principal quantum number is n can take on the following *discrete* values of the magnitude of the orbital angular momentum:[5]

Allowed values of L ▶

$$\boxed{L = \sqrt{\ell(\ell + 1)}\,\hbar \qquad \ell = 0, 1, 2, \ldots, n - 1} \tag{42.27}$$

Given these allowed values of ℓ, we see that $L = 0$ (corresponding to $\ell = 0$) is an acceptable value of the magnitude of the angular momentum. That L can be zero in this model serves to point out the inherent difficulties in any attempt to describe results based on quantum mechanics in terms of a purely particle-like (classical) model. In the quantum-mechanical interpretation, the electron cloud for the $L = 0$ state is spherically symmetric and has no fundamental rotation axis.

The Orbital Magnetic Quantum Number m_ℓ

Because angular momentum is a vector, its direction must be specified. Recall from Chapter 29 that a current loop has a corresponding magnetic moment $\vec{\boldsymbol{\mu}} = I\vec{\mathbf{A}}$ (Eq.

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[5] Equation 42.27 is a direct result of the mathematical solution of the Schrödinger equation and the application of angular boundary conditions. This development, however, is beyond the scope of this book.

29.15), where I is the current in the loop and $\vec{\mathbf{A}}$ is a vector perpendicular to the loop whose magnitude is the area of the loop. Such a moment placed in a magnetic field $\vec{\mathbf{B}}$ interacts with the field. Suppose a weak magnetic field applied along the z axis defines a direction in space. According to classical physics, the energy of the loop–field system depends on the direction of the magnetic moment of the loop with respect to the magnetic field as described by Equation 29.18, $U = -\vec{\boldsymbol{\mu}} \cdot \vec{\mathbf{B}}$. Any energy between $-\mu B$ and $+\mu B$ is allowed by classical physics.

In the Bohr theory, the circulating electron represents a current loop. In the quantum-mechanical approach to the hydrogen atom, we abandon the circular orbit viewpoint of the Bohr theory, but the atom still possesses an orbital angular momentum. Therefore, there is some sense of rotation of the electron around the nucleus and a magnetic moment is present due to this angular momentum.

As mentioned in Section 42.3, spectral lines from some atoms are observed to split into groups of three closely spaced lines when the atoms are placed in a magnetic field. Suppose the hydrogen atom is located in a magnetic field. According to quantum mechanics, there are *discrete* directions allowed for the magnetic moment vector $\vec{\boldsymbol{\mu}}$ with respect to the magnetic field vector $\vec{\mathbf{B}}$. This situation is very different from that in classical physics, in which all directions are allowed.

Because the magnetic moment $\vec{\boldsymbol{\mu}}$ of the atom can be related[6] to the angular momentum vector $\vec{\mathbf{L}}$, the discrete directions of $\vec{\boldsymbol{\mu}}$ translate to the direction of $\vec{\mathbf{L}}$ being quantized. This quantization means that L_z (the projection of $\vec{\mathbf{L}}$ along the z axis) can have only discrete values. The orbital magnetic quantum number m_ℓ specifies the allowed values of the z component of the orbital angular momentum according to the expression[7]

$$\boxed{L_z = m_\ell \hbar} \qquad \textbf{(42.28)}$$

◀ **Allowed values of L_z**

The quantization of the possible orientations of $\vec{\mathbf{L}}$ with respect to an external magnetic field is often referred to as **space quantization.**

Let's look at the possible magnitudes and orientations of $\vec{\mathbf{L}}$ for a given value of ℓ. Recall that m_ℓ can have values ranging from $-\ell$ to ℓ. If $\ell = 0$, then $L = 0$; the only allowed value of m_ℓ is $m_\ell = 0$ and $L_z = 0$. If $\ell = 1$, then $L = \sqrt{2}\hbar$. The possible values of m_ℓ are -1, 0, and 1, so L_z may be $-\hbar$, 0, or $\hbar$. If $\ell = 2$, the magnitude of the orbital angular momentum is $\sqrt{6}\,\hbar$. The value of m_ℓ can be -2, -1, 0, 1, or 2, corresponding to L_z values of $-2\hbar$, $-\hbar$, 0, $\hbar$, or $2\hbar$, and so on.

Figure 42.13a on page 1268 shows a **vector model** that describes space quantization for the case $\ell = 2$. Notice that $\vec{\mathbf{L}}$ can never be aligned parallel or antiparallel to $\vec{\mathbf{B}}$ because the maximum value of L_z is $\ell\hbar$, which is less than the magnitude of the angular momentum $L = \sqrt{\ell(\ell + 1)}\,\hbar$. The angular momentum vector $\vec{\mathbf{L}}$ is allowed to be perpendicular to $\vec{\mathbf{B}}$, which corresponds to the case of $L_z = 0$ and $\ell = 0$.

The vector $\vec{\mathbf{L}}$ does not point in one specific direction even though its z component is fixed. If $\vec{\mathbf{L}}$ were known exactly, all three components L_x, L_y, and L_z would be specified, which is inconsistent with the uncertainty principle. How can the magnitude and z component of a vector be specified, but the vector not be completely specified? To answer, imagine that L_x and L_y are completely unspecified so that $\vec{\mathbf{L}}$ lies anywhere on the surface of a cone that makes an angle θ with the z axis as shown in Figure 42.13b. From the figure, we see that θ is also quantized and that its values are specified through the relationship

$$\cos\theta = \frac{L_z}{L} = \frac{m_\ell}{\sqrt{\ell(\ell + 1)}} \qquad \textbf{(42.29)}$$

If the atom is placed in a magnetic field, the energy $U = -\vec{\boldsymbol{\mu}} \cdot \vec{\mathbf{B}}$ is additional energy for the atom–field system beyond that described in Equation 42.21. Because

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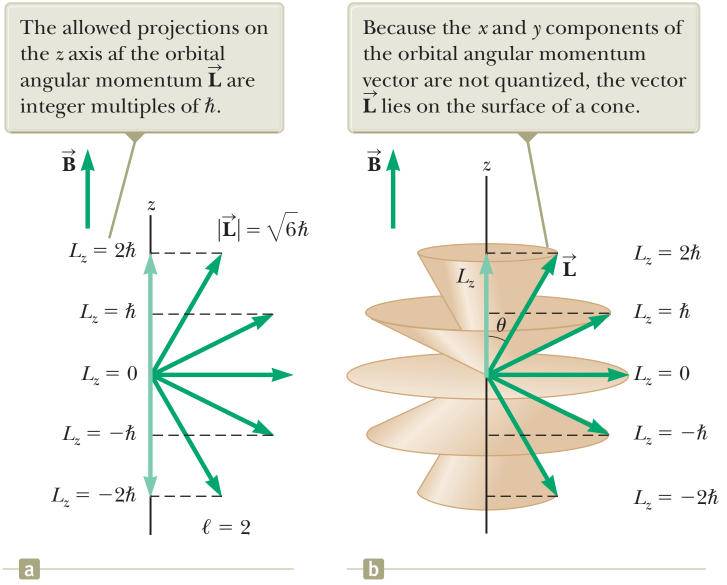
[6] See Equation 30.22 for this relationship as derived from a classical viewpoint. Quantum mechanics arrives at the same result.

[7] As with Equation 42.27, the relationship expressed in Equation 42.28 arises from the solution to the Schrödinger equation and application of boundary conditions.

Figure 42.13 A vector model for $\ell = 2$.

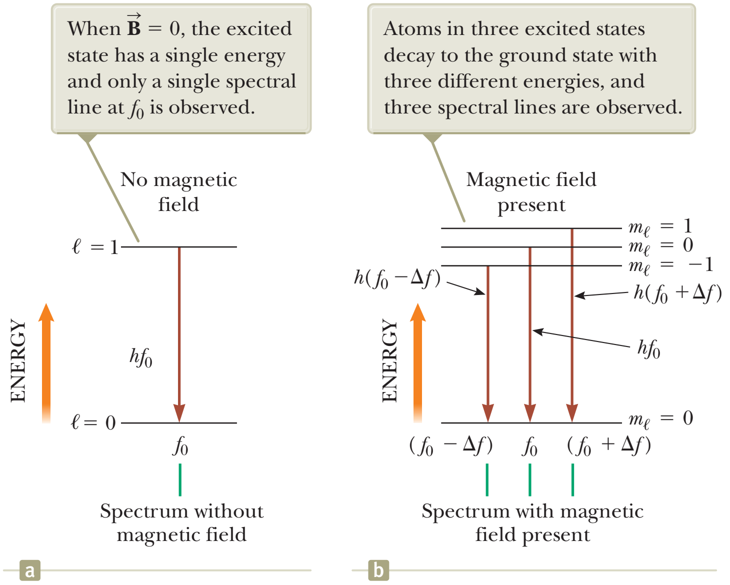

The allowed projections on the z axis af the orbital angular momentum $\vec{\mathbf{L}}$ are integer multiples of $\hbar$.

Because the x and y components of the orbital angular momentum vector are not quantized, the vector $\vec{\mathbf{L}}$ lies on the surface of a cone.

the directions of $\vec{\boldsymbol{\mu}}$ are quantized, there are discrete total energies for the atom corresponding to different values of m_ℓ. Figure 42.14a shows a transition between two atomic levels in the absence of a magnetic field. In Figure 42.14b, a magnetic field is applied and the upper level, with $\ell = 1$, splits into three levels corresponding to the different directions of $\vec{\boldsymbol{\mu}}$. There are now three possible transitions from the $\ell = 1$ subshell to the $\ell = 0$ subshell. Therefore, in a collection of atoms, there are atoms in all three states and the single spectral line in Figure 42.14a splits into three spectral lines. This phenomenon is called the *Zeeman effect.*

The Zeeman effect can be used to measure extraterrestrial magnetic fields. For example, the splitting of spectral lines in light from hydrogen atoms in the surface of the Sun can be used to calculate the magnitude of the magnetic field at that location. The Zeeman effect is one of many phenomena that cannot be explained with the Bohr model but are successfully explained by the quantum model of the atom.

Figure 42.14 The Zeeman effect. (a) Energy levels for the ground and first excited states of a hydrogen atom. (b) When the atom is immersed in a magnetic field $\vec{\mathbf{B}}$, the state with $\ell = 1$ splits into three states, giving rise to emission lines at f_0, $f_0 + \Delta f$, and $f_0 - \Delta f$, where Δf is the frequency shift of the emission caused by the magnetic field.


When $\vec{\mathbf{B}} = 0$, the excited state has a single energy and only a single spectral line at f_0 is observed.

Atoms in three excited states decay to the ground state with three different energies, and three spectral lines are observed.

Example 42.4 Space Quantization for Hydrogen

Consider the hydrogen atom in the $\ell = 3$ state. Calculate the magnitude of $\vec{\mathbf{L}}$, the allowed values of L_z, and the corresponding angles θ that $\vec{\mathbf{L}}$ makes with the z axis.

SOLUTION

Conceptualize Consider Figure 42.13, which is a vector model for $\ell = 2$. Draw such a vector model for $\ell = 3$ to help with this problem.

Categorize We evaluate results using equations developed in this section, so we categorize this example as a substitution problem.

Calculate the magnitude of the orbital angular momentum using Equation 42.27:

$$L = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{3(3 + 1)}\hbar = \boxed{2\sqrt{3}\,\hbar}$$

Calculate the allowed values of L_z using Equation 42.28 with $m_\ell = -3, -2, -1, 0, 1, 2$, and 3:

$$L_z = \boxed{-3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar}$$

Calculate the allowed values of $\cos\theta$ using Equation 42.29:

$$\cos\theta = \frac{\pm 3}{2\sqrt{3}} = \pm 0.866 \qquad \cos\theta = \frac{\pm 2}{2\sqrt{3}} = \pm 0.577$$

$$\cos\theta = \frac{\pm 1}{2\sqrt{3}} = \pm 0.289 \qquad \cos\theta = \frac{0}{2\sqrt{3}} = 0$$

Find the angles corresponding to these values of $\cos\theta$:

$$\theta = \boxed{30.0°, 54.7°, 73.2°, 90.0°, 107°, 125°, 150°}$$

WHAT IF? What if the value of ℓ is an arbitrary integer? For an arbitrary value of ℓ, how many values of m_ℓ are allowed?

Answer For a given value of ℓ, the values of m_ℓ range from $-\ell$ to $+\ell$ in steps of 1. Therefore, there are 2ℓ nonzero values of m_ℓ (specifically, $\pm 1, \pm 2, \ldots, \pm\ell$). In addition, one more value of $m_\ell = 0$ is possible, for a total of $2\ell + 1$ values of m_ℓ. This result is critical in understanding the results of the Stern–Gerlach experiment described below with regard to spin.

The Spin Magnetic Quantum Number m_s

The three quantum numbers n, ℓ, and m_ℓ discussed so far are generated by applying boundary conditions to solutions of the Schrödinger equation, and we can assign a physical interpretation to each quantum number. Let's now consider **electron spin,** which does *not* come from the Schrödinger equation.

In Example 42.2, we found four quantum states corresponding to $n = 2$. In reality, however, eight such states occur. The additional four states can be explained by requiring a fourth quantum number for each state, the **spin magnetic quantum number m_s.**

The need for this new quantum number arises because of an unusual feature observed in the spectra of certain gases, such as sodium vapor. Close examination of one prominent line in the emission spectrum of sodium reveals that the line is, in fact, two closely spaced lines called a *doublet.*[8] The wavelengths of these lines occur in the yellow region of the electromagnetic spectrum at 589.0 nm and 589.6 nm. In 1925, when this doublet was first observed, it could not be explained with the existing atomic theory. To resolve this dilemma, Samuel Goudsmit (1902–1978) and George Uhlenbeck (1900–1988), following a suggestion made by Austrian physicist Wolfgang Pauli, proposed the spin quantum number.

To describe this new quantum number, it is convenient (but technically incorrect) to imagine the electron spinning about its axis as it orbits the nucleus as


Courtesy of AIP Niels Bohr Library, Margarethe Bohr Collection

Wolfgang Pauli and Niels Bohr watch a spinning top. The spin of the electron is analogous to the spin of the top but is different in many ways.

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[8] This phenomenon is a Zeeman effect for spin and is identical in nature to the Zeeman effect for orbital angular momentum discussed before Example 42.4 except that no external magnetic field is required. The magnetic field for this Zeeman effect is internal to the atom and arises from the relative motion of the electron and the nucleus.

