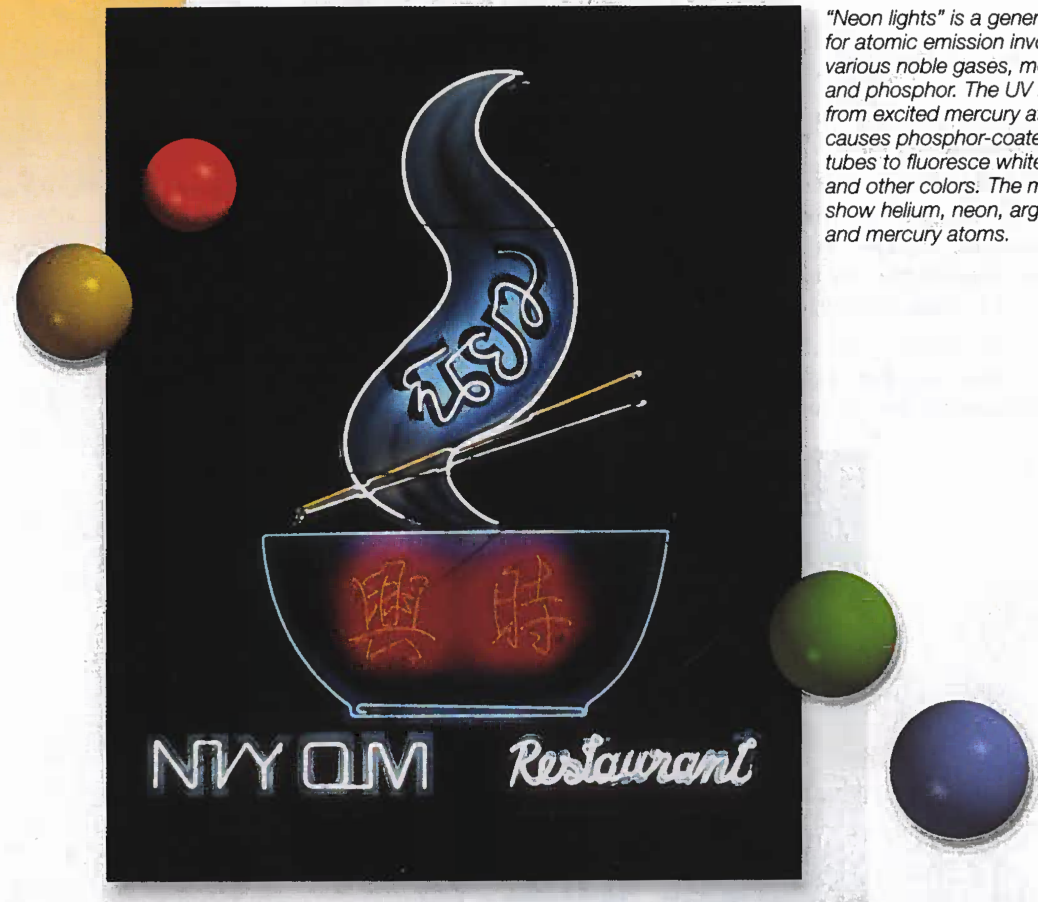
7



"Neon lights" is a generic term for atomic emission involving various noble gases, mercury, and phosphor. The UV light from excited mercury atoms causes phosphor-coated tubes to fluoresce white light and other colors. The models show helium, neon, argon, and mercury atoms.

Quantum Theory and the Electronic Structure of Atoms

A LOOK AHEAD

- We begin by discussing the transition from classical physics to quantum theory. In particular, we become familiar with properties of waves and electromagnetic radiation and Planck's formulation of the quantum theory. (7.1)
- Einstein's explanation of the photoelectric effect is another step toward the development of the quantum theory. To explain experimental observations, Einstein suggested that light behaves like a bundle of particles called photons. (7.2)
- We then study Bohr's theory for the emission spectrum of the hydrogen atom. In particular, Bohr postulated that the energies of an electron in the atom are quantized and transitions from higher levels to lower ones account for the emission lines. (7.3)
- Some of the mysteries of Bohr's theory are explained by de Broglie, who suggested that electrons can behave like waves. (7.4)
- We see that the early ideas of quantum theory led to a new era in physics called quantum mechanics. The Heisenberg uncertainty principle sets the limits for measurement of quantum mechanical systems. The Schrödinger wave equation describes the behavior of electrons in atoms and molecules. (7.5)
- We learn that there are four quantum numbers to describe an electron in an atom and the characteristics of orbitals in which the electrons reside. (7.6 and 7.7)
- Electron configuration enables us to keep track of the distribution of electrons in an atom and understand its magnetic properties. (7.8)
- Finally, we apply the rules in writing electron configurations to the entire periodic table. In particular, we group elements according to their outer electron configurations. (7.9)

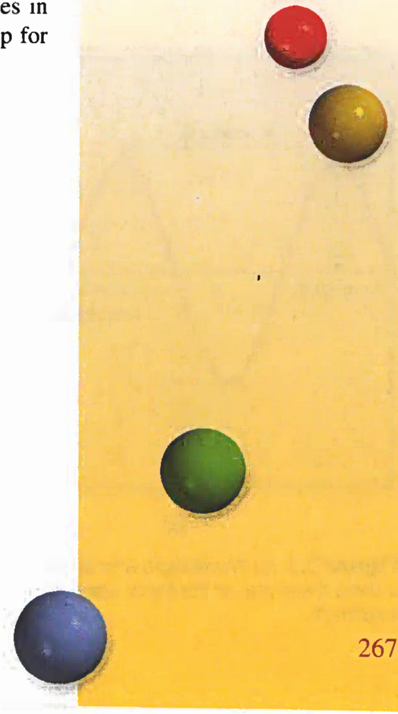
Interactive Activity Summary

1. Interactivity: Wavelength, Frequency, Amplitude (7.1)
2. Animation: Emission Spectra (7.3)
3. Interactivity: Orbital Shapes and Energy (7.7)
4. Animation: Electron Configurations (7.8)
5. Interactivity: Pauli Exclusion Principle (7.8)
6. Interactivity: Orbital Filling Rules (7.8)

Quantum theory enables us to predict and understand the critical role that electrons play in chemistry. In one sense, studying atoms amounts to asking the following questions:

1. How many electrons are present in a particular atom?
2. What energies do individual electrons possess?
3. Where in the atom can electrons be found?

The answers to these questions have a direct relationship to the behavior of all substances in chemical reactions, and the story of the search for answers provides a fascinating backdrop for our discussion.



7.1 From Classical Physics to Quantum Theory

Early attempts by nineteenth-century physicists to understand atoms and molecules met with only limited success. By assuming that molecules behave like rebounding balls, physicists were able to predict and explain some macroscopic phenomena, such as the pressure exerted by a gas. However, this model did not account for the stability of molecules; that is, it could not explain the forces that hold atoms together. It took a long time to realize—and an even longer time to accept—that the properties of atoms and molecules are *not* governed by the same physical laws as larger objects.

The new era in physics started in 1900 with a young German physicist named Max Planck.[†] While analyzing the data on radiation emitted by solids heated to various temperatures, Planck discovered that atoms and molecules emit energy only in certain discrete quantities, or *quanta.* Physicists had always assumed that energy is continuous and that any amount of energy could be released in a radiation process. Planck's *quantum theory* turned physics upside down. Indeed, the flurry of research that ensued altered our concept of nature forever.

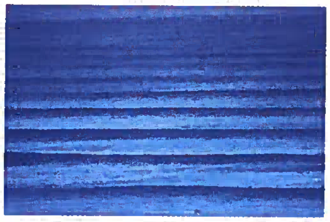


Figure 7.1 *Ocean water waves.*

Properties of Waves

To understand Planck's quantum theory, we must know something about the nature of waves. A ***wave*** can be thought of as *a vibrating disturbance by which energy is transmitted.* The fundamental properties of a wave are illustrated by a familiar type—water waves. (Figure 7.1). The regular variation of the peaks and troughs enable us to sense the propagation of the waves.

Waves are characterized by their length and height and by the number of waves that pass through a certain point in one second (Figure 7.2). ***Wavelength*** λ (lambda) is *the distance between identical points on successive waves.* The ***frequency*** ν (nu) is *the number of waves that pass through a particular point in 1 second.* ***Amplitude*** is *the vertical distance from the midline of a wave to the peak or trough.*

Interactivity:
Wavelength, Frequency, Amplitude
ARIS, Interactives

[†] Max Karl Ernst Ludwig Planck (1858–1947). German physicist. Planck received the Nobel Prize in Physics in 1918 for his quantum theory. He also made significant contributions in thermodynamics and other areas of physics.

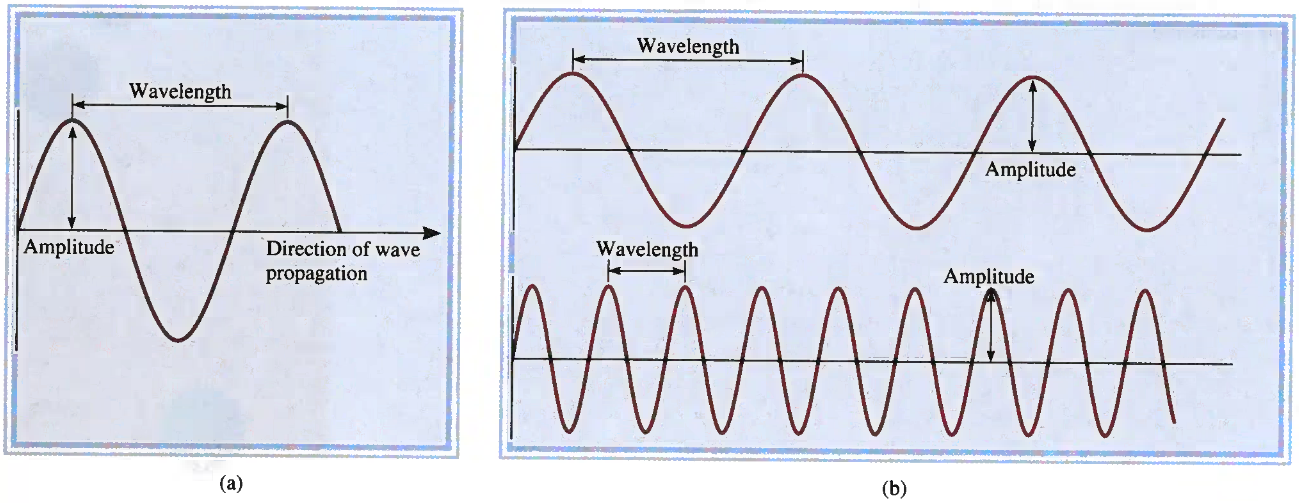


Figure 7.2 *(a) Wavelength and amplitude. (b) Two waves having different wavelengths and frequencies. The wavelength of the top wave is three times that of the lower wave, but its frequency is only one-third that of the lower wave. Both waves have the same speed and amplitude.*

Another important property of waves is their speed, which depends on the type of wave and the nature of the medium through which the wave is traveling (for example, air, water, or a vacuum). The speed (u) of a wave is the product of its wavelength and its frequency:

$$u = \lambda\nu \tag{7.1}$$

The inherent "sensibility" of Equation (7.1) becomes apparent if we analyze the physical dimensions involved in the three terms. The wavelength (λ) expresses the length of a wave, or distance/wave. The frequency (ν) indicates the number of these waves that pass any reference point per unit of time, or waves/time. Thus, the product of these terms results in dimensions of distance/time, which is speed:

$$\frac{\text{distance}}{\text{time}} = \frac{\text{distance}}{\cancel{\text{wave}}} \times \frac{\cancel{\text{waves}}}{\text{time}}$$

Wavelength is usually expressed in units of meters, centimeters, or nanometers, and frequency is measured in hertz (Hz), where

$$1\ \text{Hz} = 1\ \text{cycle/s}$$

The word "cycle" may be left out and the frequency expressed as, for example, 25/s or 25 s^{-1} (read as "25 per second").

Example 7.1

Calculate the speed of a wave whose wavelength and frequency are 17.4 cm and 87.4 Hz, respectively.

Solution Recall that 87.4 Hz is the same as 87.4/s. From Equation (7.1),

$$\begin{aligned} u &= \lambda\nu \\ &= 17.4\ \text{cm} \times 87.4\ \text{Hz} \\ &= 17.4\ \text{cm} \times 87.4/\text{s} \\ &= 1.52 \times 10^3\ \text{cm/s} \end{aligned}$$

Practice Exercise Calculate the frequency (in Hz) of a wave whose speed and wavelength are 713 m/s and 1.14 m, respectively.

Similar problem: 7.8.

Electromagnetic Radiation

There are many kinds of waves, such as water waves, sound waves, and light waves. In 1873 James Clerk Maxwell proposed that visible light consists of electromagnetic waves. According to Maxwell's theory, an ***electromagnetic wave*** *has an electric field component and a magnetic field component.* These two components have the same wavelength and frequency, and hence the same speed, but they travel in mutually perpendicular planes (Figure 7.3). The significance of Maxwell's theory is that it provides a mathematical description of the general behavior of light. In particular, his model accurately describes how energy in the form of radiation can be propagated through space as vibrating electric and magnetic fields. ***Electromagnetic radiation*** is *the emission and transmission of energy in the form of electromagnetic waves.*

Sound waves and water waves are not electromagnetic waves, but X rays and radio waves are.

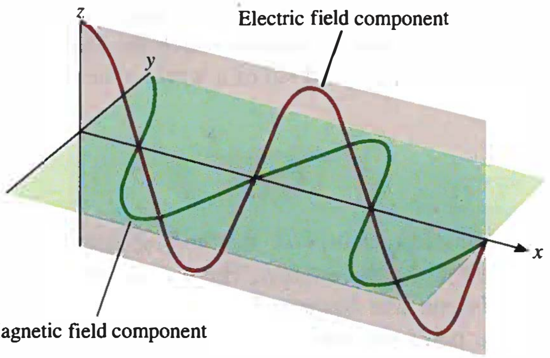


Figure 7.3 *The electric field and magnetic field components of an electromagnetic wave. These two components have the same wavelength, frequency, and amplitude, but they vibrate in two mutually perpendicular planes.*

A more accurate value for the speed of light is given on the inside back cover of the book.

Electromagnetic waves travel 3.00×10^8 meters per second (rounded off), or 186,000 miles per second in a vacuum. This speed does differ from one medium to another, but not enough to distort our calculations significantly. By convention, we use the symbol *c* for the speed of electromagnetic waves, or as it is more commonly called, the *speed of light.* The wavelength of electromagnetic waves is usually given in nanometers (nm).

Example 7.2

The wavelength of the green light from a traffic signal is centered at 522 nm. What is the frequency of this radiation?

Strategy We are given the wavelength of an electromagnetic wave and asked to calculate its frequency. Rearranging Equation (7.1) and replacing *u* with *c* (the speed of light) gives

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

Solution Because the speed of light is given in meters per second, it is convenient to first convert wavelength to meters. Recall that $1 \text{ nm} = 1 \times 10^{-9}$ m (see Table 1.3). We write

$$\lambda = 522\,\cancel{\text{nm}} \times \frac{1 \times 10^{-9}\text{ m}}{1\,\cancel{\text{nm}}} = 522 \times 10^{-9}\text{ m}$$
$$= 5.22 \times 10^{-7}\text{ m}$$

Substituting in the wavelength and the speed of light (3.00×10^8 m/s), the frequency is

$$\nu = \frac{3.00 \times 10^8\text{ m/s}}{5.22 \times 10^{-7}\text{ m}}$$
$$= 5.75 \times 10^{14}\text{/s, or } \boxed{5.75 \times 10^{14}\text{ Hz}}$$

Check The answer shows that 5.75×10^{14} waves pass a fixed point every second. This very high frequency is in accordance with the very high speed of light.