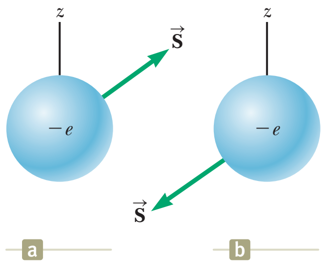

Figure 42.15 The spin of an electron can be either (a) up or (b) down relative to a specified z axis. As in the case of orbital angular momentum, the x and y components of the spin angular momentum vector are not quantized.

described in Section 30.6. As illustrated in Figure 42.15, only two directions exist for the electron spin. If the direction of spin is as shown in Figure 42.15a, the electron is said to have *spin up*. If the direction of spin is as shown in Figure 42.15b, the electron is said to have *spin down*. In the presence of a magnetic field, the energy of the electron is slightly different for the two spin directions. This energy difference accounts for the sodium doublet.

The classical description of electron spin—as resulting from a spinning electron—is incorrect. More recent theory indicates that the electron is a point particle, without spatial extent. Therefore, the electron cannot be considered to be spinning. Despite this conceptual difficulty, all experimental evidence supports the idea that an electron does have some intrinsic angular momentum that can be described by the spin magnetic quantum number. Paul Dirac (1902–1984) showed that this fourth quantum number originates in the relativistic properties of the electron.

In 1921, Otto Stern (1888–1969) and Walter Gerlach (1889–1979) performed an experiment that demonstrated space quantization. Their results, however, were not in quantitative agreement with the atomic theory that existed at that time. In their experiment, a beam of silver atoms sent through a nonuniform magnetic field was split into two discrete components (Fig. 42.16). Stern and Gerlach repeated the experiment using other atoms, and in each case the beam split into two or more components. The classical argument is as follows. If the z direction is chosen to be the direction of the maximum nonuniformity of $\vec{\mathbf{B}}$, the net magnetic force on the atoms is along the z axis and is proportional to the component of the magnetic moment $\vec{\boldsymbol{\mu}}$ of the atom in the z direction. Classically, $\vec{\boldsymbol{\mu}}$ can have any orientation, so the deflected beam should be spread out continuously. According to quantum mechanics, however, the deflected beam has an integral number of discrete components and the number of components determines the number of possible values of μ_z. Therefore, because the Stern–Gerlach experiment showed split beams, space quantization was at least qualitatively verified.

Pitfall Prevention 42.5

The Electron Is Not Spinning

Although the concept of a spinning electron is conceptually useful, it should not be taken literally. The spin of the Earth is a mechanical rotation. On the other hand, electron spin is a purely quantum effect that gives the electron an angular momentum as if it were physically spinning.

For the moment, let's assume the magnetic moment of the atom is due to the orbital angular momentum. Because μ_z is proportional to m_ℓ, the number of possible values of μ_z is $2\ell + 1$ as found in the What If? section of Example 42.4. Furthermore, because ℓ is an integer, the number of values of μ_z is always odd. This prediction is not consistent with Stern and Gerlach's observation of two components (an *even* number) in the deflected beam of silver atoms. Hence, either quantum mechanics is incorrect or the model is in need of refinement.

In 1927, T. E. Phipps and J. B. Taylor repeated the Stern–Gerlach experiment using a beam of hydrogen atoms. Their experiment was important because it involved an atom containing a single electron in its ground state, for which the quantum theory makes reliable predictions. Recall that $\ell = 0$ for hydrogen in its ground state, so $m_\ell = 0$. Therefore, we would not expect the beam to be deflected

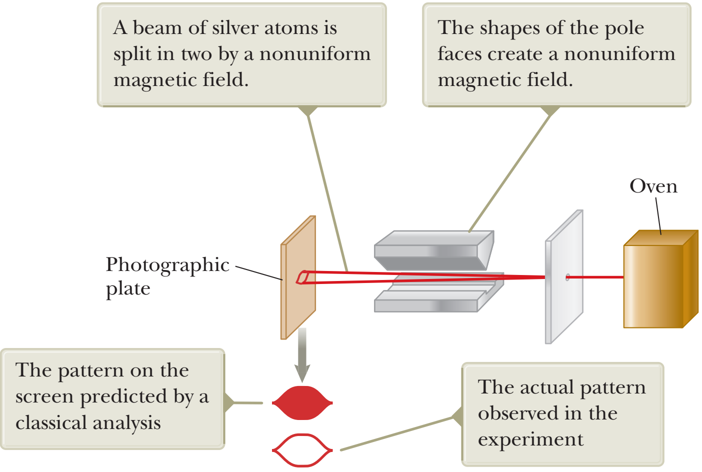

Figure 42.16 The technique used by Stern and Gerlach to verify space quantization.

by the magnetic field at all because the magnetic moment $\vec{\boldsymbol{\mu}}$ of the atom is zero. The beam in the Phipps–Taylor experiment, however, was again split into two components! On the basis of that result, we must conclude that something other than the electron's orbital motion is contributing to the atomic magnetic moment.

As we learned earlier, Goudsmit and Uhlenbeck had proposed that the electron has an intrinsic angular momentum, spin, apart from its orbital angular momentum. In other words, the total angular momentum of the electron in a particular electronic state contains both an orbital contribution $\vec{\mathbf{L}}$ and a spin contribution $\vec{\mathbf{S}}$. The Phipps–Taylor result confirmed the hypothesis of Goudsmit and Uhlenbeck.

In 1929, Dirac used the relativistic form of the total energy of a system to solve the relativistic wave equation for the electron in a potential well. His analysis confirmed the fundamental nature of electron spin. (Spin, like mass and charge, is an *intrinsic* property of a particle, independent of its surroundings.) Furthermore, the analysis showed that electron spin[9] can be described by a single quantum number s, whose value can be only $s = \frac{1}{2}$. The spin angular momentum of the electron *never changes*. This notion contradicts classical laws, which dictate that a rotating charge slows down in the presence of an applied magnetic field because of the Faraday emf that accompanies the changing field. Furthermore, if the electron is viewed as a spinning ball of charge subject to classical laws, parts of the electron near its surface would be rotating with speeds exceeding the speed of light. Therefore, the classical picture must not be pressed too far; ultimately, spin of an electron is a quantum entity defying any simple classical description.

Because spin is a form of angular momentum, it must follow the same quantum rules as orbital angular momentum. In accordance with Equation 42.27, the magnitude of the **spin angular momentum** $\vec{\mathbf{S}}$ for the electron is

$$S = \sqrt{s(s+1)}\,\hbar = \frac{\sqrt{3}}{2}\hbar \tag{42.30}$$

◀ **Magnitude of the spin angular momentum of an electron**

Like orbital angular momentum $\vec{\mathbf{L}}$, spin angular momentum $\vec{\mathbf{S}}$ exhibits space quantization as described in Figure 42.17. It can have two orientations relative to a z axis, specified by the **spin magnetic quantum number** $m_s = \pm\frac{1}{2}$. Similar to Equation 42.28 for orbital angular momentum, the z component of spin angular momentum is

$$S_z = m_s\hbar = \pm\tfrac{1}{2}\hbar \tag{42.31}$$

◀ **Allowed values of S_z**

The two values $\pm\hbar/2$ for S_z correspond to the two possible orientations for $\vec{\mathbf{S}}$ shown in Figure 42.17. The value $m_s = +\frac{1}{2}$ refers to the spin-up case, and $m_s = -\frac{1}{2}$ refers to the spin-down case. Notice that Equations 42.30 and 42.31 do not allow the spin vector to lie along the z axis. The actual direction of $\vec{\mathbf{S}}$ is at a relatively large angle with respect to the z axis as shown in Figures 42.15 and 42.17.

As discussed in the What if? feature of Example 42.4, there are $2\ell + 1$ possible values of m_ℓ for orbital angular momentum. Similarly, for spin angular momentum, there are $2s + 1$ values of m_s. For a spin of $s = \frac{1}{2}$, the number of values of m_s is $2s + 1 = 2$. These two possibilities for m_s lead to the splitting of the beams into two components in the Stern–Gerlach and Phipps–Taylor experiments.

The spin magnetic moment $\vec{\boldsymbol{\mu}}_{\text{spin}}$ of the electron is related to its spin angular momentum $\vec{\mathbf{S}}$ by the expression

$$\vec{\boldsymbol{\mu}}_{\text{spin}} = -\frac{e}{m_e}\vec{\mathbf{S}} \tag{42.32}$$

where e is the electronic charge and m_e is the mass of the electron. Because $S_z = \pm\frac{1}{2}\hbar$, the z component of the spin magnetic moment can have the values

$$\vec{\boldsymbol{\mu}}_{\text{spin},z} = \pm\frac{e\hbar}{2m_e} \tag{42.33}$$

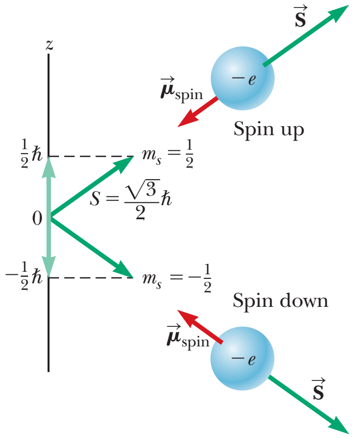

Figure 42.17 Spin angular momentum $\vec{\mathbf{S}}$ exhibits space quantization. This figure shows the two allowed orientations of the spin angular momentum vector $\vec{\mathbf{S}}$ and the spin magnetic moment $\vec{\boldsymbol{\mu}}_{\text{spin}}$ for a spin-$\frac{1}{2}$ particle, such as the electron.

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[9] Scientists often use the word *spin* when referring to the spin angular momentum quantum number. For example, it is common to say, "The electron has a spin of one half."

TABLE 42.4 *Quantum Numbers for the $n = 2$ State of Hydrogen*

n	ℓ	m_ℓ	m_s	Subshell	Shell	Number of States in Subshell
2	0	0	$\frac{1}{2}$	$2s$	L	2
2	0	0	$-\frac{1}{2}$			
2	1	1	$\frac{1}{2}$	$2p$	L	6
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	$-\frac{1}{2}$			

As we learned in Section 30.6, the quantity $e\hbar/2m_e$ is the Bohr magneton $\mu_B = 9.27 \times 10^{-24}$ J/T. The ratio of magnetic moment to angular momentum is twice as great for spin angular momentum (Eq. 42.32) as it is for orbital angular momentum (Eq. 30.22). The factor of 2 is explained in a relativistic treatment first carried out by Dirac.

Today, physicists explain the Stern–Gerlach and Phipps–Taylor experiments as follows. The observed magnetic moments for both silver and hydrogen are due to spin angular momentum only, with no contribution from orbital angular momentum. In the Phipps–Taylor experiment, the single electron in the hydrogen atom has its electron spin quantized in the magnetic field in such a way that the z component of spin angular momentum is either $\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$, corresponding to $m_s = \pm\frac{1}{2}$. Electrons with spin $+\frac{1}{2}$ are deflected downward, and those with spin $-\frac{1}{2}$ are deflected upward. In the Stern–Gerlach experiment, 46 of a silver atom's 47 electrons are in filled subshells with paired spins. Therefore, these 46 electrons have a net zero contribution to both orbital and spin angular momentum for the atom. The angular momentum of the atom is due to only the 47th electron. This electron lies in the $5s$ subshell, so there is no contribution from orbital angular momentum. As a result, the silver atoms have angular momentum due to just the spin of one electron and behave in the same way in a nonuniform magnetic field as the hydrogen atoms in the Phipps–Taylor experiment.

The Stern–Gerlach experiment provided two important results. First, it verified the concept of space quantization. Second, it showed that spin angular momentum exists, even though this property was not recognized until four years after the experiments were performed.

As mentioned earlier, there are eight quantum states corresponding to $n = 2$ in the hydrogen atom, not four as found in Example 42.2. Each of the four states in Example 42.2 is actually two states because of the two possible values of m_s. Table 42.4 shows the quantum numbers corresponding to these eight states.

42.7 The Exclusion Principle and the Periodic Table

We have found that the state of a hydrogen atom is specified by four quantum numbers: n, ℓ, m_ℓ, and m_s. As it turns out, the number of states available to other atoms may also be predicted by this same set of quantum numbers. In fact, these four quantum numbers can be used to describe all the electronic states of an atom, regardless of the number of electrons in its structure.

For our discussion of atoms with many electrons, it is often easiest to assign the quantum numbers to the electrons in the atom as opposed to the entire atom. An obvious question that arises here is, "How many electrons can be in a particular quantum state?" Pauli answered this important question in 1925, in a statement known as the **exclusion principle:**

Pitfall Prevention 42.6

The Exclusion Principle Is More General

A more general form of the exclusion principle, discussed in Chapter 46, states that no two *fermions* can be in the same quantum state. Fermions are particles with half-integral spin ($\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, and so on).

TABLE 42.5 *Allowed Quantum States for an Atom Up to $n = 3$*

Shell	n	1	2				3								
Subshell	ℓ	0	0	1			0	1			2				
Orbital	m_ℓ	0	0	1	0	−1	0	1	0	−1	2	1	0	−1	−2
	m_s	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

> No two electrons can ever be in the same quantum state; therefore, no two electrons in the same atom can have the same set of quantum numbers.

If this principle were not valid, an atom could radiate energy until every electron in the atom is in the lowest possible energy state and therefore the chemical behavior of the elements would be grossly modified. Nature as we know it would not exist.

In reality, we can view the electronic structure of complex atoms as a succession of filled levels increasing in energy. As a general rule, the order of filling of an atom's subshells is as follows. Once a subshell is filled, the next electron goes into the lowest-energy vacant subshell. We can understand this behavior by recognizing that if the atom were not in the lowest energy state available to it, it would radiate energy until it reached this state.

Before we discuss the electronic configuration of various elements, it is convenient to define an *orbital* as the atomic state characterized by the quantum numbers n, ℓ, and m_ℓ. The exclusion principle tells us that only two electrons can be present in any orbital. One of these electrons has a spin magnetic quantum number $m_s = +\frac{1}{2}$, and the other has $m_s = -\frac{1}{2}$. Because each orbital is limited to two electrons, the number of electrons that can occupy the various shells is also limited.

Table 42.5 shows the allowed quantum states for an atom up to $n = 3$. The arrows pointing upward indicate an electron described by $m_s = +\frac{1}{2}$, and those pointing downward indicate that $m_s = -\frac{1}{2}$. The $n = 1$ shell can accommodate only two electrons because $m_\ell = 0$ means that only one orbital is allowed. (The three quantum numbers describing this orbital are $n = 1$, $\ell = 0$, and $m_\ell = 0$.) The $n = 2$ shell has two subshells, one for $\ell = 0$ and one for $\ell = 1$. The $\ell = 0$ subshell is limited to two electrons because $m_\ell = 0$. The $\ell = 1$ subshell has three allowed orbitals, corresponding to $m_\ell = 1$, 0, and −1. Because each orbital can accommodate two electrons, the $\ell = 1$ subshell can hold six electrons. Therefore, the $n = 2$ shell can contain eight electrons as shown in Table 42.4. The $n = 3$ shell has three subshells ($\ell = 0, 1, 2$) and nine orbitals, accommodating up to 18 electrons. In general, each shell can accommodate up to $2n^2$ electrons.

The exclusion principle can be illustrated by examining the electronic arrangement in a few of the lighter atoms. The atomic number Z of any element is the number of protons in the nucleus of an atom of that element. A neutral atom of that element has Z electrons. Hydrogen ($Z = 1$) has only one electron, which, in the ground state of the atom, can be described by either of two sets of quantum numbers n, ℓ, m_ℓ, m_s: 1, 0, 0, $\frac{1}{2}$ or 1, 0, 0, $-\frac{1}{2}$. This electronic configuration is often written $1s^1$. The notation $1s$ refers to a state for which $n = 1$ and $\ell = 0$, and the superscript indicates that one electron is present in the s subshell.

Helium ($Z = 2$) has two electrons. In the ground state, their quantum numbers 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. This electronic configuration is written $1s^2$.

Lithium ($Z = 3$) has three electrons. In the ground state, two of them are in the $1s$ subshell. The third is in the $2s$ subshell because this subshell is slightly lower in energy than the $2p$ subshell.[10] Hence, the electronic configuration for lithium is $1s^2 2s^1$.


CERN, courtesy of AIP Emilio Segrè Visual Archive

Wolfgang Pauli

Austrian Theoretical Physicist (1900–1958)

An extremely talented theoretician who made important contributions in many areas of modern physics, Pauli gained public recognition at the age of 21 with a masterful review article on relativity that is still considered one of the finest and most comprehensive introductions to the subject. His other major contributions were the discovery of the exclusion principle, the explanation of the connection between particle spin and statistics, theories of relativistic quantum electrodynamics, the neutrino hypothesis, and the hypothesis of nuclear spin.

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[10] To a first approximation, energy depends only on the quantum number n, as we have discussed. Because of the effect of the electronic charge shielding the nuclear charge, however, energy depends on ℓ also in multielectron atoms. We shall discuss these shielding effects in Section 42.8.

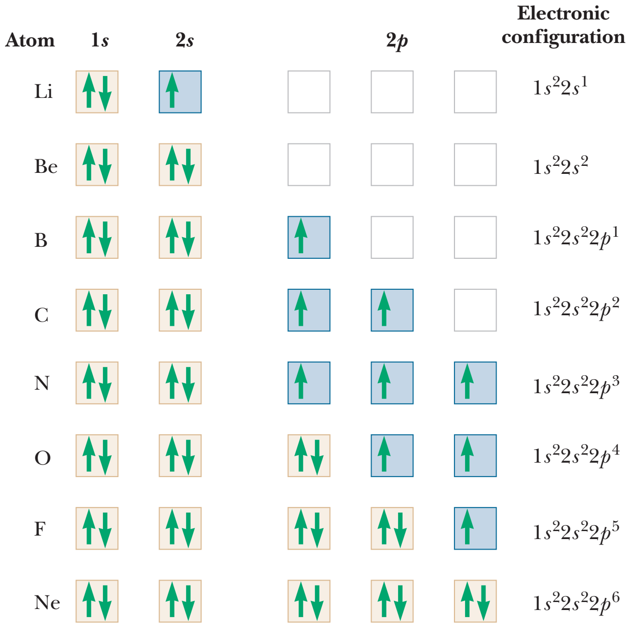


Figure 42.18 The filling of electronic states must obey both the exclusion principle and Hund's rule.

The electronic configurations of lithium and the next several elements are provided in Figure 42.18. The electronic configuration of beryllium ($Z = 4$), with its four electrons, is $1s^2 2s^2$, and boron ($Z = 5$) has a configuration of $1s^2 2s^2 2p^1$. The $2p$ electron in boron may be described by any of the six equally probable sets of quantum numbers listed in Table 42.4. In Figure 42.18, we show this electron in the leftmost $2p$ box with spin up, but it is equally likely to be in any $2p$ box with spin either up or down.

Carbon ($Z = 6$) has six electrons, giving rise to a question concerning how to assign the two $2p$ electrons. Do they go into the same orbital with paired spins (↑↓), or do they occupy different orbitals with unpaired spins (↑↑)? Experimental data show that the most stable configuration (that is, the one with the lowest energy) is the latter, in which the spins are unpaired. Hence, the two $2p$ electrons in carbon and the three $2p$ electrons in nitrogen ($Z = 7$) have unpaired spins as Figure 42.18 shows. The general rule that governs such situations, called **Hund's rule,** states that

> when an atom has orbitals of equal energy, the order in which they are filled by electrons is such that a maximum number of electrons have unpaired spins.

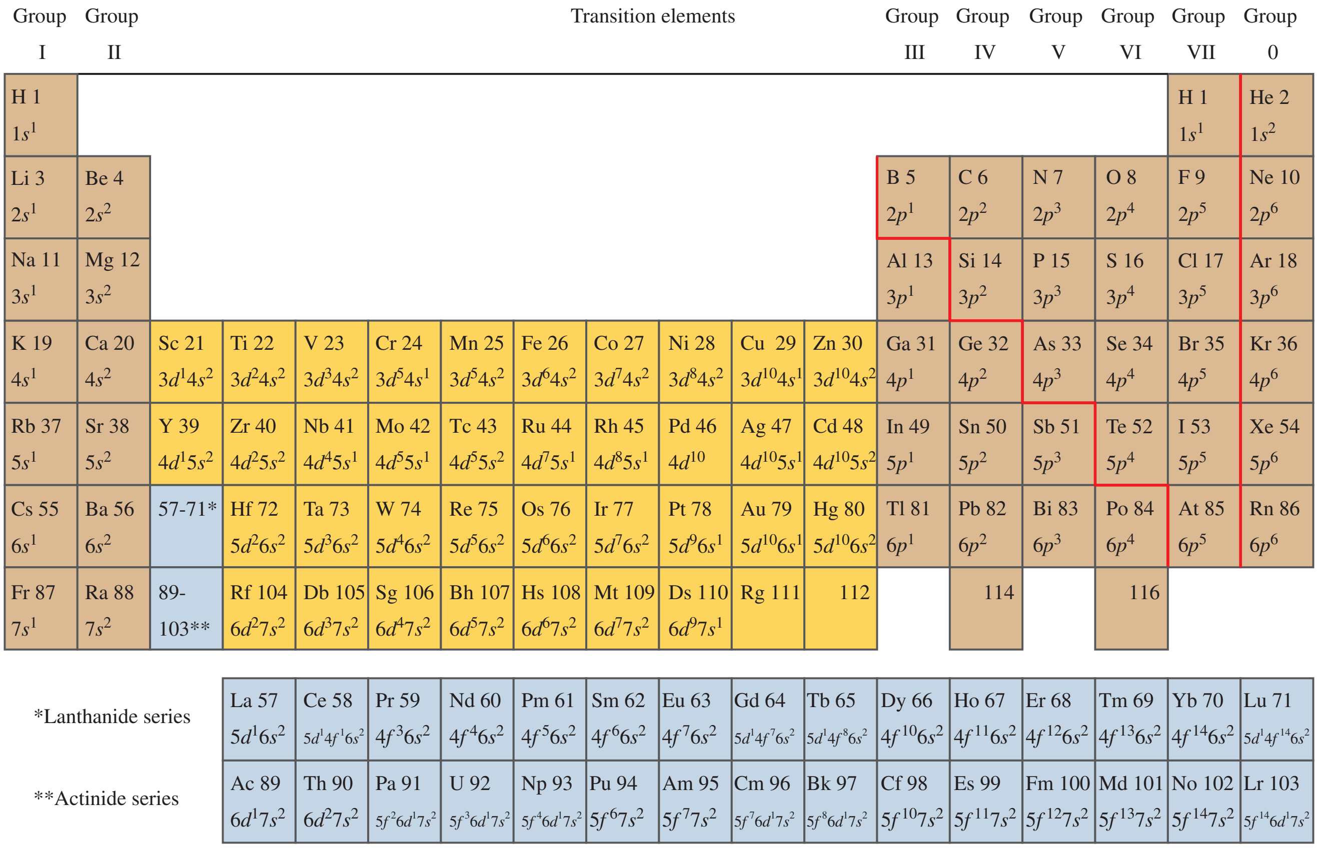
Some exceptions to this rule occur in elements having subshells that are close to being filled or half-filled.

In 1871, long before quantum mechanics was developed, the Russian chemist Dmitri Mendeleev (1834–1907) made an early attempt at finding some order among the chemical elements. He was trying to organize the elements for the table of contents of a book he was writing. He arranged the atoms in a table similar to that shown in Figure 42.19, according to their atomic masses and chemical similarities. The first table Mendeleev proposed contained many blank spaces, and he boldly stated that the gaps were there only because the elements had not yet been discovered. By noting the columns in which some missing elements should be located, he was able to make rough predictions about their chemical properties. Within 20 years of this announcement, most of these elements were indeed discovered.

The elements in the **periodic table** (Fig. 42.19) are arranged so that all those in a column have similar chemical properties. For example, consider the elements in the last column, which are all gases at room temperature: He (helium), Ne (neon), Ar (argon), Kr (krypton), Xe (xenon), and Rn (radon). The outstanding characteristic of all these elements is that they do not normally take part in chemical reactions; that is, they do not readily join with other atoms to form molecules. They are therefore called *inert gases* or *noble gases.*

We can partially understand this behavior by looking at the electronic configurations in Figure 42.19. The chemical behavior of an element depends on the outermost shell that contains electrons. The electronic configuration for helium is $1s^2$, and the $n = 1$ shell (which is the outermost shell because it is the only shell) is filled. Also, the energy of the atom in this configuration is considerably lower than the energy for the configuration in which an electron is in the next available level, the $2s$ subshell. Next, look at the electronic configuration for neon, $1s^2 2s^2 2p^6$. Again, the outermost shell ($n = 2$ in this case) is filled and a wide gap in energy occurs between the filled $2p$ subshell and the next available one, the $3s$ subshell. Argon has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. Here, it is only the $3p$ subshell that is filled, but again a wide gap in energy occurs between the filled $3p$ subshell and the next available one, the $3d$ subshell. This pattern continues through all the noble gases. Krypton has a filled $4p$ subshell, xenon a filled $5p$ subshell, and radon a filled $6p$ subshell.

The column to the left of the noble gases in the periodic table consists of a group of elements called the *halogens:* fluorine, chlorine, bromine, iodine, and astatine. At room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine and astatine are solids. In each of these atoms, the outer subshell is one electron short of being filled. As a result, the halogens are chemically very active, readily accepting an electron from another atom to form a closed shell. The halogens tend to form strong ionic bonds with atoms at the other side of the periodic table. (We



Group I	Group II	Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group 0
H 1 $1s^1$																H 1 $1s^1$	He 2 $1s^2$
Li 3 $2s^1$	Be 4 $2s^2$											B 5 $2p^1$	C 6 $2p^2$	N 7 $2p^3$	O 8 $2p^4$	F 9 $2p^5$	Ne 10 $2p^6$
Na 11 $3s^1$	Mg 12 $3s^2$											Al 13 $3p^1$	Si 14 $3p^2$	P 15 $3p^3$	S 16 $3p^4$	Cl 17 $3p^5$	Ar 18 $3p^6$
K 19 $4s^1$	Ca 20 $4s^2$	Sc 21 $3d^1 4s^2$	Ti 22 $3d^2 4s^2$	V 23 $3d^3 4s^2$	Cr 24 $3d^5 4s^1$	Mn 25 $3d^5 4s^2$	Fe 26 $3d^6 4s^2$	Co 27 $3d^7 4s^2$	Ni 28 $3d^8 4s^2$	Cu 29 $3d^{10} 4s^1$	Zn 30 $3d^{10} 4s^2$	Ga 31 $4p^1$	Ge 32 $4p^2$	As 33 $4p^3$	Se 34 $4p^4$	Br 35 $4p^5$	Kr 36 $4p^6$
Rb 37 $5s^1$	Sr 38 $5s^2$	Y 39 $4d^1 5s^2$	Zr 40 $4d^2 5s^2$	Nb 41 $4d^4 5s^1$	Mo 42 $4d^5 5s^1$	Tc 43 $4d^5 5s^2$	Ru 44 $4d^7 5s^1$	Rh 45 $4d^8 5s^1$	Pd 46 $4d^{10}$	Ag 47 $4d^{10} 5s^1$	Cd 48 $4d^{10} 5s^2$	In 49 $5p^1$	Sn 50 $5p^2$	Sb 51 $5p^3$	Te 52 $5p^4$	I 53 $5p^5$	Xe 54 $5p^6$
Cs 55 $6s^1$	Ba 56 $6s^2$	57-71*	Hf 72 $5d^2 6s^2$	Ta 73 $5d^3 6s^2$	W 74 $5d^4 6s^2$	Re 75 $5d^5 6s^2$	Os 76 $5d^6 6s^2$	Ir 77 $5d^7 6s^2$	Pt 78 $5d^9 6s^1$	Au 79 $5d^{10} 6s^1$	Hg 80 $5d^{10} 6s^2$	Tl 81 $6p^1$	Pb 82 $6p^2$	Bi 83 $6p^3$	Po 84 $6p^4$	At 85 $6p^5$	Rn 86 $6p^6$
Fr 87 $7s^1$	Ra 88 $7s^2$	89- 103**	Rf 104 $6d^2 7s^2$	Db 105 $6d^3 7s^2$	Sg 106 $6d^4 7s^2$	Bh 107 $6d^5 7s^2$	Hs 108 $6d^6 7s^2$	Mt 109 $6d^7 7s^2$	Ds 110 $6d^9 7s^1$	Rg 111	112		114		116		

*Lanthanide series	La 57 $5d^1 6s^2$	Ce 58 $5d^1 4f^1 6s^2$	Pr 59 $4f^3 6s^2$	Nd 60 $4f^4 6s^2$	Pm 61 $4f^5 6s^2$	Sm 62 $4f^6 6s^2$	Eu 63 $4f^7 6s^2$	Gd 64 $5d^1 4f^7 6s^2$	Tb 65 $5d^1 4f^8 6s^2$	Dy 66 $4f^{10} 6s^2$	Ho 67 $4f^{11} 6s^2$	Er 68 $4f^{12} 6s^2$	Tm 69 $4f^{13} 6s^2$	Yb 70 $4f^{14} 6s^2$	Lu 71 $5d^1 4f^{14} 6s^2$
**Actinide series	Ac 89 $6d^1 7s^2$	Th 90 $6d^2 7s^2$	Pa 91 $5f^2 6d^1 7s^2$	U 92 $5f^3 6d^1 7s^2$	Np 93 $5f^4 6d^1 7s^2$	Pu 94 $5f^6 7s^2$	Am 95 $5f^7 7s^2$	Cm 96 $5f^7 6d^1 7s^2$	Bk 97 $5f^8 6d^1 7s^2$	Cf 98 $5f^{10} 7s^2$	Es 99 $5f^{11} 7s^2$	Fm 100 $5f^{12} 7s^2$	Md 101 $5f^{13} 7s^2$	No 102 $5f^{14} 7s^2$	Lr 103 $5f^{14} 6d^1 7s^2$

Figure 42.19 The periodic table of the elements is an organized tabular representation of the elements that shows their periodic chemical behavior. Elements in a given column have similar chemical behavior. This table shows the chemical symbol for the element, the atomic number, and the electron configuration. A more complete periodic table is available in Appendix C.