Similar problem: 7.7.

Practice Exercise What is the wavelength (in meters) of an electromagnetic wave whose frequency is 3.64×10^7 Hz?

Figure 7.4 shows various types of electromagnetic radiation, which differ from one another in wavelength and frequency. The long radio waves are emitted by large antennas, such as those used by broadcasting stations. The shorter, visible light waves

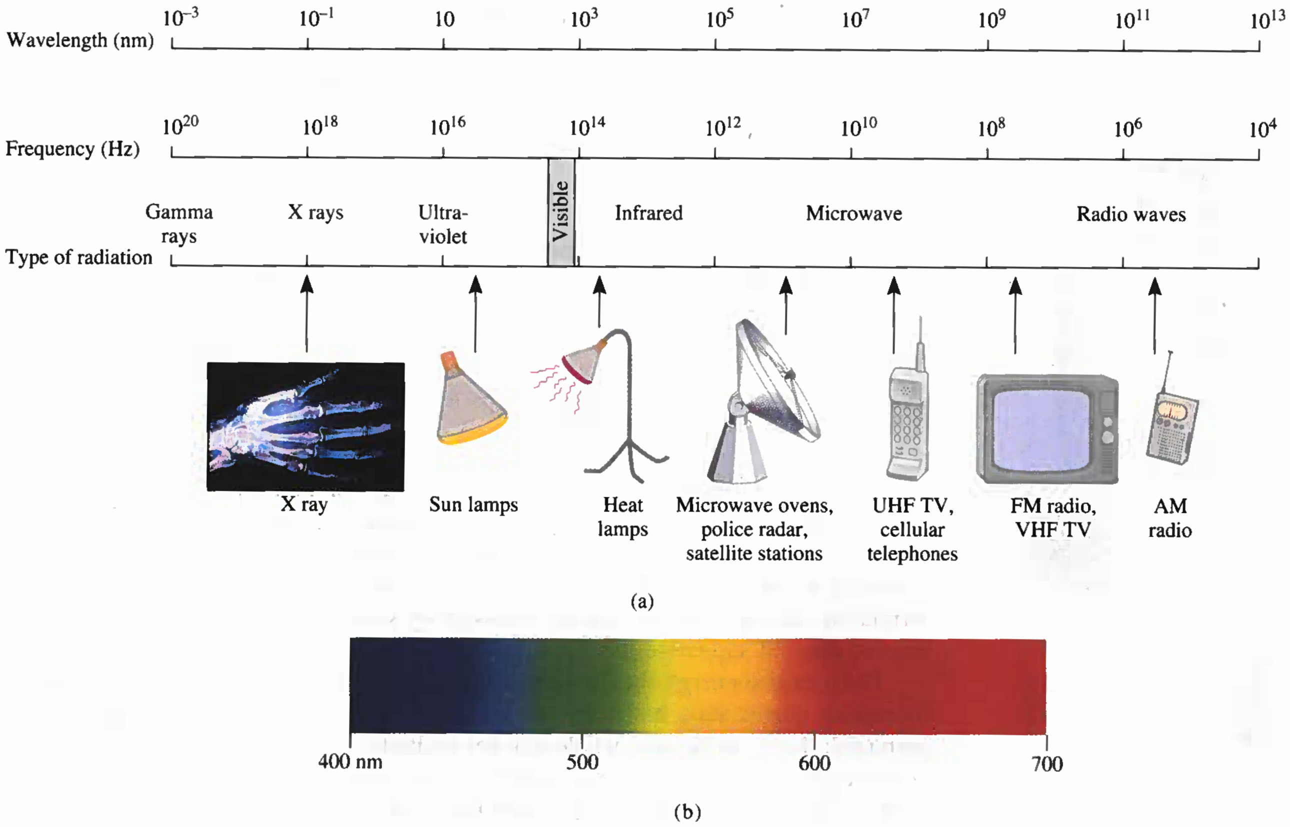


Figure 7.4 *(a) Types of electromagnetic radiation. Gamma rays have the shortest wavelength and highest frequency; radio waves have the longest wavelength and the lowest frequency. Each type of radiation is spread over a specific range of wavelengths (and frequencies). (b) Visible light ranges from a wavelength of 400 nm (violet) to 700 nm (red).*

are produced by the motions of electrons within atoms and molecules. The shortest waves, which also have the highest frequency, are associated with γ (gamma) rays, which result from changes within the nucleus of the atom (see Chapter 2). As we will see shortly, the higher the frequency, the more energetic the radiation. Thus, ultraviolet radiation, X rays, and γ rays are high-energy radiation.

Planck's Quantum Theory

When solids are heated, they emit electromagnetic radiation over a wide range of wavelengths. The dull red glow of an electric heater and the bright white light of a tungsten lightbulb are examples of radiation from heated solids.

Measurements taken in the latter part of the nineteenth century showed that the amount of radiation energy emitted by an object at a certain temperature depends on its wavelength. Attempts to account for this dependence in terms of established wave theory and thermodynamic laws were only partially successful. One theory explained short-wavelength dependence but failed to account for the longer wavelengths. Another theory accounted for the longer wavelengths but failed for short wavelengths. It seemed that something fundamental was missing from the laws of classical physics.

Planck solved the problem with an assumption that departed drastically from accepted concepts. Classical physics assumed that atoms and molecules could emit (or absorb) any arbitrary amount of radiant energy. Planck said that atoms and molecules could emit (or absorb) energy only in discrete quantities, like small packages or bundles. Planck gave the name ***quantum*** to *the smallest quantity of energy that can be emitted (or absorbed) in the form of electromagnetic radiation.* The energy E of a single quantum of energy is given by

$$E = h\nu \tag{7.2}$$

where h is called *Planck's constant* and ν is the frequency of radiation. The value of Planck's constant is 6.63×10^{-34} J · s. Because $\nu = c/\lambda$, Equation (7.2) can also be expressed as

$$E = h\frac{c}{\lambda} \tag{7.3}$$

According to quantum theory, energy is always emitted in multiples of $h\nu$; for example, $h\nu$, $2\,h\nu$, $3\,h\nu$, . . . , but never, for example, $1.67\,h\nu$ or $4.98\,h\nu$. At the time Planck presented his theory, he could not explain why energies should be fixed or quantized in this manner. Starting with this hypothesis, however, he had no trouble correlating the experimental data for emission by solids over the *entire* range of wavelengths; they all supported the quantum theory.

The idea that energy should be quantized or "bundled" may seem strange, but the concept of quantization has many analogies. For example, an electric charge is also quantized; there can be only whole-number multiples of e, the charge of one electron. Matter itself is quantized, for the numbers of electrons, protons, and neutrons and the numbers of atoms in a sample of matter must also be integers. Our money system is based on a "quantum" of value called a penny. Even processes in living systems involve quantized phenomena. The eggs laid by hens are quantized, and a pregnant cat gives birth to an integral number of kittens, not to one-half or three-quarters of a kitten.

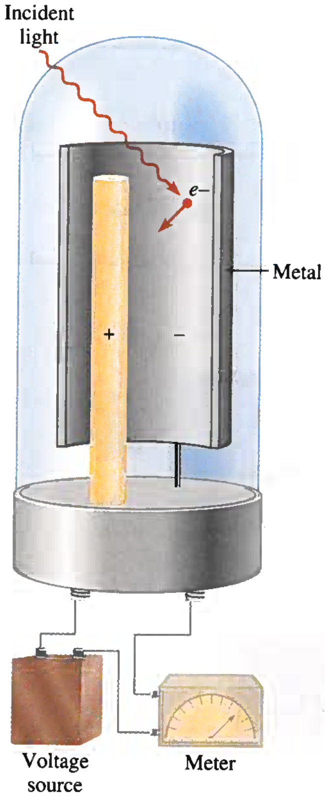


Figure 7.5 *An apparatus for studying the photoelectric effect. Light of a certain frequency falls on a clean metal surface. Ejected electrons are attracted toward the positive electrode. The flow of electrons is registered by a detecting meter. Light meters used in cameras are based on photoelectric effect.*

7.2 The Photoelectric Effect

In 1905, only five years after Planck presented his quantum theory, Albert Einstein[†] used the theory to solve another mystery in physics, the ***photoelectric effect,*** a phenomenon in which *electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency,* called *the threshold frequency* (Figure 7.5). The number of electrons ejected was proportional to the intensity (or brightness) of the light, but the energies of the ejected electrons were not. Below the threshold frequency no electrons were ejected no matter how intense the light.

The photoelectric effect could not be explained by the wave theory of light. Einstein, however, made an extraordinary assumption. He suggested that a beam of light is really a stream of particles. These *particles of light* are now called ***photons.*** Using Planck's quantum theory of radiation as a starting point, Einstein deduced that each photon must possess energy E, given by the equation

This equation has the same form as Equation (7.2) because, as we will see shortly, electromagnetic radiation is emitted as well as absorbed in the form of photons.

$$E = h\nu$$

[†] Albert Einstein (1879–1955). German-born American physicist. Regarded by many as one of the two greatest physicists the world has known (the other is Isaac Newton). The three papers (on special relativity, Brownian motion, and the photoelectric effect) that he published in 1905 while employed as a technical assistant in the Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

where ν is the frequency of light. Electrons are held in a metal by attractive forces, and so removing them from the metal requires light of a sufficiently high frequency (which corresponds to sufficiently high energy) to break them free. Shining a beam of light onto a metal surface can be thought of as shooting a beam of particles—photons—at the metal atoms. If the frequency of photons is such that $h\nu$ is exactly equal to the energy that binds the electrons in the metal, then the light will have just enough energy to knock the electrons loose. If we use light of a higher frequency, then not only will the electrons be knocked loose, but they will also acquire some kinetic energy. This situation is summarized by the equation

$$h\nu = \text{KE} + \text{BE} \tag{7.4}$$

where KE is the kinetic energy of the ejected electron and BE is the binding energy of the electron in the metal. Rewriting Equation (7.4) as

$$\text{KE} = h\nu - \text{BE}$$

shows that the more energetic the photon (that is, the higher its frequency), the greater the kinetic energy of the ejected electron.

Now consider two beams of light having the same frequency (which is greater than the threshold frequency) but different intensities. The more intense beam of light consists of a larger number of photons; consequently, it ejects more electrons from the metal's surface than the weaker beam of light. Thus, the more intense the light, the greater the number of electrons emitted by the target metal; the higher the frequency of the light, the greater the kinetic energy of the ejected electrons.

Example 7.3

Calculate the energy (in joules) of (a) a photon with a wavelength of 5.00×10^4 nm (infrared region) and (b) a photon with a wavelength of 5.00×10^{-2} nm (X ray region).

Strategy In both (a) and (b) we are given the wavelength of a photon and asked to calculate its energy. We need to use Equation (7.3) to calculate the energy. Planck's constant is given in the text and also on the back inside cover.

Solution (a) From Equation (7.3),

$$\begin{aligned} E &= h\frac{c}{\lambda} \\ &= \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{(5.00 \times 10^{4}\ \text{nm})\dfrac{1 \times 10^{-9}\ \text{m}}{1\ \text{nm}}} \\ &= 3.98 \times 10^{-21}\ \text{J} \end{aligned}$$

This is the energy of a single photon with a 5.00×10^4 nm wavelength.

(b) Following the same procedure as in (a), we can show that the energy of the photon that has a wavelength of 5.00×10^{-2} nm is 3.98×10^{-15} J.

Check Because the energy of a photon increases with decreasing wavelength, we see that an "X-ray" photon is 1×10^6, or a million times, more energetic than an "infrared" photon.

Similar problem: 7.15.

Practice Exercise The energy of a photon is 5.87×10^{-20} J. What is its wavelength (in nanometers)?

Einstein's theory of light posed a dilemma for scientists. On the one hand, it explains the photoelectric effect satisfactorily. On the other hand, the particle theory of light is not consistent with the known wave behavior of light. The only way to resolve the dilemma is to accept the idea that light possesses *both* particlelike and wavelike properties. Depending on the experiment, light behaves either as a wave or as a stream of particles. This concept, called particle-wave duality, was totally alien to the way physicists had thought about matter and radiation, and it took a long time for them to accept it. We will see in Section 7.4 that a dual nature (particles and waves) is not unique to light but is characteristic of all matter, including electrons.

7.3 Bohr's Theory of the Hydrogen Atom

Einstein's work paved the way for the solution of yet another nineteenth-century "mystery" in physics: the emission spectra of atoms.

Emission Spectra

Animation:
Emission Spectra
ARIS, Animations

Ever since the seventeenth century, when Newton showed that sunlight is composed of various color components that can be recombined to produce white light, chemists and physicists have studied the characteristics of ***emission spectra,*** that is, *either continuous or line spectra of radiation emitted by substances.* The emission spectrum of a substance can be seen by energizing a sample of material either with thermal energy or with some other form of energy (such as a high-voltage electrical discharge). A "red-hot" or "white-hot" iron bar freshly removed from a high-temperature source produces a characteristic glow. This visible glow is the portion of its emission spectrum that is sensed by eye. The warmth of the same iron bar represents another portion of its emission spectrum—the infrared region. A feature common to the emission spectra of the sun and of a heated solid is that both are continuous; that is, all wavelengths of visible light are represented in the spectra (see the visible region in Figure 7.4).

The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelengths from red to violet; rather, the atoms produce bright lines in different parts of the visible spectrum. These ***line spectra*** are *the light emission only at specific wavelengths.* Figure 7.6 is a schematic diagram of a discharge tube that is used to study emission spectra, and Figure 7.7 shows the color emitted by hydrogen atoms in a discharge tube.


When a high voltage is applied between the forks, some of the sodium ions in the pickle are converted to sodium atoms in an excited state. These atoms emit the characteristic yellow light as they relax to the ground state.

Every element has a unique emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms, much as fingerprints are used to identify people. When the lines of the emission spectrum of a known element exactly match the lines of the emission spectrum of an unknown sample, the identity of the sample is established. Although the utility of this procedure was recognized some time ago in chemical analysis, the origin of these lines was unknown until early in the twentieth century. Figure 7.8 on p. 276 shows the emission spectra of several elements.

Emission Spectrum of the Hydrogen Atom

In 1913, not too long after Planck's and Einstein's discoveries, a theoretical explanation of the emission spectrum of the hydrogen atom was presented by the Danish physicist Niels Bohr.† Bohr's treatment is very complex and is no longer considered

---

†Niels Henrik David Bohr (1885–1962). Danish physicist. One of the founders of modern physics, he received the Nobel Prize in Physics in 1922 for his theory explaining the spectrum of the hydrogen atom.

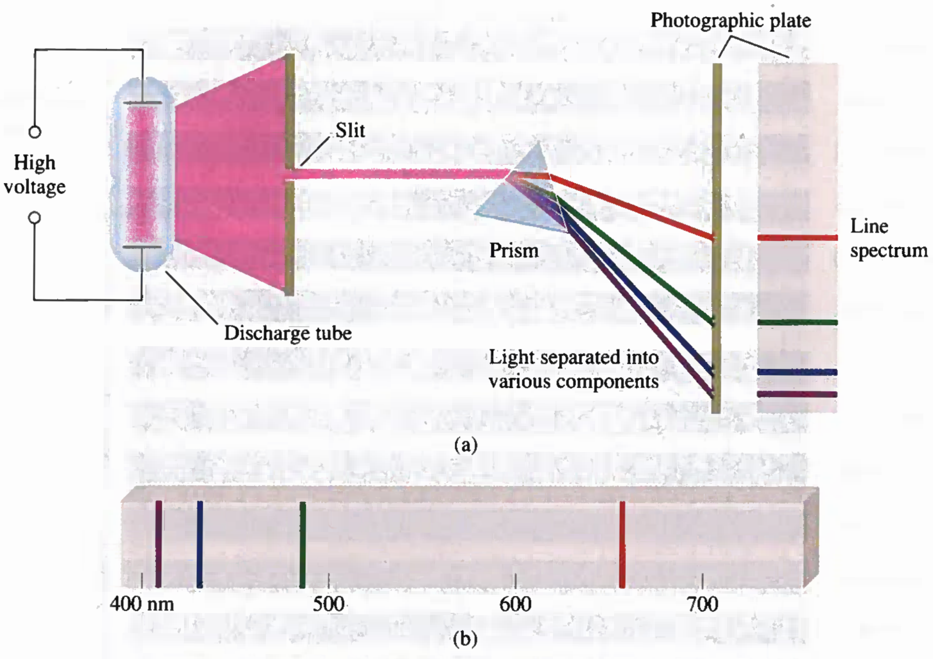


Figure 7.6 *(a) An experimental arrangement for studying the emission spectra of atoms and molecules. The gas under study is in a discharge tube containing two electrodes. As electrons flow from the negative electrode to the positive electrode, they collide with the gas. This collision process eventually leads to the emission of light by the atoms (or molecules). The emitted light is separated into its components by a prism. Each component color is focused at a definite position, according to its wavelength, and forms a colored image of the slit on the photographic plate. The colored images are called spectral lines. (b) The line emission spectrum of hydrogen atoms.*

to be correct in all its details. Thus, we will concentrate only on his important assumptions and final results, which do account for the spectral lines.

When Bohr first tackled this problem, physicists already knew that the atom contains electrons and protons. They thought of an atom as an entity in which electrons whirled around the nucleus in circular orbits at high velocities. This was an appealing model because it resembled the motions of the planets around the sun. In the hydrogen atom, it was believed that the electrostatic attraction between the positive "solar" proton and the negative "planetary" electron pulls the electron inward and that this force is balanced exactly by the outward acceleration due to the circular motion of the electron.

Bohr's model of the atom included the idea of electrons moving in circular orbits, but he imposed a rather severe restriction: The single electron in the hydrogen atom could be located only in certain orbits. Because each orbit has a particular energy associated with it, the energies associated with electron motion in the permitted orbits must be fixed in value, or *quantized.* Bohr attributed the emission of radiation by an energized hydrogen atom to the electron dropping from a higher-energy orbit to a lower one and giving up a quantum of energy (a photon) in the form of light (Figure 7.9). Using arguments based on electrostatic interaction and Newton's laws of motion, Bohr showed that the energies that the electron in the hydrogen atom can possess are given by

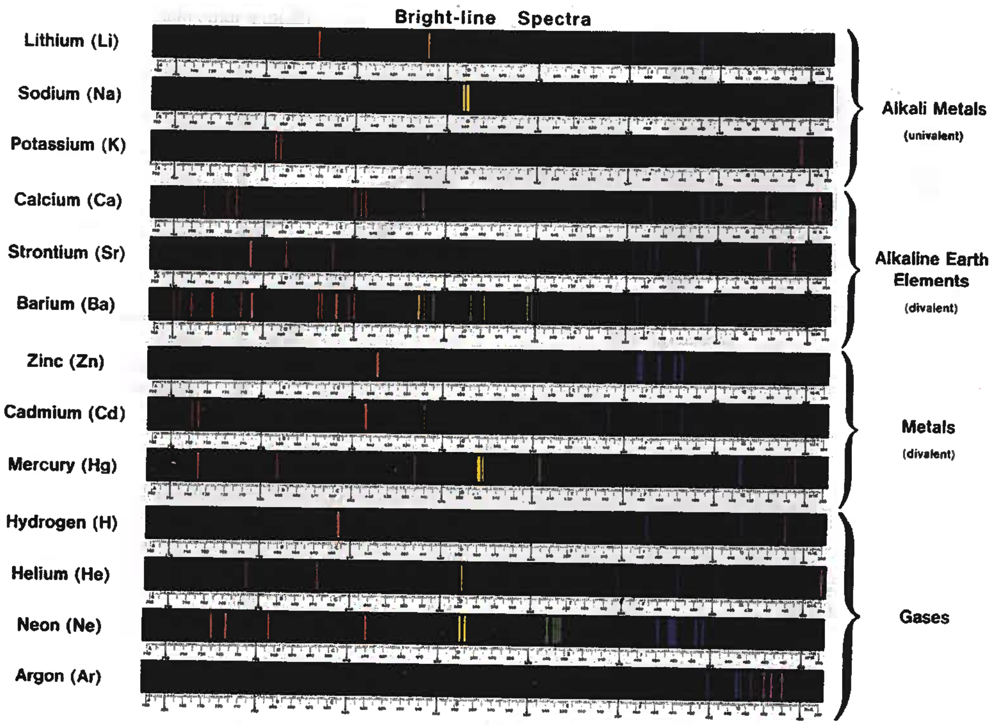
$$E_n = -R_{\mathrm{H}}\left(\frac{1}{n^2}\right) \tag{7.5}$$

where R_{H}, the Rydberg[†] constant, has the value 2.18×10^{-18} J. The number n is an integer called the principal quantum number; it has the values $n = 1, 2, 3, \ldots$.

Figure 7.7 *Color emitted by hydrogen atoms in a discharge tube. The color observed results from the combination of the colors emitted in the visible spectrum.*

[†] Johannes Robert Rydberg (1854–1919). Swedish physicist. Rydberg's major contribution to physics was his study of the line spectra of many elements.

Figure 7.8 *The emission spectra of various elements.*



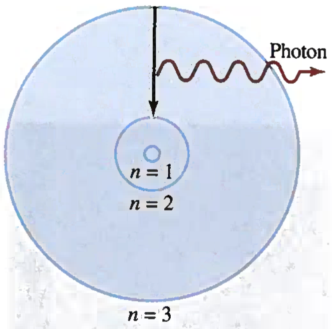


Figure 7.9 *The emission process in an excited hydrogen atom, according to Bohr's theory. An electron originally in a higher-energy orbit (n = 3) falls back to a lower-energy orbit (n = 2). As a result, a photon with energy hν is given off. The value of hν is equal to the difference in energies of the two orbits occupied by the electron in the emission process. For simplicity, only three orbits are shown.*

The negative sign in Equation (7.5) is an arbitrary convention, signifying that the energy of the electron in the atom is *lower* than the energy of a *free electron,* which is an electron that is infinitely far from the nucleus. The energy of a free electron is arbitrarily assigned a value of zero. Mathematically, this corresponds to setting n equal to infinity in Equation (7.5), so that $E_\infty = 0$. As the electron gets closer to the nucleus (as n decreases), E_n becomes larger in absolute value, but also more negative. The most negative value, then, is reached when $n = 1$, which corresponds to the most stable energy state. We call this the ***ground state,*** or the ***ground level,*** which refers to *the lowest energy state of a system* (which is an atom in our discussion). The stability of the electron diminishes for $n = 2, 3, \ldots$. Each of these levels is called an ***excited state,*** or ***excited level,*** which is *higher in energy than the ground state.* A hydrogen electron for which n is greater than 1 is said to be in an excited state. The radius of each circular orbit in Bohr's model depends on n^2. Thus, as n increases from 1 to 2 to 3, the orbit radius increases very rapidly. The higher the excited state, the farther away the electron is from the nucleus (and the less tightly it is held by the nucleus).

Bohr's theory enables us to explain the line spectrum of the hydrogen atom. Radiant energy absorbed by the atom causes the electron to move from a lower-energy state (characterized by a smaller n value) to a higher-energy state (characterized by a larger n value). Conversely, radiant energy (in the form of a photon) is emitted when the electron moves from a higher-energy state to a lower-energy state. The quantized movement of the electron from one energy state to another is analogous to the movement of a tennis ball either up or down a set of stairs (Figure 7.10). The ball can be on any of several steps but never between steps. The journey from a lower step to a higher one is an energy-requiring process, whereas movement from a higher step to a lower step is an energy-releasing process. The quantity of energy involved in either type of change is determined by the distance between the beginning and ending steps.

Similarly, the amount of energy needed to move an electron in the Bohr atom depends on the difference in energy levels between the initial and final states.

To apply Equation (7.5) to the emission process in a hydrogen atom, let us suppose that the electron is initially in an excited state characterized by the principal quantum number n_i. During emission, the electron drops to a lower energy state characterized by the principal quantum number n_f (the subscripts i and f denote the initial and final states, respectively). This lower energy state may be either a less excited state or the ground state. The difference between the energies of the initial and final states is

$$\Delta E = E_\mathrm{f} - E_\mathrm{i}$$

From Equation (7.5),

$$E_\mathrm{f} = -R_\mathrm{H}\left(\frac{1}{n_\mathrm{f}^2}\right)$$

and

$$E_\mathrm{i} = -R_\mathrm{H}\left(\frac{1}{n_\mathrm{i}^2}\right)$$

Therefore,

$$\Delta E = \left(\frac{-R_\mathrm{H}}{n_\mathrm{f}^2}\right) - \left(\frac{-R_\mathrm{H}}{n_\mathrm{i}^2}\right)$$

$$= R_\mathrm{H}\left(\frac{1}{n_\mathrm{i}^2} - \frac{1}{n_\mathrm{f}^2}\right)$$

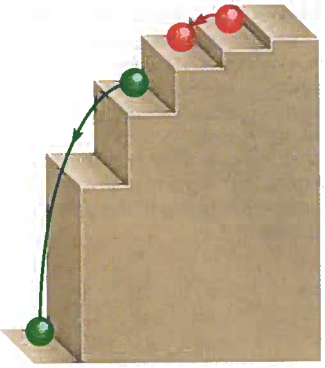


Figure 7.10 *A mechanical analogy for the emission processes. The ball can rest on any step but not between steps.*

Because this transition results in the emission of a photon of frequency ν and energy $h\nu$, we can write

$$\Delta E = h\nu = R_\mathrm{H}\left(\frac{1}{n_\mathrm{i}^2} - \frac{1}{n_\mathrm{f}^2}\right) \tag{7.6}$$

When a photon is emitted, $n_\mathrm{i} > n_\mathrm{f}$. Consequently the term in parentheses is negative and ΔE is negative (energy is lost to the surroundings). When energy is absorbed, $n_\mathrm{i} < n_\mathrm{f}$ and the term in parentheses is positive, so ΔE is positive. Each spectral line in the emission spectrum corresponds to a particular transition in a hydrogen atom. When we study a large number of hydrogen atoms, we observe all possible transitions and hence the corresponding spectral lines. The brightness of a spectral line depends on how many photons of the same wavelength are emitted.

The emission spectrum of hydrogen includes a wide range of wavelengths from the infrared to the ultraviolet. Table 7.1 lists the series of transitions in the hydrogen

TABLE 7.1 The Various Series in Atomic Hydrogen Emission Spectrum

Series	n_f	n_i	Spectrum Region
Lyman	1	2, 3, 4, . . .	Ultraviolet
Balmer	2	3, 4, 5, . . .	Visible and ultraviolet
Paschen	3	4, 5, 6, . . .	Infrared
Brackett	4	5, 6, 7, . . .	Infrared

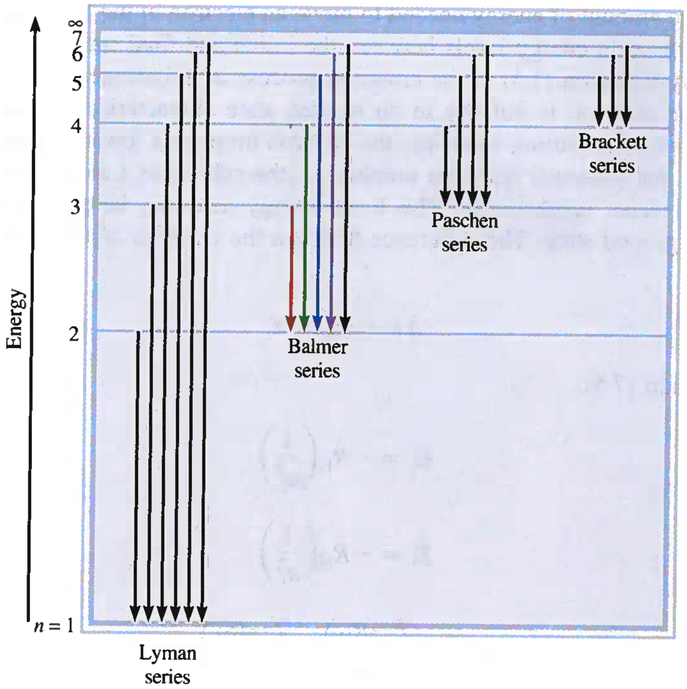


Figure 7.11 *The energy levels in the hydrogen atom and the various emission series. Each energy level corresponds to the energy associated with an allowed energy state for an orbit, as postulated by Bohr and shown in Figure 7.9. The emission lines are labeled according to the scheme in Table 7.1.*

spectrum; they are named after their discoverers. The Balmer series was particularly easy to study because a number of its lines fall in the visible range.

Figure 7.9 shows a single transition. However, it is more informative to express transitions as shown in Figure 7.11. Each horizontal line represents an allowed energy level for the electron in a hydrogen atom. The energy levels are labeled with their principal quantum numbers.

Example 7.4 illustrates the use of Equation (7.6).

Example 7.4

What is the wavelength of a photon (in nanometers) emitted during a transition from the $n_i = 5$ state to the $n_f = 2$ state in the hydrogen atom?

Strategy We are given the initial and final states in the emission process. We can calculate the energy of the emitted photon using Equation (7.6). Then from Equations (7.2) and (7.1) we can solve for the wavelength of the photon. The value of Rydberg's constant is given in the text.

Solution From Equation (7.6) we write

$$\Delta E = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$
$$= 2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{5^2} - \frac{1}{2^2}\right)$$
$$= -4.58 \times 10^{-19}\,\text{J}$$

The negative sign is in accord with our convention that energy is given off to the surroundings.

The negative sign indicates that this is energy associated with an emission process. To calculate the wavelength, we will omit the minus sign for ΔE because the wavelength of

(Continued)

the photon must be positive. Because $\Delta E = h\nu$ or $\nu = \Delta E/h$, we can calculate the wavelength of the photon by writing

$$\begin{aligned}\lambda &= \frac{c}{\nu}\\ &= \frac{ch}{\Delta E}\\ &= \frac{(3.00 \times 10^{8}\ \text{m/s})(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})}{4.58 \times 10^{-19}\ \text{J}}\\ &= 4.34 \times 10^{-7}\ \text{m}\\ &= 4.34 \times 10^{-7}\ \text{m} \times \left(\frac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}}\right) = 434\ \text{nm}\end{aligned}$$

Check The wavelength is in the visible region of the electromagnetic region (see Figure 7.4). This is consistent with the fact that because $n_f = 2$, this transition gives rise to a spectral line in the Balmer series (see Figure 7.6).

Similar problems: 7.31, 7.32.