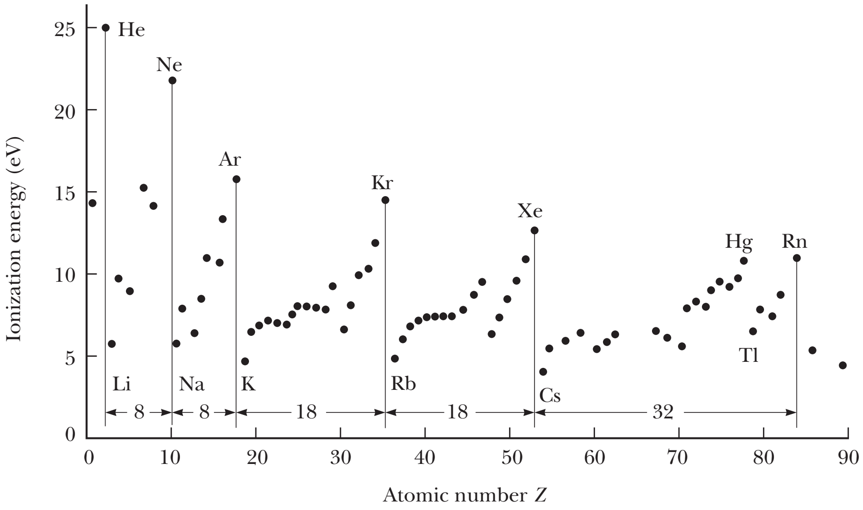


Figure 42.20 Ionization energy of the elements versus atomic number.

shall discuss ionic bonds in Chapter 43.) In a halogen lightbulb, bromine or iodine atoms combine with tungsten atoms evaporated from the filament and return them to the filament, resulting in a longer-lasting lightbulb. In addition, the filament can be operated at a higher temperature than in ordinary lightbulbs, giving a brighter and whiter light.

At the left side of the periodic table, the Group I elements consist of hydrogen and the *alkali metals:* lithium, sodium, potassium, rubidium, cesium, and francium. Each of these atoms contains one electron in a subshell outside of a closed subshell. Therefore, these elements easily form positive ions because the lone electron is bound with a relatively low energy and is easily removed. Therefore, the alkali metal atoms are chemically active and form very strong bonds with halogen atoms. For example, table salt, NaCl, is a combination of an alkali metal and a halogen. Because the outer electron is weakly bound, pure alkali metals tend to be good electrical conductors. Because of their high chemical activity, however, they are not generally found in nature in pure form.

It is interesting to plot ionization energy versus atomic number Z as in Figure 42.20. Notice the pattern of $\Delta Z = 2, 8, 8, 18, 18, 32$ for the various peaks. This pattern follows from the exclusion principle and helps explain why the elements repeat their chemical properties in groups. For example, the peaks at $Z = 2$, 10, 18, and 36 correspond to the noble gases helium, neon, argon, and krypton, respectively, which, as we have mentioned, all have filled outermost shells. These elements have relatively high ionization energies and similar chemical behavior.

42.8 More on Atomic Spectra: Visible and X-Ray

In Section 42.1, we discussed the observation and early interpretation of visible spectral lines from gases. These spectral lines have their origin in transitions between quantized atomic states. We shall investigate these transitions more deeply in these final three sections of this chapter.

A modified energy-level diagram for hydrogen is shown in Figure 42.21. In this diagram, the allowed values of ℓ for each shell are separated horizontally. Figure 42.21 shows only those states up to $\ell = 2$; the shells from $n = 4$ upward would have more sets of states to the right, which are not shown. Transitions for which ℓ does not change are very unlikely to occur and are called *forbidden transitions.* (Such transitions actually can occur, but their probability is very low relative to the probability of "allowed" transitions.) The various diagonal lines represent allowed transitions between stationary states. Whenever an atom makes a transition from a higher energy state to a lower one, a photon of light is emitted. The frequency of

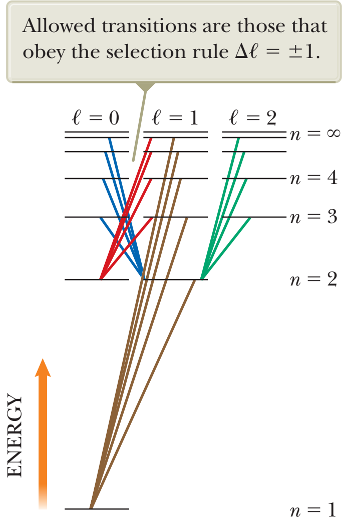

Allowed transitions are those that obey the selection rule $\Delta\ell = \pm 1$.

Figure 42.21 Some allowed electronic transitions for hydrogen, represented by the colored lines.

this photon is $f = \Delta E/h$, where ΔE is the energy difference between the two states and h is Planck's constant. The **selection rules** for the *allowed transitions* are

$$\Delta\ell = \pm 1 \quad \text{and} \quad \Delta m_\ell = 0, \pm 1 \tag{42.34}$$

Selection rules for allowed atomic transitions

Because the orbital angular momentum of an atom changes when a photon is emitted or absorbed (that is, as a result of a transition between states) and because angular momentum of the isolated atom–photon system must be conserved, we conclude that the photon involved in the process must carry angular momentum. In fact, the photon has an angular momentum equivalent to that of a particle having a spin of 1. Therefore, a photon has energy, linear momentum, and angular momentum.

Recall from Equation 42.19 that the allowed energies for one-electron atoms and ions, such as hydrogen and He$^+$, are

$$E_n = -\frac{k_e e^2}{2a_0}\left(\frac{Z^2}{n^2}\right) = -\frac{(13.6\ \text{eV})Z^2}{n^2} \tag{42.35}$$

This equation was developed from the Bohr theory, but it serves as a good first approximation in quantum theory as well. For multielectron atoms, the positive nuclear charge Ze is largely shielded by the negative charge of the inner-shell electrons. Therefore, the outer electrons interact with a net charge that is smaller than the nuclear charge. The expression for the allowed energies for multielectron atoms has the same form as Equation 42.35 with Z replaced by an effective atomic number Z_{eff}:

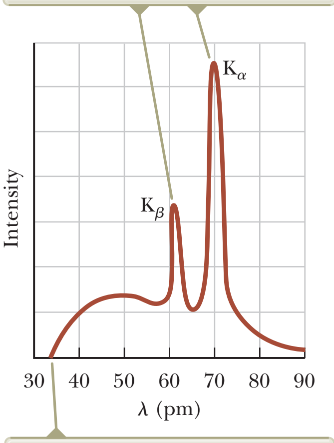
$$E_n = -\frac{(13.6\ \text{eV})Z_{\text{eff}}^2}{n^2} \tag{42.36}$$

where Z_{eff} depends on n and ℓ.

X-Ray Spectra

X-rays are emitted when high-energy electrons or any other charged particles bombard a metal target. The x-ray spectrum typically consists of a broad continuous band containing a series of sharp lines as shown in Figure 42.22. In Section 34.6, we mentioned that an accelerated electric charge emits electromagnetic radiation. The x-rays in Figure 42.22 are the result of the slowing down of high-energy electrons as they strike the target. It may take several interactions with the atoms of the target before the electron loses all its kinetic energy. The amount of kinetic energy lost in any given interaction can vary from zero up to the entire kinetic energy of the electron. Therefore, the wavelength of radiation from these interactions lies in a continuous range from some minimum value up to infinity. It is this general slowing down of the electrons that provides the continuous curve in Figure 42.22, which shows the cutoff of x-rays below a minimum wavelength value that depends on the kinetic energy of the incoming electrons. X-ray radiation with its origin in the slowing down of electrons is called **bremsstrahlung,** the German word for "braking radiation."

The peaks represent *characteristic x-rays*. Their appearance depends on the target material.



The continuous curve represents *bremsstrahlung*. The shortest wavelength depends on the accelerating voltage.

Figure 42.22 The x-ray spectrum of a metal target. The data shown were obtained when 37-keV electrons bombarded a molybdenum target.

Extremely high-energy bremsstrahlung can be used for the treatment of cancerous tissues. Figure 42.23 shows a machine that uses a linear accelerator to accelerate electrons up to 18 MeV and smash them into a tungsten target. The result is a beam of photons, up to a maximum energy of 18 MeV, which is actually in the gamma-ray range in Figure 34.13. This radiation is directed at the tumor in the patient.


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Figure 42.23 Bremsstrahlung is created by this machine and used to treat cancer in a patient.

The discrete lines in Figure 42.22, called **characteristic x-rays** and discovered in 1908, have a different origin. Their origin remained unexplained until the details of atomic structure were understood. The first step in the production of characteristic x-rays occurs when a bombarding electron collides with a target atom. The electron must have sufficient energy to remove an inner-shell electron from the atom. The vacancy created in the shell is filled when an electron in a higher level

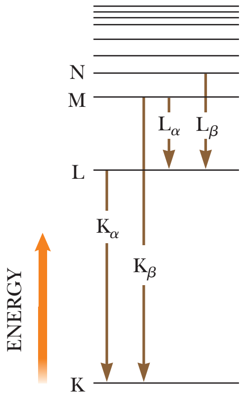


Figure 42.24 Transitions between higher and lower atomic energy levels that give rise to x-ray photons from heavy atoms when they are bombarded with high-energy electrons.

drops down into the level containing the vacancy. The time interval for that to happen is very short, less than 10^{-9} s. This transition is accompanied by the emission of a photon whose energy equals 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.

Let's 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 has an energy corresponding to the K_α characteristic x-ray line on the curve of Figure 42.22. In this notation, K refers to the final level of the electron and the subscript α, as the *first* letter of the Greek alphabet, refers to the initial level as the *first* one above the final level. Figure 42.24 shows this transition as well as others discussed below. If the vacancy in the K shell is filled by an electron dropping from the M shell, the K_β line in Figure 42.22 is produced.

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.

Although multielectron atoms cannot be analyzed exactly with either the Bohr model or the Schrödinger equation, we can apply Gauss's law from Chapter 24 to make some surprisingly accurate estimates of expected x-ray energies and wavelengths. Consider an atom of atomic number Z in which one of the two electrons in the K shell has been ejected. Imagine drawing a gaussian sphere immediately inside the most probable radius of the L electrons. The electric field at the position of the L electrons is a combination of the fields created by the nucleus, the single K electron, the other L electrons, and the outer electrons. The wave functions of the outer electrons are such that the electrons have a very high probability of being farther from the nucleus than the L electrons are. Therefore, the outer electrons are much more likely to be outside the gaussian surface than inside and, on average, do not contribute significantly to the electric field at the position of the L electrons. The effective charge inside the gaussian surface is the positive nuclear charge and one negative charge due to the single K electron. Ignoring the interactions between L electrons, a single L electron behaves as if it experiences an electric field due to a charge $(Z - 1)e$ enclosed by the gaussian surface. The nuclear charge is shielded by the electron in the K shell such that Z_{eff} in Equation 42.36 is $Z - 1$. For higher-level shells, the nuclear charge is shielded by electrons in all the inner shells.

We can now use Equation 42.36 to estimate the energy associated with an electron in the L shell:

$$E_{\text{L}} = -(Z - 1)^2 \frac{13.6 \text{ eV}}{2^2}$$

After the atom makes the transition, there are two electrons in the K shell. We can approximate the energy associated with one of these electrons as that of a one-electron atom. (In reality, the nuclear charge is reduced somewhat by the negative charge of the other electron, but let's ignore this effect.) Therefore,

$$E_{\text{K}} \approx -Z^2(13.6 \text{ eV}) \qquad \textbf{(42.37)}$$

As Example 42.5 shows, the energy of the atom with an electron in an M shell can be estimated in a similar fashion. Taking the energy difference between the initial and final levels, we can then calculate the energy and wavelength of the emitted photon.

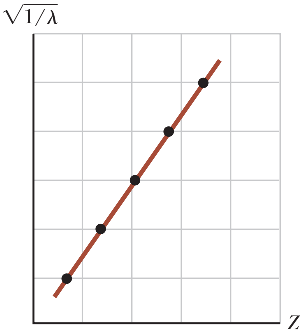


Figure 42.25 A Moseley plot of $\sqrt{1/\lambda}$ versus Z, where λ is the wavelength of the K_α x-ray line of the element of atomic number Z.

In 1914, Henry G. J. Moseley (1887–1915) plotted $\sqrt{1/\lambda}$ versus the Z values for a number of elements where λ is the wavelength of the K_α line of each element. He found that the plot is a straight line as in Figure 42.25, which is consistent with rough calculations of the energy levels given by Equation 42.37. From this plot, Moseley determined the Z values of elements that had not yet been discovered and produced a periodic table in excellent agreement with the known chemical properties of the elements. Until that experiment, atomic numbers had been merely placeholders for the elements that appeared in the periodic table, the elements being ordered according to mass.

***Quick Quiz* 42.5** In an x-ray tube, as you increase the energy of the electrons striking the metal target, do the wavelengths of the characteristic x-rays **(a)** increase, **(b)** decrease, or **(c)** remain constant?

***Quick Quiz* 42.6** True or False: It is possible for an x-ray spectrum to show the continuous spectrum of x-rays without the presence of the characteristic x-rays.

Example 42.5 Estimating the Energy of an X-Ray

Estimate the energy 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). The atomic number for tungsten is $Z = 74$.

SOLUTION

Conceptualize Imagine an accelerated electron striking a tungsten atom and ejecting an electron from the K shell. Subsequently, an electron in the M shell drops down to fill the vacancy and the energy difference between the states is emitted as an x-ray photon.

Categorize We estimate the results using equations developed in this section, so we categorize this example as a substitution problem.