Practice Exercise What is the wavelength (in nanometers) of a photon emitted during a transition from $n_i = 6$ to $n_f = 4$ state in the H atom?

The Chemistry in Action essay on p. 280 discusses a special type of atomic emission—lasers.

7.4 The Dual Nature of the Electron

Physicists were both mystified and intrigued by Bohr's theory. They questioned why the energies of the hydrogen electron are quantized. Or, phrasing the question in a more concrete way, Why is the electron in a Bohr atom restricted to orbiting the nucleus at certain fixed distances? For a decade no one, not even Bohr himself, had a logical explanation. In 1924 Louis de Broglie[†] provided a solution to this puzzle. De Broglie reasoned that if light waves can behave like a stream of particles (photons), then perhaps particles such as electrons can possess wave properties. According to de Broglie, an electron bound to the nucleus behaves like a *standing wave.* Standing waves can be generated by plucking, say, a guitar string (Figure 7.12). The waves are described as standing, or stationary, because they do not travel along the string. Some points on the string, called ***nodes,*** do not move at all; that is, *the amplitude of the wave at these points is zero.* There is a node at each end, and there may be nodes between the ends. The greater the frequency of vibration, the shorter the wavelength of the standing wave and the greater the number of nodes. As Figure 7.12 shows, there can be only certain wavelengths in any of the allowed motions of the string.

[†] Louis Victor Pierre Raymond Duc de Broglie (1892–1977). French physicist. Member of an old and noble family in France, he held the title of a prince. In his doctoral dissertation, he proposed that matter and radiation have the properties of both wave and particle. For this work, de Broglie was awarded the Nobel Prize in Physics in 1929.

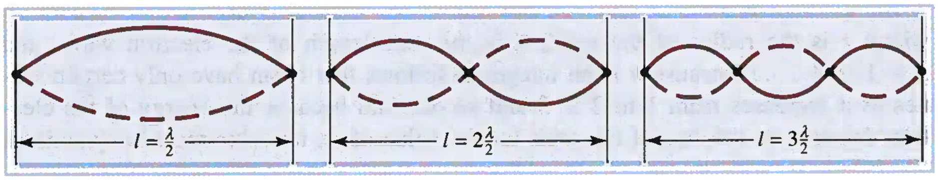
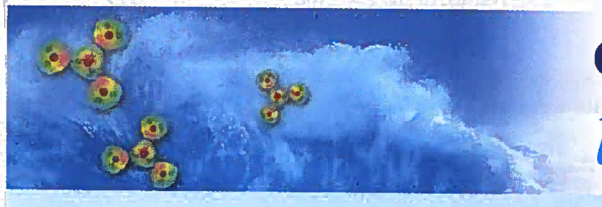


Figure 7.12 *The standing waves generated by plucking a guitar string. Each dot represents a node. The length of the string (l) must be equal to a whole number times one-half the wavelength ($\lambda/2$).*

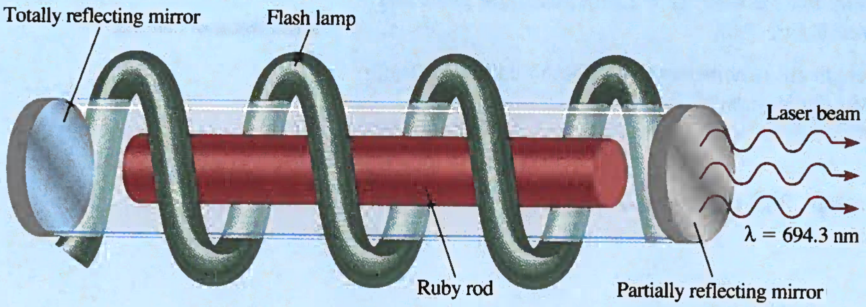


CHEMISTRY *in Action*

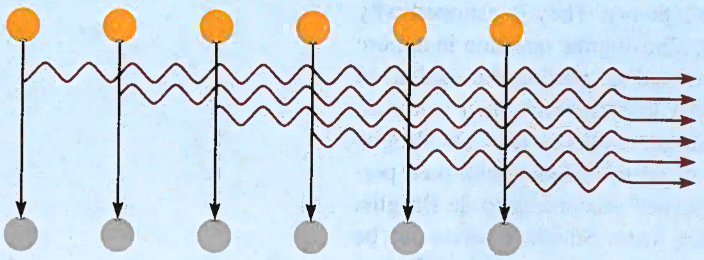
Laser—The Splendid Light

Laser is an acronym for light amplification by stimulated emission of radiation. It is a special type of emission that involves either atoms or molecules. Since the discovery of laser in 1960, it has been used in numerous systems designed to operate in the gas, liquid, and solid states. These systems emit radiation with wavelengths ranging from infrared through visible and ultraviolet. The advent of laser has truly revolutionized science, medicine, and technology.

Ruby laser was the first known laser. Ruby is a deep-red mineral containing corundum, Al_2O_3, in which some of the Al^{3+}



The emission of laser light from a ruby laser.



The stimulated emission of one photon by another photon in a cascade event that leads to the emission of laser light. The synchronization of the light waves produces an intensely penetrating laser beam.

De Broglie argued that if an electron does behave like a standing wave in the hydrogen atom, the length of the wave must fit the circumference of the orbit exactly (Figure 7.13). Otherwise the wave would partially cancel itself on each successive orbit. Eventually the amplitude of the wave would be reduced to zero, and the wave would not exist.

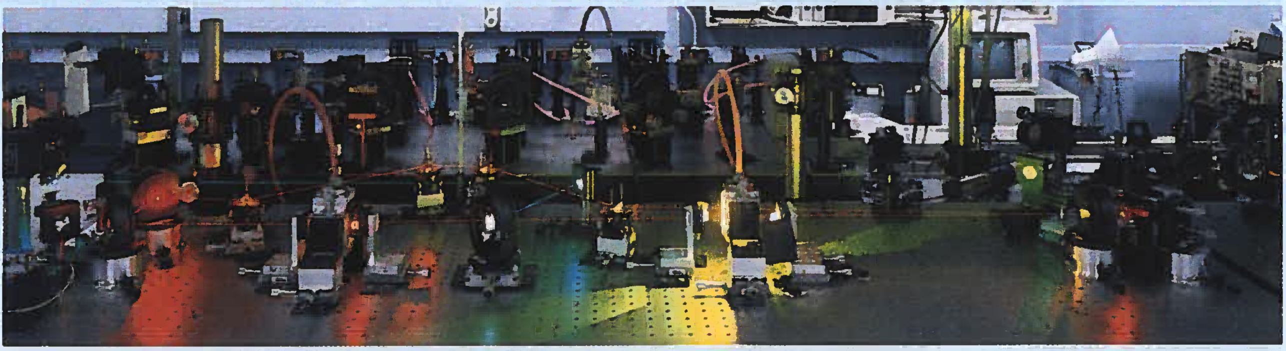
The relation between the circumference of an allowed orbit ($2\pi r$) and the wavelength (λ) of the electron is given by

$$2\pi r = n\lambda \tag{7.7}$$

where r is the radius of the orbit, λ is the wavelength of the electron wave, and $n = 1, 2, 3, \ldots$. Because n is an integer, it follows that r can have only certain values as n increases from 1 to 2 to 3 and so on. And because the energy of the electron depends on the size of the orbit (or the value of r), its value must be quantized.

ions have been replaced by Cr^{3+} ions. A flashlamp is used to excite the chromium atoms to a higher energy level. The excited atoms are unstable, so at a given instant some of them will return to the ground state by emitting a photon in the red region of the spectrum. The photon bounces back and forth many times between mirrors at opposite ends of the laser tube. This photon can stimulate the emission of photons of exactly the same wavelength from other excited chromium atoms; these photons in turn can stimulate the emission of more photons, and so on. Because the light waves are *in phase*—that is, their maxima and minima coincide—the photons enhance one another, increasing their power with each passage between the mirrors. One of the mirrors is only partially reflecting, so that when the light reaches a certain intensity it emerges from the mirror as a laser beam. Depending on the mode of operation, the laser light may be emitted in pulses (as in the ruby laser case) or in continuous waves.

Laser light is characterized by three properties: It is intense, it has precisely known wavelength and hence energy, and it is coherent. By *coherent* we mean that the light waves are all in phase. The applications of lasers are quite numerous. Their high intensity and ease of focus make them suitable for doing eye surgery, for drilling holes in metals and welding, and for carrying out nuclear fusion. The fact that they are highly directional and have precisely known wavelengths makes them very useful for telecommunications. Lasers are also used in isotope separation, in holography (three-dimensional photography), in compact disc players, and in supermarket scanners. Lasers have played an important role in the spectroscopic investigation of molecular properties and of many chemical and biological processes. Laser lights are increasingly being used to probe the details of chemical reactions (see Chapter 13).

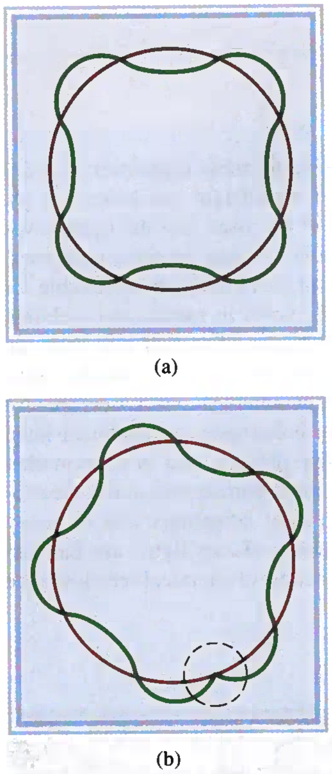


State-of-the-art lasers used in the research laboratory of Dr. A. H. Zewail at the California Institute of Technology.

De Broglie's reasoning led to the conclusion that waves can behave like particles and particles can exhibit wavelike properties. De Broglie deduced that the particle and wave properties are related by the expression

$$\lambda = \frac{h}{mu} \tag{7.8}$$

where λ, m, and u are the wavelengths associated with a moving particle, its mass, and its velocity, respectively. Equation (7.8) implies that a particle in motion can be treated as a wave, and a wave can exhibit the properties of a particle. Note that the left side of Equation (7.8) involves the wavelike property of wavelength, whereas the right side makes references to mass, a distinctly particlelike property.


(a)

(b)

Figure 7.13 *(a) The circumference of the orbit is equal to an integral number of wavelengths. This is an allowed orbit. (b) The circumference of the orbit is not equal to an integral number of wavelengths. As a result, the electron wave does not close in on itself. This is a nonallowed orbit.*

Example 7.5

Calculate the wavelength of the "particle" in the following two cases: (a) The fastest serve in tennis is about 150 miles per hour, or 68 m/s. Calculate the wavelength associated with a 6.0×10^{-2}-kg tennis ball traveling at this speed. (b) Calculate the wavelength associated with an electron (9.1094×10^{-31} kg) moving at 63 m/s.

Strategy We are given the mass and the speed of the particle in (a) and (b) and asked to calculate the wavelength so we need Equation (7.8). Note that because the units of Planck's constants are J · s, m and u must be in kg and m/s ($1\ \text{J} = 1\ \text{kg m}^2/\text{s}^2$), respectively.

Solution (a) Using Equation (7.8) we write

$$\lambda = \frac{h}{mu}$$
$$= \frac{6.68 \times 10^{-34}\ \text{J}\cdot\text{s}}{(6.0 \times 10^{-2}\ \text{kg}) \times 63\ \text{m/s}}$$
$$= 1.6 \times 10^{-34}\ \text{m}$$

Comment This is an exceedingly small wavelength considering that the size of an atom itself is on the order of 1×10^{-10} m. For this reason, the wave properties of a tennis ball cannot be detected by any existing measuring device.

(b) In this case,

$$\lambda = \frac{h}{mu}$$
$$= \frac{6.63 \times 10^{-34}\ \text{J}\cdot\text{s}}{(9.1094 \times 10^{-31}\ \text{kg}) \times 68\ \text{m/s}}$$
$$= 1.1 \times 10^{-5}\ \text{m}$$

Comment This wavelength (1.1×10^{-5} m or 1.1×10^{4} nm) is in the infrared region. This calculation shows that only electrons (and other submicroscopic particles) have measurable wavelengths.

Practice Exercise Calculate the wavelength (in nanometers) of a H atom (mass = 1.674×10^{-27} kg) moving at 7.00×10^{2} cm/s.

Similar problems: 7.40, 7.41.

Example 7.5 shows that although de Broglie's equation can be applied to diverse systems, the wave properties become observable only for submicroscopic objects. This distinction is due to the smallness of Planck's constant, h, which appears in the numerator in Equation (7.8).

Shortly after de Broglie introduced his equation, Clinton Davisson[†] and Lester Germer[‡] in the United States and G. P. Thomson[§] in England demonstrated that electrons do indeed possess wavelike properties. By directing a beam of electrons through a thin piece of gold foil, Thomson obtained a set of concentric rings on a screen,

---

[†] Clinton Joseph Davisson (1881–1958). American physicist. He and G. P. Thomson shared the Nobel Prize in Physics in 1937 for demonstrating wave properties of electrons.

[‡] Lester Halbert Germer (1896–1972). American physicist. Discoverer (with Davisson) of the wave properties of electrons.

[§] George Paget Thomson (1892–1975). English physicist. Son of J. J. Thomson, he received the Nobel Prize in Physics in 1937, along with Clinton Davisson, for demonstrating wave properties of electrons.

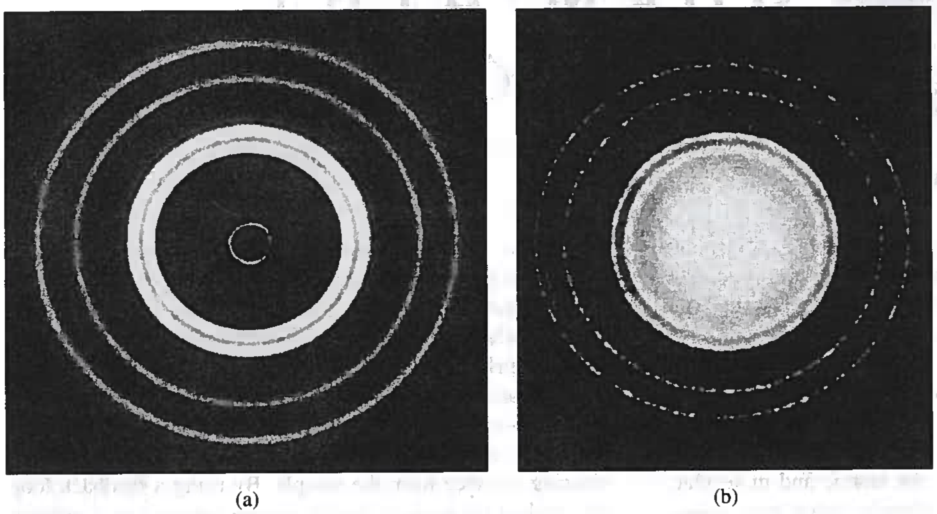


Figure 7.14 *(a) X-ray diffraction pattern of aluminum foil. (b) Electron diffraction of aluminum foil. The similarity of these two patterns shows that electrons can behave like X rays and display wave properties.*

similar to the pattern observed when X rays (which are waves) were used. Figure 7.14 shows such a pattern for aluminum.

The Chemistry in Action essay on p. 284 describes electron microscopy.

7.5 Quantum Mechanics

The spectacular success of Bohr's theory was followed by a series of disappointments. Bohr's approach did not account for the emission spectra of atoms containing more than one electron, such as atoms of helium and lithium. Nor did it explain why extra lines appear in the hydrogen emission spectrum when a magnetic field is applied. Another problem arose with the discovery that electrons are wavelike: How can the "position" of a wave be specified? We cannot define the precise location of a wave because a wave extends in space.

In reality, Bohr's theory accounted for the observed emission spectra of He^+ and Li^{2+} ions, as well as that of hydrogen. However, all three systems have one feature in common—each contains a single electron. Thus, the Bohr model worked successfully only for the hydrogen atom and for "hydrogenlike ions."

To describe the problem of trying to locate a subatomic particle that behaves like a wave, Werner Heisenberg[†] formulated what is now known as the ***Heisenberg uncertainty principle:*** *it is impossible to know simultaneously both the momentum p* (defined as mass times velocity) *and the position of a particle with certainty.* Stated mathematically,

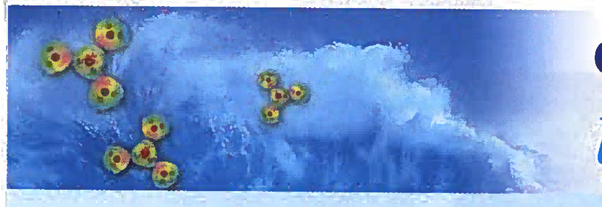
$$\Delta x \Delta p \geq \frac{h}{4\pi} \tag{7.9}$$

The ≥ sign means that the product $\Delta x \Delta p$ can be greater than or equal to $h/4\pi$, but it can never be smaller than $h/4\pi$.

where Δx and Δp are the uncertainties in measuring the position and momentum, respectively. Equation (7.9) says that if we make the measurement of the momentum of a particle more precise (that is, if we make Δp a small quantity), our knowledge of the position will become correspondingly less precise (that is, Δx will become larger). Similarly, if the position of the particle is known more precisely, then its momentum measurement must be less precise. Applying the Heisenberg uncertainty principle to the hydrogen atom, we see that in reality the electron does not orbit the nucleus in a

---

[†] Werner Karl Heisenberg (1901–1976). German physicist. One of the founders of modern quantum theory, Heisenberg received the Nobel Prize in Physics in 1932.



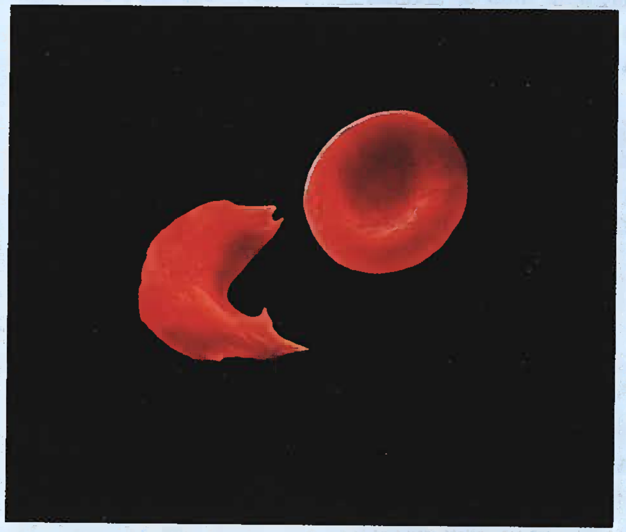
CHEMISTRY *in Action*

Electron Microscopy

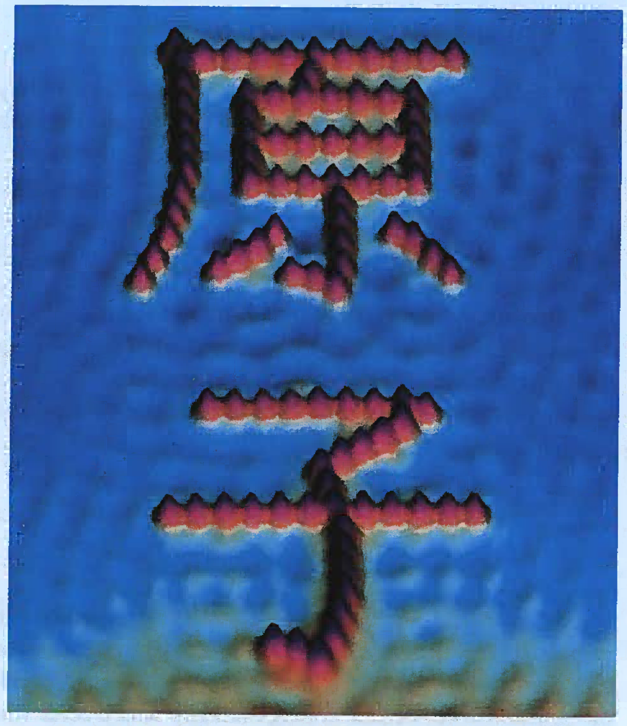
The electron microscope is an extremely valuable application of the wavelike properties of electrons because it produces images of objects that cannot be seen with the naked eye or with light microscopes. According to the laws of optics, it is impossible to form an image of an object that is smaller than half the wavelength of the light used for the observation. Because the range of visible light wavelengths starts at around 400 nm, or 4×10^{-5} cm, we cannot see anything smaller than 2×10^{-5} cm. In principle, we can see objects on the atomic and molecular scale by using X rays, whose wavelengths range from about 0.01 nm to 10 nm. However, X rays cannot be focused, so they do not produce well-formed images. Electrons, on the other hand, are charged particles, which can be focused in the same way the image on a TV screen is focused, that is, by applying an electric field or a magnetic field. According to Equation (7.8), the wavelength of an electron is inversely proportional to its velocity. By accelerating electrons to very high velocities, we can obtain wavelengths as short as 0.004 nm.

A different type of electron microscope, called the *scanning tunneling microscope* (*STM*), makes use of another quantum mechanical property of the electron to produce an image of the atoms on the surface of a sample. Because of its extremely small mass, an electron is able to move or "tunnel" through an energy barrier (instead of going over it). The STM consists of a tungsten metal needle with a very fine point, the source of the tunneling electrons. A voltage is maintained between the needle and the surface of the sample to induce electrons to tunnel through space to the sample. As the needle moves over the sample, at a distance of a few atomic diameters from the surface, the tunneling current is measured. This current decreases with increasing distance from the sample. By using a feedback loop, the vertical position of the tip can be adjusted to a constant distance from the surface. The extent of these adjustments, which profile the sample, is recorded and displayed as a three-dimensional false-colored image.

Both the electron microscope and the STM are among the most powerful tools in chemical and biological research.



An electron micrograph showing a normal red blood cell and a sickled red blood cell from the same person.



STM image of iron atoms arranged to display the Chinese characters for atom on a copper surface.

well-defined path, as Bohr thought. If it did, we could determine precisely both the position of the electron (from its location on a particular orbit) and its momentum (from its kinetic energy) at the same time, a violation of the uncertainty principle.

To be sure, Bohr made a significant contribution to our understanding of atoms, and his suggestion that the energy of an electron in an atom is quantized remains unchallenged. But his theory did not provide a complete description of electronic behavior in atoms. In 1926 the Austrian physicist Erwin Schrödinger,[†] using a complicated mathematical technique, formulated an equation that describes the behavior and energies of submicroscopic particles in general, an equation analogous to Newton's laws of motion for macroscopic objects. The *Schrödinger equation* requires advanced calculus to solve, and we will not discuss it here. It is important to know, however, that the equation incorporates both particle behavior, in terms of mass m, and wave behavior, in terms of a *wave function* ψ (psi), which depends on the location in space of the system (such as an electron in an atom).

The wave function itself has no direct physical meaning. However, the probability of finding the electron in a certain region in space is proportional to the square of the wave function, ψ^2. The idea of relating ψ^2 to probability stemmed from a wave theory analogy. According to wave theory, the intensity of light is proportional to the square of the amplitude of the wave, or ψ^2. The most likely place to find a photon is where the intensity is greatest, that is, where the value of ψ^2 is greatest. A similar argument associates ψ^2 with the likelihood of finding an electron in regions surrounding the nucleus.

Schrödinger's equation began a new era in physics and chemistry, for it launched a new field, *quantum mechanics* (also called *wave mechanics*). We now refer to the developments in quantum theory from 1913—the time Bohr presented his analysis for the hydrogen atom—to 1926 as "old quantum theory."

The Quantum Mechanical Description of the Hydrogen Atom

The Schrödinger equation specifies the possible energy states the electron can occupy in a hydrogen atom and identifies the corresponding wave functions (ψ^2). These energy states and wave functions are characterized by a set of quantum numbers (to be discussed shortly), with which we can construct a comprehensive model of the hydrogen atom.

Although quantum mechanics tells us that we cannot pinpoint an electron in an atom, it does define the region where the electron might be at a given time. The concept of ***electron density*** *gives the probability that an electron will be found in a particular region of an atom.* The square of the wave function, ψ^2, defines the distribution of electron density in three-dimensional space around the nucleus. Regions of high electron density represent a high probability of locating the electron, whereas the opposite holds for regions of low electron density (Figure 7.15).

To distinguish the quantum mechanical description of an atom from Bohr's model, we speak of an atomic orbital, rather than an orbit. An ***atomic orbital*** can be thought of as *the wave function of an electron in an atom.* When we say that an electron is in a certain orbital, we mean that the distribution of the electron density or the probability of locating the electron in space is described by the square of the wave function associated with that orbital. An atomic orbital, therefore, has a characteristic energy, as well as a characteristic distribution of electron density.

The Schrödinger equation works nicely for the simple hydrogen atom with its one proton and one electron, but it turns out that it cannot be solved exactly for any

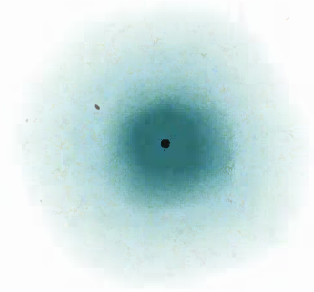


Figure 7.15 *A representation of the electron density distribution surrounding the nucleus in the hydrogen atom. It shows a high probability of finding the electron closer to the nucleus.*

[†] Erwin Schrödinger (1887–1961). Austrian physicist. Schrödinger formulated wave mechanics, which laid the foundation for modern quantum theory. He received the Nobel Prize in Physics in 1933.

atom containing more than one electron! Fortunately, chemists and physicists have learned to get around this kind of difficulty by approximation. For example, although the behavior of electrons in ***many-electron atoms*** (that is, *atoms containing two or more electrons*) is not the same as in the hydrogen atom, we assume that the difference is probably not too great. Thus we can use the energies and wave functions obtained from the hydrogen atom as good approximations of the behavior of electrons in more complex atoms. In fact, this approach provides fairly reliable descriptions of electronic behavior in many-electron atoms.

Although the helium atom has only two electrons, in quantum mechanics it is regarded as a many-electron atom.

7.6 Quantum Numbers

In quantum mechanics, three ***quantum numbers*** are required to *describe the distribution of electrons in hydrogen and other atoms.* These numbers are derived from the mathematical solution of the Schrödinger equation for the hydrogen atom. They are called the *principal quantum number,* the *angular momentum quantum number,* and the *magnetic quantum number.* These quantum numbers will be used to describe atomic orbitals and to label electrons that reside in them. A fourth quantum number—the *spin quantum number*—describes the behavior of a specific electron and completes the description of electrons in atoms.

The Principal Quantum Number (n)

The principal quantum number (n) can have integral values 1, 2, 3, and so forth; it corresponds to the quantum number in Equation (7.5). In a hydrogen atom, the value of n determines the energy of an orbital. As we will see shortly, this is not the case for a many-electron atom. The principal quantum number also relates to the average distance of the electron from the nucleus in a particular orbital. The larger n is, the greater the average distance of an electron in the orbital from the nucleus and therefore the larger the orbital.

Equation (7.5) holds only for the hydrogen atom.

The Angular Momentum Quantum Number (ℓ)

The angular momentum quantum number (ℓ) tells us the "shape" of the orbitals (see Section 7.7). The values of ℓ depend on the value of the principal quantum number, n. For a given value of n, ℓ has possible integral values from 0 to $(n - 1)$. If $n = 1$, there is only one possible value of ℓ; that is, $\ell = n - 1 = 1 - 1 = 0$. If $n = 2$, there are two values of ℓ, given by 0 and 1. If $n = 3$, there are three values of ℓ, given by 0, 1, and 2. The value of ℓ is generally designated by the letters *s*, *p*, *d*, . . . as follows:

ℓ	0	1	2	3	4	5
Name of orbital	*s*	*p*	*d*	*f*	*g*	*h*

Thus if $\ell = 0$, we have an *s* orbital; if $\ell = 1$, we have a *p* orbital; and so on.

The unusual sequence of letters (*s*, *p*, and *d*) has a historical origin. Physicists who studied atomic emission spectra tried to correlate the observed spectral lines with the particular energy states involved in the transitions. They noted that some of the lines were ***s**harp*; some were rather spread out, or ***d**iffuse*; and some were very strong and hence referred to as ***p**rincipal* lines. Subsequently, the initial letters of each adjective were assigned to those energy states. However, after the letter *d* and starting with the letter *f* (for ***f**undamental*), the orbital designations follow alphabetical order.

A collection of orbitals with the same value of n is frequently called a shell. One or more orbitals with the same n and ℓ values are referred to as a subshell. For example, the shell with $n = 2$ is composed of two subshells, $\ell = 0$ and 1 (the allowed values for $n = 2$). These subshells are called the 2*s* and 2*p* subshells where 2 denotes the value of n, and *s* and *p* denote the values of ℓ.

Remember that the "2" in 2*s* refers to the value of *n* and the "s" symbolizes the value of ℓ.

The Magnetic Quantum Number (m_ℓ)

The magnetic quantum number (m_ℓ) describes the orientation of the orbital in space (to be discussed in Section 7.7). Within a subshell, the value of m_ℓ depends on the value of the angular momentum quantum number, ℓ. For a certain value of ℓ, there are $(2\ell + 1)$ integral values of m_ℓ as follows:

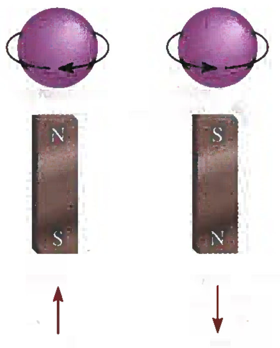
$$-\ell, (-\ell + 1), \ldots 0, \ldots (+\ell - 1), +\ell$$

If $\ell = 0$, then $m_\ell = 0$. If $\ell = 1$, then there are $[(2 \times 1) + 1]$, or three values of m_ℓ, namely, -1, 0, and 1. If $\ell = 2$, there are $[(2 \times 2) + 1]$, or five values of m_ℓ, namely, -2, -1, 0, 1, and 2. The number of m_ℓ values indicates the number of orbitals in a subshell with a particular ℓ value.

To conclude our discussion of these three quantum numbers, let us consider a situation in which $n = 2$ and $\ell = 1$. The values of n and ℓ indicate that we have a 2*p* subshell, and in this subshell we have *three* 2*p* orbitals (because there are three values of m_ℓ, given by -1, 0, and 1).