Use Equation 42.37 and $Z = 74$ for tungsten to estimate the energy associated with the electron in the K shell:

$$E_K \approx -(74)^2(13.6 \text{ eV}) = -7.4 \times 10^4 \text{ eV}$$

Use Equation 42.36 and that nine electrons shield the nuclear charge (eight electrons in the $n = 2$ state and one electron in the $n = 1$ state) to estimate the energy of the M shell:

$$E_M \approx -\frac{(13.6 \text{ eV})(74 - 9)^2}{(3)^2} \approx -6.4 \times 10^3 \text{ eV}$$

Find the energy of the emitted x-ray photon:

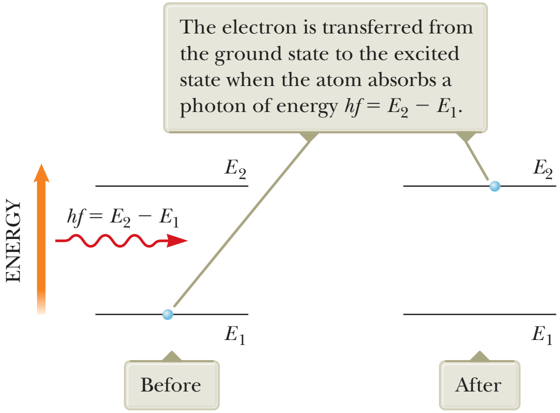
$$hf = E_M - E_K \approx -6.4 \times 10^3 \text{ eV} - (-7.4 \times 10^4 \text{ eV})$$

$$\approx 6.8 \times 10^4 \text{ eV} = \boxed{68 \text{ keV}}$$

Consultation of x-ray tables shows that the M–K transition energies in tungsten vary from 66.9 keV to 67.7 keV, where the range of energies is due to slightly different energy values for states of different ℓ. Therefore, our estimate differs from the midpoint of this experimentally measured range by approximately 1%.

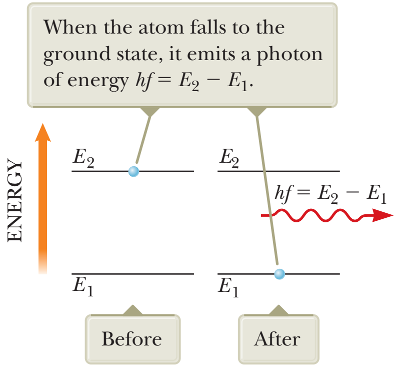
42.9 Spontaneous and Stimulated Transitions

We have seen that an atom absorbs and emits electromagnetic radiation only at frequencies that correspond to the energy differences between allowed states. Let's now examine more details of these processes. Consider an atom having the allowed energy levels labeled $E_1, E_2, E_3, \ldots$. When radiation is incident on the atom, only those photons whose energy hf matches the energy separation ΔE between two energy levels can be absorbed by the atom as represented in Active Figure 42.26 on page 1280. This process is called **stimulated absorption** because the photon stimulates the atom to make the upward transition. At ordinary temperatures, most of the atoms in a sample are in the ground state. If a vessel containing many atoms of a gaseous element is illuminated with radiation of all possible photon frequencies (that is, a continuous spectrum), only those photons having energy $E_2 - E_1$,


The electron is transferred from the ground state to the excited state when the atom absorbs a photon of energy $hf = E_2 - E_1$.

ACTIVE FIGURE 42.26

Stimulated absorption of a photon.


When the atom falls to the ground state, it emits a photon of energy $hf = E_2 - E_1$.

ACTIVE FIGURE 42.27

Spontaneous emission of a photon by an atom that is initially in the excited state E_2.

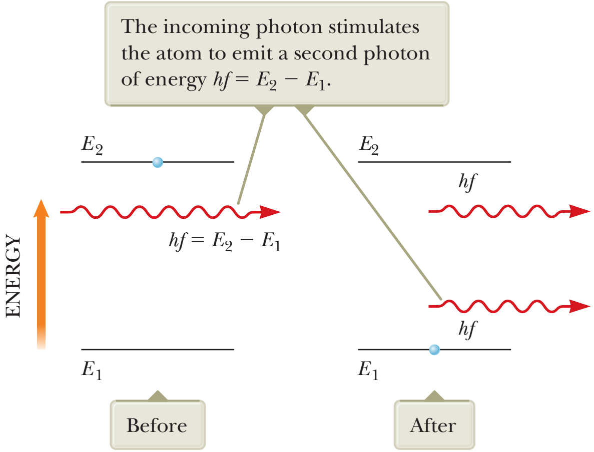
$E_3 - E_1$, $E_4 - E_1$, and so on are absorbed by the atoms. As a result of this absorption, some of the atoms are raised to excited states.

Once an atom is in an excited state, the excited atom can make a transition back to a lower energy level, emitting a photon in the process as in Active Figure 42.27. This process is known as **spontaneous emission** because it happens naturally, without requiring an event to trigger the transition. Typically, an atom remains in an excited state for only about 10^{-8} s.

In addition to spontaneous emission, **stimulated emission** occurs. Suppose an atom is in an excited state E_2 as in Active Figure 42.28. If the excited state is a *metastable state*—that is, if its lifetime is much longer than the typical 10^{-8} s lifetime of excited states—the time interval until spontaneous emission occurs is relatively long. Let's imagine that during that interval a photon of energy $hf = E_2 - E_1$ is incident on the atom. One possibility is that the photon energy is sufficient for the photon to ionize the atom. Another possibility is that the interaction between the incoming photon and the atom causes the atom to return to the ground state[11] and thereby emit a second photon with energy $hf = E_2 - E_1$. In this process, the incident photon is not absorbed; therefore, after the stimulated emission, two photons with

ACTIVE FIGURE 42.28

Stimulated emission of a photon by an incoming photon of energy $hf = E_2 - E_1$. Initially, the atom is in the excited state.


The incoming photon stimulates the atom to emit a second photon of energy $hf = E_2 - E_1$.

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[11] This phenomenon is fundamentally due to *resonance.* The incoming photon has a frequency and drives the system of the atom at that frequency. Because the driving frequency matches that associated with a transition between states—one of the natural frequencies of the atom—there is a large response: the atom makes the transition.

identical energy exist: the incident photon and the emitted photon. The two are in phase and travel in the same direction, which is an important consideration in lasers, discussed next.

42.10 Lasers

In this section, we explore the nature of laser light and a variety of applications of lasers in our technological society. The primary properties of laser light that make it useful in these technological applications are the following:

- Laser light is coherent. The individual rays of light in a laser beam maintain a fixed phase relationship with one another.
- Laser light is monochromatic. Light in a laser beam has a very narrow range of wavelengths.
- Laser light has a small angle of divergence. The beam spreads out very little, even over large distances.

To understand the origin of these properties, let's combine our knowledge of atomic energy levels from this chapter with some special requirements for the atoms that emit laser light.

We have described how an incident photon can cause atomic energy transitions either upward (stimulated absorption) or downward (stimulated emission). The two processes are equally probable. When light is incident on a collection of atoms, a net absorption of energy usually occurs because when the system is in thermal equilibrium, many more atoms are in the ground state than in excited states. If the situation can be inverted so that more atoms are in an excited state than in the ground state, however, a net emission of photons can result. Such a condition is called **population inversion.**

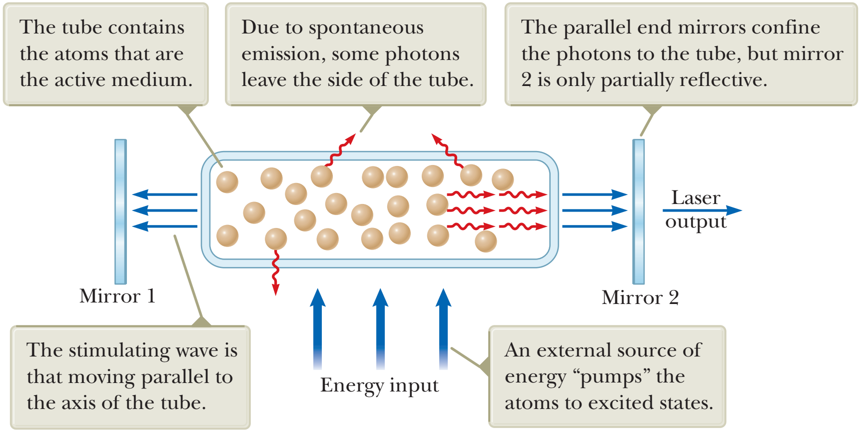
Population inversion is, in fact, the fundamental principle involved in the operation of a **laser** (an acronym for *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation). The full name indicates one of the requirements for laser light: to achieve laser action, the process of stimulated emission must occur.

Suppose an atom is in the excited state E_2 as in Active Figure 42.28 and a photon with energy $hf = E_2 - E_1$ is incident on it. As described in Section 42.9, the incoming photon can stimulate the excited atom to return to the ground state and thereby emit a second photon having the same energy hf and traveling in the same direction. The incident photon is not absorbed, so after the stimulated emission, there are two identical photons: the incident photon and the emitted photon. The emitted photon is in phase with the incident photon. These photons can stimulate other atoms to emit photons in a chain of similar processes. The many photons produced in this fashion are the source of the intense, coherent light in a laser.

For the stimulated emission to result in laser light, there must be a buildup of photons in the system. The following three conditions must be satisfied to achieve this buildup:

- The system must be in a state of population inversion: there must be more atoms in an excited state than in the ground state. That must be true because the number of photons emitted must be greater than the number absorbed.
- The excited state of the system must be a *metastable state,* meaning that its lifetime must be long compared with the usually short lifetimes of excited states, which are typically 10^{-8} s. In this case, the population inversion can be established and stimulated emission is likely to occur before spontaneous emission.
- The emitted photons must be confined in the system long enough to enable them to stimulate further emission from other excited atoms. That is achieved by using reflecting mirrors at the ends of the system. One end is made totally reflecting, and the other is partially reflecting. A fraction of the

Figure 42.29 Schematic diagram of a laser design.



light intensity passes through the partially reflecting end, forming the beam of laser light (Fig. 42.29).

One device that exhibits stimulated emission of radiation is the helium–neon gas laser. Figure 42.30 is an energy-level diagram for the neon atom in this system. The mixture of helium and neon is confined to a glass tube that is sealed at the ends by mirrors. A voltage applied across the tube causes electrons to sweep through the tube, colliding with the atoms of the gases and raising them into excited states. Neon atoms are excited to state E_3^* through this process (the asterisk indicates a metastable state) and also as a result of collisions with excited helium atoms. Stimulated emission occurs, causing neon atoms to make transitions to state E_2. Neighboring excited atoms are also stimulated. The result is the production of coherent light at a wavelength of 632.8 nm.

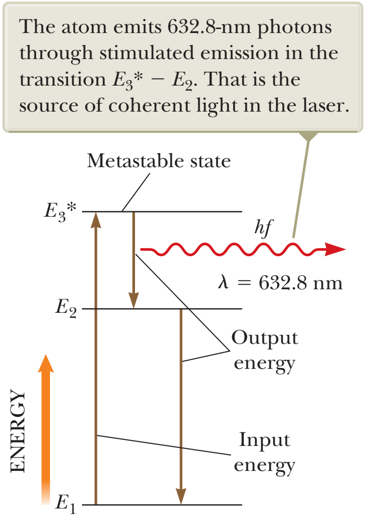


Figure 42.30 Energy-level diagram for a neon atom in a helium–neon laser.

Applications

Since the development of the first laser in 1960, tremendous growth has occurred in laser technology. Lasers that cover wavelengths in the infrared, visible, and ultraviolet regions are now available. Applications include surgical "welding" of detached retinas, precision surveying and length measurement, precision cutting of metals and other materials (such as the fabric in Fig. 42.31), and telephone communication along optical fibers. These and other applications are possible because of the unique characteristics of laser light. In addition to being highly monochromatic, laser light is also highly directional and can be sharply focused to produce regions of extremely intense light energy (with energy densities 10^{12} times the density in the flame of a typical cutting torch).

Philippe Plailly/SPL/Photo Researchers, Inc.

Figure 42.31 This robot carrying laser scissors, which can cut up to 50 layers of fabric at a time, is one of the many applications of laser technology.

Lasers are used in precision long-range distance measurement (range finding). In recent years, it has become important in astronomy and geophysics to measure as precisely as possible the distances from various points on the surface of the Earth to a point on the Moon's surface. To facilitate these measurements, the *Apollo* astronauts set up a 0.5-m square of reflector prisms on the Moon, which enables laser pulses directed from an Earth-based station to be retroreflected to the same station (see Fig. 35.8a). Using the known speed of light and the measured round-trip travel time of a laser pulse, the Earth–Moon distance can be determined to a precision of better than 10 cm.

Because various laser wavelengths can be absorbed in specific biological tissues, lasers have a number of medical applications. For example, certain laser procedures have greatly reduced blindness in patients with glaucoma and diabetes. Glaucoma is a widespread eye condition characterized by a high fluid pressure in the eye, a condition that can lead to destruction of the optic nerve. A simple laser operation (iridectomy) can "burn" open a tiny hole in a clogged membrane, relieving the destructive pressure. A serious side effect of diabetes is neovascularization, the proliferation of weak blood vessels, which often leak blood. When neovascularization occurs in the retina, vision deteriorates (diabetic retinopathy) and finally is destroyed. Today, it is possible to direct the green light from an argon ion laser through the clear eye lens and eye fluid, focus on the retina edges, and photocoagulate the leaky vessels. Even people who have only minor vision defects such as nearsightedness are benefiting from the use of lasers to reshape the cornea, changing its focal length and reducing the need for eyeglasses.

Laser surgery is now an everyday occurrence at hospitals and medical clinics around the world. Infrared light at 10 μm from a carbon dioxide laser can cut through muscle tissue, primarily by vaporizing the water contained in cellular material. Laser power of approximately 100 W is required in this technique. The advantage of the "laser knife" over conventional methods is that laser radiation cuts tissue and coagulates blood at the same time, leading to a substantial reduction in blood loss. In addition, the technique virtually eliminates cell migration, an important consideration when tumors are being removed.

A laser beam can be trapped in fine optical fiber light guides (endoscopes) by means of total internal reflection. An endoscope can be introduced through natural orifices, conducted around internal organs, and directed to specific interior body locations, eliminating the need for invasive surgery. For example, bleeding in the gastrointestinal tract can be optically cauterized by endoscopes inserted through the patient's mouth.

In biological and medical research, it is often important to isolate and collect unusual cells for study and growth. A laser cell separator exploits the tagging of specific cells with fluorescent dyes. All cells are then dropped from a tiny charged nozzle and laser-scanned for the dye tag. If triggered by the correct light-emitting tag, a small voltage applied to parallel plates deflects the falling electrically charged cell into a collection beaker.

An exciting area of research and technological applications arose in the 1990s with the development of *laser trapping* of atoms. One scheme, called *optical molasses* and developed by Steven Chu of Stanford University and his colleagues, involves focusing six laser beams onto a small region in which atoms are to be trapped. Each pair of lasers is along one of the x, y, and z axes and emits light in opposite directions (Fig. 42.32). The frequency of the laser light is tuned to be slightly below the absorption frequency of the subject atom. Imagine that an atom has been placed into the trap region and moves along the positive x axis toward the laser that is emitting light toward it (the rightmost laser in Fig. 42.32). Because the atom is moving, the light from the laser appears Doppler-shifted upward in frequency in the reference frame of the atom. Therefore, a match between the Doppler-shifted laser frequency and the absorption frequency of the atom exists and the atom absorbs photons.[12] The momentum carried by these photons results in the atom being pushed back to the center of the trap. By incorporating six lasers, the atoms are pushed back into the trap regardless of which way they move along any axis.