The Electron Spin Quantum Number (m_s)

Experiments on the emission spectra of hydrogen and sodium atoms indicated that lines in the emission spectra could be split by the application of an external magnetic field. The only way physicists could explain these results was to assume that electrons act like tiny magnets. If electrons are thought of as spinning on their own axes, as Earth does, their magnetic properties can be accounted for. According to electromagnetic theory, a spinning charge generates a magnetic field, and it is this motion that causes an electron to behave like a magnet. Figure 7.16 shows the two possible spinning motions of an electron, one clockwise and the other counterclockwise. To take the electron spin into account, it is necessary to introduce a fourth quantum number, called the electron spin quantum number (m_s), which has a value of $+\frac{1}{2}$ or $-\frac{1}{2}$.



(a) (b)

Figure 7.16 *The (a) clockwise and (b) counterclockwise spins of an electron. The magnetic fields generated by these two spinning motions are analogous to those from the two magnets. The upward and downward arrows are used to denote the direction of spin.*

Conclusive proof of electron spin was provided by Otto Stern[†] and Walther Gerlach[‡] in 1924. Figure 7.17 shows the basic experimental arrangement. A beam of

In their experiment, Stern and Gerlach used silver atoms, which contain just one unpaired electron. To illustrate the principle, we can assume that hydrogen atoms are used in the study.

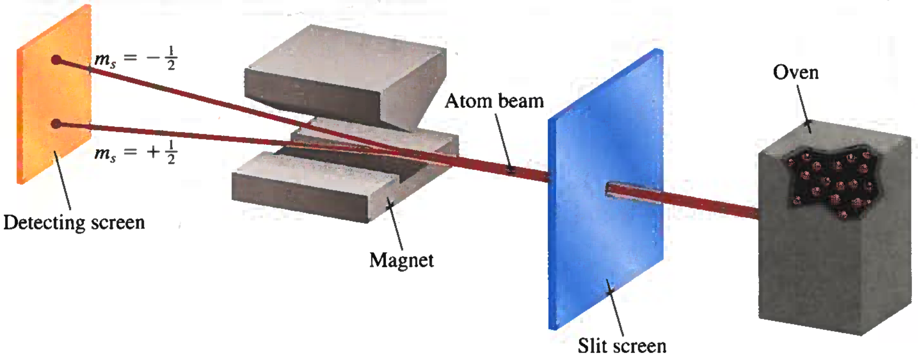


Figure 7.17 *Experimental arrangement for demonstrating the spinning motion of electrons. A beam of atoms is directed through a magnetic field. For example, when a hydrogen atom with a single electron passes through the field, it is deflected in one direction or the other, depending on the direction of the spin. In a stream consisting of many atoms, there will be equal distributions of the two kinds of spins, so that two spots of equal intensity are detected on the screen.*

[†] Otto Stern (1888–1969). German physicist. He made important contributions to the study of magnetic properties of atoms and the kinetic theory of gases. Stern was awarded the Nobel Prize in Physics in 1943.

[‡] Walther Gerlach (1889–1979). German physicist. Gerlach's main area of research was in quantum theory.

gaseous atoms generated in a hot furnace passes through a nonhomogeneous magnetic field. The interaction between an electron and the magnetic field causes the atom to be deflected from its straight-line path. Because the spinning motion is completely random, the electrons in half of the atoms will be spinning in one direction, and those atoms will be deflected in one way; the electrons in the other half of the atoms will be spinning in the opposite direction, and those atoms will be deflected in the other direction. Thus, two spots of equal intensity are observed on the detecting screen.

7.7 Atomic Orbitals

Interactivity:
Orbital Shapes and Energy
ARIS, Interactives

Table 7.2 shows the relation between quantum numbers and atomic orbitals. We see that when $\ell = 0$, $(2\ell + 1) = 1$ and there is only one value of m_ℓ, thus we have an s orbital. When $\ell = 1$, $(2\ell + 1) = 3$, so there are three values of m_ℓ or three p orbitals, labeled p_x, p_y, and p_z. When $\ell = 2$, $(2\ell + 1) = 5$ and there are five values of m_ℓ, and the corresponding five d orbitals are labeled with more elaborate subscripts. In the following sections we will consider the s, p, and d orbitals separately.

That the wave function for an orbital theoretically has no outer limit as one moves outward from the nucleus raises interesting philosophical questions regarding the sizes of atoms. Chemists have agreed on an operational definition of atomic size, as we will see in later chapters.

***s* Orbitals.** One of the important questions we ask when studying the properties of atomic orbitals is, What are the shapes of the orbitals? Strictly speaking, an orbital does not have a well-defined shape because the wave function characterizing the orbital extends from the nucleus to infinity. In that sense, it is difficult to say what an orbital looks like. On the other hand, it is certainly convenient to think of orbitals as having specific shapes, particularly in discussing the formation of chemical bonds between atoms, as we will do in Chapters 9 and 10.

Although in principle an electron can be found anywhere, we know that most of the time it is quite close to the nucleus. Figure 7.18(a) shows the distribution of electron density in a hydrogen 1*s* orbital moving outward from the nucleus. As you can see, the electron density falls off rapidly as the distance from the nucleus increases. Roughly speaking, there is about a 90 percent probability of finding the electron within a sphere of radius 100 pm (1 pm = 1×10^{-12} m) surrounding the nucleus. Thus, we can represent the 1*s* orbital by drawing a ***boundary surface diagram*** that *encloses about 90 percent of the total electron density in an orbital,* as shown in Figure 7.18(b). A 1*s* orbital represented in this manner is merely a sphere.

An *s* subshell has one orbital, a *p* subshell has three orbitals, and a *d* subshell has five orbitals.

TABLE 7.2 Relation Between Quantum Numbers and Atomic Orbitals

n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	1*s*
2	0	0	1	2*s*
	1	−1, 0, 1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	3*s*
	1	−1, 0, 1	3	$3p_x$, $3p_y$, $3p_z$
	2	−2, −1, 0, 1, 2	5	$3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

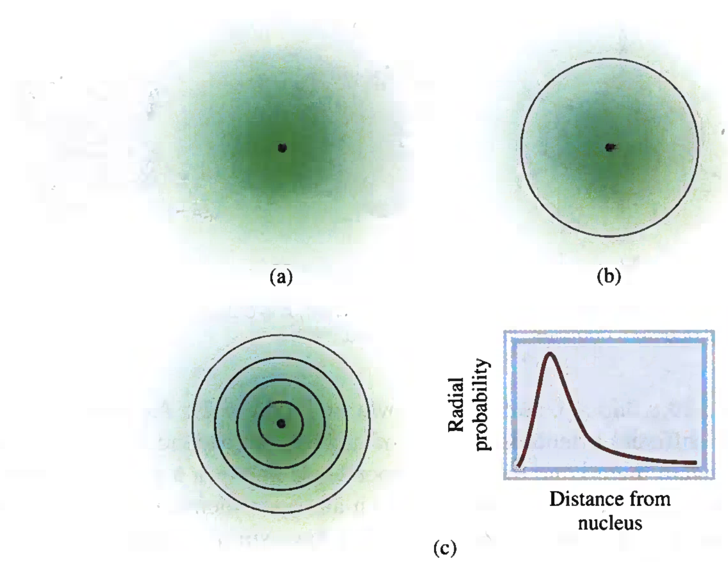


Figure 7.18 *(a) Plot of electron density in the hydrogen 1s orbital as a function of the distance from the nucleus. The electron density falls off rapidly as the distance from the nucleus increases. (b) Boundary surface diagram of the hydrogen 1s orbital. (c) A more realistic way of viewing electron density distribution is to divide the 1s orbital into successive spherical thin shells. A plot of the probability of finding the electron in each shell, called radial probability, as a function of distance shows a maximum at 52.9 pm from the nucleus. Interestingly, this is equal to the radius of the innermost orbit in the Bohr model.*

Figure 7.19 shows boundary surface diagrams for the 1*s*, 2*s*, and 3*s* hydrogen atomic orbitals. All *s* orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases. Although the details of electron density variation within each boundary surface are lost, there is no serious disadvantage. For us the most important features of atomic orbitals are their shapes and *relative* sizes, which are adequately represented by boundary surface diagrams.

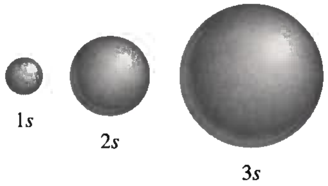


Figure 7.19 *Boundary surface diagrams of the hydrogen 1s, 2s, and 3s orbitals. Each sphere contains about 90 percent of the total electron density. All s orbitals are spherical. Roughly speaking, the size of an orbital is proportional to n^2, where n is the principal quantum number.*

***p* Orbitals.** It should be clear that the *p* orbitals start with the principal quantum number $n = 2$. If $n = 1$, then the angular momentum quantum number ℓ can assume only the value of zero; therefore, there is only a 1*s* orbital. As we saw earlier, when $\ell = 1$, the magnetic quantum number m_ℓ can have values of $-1, 0, 1$. Starting with $n = 2$ and $\ell = 1$, we therefore have three 2*p* orbitals: $2p_x$, $2p_y$, and $2p_z$ (Figure 7.20). The letter subscripts indicate the axes along which the orbitals are oriented. These three *p* orbitals are identical in size, shape, and energy; they differ from one another only in orientation. Note, however, that there is no simple relation between the values of m_ℓ and the *x*, *y*, and *z* directions. For our purpose, you need only remember that because there are three possible values of m_ℓ, there are three *p* orbitals with different orientations.

The boundary surface diagrams of *p* orbitals in Figure 7.20 show that each *p* orbital can be thought of as two lobes on opposite sides of the nucleus. Like *s* orbitals, *p* orbitals increase in size from 2*p* to 3*p* to 4*p* orbital and so on.

***d* Orbitals and Other Higher-Energy Orbitals.** When $\ell = 2$, there are five values of m_ℓ, which correspond to five *d* orbitals. The lowest value of *n* for a *d* orbital is 3. Because ℓ can never be greater than $n - 1$, when $n = 3$ and $\ell = 2$, we have five 3*d*

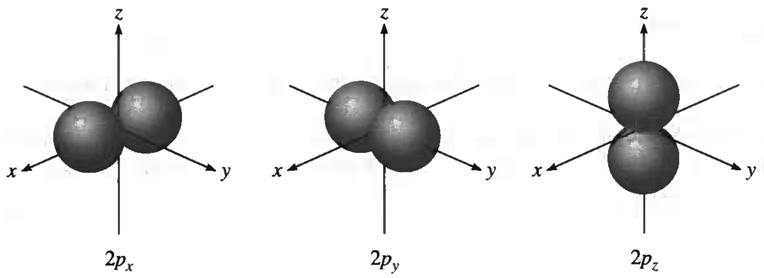
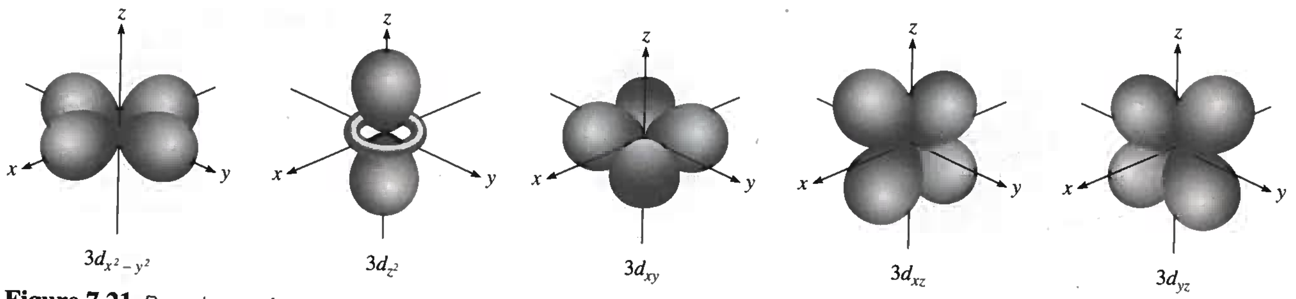


Figure 7.20 *The boundary surface diagrams of the three 2p orbitals. These orbitals are identical in shape and energy, but their orientations are different. The p orbitals of higher principal quantum numbers have a similar shape.*



$3d_{x^2-y^2}$ $3d_{z^2}$ $3d_{xy}$ $3d_{xz}$ $3d_{yz}$

Figure 7.21 *Boundary surface diagrams of the five 3d orbitals. Although the* $3d_{z^2}$ *orbital looks different, it is equivalent to the other four orbitals in all other respects. The d orbitals of higher principal quantum numbers have similar shapes.*

orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, and $3d_{z^2}$), shown in Figure 7.21. As in the case of the *p* orbitals, the different orientations of the *d* orbitals correspond to the different values of m_ℓ, but again there is no direct correspondence between a given orientation and a particular m_ℓ value. All the 3*d* orbitals in an atom are identical in energy. The *d* orbitals for which *n* is greater than 3 (4*d*, 5*d*, . . .) have similar shapes.

Orbitals having higher energy than *d* orbitals are labeled *f*, *g*, . . . and so on. The *f* orbitals are important in accounting for the behavior of elements with atomic numbers greater than 57, but their shapes are difficult to represent. In general chemistry, we are not concerned with orbitals having ℓ values greater than 3 (the *g* orbitals and beyond).

Examples 7.6 and 7.7 illustrate the labeling of orbitals with quantum numbers and the calculation of total number of orbitals associated with a given principal quantum number.

Example 7.6

List the values of n, ℓ, and m_ℓ for orbitals in the 4*d* subshell.

Strategy What are the relationships among n, ℓ, and m_ℓ? What do "4" and "*d*" represent in 4*d*?

Solution As we saw earlier, the number given in the designation of the subshell is the principal quantum number, so in this case $n = 4$. The letter designates the type of orbital. Because we are dealing with *d* orbitals, $\ell = 2$. The values of m_ℓ can vary from $-\ell$ to ℓ. Therefore, m_ℓ can be $-2, -1, 0, 1$, or 2.

Check The values of n and ℓ are fixed for 4*d*, but m_ℓ can have any one of the five values, which correspond to the five *d* orbitals.

Similar problem: 7.57.

Practice Exercise Give the values of the quantum numbers associated with the orbitals in the 3*p* subshell.

Example 7.7

What is the total number of orbitals associated with the principal quantum number $n = 3$?

Strategy To calculate the total number of orbitals for a given n value, we need to first write the possible values of ℓ. We then determine how many m_ℓ values are

(Continued)

associated with each value of ℓ. The total number of orbitals is equal to the sum of all the m_ℓ values.

Solution For $n = 3$, the possible values of ℓ are 0, 1, and 2. Thus, there is one 3*s* orbital ($n = 3$, $\ell = 0$, and $m_\ell = 0$); there are three 3*p* orbitals ($n = 3$, $\ell = 1$, and $m_\ell = -1, 0, 1$); there are five 3*d* orbitals ($n = 3$, $\ell = 2$, and $m_\ell = -2, -1, 0, 1, 2$). The total number of orbitals is $1 + 3 + 5 = 9$.

Check The total number of orbitals for a given value of n is n^2. So here we have $3^2 = 9$. Can you prove the validity of this relationship?

Practice Exercise What is the total number of orbitals associated with the principal quantum number $n = 4$?

Similar problem: 7.62.

The Energies of Orbitals

Now that we have some understanding of the shapes and sizes of atomic orbitals, we are ready to inquire into their relative energies and look at how energy levels affect the actual arrangement of electrons in atoms.

According to Equation (7.5), the energy of an electron in a hydrogen atom is determined solely by its principal quantum number. Thus, the energies of hydrogen orbitals increase as follows (Figure 7.22):

$$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f < \cdots$$

Although the electron density distributions are different in the 2*s* and 2*p* orbitals, hydrogen's electron has the same energy whether it is in the 2*s* orbital or a 2*p* orbital. The 1*s* orbital in a hydrogen atom corresponds to the most stable condition, the ground state. An electron residing in this orbital is most strongly held by the nucleus because it is closest to the nucleus. An electron in the 2*s*, 2*p*, or higher orbitals in a hydrogen atom is in an excited state.

The energy picture is more complex for many-electron atoms than for hydrogen. The energy of an electron in such an atom depends on its angular momentum quantum number as well as on its principal quantum number (Figure 7.23). For many-electron atoms, the 3*d* energy level is very close to the 4*s* energy level. The total energy of an

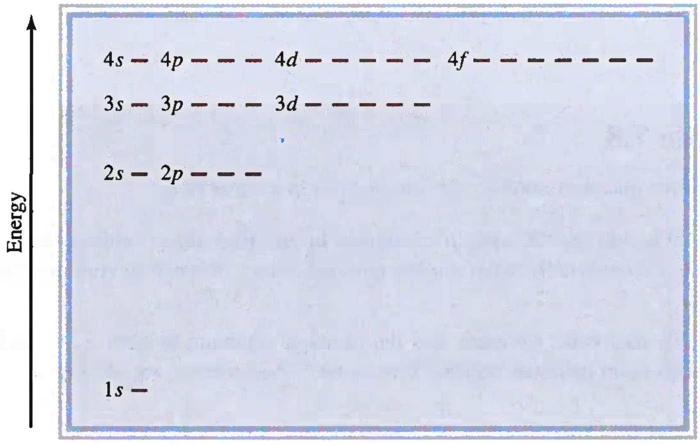


Figure 7.22 *Orbital energy levels in the hydrogen atom. Each short horizontal line represents one orbital. Orbitals with the same principal quantum number (n) all have the same energy.*

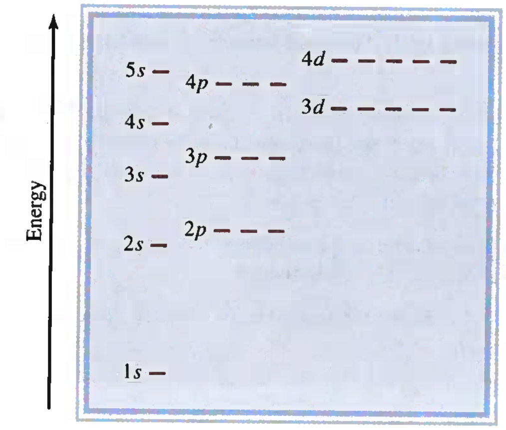


Figure 7.23 *Orbital energy levels in a many-electron atom. Note that the energy level depends on both n and ℓ values.*

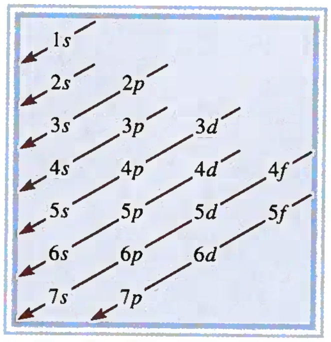


Figure 7.24 *The order in which atomic subshells are filled in a many-electron atom. Start with the 1s orbital and move downward, following the direction of the arrows. Thus, the order goes as follows: 1s < 2s < 2p < 3s < 3p < 4s < 3d < . . . .*

atom, however, depends not only on the sum of the orbital energies but also on the energy of repulsion between the electrons in these orbitals (each orbital can accommodate up to two electrons, as we will see in Section 7.8). It turns out that the total energy of an atom is lower when the 4*s* subshell is filled before a 3*d* subshell. Figure 7.24 depicts the order in which atomic orbitals are filled in a many-electron atom. We will consider specific examples in Section 7.8.

7.8 Electron Configuration

Animation:
Electron Configurations
ARIS, Animations

The four quantum numbers n, ℓ, m_ℓ, and m_s enable us to label completely an electron in any orbital in any atom. In a sense, we can regard the set of four quantum numbers as the "address" of an electron in an atom, somewhat in the same way that a street address, city, state, and postal ZIP code specify the address of an individual. For example, the four quantum numbers for a 2*s* orbital electron are $n = 2$, $\ell = 0$, $m_\ell = 0$, and $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$. It is inconvenient to write out all the individual quantum numbers, and so we use the simplified notation (n, ℓ, m_ℓ, m_s). For the preceding example, the quantum numbers are either $(2, 0, 0, +\frac{1}{2})$ or $(2, 0, 0, -\frac{1}{2})$. The value of m_s has no effect on the energy, size, shape, or orientation of an orbital, but it determines how electrons are arranged in an orbital.

Example 7.8 shows how quantum numbers of an electron in an orbital are assigned.

Example 7.8

Write the four quantum numbers for an electron in a 3*p* orbital.

Strategy What do the "3" and "*p*" designate in 3*p*? How many orbitals (values of m_ℓ) are there in a 3*p* subshell? What are the possible values of electron spin quantum number?

Solution To start with, we know that the principal quantum number n is 3 and the angular momentum quantum number ℓ must be 1 (because we are dealing with a *p* orbital).

(Continued)

For $\ell = 1$, there are three values of m_ℓ given by -1, 0, and 1. Because the electron spin quantum number m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$, we conclude that there are six possible ways to designate the electron using the (n, ℓ, m_ℓ, m_s) notation:

$$\begin{array}{ll} (3, 1, -1, +\frac{1}{2}) & (3, 1, -1, -\frac{1}{2}) \\ (3, 1, 0, +\frac{1}{2}) & (3, 1, 0, -\frac{1}{2}) \\ (3, 1, 1, +\frac{1}{2}) & (3, 1, 1, -\frac{1}{2}) \end{array}$$

Check In these six designations we see that the values of n and ℓ are constant, but the values of m_ℓ and m_s can vary.

Practice Exercise Write the four quantum numbers for an electron in a $5p$ orbital.

Similar problem: 7.58.

The hydrogen atom is a particularly simple system because it contains only one electron. The electron may reside in the $1s$ orbital (the ground state), or it may be found in some higher-energy orbital (an excited state). For many-electron atoms, however, we must know the ***electron configuration*** of the atom, that is, *how the electrons are distributed among the various atomic orbitals,* in order to understand electronic behavior. We will use the first 10 elements (hydrogen to neon) to illustrate the rules for writing electron configurations for atoms in the *ground state.* (Section 7.9 will describe how these rules can be applied to the remainder of the elements in the periodic table.) For this discussion, recall that the number of electrons in an atom is equal to its atomic number Z.

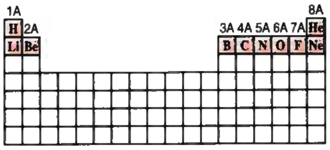
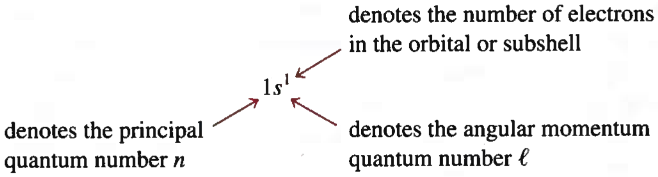
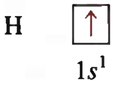


Figure 7.22 indicates that the electron in a ground-state hydrogen atom must be in the $1s$ orbital, so its electron configuration is $1s^1$:



The electron configuration can also be represented by an *orbital diagram* that shows the spin of the electron (see Figure 7.16):



The upward arrow denotes one of the two possible spinning motions of the electron. (Alternatively, we could have represented the electron with a downward arrow.) The box represents an atomic orbital.

Remember that the direction of electron spin has no effect on the energy of the electron.

The Pauli Exclusion Principle

For many-electron atoms we use the ***Pauli***[†] ***exclusion principle*** to determine electron configurations. This principle states that *no two electrons in an atom can have the same four quantum numbers.* If two electrons in an atom should have the same n, ℓ, and m_ℓ values (that is, these two electrons are in the *same* atomic orbital), then they

Interactivity:
Pauli Exclusion Principle
ARIS, Interactives

[†] Wolfgang Pauli (1900–1958). Austrian physicist. One of the founders of quantum mechanics, Pauli was awarded the Nobel Prize in Physics in 1945.

must have different values of m_s. In other words, only two electrons may occupy the same atomic orbital, and these electrons must have opposite spins. Consider the helium atom, which has two electrons. The three possible ways of placing two electrons in the 1*s* orbital are as follows:

$$\text{He} \quad \underset{\text{(a)}}{\underset{1s^2}{\boxed{\uparrow\uparrow}}} \qquad \underset{\text{(b)}}{\underset{1s^2}{\boxed{\downarrow\downarrow}}} \qquad \underset{\text{(c)}}{\underset{1s^2}{\boxed{\uparrow\downarrow}}}$$

Diagrams (a) and (b) are ruled out by the Pauli exclusion principle. In (a), both electrons have the same upward spin and would have the quantum numbers $(1, 0, 0, +\frac{1}{2})$; in (b), both electrons have downward spins and would have the quantum numbers $(1, 0, 0, -\frac{1}{2})$. Only the configuration in (c) is physically acceptable, because one electron has the quantum numbers $(1, 0, 0, +\frac{1}{2})$ and the other has $(1, 0, 0, -\frac{1}{2})$. Thus, the helium atom has the following configuration:

$$\text{He} \quad \underset{1s^2}{\boxed{\uparrow\downarrow}}$$

Electrons that have opposite spins are said to be paired. In helium, $m_s = +\frac{1}{2}$ for one electron; $m_s = -\frac{1}{2}$ for the other.

Note that $1s^2$ is read "one *s* two," not "one *s* squared."

Diamagnetism and Paramagnetism

The Pauli exclusion principle is one of the fundamental principles of quantum mechanics. It can be tested by a simple observation. If the two electrons in the 1*s* orbital of a helium atom had the same, or parallel, spins (↑↑ or ↓↓), their net magnetic fields would reinforce each other [Figure 7.25(a)]. Such an arrangement would make the helium gas paramagnetic. ***Paramagnetic*** substances are those that *contain net unpaired spins and are attracted by a magnet.* On the other hand, if the electron spins are paired, or antiparallel to each other (↑↓ or ↓↑), the magnetic effects cancel out [Figure 7.25(b)]. ***Diamagnetic*** substances *do not contain net unpaired spins and are slightly repelled by a magnet.*

Measurements of magnetic properties provide the most direct evidence for specific electron configurations of elements. Advances in instrument design during the last 30 years or so enable us to determine the number of unpaired electrons in an atom (Figure 7.26). By experiment we find that the helium atom in its ground state has no net magnetic field. Therefore, the two electrons in the 1*s* orbital must be paired in accord with the Pauli exclusion principle and the helium gas is diamagnetic. A useful rule to keep in mind is that any atom with an *odd* number of electrons will always

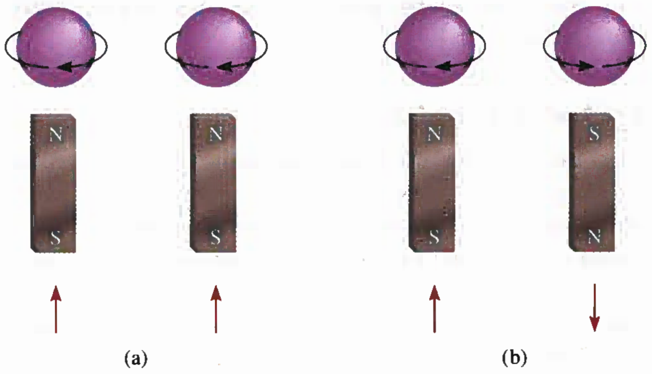


Figure 7.25 *The (a) parallel and (b) antiparallel spins of two electrons. In (a) the two magnetic fields reinforce each other. In (b) the two magnetic fields cancel each other.*

contain one or more unpaired spins because we need an even number of electrons for complete pairing. On the other hand, atoms containing an even number of electrons may or may not contain unpaired spins. We will see the reason for this behavior shortly.

As another example, consider the lithium atom ($Z = 3$) which has three electrons. The third electron cannot go into the 1*s* orbital because it would inevitably have the same four quantum numbers as one of the first two electrons. Therefore, this electron "enters" the next (energetically) higher orbital, which is the 2*s* orbital (see Figure 7.23). The electron configuration of lithium is $1s^22s^1$, and its orbital diagram is

$$\text{Li} \quad \underset{1s^2}{\boxed{\uparrow\downarrow}} \quad \underset{2s^1}{\boxed{\uparrow}}$$

The lithium atom contains one unpaired electron and the lithium metal is therefore paramagnetic.

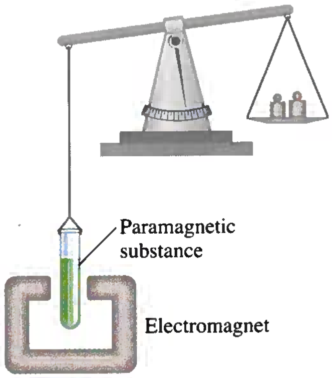


Figure 7.26 *Initially the paramagnetic substance was weighed on a balance. When the electromagnet is turned on, the balance is offset because the sample tube is drawn into the magnetic field. Knowing the concentration and the additional mass needed to reestablish balance, it is possible to calculate the number of unpaired electrons in the substance.*

The Shielding Effect in Many-Electron Atoms

Experimentally we find that the 2*s* orbital lies at a lower energy level than the 2*p* orbital in a many-electron atom. Why? In comparing the electron configurations of $1s^22s^1$ and $1s^22p^1$, we note that, in both cases, the 1*s* orbital is filled with two electrons. Figure 7.27 shows the radial probability plots for the 1*s*, 2*s*, and 2*p* orbitals. Because the 2*s* and 2*p* orbitals are larger than the 1*s* orbital, an electron in either of these orbitals will spend more time away from the nucleus than an electron in the 1*s* orbital. Thus, we can speak of a 2*s* or 2*p* electron being partly "shielded" from the attractive force of the nucleus by the 1*s* electrons. The important consequence of the shielding effect is that it *reduces* the electrostatic attraction between the protons in the nucleus and the electron in the 2*s* or 2*p* orbital.

The manner in which the electron density varies as we move from the nucleus outward depends on the type of orbital. Although a 2*s* electron spends most of its time (on average) slightly farther from the nucleus than a 2*p* electron, the electron density near the nucleus is actually greater for the 2*s* electron (see the small maximum for the 2*s* orbital in Figure 7.27). For this reason, the 2*s* orbital is said to be more "penetrating" than the 2*p* orbital. Therefore, a 2*s* electron is less shielded by the 1*s* electrons and is more strongly held by the nucleus. In fact, for the same principal quantum number *n*, the penetrating power decreases as the angular momentum quantum number ℓ increases, or

$$s > p > d > f > \cdots$$

Because the stability of an electron is determined by the strength of its attraction to the nucleus, it follows that a 2*s* electron will be lower in energy than a 2*p* electron. To put it another way, less energy is required to remove a 2*p* electron than a 2*s* electron because a 2*p* electron is not held quite as strongly by the nucleus. The hydrogen atom has only one electron and, therefore, is without such a shielding effect.

Continuing our discussion of atoms of the first 10 elements, we go next to beryllium ($Z = 4$). The ground-state electron configuration of beryllium is $1s^22s^2$, or

$$\text{Be} \quad \underset{1s^2}{\boxed{\uparrow\downarrow}} \quad \underset{2s^2}{\boxed{\uparrow\downarrow}}$$

Beryllium is diamagnetic, as we would expect.