In 1986, Chu developed *optical tweezers,* a device that uses a single tightly focused laser beam to trap and manipulate small particles. In combination with microscopes, optical tweezers have opened up many new possibilities for biologists. Optical tweezers have been used to manipulate live bacteria without damage, move chromosomes within a cell nucleus, and measure the elastic properties of a single DNA molecule. Chu shared the 1997 Nobel Prize in Physics with two of his colleagues for the development of the techniques of optical trapping.

An extension of laser trapping, *laser cooling,* is possible because the normal high speeds of the atoms are reduced when they are restricted to the region of the trap. As a result, the temperature of the collection of atoms can be reduced to a few microkelvins. The technique of laser cooling allows scientists to study the behavior of atoms at extremely low temperatures (Fig. 42.33).

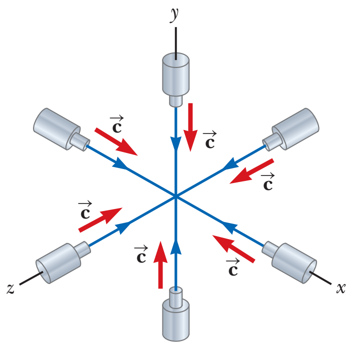
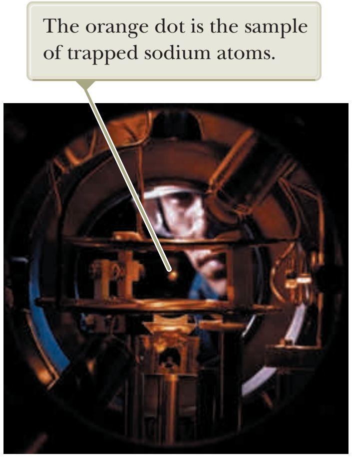


Figure 42.32 An optical trap for atoms is formed at the intersection point of six counterpropagating laser beams along mutually perpendicular axes.



The orange dot is the sample of trapped sodium atoms.

Courtesy of National Institute of Standards and Technology, U.S. Dept. of Commerce

Figure 42.33 A staff member of the National Institute of Standards and Technology views a sample of trapped sodium atoms cooled to a temperature of less than 1 mK.

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[12] The laser light traveling in the same direction as the atom is Doppler-shifted further downward in frequency, so there is no absorption. Therefore, the atom is not pushed out of the trap by the diametrically opposed laser.

Summary

Concepts and Principles

The wavelengths of spectral lines from hydrogen, called the **Balmer series,** can be described by the equation

$$\frac{1}{\lambda} = R_{\mathrm{H}}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad n = 3, 4, 5, \ldots \qquad \textbf{(42.1)}$$

where R_{H} is the **Rydberg constant.** The spectral lines corresponding to values of n from 3 to 6 are in the visible range of the electromagnetic spectrum. Values of n higher than 6 correspond to spectral lines in the ultraviolet region of the spectrum.

The Bohr model of the atom is successful in describing some details of the spectra of atomic hydrogen and hydrogen-like ions. One basic assumption of the model is that the electron can exist only in discrete orbits such that the angular momentum of the electron is an integral multiple of $h/2\pi = \hbar$. When we assume circular orbits and a simple Coulomb attraction between electron and proton, the energies of the quantum states for hydrogen are calculated to be

$$E_n = -\frac{k_e e^2}{2a_0}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots \qquad \textbf{(42.13)}$$

where n is an integer called the **quantum number,** k_e is the Coulomb constant, e is the electronic charge, and $a_0 = 0.052\,9$ nm is the **Bohr radius.**

If the electron in a hydrogen atom makes a transition from an orbit whose quantum number is n_i to one whose quantum number is n_f, where $n_f < n_i$, a photon is emitted by the atom. The frequency of this photon is

$$f = \frac{k_e e^2}{2a_0 h}\left(\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right) \qquad \textbf{(42.15)}$$

Quantum mechanics can be applied to the hydrogen atom by the use of the potential energy function $U(r) = -k_e e^2/r$ in the Schrödinger equation. The solution to this equation yields wave functions for allowed states and allowed energies:

$$E_n = -\left(\frac{k_e e^2}{2a_0}\right)\frac{1}{n^2} = -\frac{13.606 \text{ eV}}{n^2} \qquad n = 1, 2, 3, \ldots \qquad \textbf{(42.21)}$$

where n is the **principal quantum number.** The allowed wave functions depend on three quantum numbers: n, ℓ, and m_ℓ, where ℓ is the **orbital quantum number** and m_ℓ is the **orbital magnetic quantum number.** The restrictions on the quantum numbers are

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

$$\ell = 0, 1, 2, \ldots, n-1$$

$$m_\ell = -\ell, -\ell + 1, \ldots \ell - 1, \ell$$

All states having the same principal quantum number n form a **shell,** identified by the letters K, L, M, . . . (corresponding to $n = 1, 2, 3, \ldots$). All states having the same values of n and ℓ form a **subshell,** designated by the letters $s, p, d, f, \ldots$ (corresponding to $\ell = 0, 1, 2, 3, \ldots$).

An atom in a state characterized by a specific value of n can have the following values of L, the magnitude of the atom's orbital angular momentum $\vec{\mathbf{L}}$:

$$L = \sqrt{\ell(\ell + 1)}\,\hbar$$

$$\ell = 0, 1, 2, \ldots, n-1 \qquad \textbf{(42.27)}$$

The allowed values of the projection of $\vec{\mathbf{L}}$ along the z axis are

$$L_z = m_\ell \hbar \qquad \textbf{(42.28)}$$

Only discrete values of L_z are allowed as determined by the restrictions on m_ℓ. This quantization of L_z is referred to as **space quantization.**

The electron has an intrinsic angular momentum called the **spin angular momentum.** Electron spin can be described by a single quantum number $s = \frac{1}{2}$. To describe a quantum state completely, it is necessary to include a fourth quantum number m_s, called the **spin magnetic quantum number.** This quantum number can have only two values, $\pm\frac{1}{2}$. The magnitude of the spin angular momentum is

$$S = \frac{\sqrt{3}}{2}\hbar \tag{42.30}$$

and the z component of $\vec{\mathbf{S}}$ is

$$S_z = m_s\hbar = \pm\tfrac{1}{2}\hbar \tag{42.31}$$

That is, the spin angular momentum is also quantized in space, as specified by the spin magnetic quantum number $m_s = \pm\frac{1}{2}$.

The **exclusion principle** states that **no two electrons in an atom can be in the same quantum state.** In other words, no two electrons can have the same set of quantum numbers n, ℓ, m_ℓ, and m_s. Using this principle, the electronic configurations of the elements can be determined. This principle serves as a basis for understanding atomic structure and the chemical properties of the elements.

The magnetic moment $\vec{\boldsymbol{\mu}}_{\text{spin}}$ associated with the spin angular momentum of an electron is

$$\vec{\boldsymbol{\mu}}_{\text{spin}} = -\frac{e}{m_e}\vec{\mathbf{S}} \tag{42.32}$$

The z component of $\vec{\boldsymbol{\mu}}_{\text{spin}}$ can have the values

$$\mu_{\text{spin},z} = \pm\frac{e\hbar}{2m_e} \tag{42.33}$$

The x-ray spectrum of a metal target consists of a set of sharp characteristic lines superimposed on a broad continuous spectrum. **Bremsstrahlung** is x-radiation with its origin in the slowing down of high-energy electrons as they encounter the target. **Characteristic x-rays** are emitted by atoms when an electron undergoes a transition from an outer shell to a vacancy in an inner shell.

Atomic transitions can be described with three processes: **stimulated absorption,** in which an incoming photon raises the atom to a higher energy state; **spontaneous emission,** in which the atom makes a transition to a lower energy state, emitting a photon; and **stimulated emission,** in which an incident photon causes an excited atom to make a downward transition, emitting a photon identical to the incident one.

Objective Questions

☐ denotes answer available in Student Solutions Manual/Study Guide

1. When an electron collides with an atom, it can transfer all or some of its energy to the atom. A hydrogen atom is in its ground state. Incident on the atom are several electrons, each having a kinetic energy of 10.5 eV. What is the result? (a) The atom can be excited to a higher allowed state. (b) The atom is ionized. (c) The electrons pass by the atom without interaction.

2. (a) Can a hydrogen atom in the ground state absorb a photon of energy less than 13.6 eV? (b) Can this atom absorb a photon of energy greater than 13.6 eV?

3. An electron in the $n = 5$ energy level of hydrogen undergoes a transition to the $n = 3$ energy level. What is the wavelength of the photon the atom emits in this process? (a) 2.28×10^{-6} m (b) 8.20×10^{-7} m (c) 3.64×10^{-7} m (d) 1.28×10^{-6} m (e) 5.92×10^{-5} m

4. Consider the $n = 3$ energy level in a hydrogen atom. How many electrons can be placed in this level? (a) 1 (b) 2 (c) 8 (d) 9 (e) 18

5. Which of the following is *not* one of the basic assumptions of the Bohr model of hydrogen? (a) Only certain electron orbits are stable and allowed. (b) The electron moves in circular orbits about the proton under the influence of the Coulomb force. (c) The charge on the electron is quantized. (d) Radiation is emitted by the atom when the electron moves from a higher energy state to a lower energy state. (e) The angular momentum associated with the electron's orbital motion is quantized.

6. When an atom emits a photon, what happens? (a) One of its electrons leaves the atom. (b) The atom moves to a state of higher energy. (c) The atom moves to a state of lower energy. (d) One of its electrons collides with another particle. (e) None of those events occur.

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

8. 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) $3f$

9. Which of the following electronic configurations are *not* allowed for an atom? Choose all correct answers. (a) $2s^22p^6$ (b) $3s^23p^7$ (c) $3d^74s^2$ (d) $3d^{10}4s^24p^6$ (e) $1s^22s^22d^1$

10. What can be concluded about a hydrogen atom with its electron in the d state? (a) The atom is ionized. (b) The orbital quantum number is $\ell = 1$. (c) The principal quantum number is $n = 2$. (d) The atom is in its ground state. (e) The orbital angular momentum of the atom is not zero.

11. **(i)** Rank the following transitions for a hydrogen atom from the transition with the greatest gain in energy to that with the greatest loss, showing any cases of equality. (a) $n_i = 2$; $n_f = 5$ (b) $n_i = 5$; $n_f = 3$ (c) $n_i = 7$; $n_f = 4$ (d) $n_i = 4$; $n_f = 7$ **(ii)** Rank the same transitions as in part (i) according to the wavelength of the photon absorbed or emitted by an otherwise isolated atom from greatest wavelength to smallest.

12. Let $-E$ represent the energy of a hydrogen atom. **(i)** What is the kinetic energy of the electron? (a) $2E$ (b) E (c) 0 (d) $-E$ (e) $-2E$ **(ii)** What is the potential energy of the atom? Choose from the same possibilities (a) through (e).

13. (a) In the hydrogen atom, can the quantum number n increase without limit? (b) Can the frequency of possible discrete lines in the spectrum of hydrogen increase without limit? (c) Can the wavelength of possible discrete lines in the spectrum of hydrogen increase without limit?

14. Consider the quantum numbers (a) n, (b) ℓ, (c) m_ℓ, and (d) m_s. **(i)** Which of these quantum numbers are fractional as opposed to being integers? **(ii)** Which can sometimes attain negative values? **(iii)** Which can be zero?

15. **(i)** What is the principal quantum number of the initial state of an atom as it emits an M_β line in an x-ray spectrum? (a) 1 (b) 2 (c) 3 (d) 4 (e) 5 **(ii)** What is the principal quantum number of the final state for this transition? Choose from the same possibilities as in part (i).

Conceptual Questions

☐ denotes answer available in Student Solutions Manual/Study Guide

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

2. (a) According to Bohr's model of the hydrogen atom, what is the uncertainty in the radial coordinate of the electron? (b) What is the uncertainty in the radial component of the velocity of the electron? (c) In what way does the model violate the uncertainty principle?

3. Why are three quantum numbers needed to describe the state of a one-electron atom (ignoring spin)?

4. Compare the Bohr theory and the Schrödinger treatment of the hydrogen atom, specifically commenting on their treatment of total energy and orbital angular momentum of the atom.

5. Could the Stern–Gerlach experiment be performed with ions rather than neutral atoms? Explain.

6. Why is a *nonuniform* magnetic field used in the Stern–Gerlach experiment?

7. Discuss some consequences of the exclusion principle.

8. An energy of about 21 eV is required to excite an electron in a helium atom from the $1s$ state to the $2s$ state. The same transition for the He^+ ion requires approximately twice as much energy. Explain.

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

10. It is easy to understand how two electrons (one spin up, one spin down) fill the $n = 1$ or K shell for a helium atom. How is it possible that eight more electrons are allowed in the $n = 2$ shell, filling the K and L shells for a neon atom?

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

12. Does the intensity of light from a laser fall off as $1/r^2$? Explain.

Problems

ENHANCED WebAssign The problems found in this chapter may be assigned online in Enhanced WebAssign

1. denotes straightforward problem; **2.** denotes intermediate problem; **3.** denotes challenging problem

1. full solution available in the *Student Solutions Manual/Study Guide*

1. denotes problems most often assigned in Enhanced WebAssign; these provide students with targeted feedback and either a Master It tutorial or a Watch It solution video.

Q|C denotes asking for quantitative and conceptual reasoning

S denotes symbolic reasoning problem

M denotes Master It tutorial available in Enhanced WebAssign

GP denotes guided problem

shaded denotes "paired problems" that develop reasoning with symbols and numerical values

Section 42.1 Atomic Spectra of Gases

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

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

(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

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

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

3. An isolated atom of a certain element emits light of wavelength 520 nm when the atom falls from its fifth excited state into its second excited state. The atom emits a photon of wavelength 410 nm when it drops from its sixth excited state into its second excited state. Find the wavelength of the light radiated when the atom makes a transition from its sixth to its fifth excited state.

4. **S** An isolated atom of a certain element emits light of wavelength λ_{m1} when the atom falls from its state with quantum number m into its ground state of quantum number 1. The atom emits a photon of wavelength λ_{n1} when the atom falls from its state with quantum number n into its ground state. (a) Find the wavelength of the light radiated when the atom makes a transition from the m state to the n state. (b) Show that $k_{mn} = |k_{m1} - k_{n1}|$, where $k_{ij} = 2\pi/\lambda_{ij}$ is the wave number of the photon. This problem exemplifies the *Ritz combination principle,* an empirical rule formulated in 1908.

5. (a) What value of n_i is associated with the 94.96-nm spectral line in the Lyman series of hydrogen? (b) **What If?** Could this wavelength be associated with the Paschen series? (c) Could this wavelength be associated with the Balmer series?

Section 42.2 Early Models of the Atom

6. According to classical physics, a charge e moving with an acceleration a radiates energy at a rate

$$\frac{dE}{dt} = -\frac{1}{6\pi\epsilon_0}\frac{e^2a^2}{c^3}$$

(a) Show that an electron in a classical hydrogen atom (see Fig. 42.5) spirals into the nucleus at a rate

$$\frac{dr}{dt} = -\frac{e^4}{12\pi^2\epsilon_0{}^2m_e{}^2c^3}\left(\frac{1}{r^2}\right)$$

(b) Find the time interval over which the electron reaches $r = 0$, starting from $r_0 = 2.00 \times 10^{-10}$ m.

7. **Review.** In the Rutherford scattering experiment, 4.00-MeV alpha particles scatter off gold nuclei (containing 79 protons and 118 neutrons). Assume a particular alpha particle moves directly toward the gold nucleus and scatters backward at 180°, and that the gold nucleus remains fixed throughout the entire process. Determine (a) the distance of closest approach of the alpha particle to the gold nucleus and (b) the maximum force exerted on the alpha particle.

Section 42.3 Bohr's Model of the Hydrogen Atom

Note: In this section, unless otherwise indicated, assume the hydrogen atom is treated with the Bohr model.

8. 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?

9. A photon is emitted when a hydrogen atom undergoes a transition from the $n = 5$ state to the $n = 3$ state. Calculate

(a) the energy (in electron volts), (b) the wavelength, and (c) the frequency of the emitted photon.

10. 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 P42.10. Consider the photon of longest wavelength corresponding to a transition shown in the figure. Determine (a) its energy and (b) its wavelength. Consider the spectral line of shortest wavelength corresponding to a transition shown in the figure. Find (c) its photon energy and (d) its wavelength. (e) What is the shortest possible wavelength in the Balmer series?

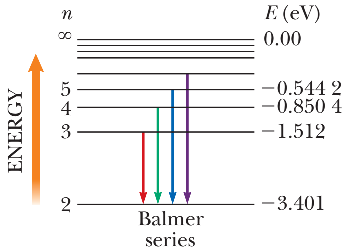

Figure P42.10

11. For a hydrogen atom in its ground state, compute (a) the orbital speed of the electron, (b) the kinetic energy of the electron, and (c) the electric potential energy of the atom.

12. Q|C A monochromatic beam of light is absorbed by a collection of ground-state hydrogen atoms in such a way that six different wavelengths are observed when the hydrogen relaxes back to the ground state. (a) What is the wavelength of the incident beam? Explain the steps in your solution. (b) What is the longest wavelength in the emission spectrum of these atoms? (c) To what portion of the electromagnetic spectrum and (d) to what series does it belong? (e) What is the shortest wavelength? (f) To what portion of the electromagnetic spectrum and (g) to what series does it belong?

13. A hydrogen atom is in its second excited state, corresponding to $n = 3$. Find (a) the radius of the electron's Bohr orbit and (b) the de Broglie wavelength of the electron in this orbit.

14. A hydrogen atom is in its first excited state ($n = 2$). 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 of the electron, (e) the potential energy of the system, and (f) the total energy of the system.

15. A photon with energy 2.28 eV is absorbed by a hydrogen atom. Find (a) the minimum n for a hydrogen atom that can be ionized by such a photon and (b) the speed of the electron released from the state in part (a) when it is far from the nucleus.

16. Q|C An electron is in the nth Bohr orbit of the hydrogen atom. (a) Show that the period of the electron is $T = n^3 t_0$ and determine the numerical value of t_0. (b) On average, an electron remains in the $n = 2$ orbit for approximately 10 μs before it jumps down to the $n = 1$ (ground-state) orbit. How many revolutions does the electron make in the excited state? (c) Define the period of one revolution as an electron year, analogous to an Earth year being the period of the Earth's motion around the Sun. Explain whether we should think of the electron in the $n = 2$ orbit as "living for a long time."

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

Section 42.4 The Quantum Model of the Hydrogen Atom

18. A general expression for the energy levels of one-electron atoms and ions is

$$E_n = -\frac{\mu k_e^{\,2} q_1^{\,2} q_2^{\,2}}{2\hbar^2 n^2}$$

Here μ is the reduced mass of the atom, given by $\mu = m_1 m_2/(m_1 + m_2)$, where m_1 is the mass of the electron and m_2 is the mass of the nucleus; k_e is the Coulomb constant; and q_1 and q_2 are the charges of the electron and the nucleus, respectively. The wavelength for the $n = 3$ to $n = 2$ transition of the hydrogen atom is 656.3 nm (visible red light). What are the wavelengths for this same transition in (a) positronium, which consists of an electron and a positron, and (b) singly ionized helium? *Note:* A positron is a positively charged electron.

19. Atoms of the same element but with different numbers of neutrons in the nucleus are called *isotopes.* Ordinary hydrogen gas is a mixture of two isotopes containing either one- or two-particle nuclei. These isotopes are hydrogen-1, with a proton nucleus, and hydrogen-2, called deuterium, with a deuteron nucleus. A deuteron is one proton and one neutron bound together. Hydrogen-1 and deuterium have identical chemical properties, but they can be separated via an ultracentrifuge or by other methods. Their emission spectra show lines of the same colors at very slightly different wavelengths. (a) Use the equation given in Problem 18 to show that the difference in wavelength between the hydrogen-1 and deuterium spectral lines associated with a particular electron transition is given by

$$\lambda_H - \lambda_D = \left(1 - \frac{\mu_H}{\mu_D}\right)\lambda_H$$

(b) Find the wavelength difference for the Balmer alpha line of hydrogen, with wavelength 656.3 nm, emitted by an atom making a transition from an $n = 3$ state to an $n = 2$ state. Harold Urey observed this wavelength difference in 1931 and so confirmed his discovery of deuterium.

20. **Q|C** **S** An electron of momentum p is at a distance r from a stationary proton. The electron has kinetic energy $K = p^2/2m_e$. The atom has potential energy $U = -k_e e^2/r$ and total energy $E = K + U$. If the electron is bound to the proton to form a hydrogen atom, its average position is at the proton but the uncertainty in its position is approximately equal to the radius r of its orbit. The electron's average vector momentum is zero, but its average squared momentum is approximately equal to the squared uncertainty in its momentum as given by the uncertainty principle. Treating the atom as a one-dimensional system, (a) estimate the uncertainty in the electron's momentum in terms of r. Estimate the electron's (b) kinetic energy and (c) total energy in terms of r. The actual value of r is the one that *minimizes the total energy,* resulting in a stable atom. Find (d) that value of r and (e) the resulting total energy. (f) State how your answers compare with the predictions of the Bohr theory.

Section 42.5 The Wave Functions for Hydrogen

21. Plot the wave function $\psi_{1s}(r)$ versus r (see Eq. 42.22) and the radial probability density function $P_{1s}(r)$ versus r (see Eq. 42.25) for hydrogen. Let r range from 0 to $1.5a_0$, where a_0 is the Bohr radius.

22. The ground-state wave function for the electron in a hydrogen atom is

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0{}^3}} e^{-r/a_0}$$

where r is the radial coordinate of the electron and a_0 is the Bohr radius. (a) Show that the wave function as given is normalized. (b) Find the probability of locating the electron between $r_1 = a_0/2$ and $r_2 = 3a_0/2$.

23. **S** The wave function for an electron in the $2p$ state of hydrogen is

$$\psi_{2p} = \frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$$

What is the most likely distance from the nucleus to find an electron in the $2p$ state?

24. **S** For a spherically symmetric state of a hydrogen atom, the Schrödinger equation in spherical coordinates is

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr}\right) - \frac{k_e e^2}{r}\psi = E\psi$$

(a) Show that the $1s$ wave function for an electron in hydrogen,

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0{}^3}} e^{-r/a_0}$$

satisfies the Schrödinger equation. (b) What is the energy of the atom for this state?

25. In an experiment, a large number of electrons are fired at a sample of neutral hydrogen atoms and observations are made of how the incident particles scatter. The electron in the ground state of a hydrogen atom is found to be momentarily at a distance $a_0/2$ from the nucleus in 1 000 of the observations. In this set of trials, how many times is the atomic electron observed at a distance $2a_0$ from the nucleus?

Section 42.6 Physical Interpretation of the Quantum Numbers

26. List the possible sets of quantum numbers for the hydrogen atom associated with (a) the $3d$ subshell and (b) the $3p$ subshell.

27. Calculate the magnitude of the orbital angular momentum for a hydrogen atom in (a) the $4d$ state and (b) the $6f$ state.

28. Find all possible values of (a) L, (b) L_z, and (c) θ for a hydrogen atom in a $3d$ state.

29. An electron in a sodium atom is in the N shell. Determine the maximum value the z component of its angular momentum could have.

30. How many sets of quantum numbers are possible for a hydrogen atom for which (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 4$, and (e) $n = 5$?

31. A hydrogen atom is in its fifth excited state, with principal quantum number 6. The atom emits a photon with a wavelength of 1 090 nm. Determine the maximum possible magnitude of the orbital angular momentum of the atom after emission.

32. **Q|C** (a) Find the mass density of a proton, modeling it as a solid sphere of radius 1.00×10^{-15} m. (b) **What If?** Consider a classical model of an electron as a uniform solid sphere with the same density as the proton. Find its radius. (c) Imagine that this electron possesses spin angular momentum $I\omega = \hbar/2$ because of classical rotation about the z axis. Determine the speed of a point on the equator of the electron. (d) State how this speed compares with the speed of light.

33. **M** The ρ^- meson has a charge of $-e$, a spin quantum number of 1, and a mass 1 507 times that of the electron. The possible values for its spin magnetic quantum number are −1, 0, and 1. **What If?** Imagine that the electrons in atoms are replaced by ρ^- mesons. List the possible sets of quantum numbers for ρ^- mesons in the $3d$ subshell.

34. *Why is the following situation impossible?* A photon of wavelength 88.0 nm strikes a clean aluminum surface, ejecting a photoelectron. The photoelectron then strikes a hydrogen atom in its ground state, transferring energy to it and exciting the atom to a higher quantum state.

Section 42.7 The Exclusion Principle and the Periodic Table

35. (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.

36. Q|C (a) As we go down the periodic table, which subshell is filled first, the $3d$ or the $4s$ subshell? (b) Which electronic configuration has a lower energy, [Ar]$3d^4 4s^2$ or [Ar]$3d^5 4s^1$? *Note:* The notation [Ar] represents the filled configuration for argon. *Suggestion:* Which has the greater number of unpaired spins? (c) Identify the element with the electronic configuration in part (b).

37. A certain element has its outermost electron in a $3p$ subshell. It has valence +3 because it has three more electrons than a certain noble gas. What element is it?

38. Devise a table similar to that shown in Figure 42.18 for atoms containing 11 through 19 electrons. Use Hund's rule and educated guesswork.

39. Two electrons in the same atom both have $n = 3$ and $\ell = 1$. Assume the electrons are distinguishable, so that interchanging them defines a new state. (a) How many states of the atom are possible considering the quantum numbers these two electrons can have? (b) **What If?** How many states would be possible if the exclusion principle were inoperative?

40. Scanning through Figure 42.19 in order of increasing atomic number, notice that the electrons usually fill the subshells in such a way that those subshells with the lowest values of $n + \ell$ are filled first. If two subshells have the same value of $n + \ell$, the one with the lower value of n is generally filled first. Using these two rules, write the order in which the subshells are filled through $n + \ell = 7$.

41. For a neutral atom of element 110, what would be the probable ground-state electronic configuration?

42. **Review.** For an electron with magnetic moment $\vec{\boldsymbol{\mu}}_s$ in a magnetic field $\vec{\mathbf{B}}$, Section 29.5 showed the following. The electron–field system can be in a higher energy state with the z component of the electron's magnetic moment opposite the field or a lower energy state with the z component of the magnetic moment in the direction of the field. The difference in energy between the two states is $2\mu_B B$.

Under high resolution, many spectral lines are observed to be doublets. The most famous doublet is the pair of two yellow lines in the spectrum of sodium (the D lines), with wavelengths of 588.995 nm and 589.592 nm. Their existence was explained in 1925 by Goudsmit and Uhlenbeck, who postulated that an electron has intrinsic spin angular momentum. When the sodium atom is excited with its outermost electron in a $3p$ state, the orbital motion of the outermost electron creates a magnetic field. The atom's energy is somewhat different depending on whether the electron is itself spin-up or spin-down in this field. Then the photon energy the atom radiates as it falls back into its ground state depends on the energy of the excited state. Calculate the magnitude of the internal magnetic field, mediating this so-called spin-orbit coupling.

Section 42.8 More on Atomic Spectra: Visible and X-Ray

43. What minimum accelerating voltage would be required to produce an x-ray with a wavelength of 70.0 pm?

44. A tungsten target is struck by electrons that have been accelerated from rest through a 40.0-keV potential difference. Find the shortest wavelength of the radiation emitted.

45. A bismuth target is struck by electrons, and x-rays are emitted. Estimate (a) the M- to L-shell transitional energy for bismuth and (b) the wavelength of the x-ray emitted when an electron falls from the M shell to the L shell.

46. Q|C The $3p$ level of sodium has an energy of −3.0 eV, and the $3d$ level has an energy of −1.5 eV. (a) Determine Z_{eff} for each of these states. (b) Explain the difference.

47. (a) Determine the possible values of the quantum numbers ℓ and m_ℓ for the He^+ ion in the state corresponding to $n = 3$. (b) What is the energy of this state?

48. The K series of the discrete x-ray 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. (a) Determine the ionization energies of the L, M, and N shells. (b) Draw a diagram of the transitions.

49. M Use the method illustrated in Example 42.5 to calculate the wavelength of the x-ray emitted from a molybdenum target ($Z = 42$) when an electron moves from the L shell ($n = 2$) to the K shell ($n = 1$).

50. Q|C In x-ray production, electrons are accelerated through a high voltage and then decelerated by striking a target. (a) To make possible the production of x-rays of wavelength λ, what is the minimum potential difference ΔV through which the electrons must be accelerated? (b) State in words how the required potential difference depends on the wavelength. (c) Explain whether your result predicts the correct minimum wavelength in Figure 42.22. (d) Does the relationship from part (a) apply to other kinds of electromagnetic radiation besides x-rays? (e) What does the potential difference approach as λ goes to zero? (f) What does the potential difference approach as λ increases without limit?

51. 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.

Section 42.9 Spontaneous and Stimulated Transitions

Section 42.10 Lasers

52. Figure P42.52 shows portions of the energy-level diagrams of the helium and neon atoms. An electrical discharge excites the He atom from its ground state (arbitrarily assigned the energy $E_1 = 0$) to its excited state of 20.61 eV.

The excited He atom collides with a Ne atom in its ground state and excites this atom to the state at 20.66 eV. Lasing action takes place for electron transitions from $E_3{}^*$ to E_2 in the Ne atoms. From the data in the figure, show that the wavelength of the red He–Ne laser light is approximately 633 nm.

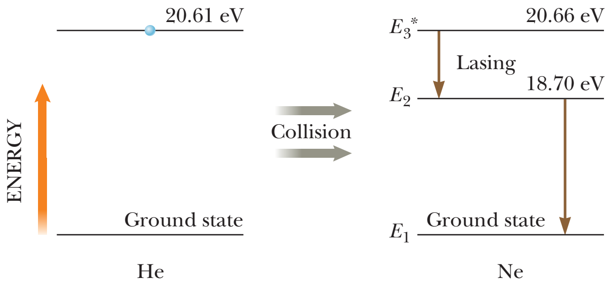

Figure P42.52

53. The carbon dioxide laser is one of the most powerful developed. The energy difference between the two laser levels is 0.117 eV. Determine (a) the frequency and (b) the wavelength of the radiation emitted by this laser. (c) In what portion of the electromagnetic spectrum is this radiation?

54. **Review.** A helium–neon laser can produce a green laser beam instead of a red one. Figure P42.54 shows the transitions involved to form the red beam and the green beam. After a population inversion is established, neon atoms make a variety of downward transitions in falling from the state labeled $E_4{}^*$ down eventually to level E_1 (arbitrarily assigned the energy $E_1 = 0$). The atoms emit both red light with a wavelength of 632.8 nm in a transition $E_4{}^* - E_3$ and green light with a wavelength of 543 nm in a competing transition $E_4{}^* - E_2$. (a) What is the energy E_2? Assume the atoms are in a cavity between mirrors designed to reflect the green light with high efficiency but to allow the red light to leave the cavity immediately. Then stimulated emission can lead to the buildup of a collimated beam of green light between the mirrors having a greater intensity than that of the red light. To constitute the radiated laser beam, a small fraction of the green light is permitted to escape by transmission through one mirror. The mirrors forming the resonant cavity can be made of layers of silicon dioxide (index of refraction $n = 1.458$) and titanium dioxide (index of refraction varies between 1.9 and 2.6). (b) How thick a layer of silicon dioxide, between layers of titanium dioxide, would minimize reflection of the red light? (c) What should be the thickness of a similar but separate layer of silicon dioxide to maximize reflection of the green light?

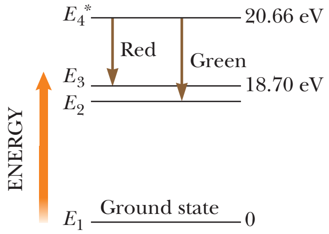

Figure P42.54 Problems 54 and 56.

55. M A ruby laser delivers a 10.0-ns pulse of 1.00-MW average power. If the photons have a wavelength of 694.3 nm, how many are contained in the pulse?

56. Q|C The number N of atoms in a particular state is called the population of that state. This number depends on the energy of that state and the temperature. In thermal equilibrium, the population of atoms in a state of energy E_n is given by a Boltzmann distribution expression

$$N = N_g e^{-(E_n - E_g)/k_B T}$$

where N_g is the population of the ground state of energy E_g, k_B is Boltzmann's constant, and T is the absolute temperature. For simplicity, assume each energy level has only one quantum state associated with it. (a) Before the power is switched on, the neon atoms in a laser are in thermal equilibrium at 27.0°C. Find the equilibrium ratio of the populations of the states $E_4{}^*$ and E_3 shown for the red transition in Figure P42.54. Lasers operate by a clever artificial production of a "population inversion" between the upper and lower atomic energy states involved in the lasing transition. This term means that more atoms are in the upper excited state than in the lower one. Consider the $E_4{}^*–E_3$ transition in Figure P42.54. Assume 2% more atoms occur in the upper state than in the lower. (b) To demonstrate how unnatural such a situation is, find the temperature for which the Boltzmann distribution describes a 2.00% population inversion. (c) Why does such a situation not occur naturally?

57. A neodymium–yttrium–aluminum garnet 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. (In the optics industry, this quantity is called the *irradiance*.) (b) What energy is delivered by the pulse to an area of molecular size, taken as a circular area 0.600 nm in diameter?

Additional Problems

58. The force on a magnetic moment μ_z in a nonuniform magnetic field B_z is given by $F_z = \mu_z(dB_z/dz)$. If a beam of silver atoms travels a horizontal distance of 1.00 m through such a field and each atom has a speed of 100 m/s, how strong must be the field gradient dB_z/dz to deflect the beam 1.00 mm?

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

60. **Review.** (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) Suppose the atom gains this energy through collisions among hydrogen atoms at a high temperature. At what temperature would the average atomic kinetic energy $\frac{3}{2}k_B T$ be great enough to excite the electron? Here k_B is Boltzmann's constant.

61. Suppose a hydrogen atom is in the 2*s* state, with its wave function given by Equation 42.26. Taking $r = a_0$, calculate values for (a) $\psi_{2s}(a_0)$, (b) $|\psi_{2s}(a_0)|^2$, and (c) $P_{2s}(a_0)$.

62. 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. Use the Bohr theory to find the kinetic energy of the Auger electron.

63. M In the technique known as electron spin resonance (ESR), a sample containing unpaired electrons is placed in a magnetic field. Consider a situation in which a single electron (*not* contained in an atom) is immersed in a magnetic field. In this simple situation, only two energy states are possible, corresponding to $m_s = \pm\frac{1}{2}$. In ESR, the absorption of a photon causes the electron's spin magnetic moment to flip from the lower energy state to the higher energy state. According to Section 29.5, the change in energy is $2\mu_B B$. (The lower energy state corresponds to the case in which the *z* component of the magnetic moment $\vec{\boldsymbol{\mu}}_{\text{spin}}$ is aligned with the magnetic field, and the higher energy state corresponds to the case in which the *z* component of $\vec{\boldsymbol{\mu}}_{\text{spin}}$ is aligned opposite to the field.) What is the photon frequency required to excite an ESR transition in a 0.350-T magnetic field?

64. *Why is the following situation impossible?* An experiment is performed on an atom. Measurements of the atom when it is in a particular excited state show five possible values of the *z* component of orbital angular momentum, ranging between $3.16 \times 10^{-34}\ \text{kg}\cdot\text{m}^2/\text{s}$ and $-3.16 \times 10^{-34}\ \text{kg}\cdot\text{m}^2/\text{s}$.

65. In the Bohr model of the hydrogen atom, an electron travels in a circular path. Consider another case in which an electron travels in a circular path: a single electron moving perpendicular to a magnetic field $\vec{\mathbf{B}}$. Lev Davidovich Landau (1908–1968) solved the Schrödinger equation for such an electron. The electron can be considered as a model atom without a nucleus or as the irreducible quantum limit of the cyclotron. Landau proved its energy is quantized in uniform steps of $e\hbar B/m_e$. In 1999, a single electron was trapped by a Harvard University research team in an evacuated centimeter-size metal can cooled to a temperature of 80 mK. In a magnetic field of magnitude 5.26 T, the electron circulated for hours in its lowest energy level. (a) Evaluate the size of a quantum jump in the electron's energy. (b) For comparison, evaluate $k_B T$ as a measure of the energy available to the electron in blackbody radiation from the walls of its container. Microwave radiation was introduced to excite the electron. Calculate (c) the frequency and (d) the wavelength of the photon the electron absorbed as it jumped to its second energy level. Measurement of the resonant absorption frequency verified the theory and permitted precise determination of properties of the electron.

66. QC S As the Earth moves around the Sun, its orbits are quantized. (a) Follow the steps of Bohr's analysis of the hydrogen atom to show that the allowed radii of the Earth's orbit are given by

$$r = \frac{n^2\hbar^2}{GM_S M_E{}^2}$$

where n is an integer quantum number, M_S is the mass of the Sun, and M_E is the mass of the Earth. (b) Calculate the numerical value of n for the Sun–Earth system. (c) Find the distance between the orbit for quantum number n and the next orbit out from the Sun corresponding to the quantum number $n + 1$. (d) Discuss the significance of your results from parts (b) and (c).

67. S An elementary theorem in statistics states that the root-mean-square uncertainty in a quantity r is given by $\Delta r = \sqrt{\langle r^2\rangle - \langle r\rangle^2}$. Determine the uncertainty in the radial position of the electron in the ground state of the hydrogen atom. Use the average value of r found in Example 42.3: $\langle r\rangle = 3a_0/2$. The average value of the squared distance between the electron and the proton is given by

$$\langle r^2\rangle = \int_{\text{all space}} |\psi|^2 r^2\, dV = \int_0^\infty P(r) r^2\, dr$$

68. Example 42.3 calculates the most probable value and the average value for the radial coordinate *r* of the electron in the ground state of a hydrogen atom. For comparison with these modal and mean values, find the median value of *r*. Proceed as follows. (a) Derive an expression for the probability, as a function of *r*, that the electron in the ground state of hydrogen will be found outside a sphere of radius *r* centered on the nucleus. (b) Make a graph of the probability as a function of r/a_0. Choose values of r/a_0 ranging from 0 to 4.00 in steps of 0.250. (c) Find the value of *r* for which the probability of finding the electron outside a sphere of radius *r* is equal to the probability of finding the electron inside this sphere. You must solve a transcendental equation numerically, and your graph is a good starting point.

69. (a) For a hydrogen atom making a transition from the $n = 4$ state to the $n = 2$ state, determine the wavelength of the photon created in the process. (b) Assuming the atom was initially at rest, determine the recoil speed of the hydrogen atom when it emits this photon.

70. QC Astronomers observe a series of spectral lines in the light from a distant galaxy. On the hypothesis that the lines form the Lyman series for a (new?) one-electron atom, they start to construct the energy-level diagram shown in Figure P42.70, which gives the wavelengths of the first four lines and the short-wavelength limit of this series. Based on this information, calculate (a) the energies of the ground state and first four excited states for this one-electron atom and (b) the wavelengths of the first three lines and the short-wavelength limit in the Balmer series for this atom. (c) Show that the wavelengths of the first four lines and the short-wavelength limit of the Lyman series for the hydrogen atom are all 60.0% of the wavelengths for the Lyman series in the one-electron atom in the distant galaxy. (d) Based on this observation, explain why this atom could be hydrogen.

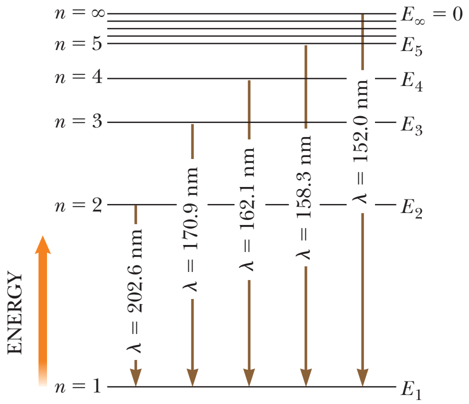

Figure P42.70

71. GP S We wish to show that the most probable radial position for an electron in the $2s$ state of hydrogen is $r = 5.236a_0$. (a) Use Equations 42.24 and 42.26 to find the radial probability density for the $2s$ state of hydrogen. (b) Calculate the derivative of the radial probability density with respect to r. (c) Set the derivative in part (b) equal to zero and identify three values of r that represent minima in the function. (d) Find two values of r that represent maxima in the function. (e) Identify which of the values in part (c) represents the highest probability.

72. Q|C All atoms have the same size, to an order of magnitude. (a) To demonstrate this fact, estimate the atomic diameters for aluminum (with molar mass 27.0 g/mol and density 2.70 g/cm^3) and uranium (molar mass 238 g/mol and density 18.9 g/cm^3). (b) What do the results of part (a) imply about the wave functions for inner-shell electrons as we progress to higher and higher atomic mass atoms?

73. 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) The beam has a circular cross section of diameter 0.600 cm. Find the number of photons per cubic millimeter.

74. S A pulsed laser emits light of wavelength λ. For a pulse of duration Δt having energy T_{ER}, find (a) the physical length of the pulse as it travels through space and (b) the number of photons in it. (c) The beam has a circular cross section having diameter d. Find the number of photons per unit volume.

75. S Assume three identical uncharged particles of mass m and spin $\frac{1}{2}$ are contained in a one-dimensional box of length L. What is the ground-state energy of this system?

76. Suppose the ionization energy of an atom is 4.10 eV. In the spectrum of this same atom, we observe emission lines with wavelengths 310 nm, 400 nm, and 1 377.8 nm. Use this information to construct the energy-level diagram with the fewest levels. Assume the higher levels are closer together.

77. For hydrogen in the $1s$ state, what is the probability of finding the electron farther than $2.50a_0$ from the nucleus?

78. S For hydrogen in the $1s$ state, what is the probability of finding the electron farther than βa_0 from the nucleus, where β is an arbitrary number?

Challenge Problems

79. The positron is the antiparticle to the electron. It has the same mass and a positive electric charge of the same magnitude as that of the electron. Positronium is a hydrogen-like atom consisting of a positron and an electron revolving around each other. Using the Bohr model, find (a) the allowed distances between the two particles and (b) the allowed energies of the system.

80. **Review.** Steven Chu, Claude Cohen-Tannoudji, and William Phillips received the 1997 Nobel Prize in Physics for "the development of methods to cool and trap atoms with laser light." One part of their work was with a beam of atoms (mass ~ 10^{-25} kg) that move at a speed on the order of 1 km/s, similar to the speed of molecules in air at room temperature. An intense laser light beam tuned to a visible atomic transition (assume 500 nm) is directed straight into the atomic beam; that is, the atomic beam and the light beam are traveling in opposite directions. An atom in the ground state immediately absorbs a photon. Total system momentum is conserved in the absorption process. After a lifetime on the order of 10^{-8} s, the excited atom radiates by spontaneous emission. It has an equal probability of emitting a photon in any direction. Therefore, the average "recoil" of the atom is zero over many absorption and emission cycles. (a) Estimate the average deceleration of the atomic beam. (b) What is the order of magnitude of the distance over which the atoms in the beam are brought to a halt?

81. **S** (a) Use Bohr's model of the hydrogen atom to show that when the electron moves from the n state to the $n - 1$ state, the frequency of the emitted light is

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

(b) Bohr's correspondence principle claims that quantum results should reduce to classical results in the limit of large quantum numbers. Show that as $n \to \infty$, this expression varies as $1/n^3$ and reduces to the classical frequency one expects the atom to emit. *Suggestion:* To calculate the classical frequency, note that the frequency of revolution is $v/2\pi r$, where v is the speed of the electron and r is given by Equation 42.10.