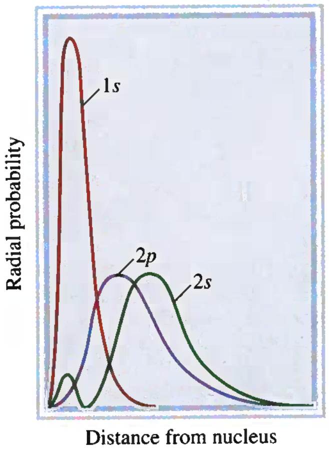
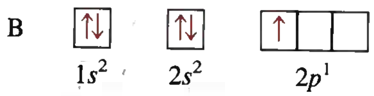


Figure 7.27 *Radial probability plots (see Figure 7.18) for the 1s, 2s, and 2p orbitals. The 1s electrons effectively shield both the 2s and 2p electrons from the nucleus. The 2s orbital is more penetrating than the 2p orbital.*

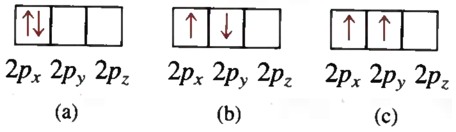
The electron configuration of boron ($Z = 5$) is $1s^22s^22p^1$, or



Note that the unpaired electron can be in the $2p_x$, $2p_y$, or $2p_z$ orbital. The choice is completely arbitrary because the three p orbitals are equivalent in energy. As the diagram shows, boron is paramagnetic.

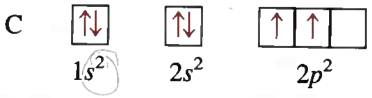
Hund's Rule

The electron configuration of carbon ($Z = 6$) is $1s^22s^22p^2$. The following are different ways of distributing two electrons among three p orbitals:



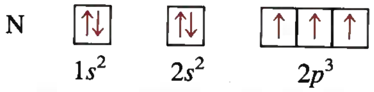
(a) (b) (c)

None of the three arrangements violates the Pauli exclusion principle, so we must determine which one will give the greatest stability. The answer is provided by ***Hund's rule,***[†] which states that *the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins.* The arrangement shown in (c) satisfies this condition. In both (a) and (b) the two spins cancel each other. Thus, the orbital diagram for carbon is



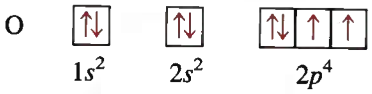
Qualitatively, we can understand why (c) is preferred to (a). In (a), the two electrons are in the same $2p_x$ orbital, and their proximity results in a greater mutual repulsion than when they occupy two separate orbitals, say $2p_x$ and $2p_y$. The choice of (c) over (b) is more subtle but can be justified on theoretical grounds. The fact that carbon atoms contain two unpaired electrons is in accord with Hund's rule.

The electron configuration of nitrogen ($Z = 7$) is $1s^22s^22p^3$:



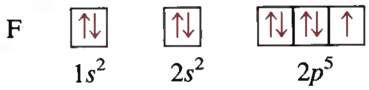
Again, Hund's rule dictates that all three $2p$ electrons have spins parallel to one another; the nitrogen atom contains three unpaired electrons.

The electron configuration of oxygen ($Z = 8$) is $1s^22s^22p^4$. An oxygen atom has two unpaired electrons:



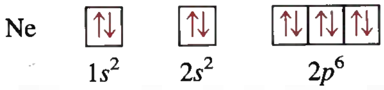
[†] Frederick Hund (1896–1997). German physicist. Hund's work was mainly in quantum mechanics. He also helped to develop the molecular orbital theory of chemical bonding.

The electron configuration of fluorine ($Z = 9$) is $1s^22s^22p^5$. The nine electrons are arranged as follows:



The fluorine atom has one unpaired electron.

In neon ($Z = 10$), the $2p$ subshell is completely filled. The electron configuration of neon is $1s^22s^22p^6$, and *all* the electrons are paired, as follows:



The neon gas should be diamagnetic, and experimental observation bears out this prediction.

General Rules for Assigning Electrons to Atomic Orbitals

Based on the preceding examples we can formulate some general rules for determining the maximum number of electrons that can be assigned to the various subshells and orbitals for a given value of n:

Interactivity:
Orbital Filling Rules
ARIS, Interactives

1. Each shell or principal level of quantum number n contains n subshells. For example, if $n = 2$, then there are two subshells (two values of ℓ) of angular momentum quantum numbers 0 and 1.
2. Each subshell of quantum number ℓ contains $(2\ell + 1)$ orbitals. For example, if $\ell = 1$, then there are three p orbitals.
3. No more than two electrons can be placed in each orbital. Therefore, the maximum number of electrons is simply twice the number of orbitals that are employed.
4. A quick way to determine the maximum number of electrons that an atom can have in a principal level n is to use the formula $2n^2$.

Examples 7.9 and 7.10 illustrate the procedure for calculating the number of electrons in orbitals and labeling electrons with the four quantum numbers.

Example 7.9

What is the maximum number of electrons that can be present in the principal level for which $n = 3$?

Strategy We are given the principal quantum number (n) so we can determine all the possible values of the angular momentum quantum number (ℓ). The preceding rule shows that the number of orbitals for each value of ℓ is $(2\ell + 1)$. Thus, we can determine the total number of orbitals. How many electrons can each orbital accommodate?

Solution When $n = 3$, $\ell = 0$, 1, and 2. The number of orbitals for each value of ℓ is given by

Value of ℓ	Number of Orbitals $(2\ell + 1)$
0	1
1	3
2	5

(Continued)

The total number of orbitals is nine. Because each orbital can accommodate two electrons, the maximum number of electrons that can reside in the orbitals is 2 × 9, or 18.

Check If we use the formula (n^2) in Example 7.7, we find that the total number of orbitals is 3^2 and the total number of electrons is $2(3^2)$ or 18. In general, the number of electrons in a given principal energy level n is $2n^2$.

Similar problems: 7.64, 7.65.

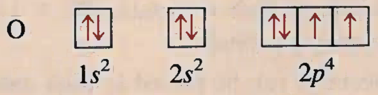
Practice Exercise Calculate the total number of electrons that can be present in the principal level for which $n = 4$.

Example 7.10

An oxygen atom has a total of eight electrons. Write the four quantum numbers for each of the eight electrons in the ground state.

Strategy We start with $n = 1$ and proceed to fill orbitals in the order shown in Figure 7.24. For each value of n we determine the possible values of ℓ. For each value of ℓ, we assign the possible values of m_ℓ. We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule.

Solution We start with $n = 1$, so $\ell = 0$, a subshell corresponding to the 1s orbital. This orbital can accommodate a total of two electrons. Next, $n = 2$, and ℓ may be either 0 or 1. The $\ell = 0$ subshell contains one 2s orbital, which can accommodate two electrons. The remaining four electrons are placed in the $\ell = 1$ subshell, which contains three 2p orbitals. The orbital diagram is



The results are summarized in the following table:

Electron	n	ℓ	m_ℓ	m_s	Orbital
1	1	0	0	$+\frac{1}{2}$	1s
2	1	0	0	$-\frac{1}{2}$	
3	2	0	0	$+\frac{1}{2}$	2s
4	2	0	0	$-\frac{1}{2}$	
5	2	1	-1	$+\frac{1}{2}$	$2p_x$, $2p_y$, $2p_z$
6	2	1	0	$+\frac{1}{2}$	
7	2	1	1	$+\frac{1}{2}$	
8	2	1	1	$-\frac{1}{2}$	

Of course, the placement of the eighth electron in the orbital labeled $m_\ell = 1$ is completely arbitrary. It would be equally correct to assign it to $m_\ell = 0$ or $m_\ell = -1$.

Similar problem: 7.91.

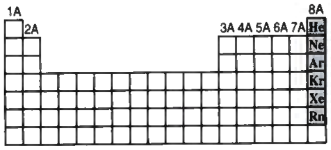
Practice Exercise Write a complete set of quantum numbers for each of the electrons in boron (B).

7.9 The Building-Up Principle

The German word "Aufbau" means "building up."

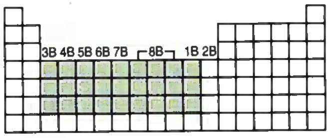
Here we will extend the rules used in writing electron configurations for the first 10 elements to the rest of the elements. This process is based on the Aufbau principle. The ***Aufbau principle*** dictates that *as protons are added one by one to the nucleus* *to build up the elements, electrons are similarly added to the atomic orbitals.* Through this process we gain a detailed knowledge of the ground-state electron configurations of the elements. As we will see later, knowledge of electron configurations helps us to understand and predict the properties of the elements; it also explains why the periodic table works so well.

Table 7.3 gives the ground-state electron configurations of elements from H ($Z = 1$) through Rg ($Z = 111$). The electron configurations of all elements except hydrogen and helium are represented by a ***noble gas core,*** which *shows in brackets the noble gas element that most nearly precedes the element being considered,* followed by the symbol for the highest filled subshells in the outermost shells. Notice that the electron configurations of the highest filled subshells in the outermost shells for the elements sodium ($Z = 11$) through argon ($Z = 18$) follow a pattern similar to those of lithium ($Z = 3$) through neon ($Z = 10$).



The noble gases.

As mentioned in Section 7.7, the 4*s* subshell is filled before the 3*d* subshell in a many-electron atom (see Figure 7.24). Thus, the electron configuration of potassium ($Z = 19$) is $1s^22s^22p^63s^23p^64s^1$. Because $1s^22s^22p^63s^23p^6$ is the electron configuration of argon, we can simplify the electron configuration of potassium by writing $[\text{Ar}]4s^1$, where [Ar] denotes the "argon core." Similarly, we can write the electron configuration of calcium ($Z = 20$) as $[\text{Ar}]4s^2$. The placement of the outermost electron in the 4*s* orbital (rather than in the 3*d* orbital) of potassium is strongly supported by experimental evidence. The following comparison also suggests that this is the correct configuration. The chemistry of potassium is very similar to that of lithium and sodium, the first two alkali metals. The outermost electron of both lithium and sodium is in an *s* orbital (there is no ambiguity in assigning their electron configurations); therefore, we expect the last electron in potassium to occupy the 4*s* rather than the 3*d* orbital.



The transition metals.

The elements from scandium ($Z = 21$) to copper ($Z = 29$) are transition metals. ***Transition metals*** either *have incompletely filled d subshells or readily give rise to cations that have incompletely filled d subshells.* Consider the first transition metal series, from scandium through copper. In this series additional electrons are placed in the 3*d* orbitals, according to Hund's rule. However, there are two irregularities. The electron configuration of chromium ($Z = 24$) is $[\text{Ar}]4s^13d^5$ and not $[\text{Ar}]4s^23d^4$, as we might expect. A similar break in the pattern is observed for copper, whose electron configuration is $[\text{Ar}]4s^13d^{10}$ rather than $[\text{Ar}]4s^23d^9$. The reason for these irregularities is that a slightly greater stability is associated with the half-filled ($3d^5$) and completely filled ($3d^{10}$) subshells. Electrons in the same subshell (in this case, the *d* orbitals) have equal energy but different spatial distributions. Consequently, their shielding of one another is relatively small, and the electrons are more strongly attracted by the nucleus when they have the $3d^5$ configuration. According to Hund's rule, the orbital diagram for Cr is

$$\text{Cr}\quad[\text{Ar}]\quad \underset{4s^1}{\boxed{\uparrow}}\qquad \underset{3d^5}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$$

Thus, Cr has a total of six unpaired electrons. The orbital diagram for copper is

$$\text{Cu}\quad[\text{Ar}]\quad \underset{4s^1}{\boxed{\uparrow}}\qquad \underset{3d^{10}}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}$$

Again, extra stability is gained in this case by having the 3*d* subshell completely filled.

For elements Zn ($Z = 30$) through Kr ($Z = 36$), the 4*s* and 4*p* subshells fill in a straightforward manner. With rubidium ($Z = 37$), electrons begin to enter the $n = 5$ energy level.

TABLE 7.3 The Ground-State Electron Configurations of the Elements*

Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration	Atomic Number	Symbol	Electron Configuration
1	H	$1s^1$	38	Sr	[Kr]$5s^2$	75	Re	[Xe]$6s^2 4f^{14} 5d^5$
2	He	$1s^2$	39	Y	[Kr]$5s^2 4d^1$	76	Os	[Xe]$6s^2 4f^{14} 5d^6$
3	Li	[He]$2s^1$	40	Zr	[Kr]$5s^2 4d^2$	77	Ir	[Xe]$6s^2 4f^{14} 5d^7$
4	Be	[He]$2s^2$	41	Nb	[Kr]$5s^1 4d^4$	78	Pt	[Xe]$6s^1 4f^{14} 5d^9$
5	B	[He]$2s^2 2p^1$	42	Mo	[Kr]$5s^1 4d^5$	79	Au	[Xe]$6s^1 4f^{14} 5d^{10}$
6	C	[He]$2s^2 2p^2$	43	Tc	[Kr]$5s^2 4d^5$	80	Hg	[Xe]$6s^2 4f^{14} 5d^{10}$
7	N	[He]$2s^2 2p^3$	44	Ru	[Kr]$5s^1 4d^7$	81	Tl	[Xe]$6s^2 4f^{14} 5d^{10} 6p^1$
8	O	[He]$2s^2 2p^4$	45	Rh	[Kr]$5s^1 4d^8$	82	Pb	[Xe]$6s^2 4f^{14} 5d^{10} 6p^2$
9	F	[He]$2s^2 2p^5$	46	Pd	[Kr]$4d^{10}$	83	Bi	[Xe]$6s^2 4f^{14} 5d^{10} 6p^3$
10	Ne	[He]$2s^2 2p^6$	47	Ag	[Kr]$5s^1 4d^{10}$	84	Po	[Xe]$6s^2 4f^{14} 5d^{10} 6p^4$
11	Na	[Ne]$3s^1$	48	Cd	[Kr]$5s^2 4d^{10}$	85	At	[Xe]$6s^2 4f^{14} 5d^{10} 6p^5$
12	Mg	[Ne]$3s^2$	49	In	[Kr]$5s^2 4d^{10} 5p^1$	86	Rn	[Xe]$6s^2 4f^{14} 5d^{10} 6p^6$
13	Al	[Ne]$3s^2 3p^1$	50	Sn	[Kr]$5s^2 4d^{10} 5p^2$	87	Fr	[Rn]$7s^1$
14	Si	[Ne]$3s^2 3p^2$	51	Sb	[Kr]$5s^2 4d^{10} 5p^3$	88	Ra	[Rn]$7s^2$
15	P	[Ne]$3s^2 3p^3$	52	Te	[Kr]$5s^2 4d^{10} 5p^4$	89	Ac	[Rn]$7s^2 6d^1$
16	S	[Ne]$3s^2 3p^4$	53	I	[Kr]$5s^2 4d^{10} 5p^5$	90	Th	[Rn]$7s^2 6d^2$
17	Cl	[Ne]$3s^2 3p^5$	54	Xe	[Kr]$5s^2 4d^{10} 5p^6$	91	Pa	[Rn]$7s^2 5f^2 6d^1$
18	Ar	[Ne]$3s^2 3p^6$	55	Cs	[Xe]$6s^1$	92	U	[Rn]$7s^2 5f^3 6d^1$
19	K	[Ar]$4s^1$	56	Ba	[Xe]$6s^2$	93	Np	[Rn]$7s^2 5f^4 6d^1$
20	Ca	[Ar]$4s^2$	57	La	[Xe]$6s^2 5d^1$	94	Pu	[Rn]$7s^2 5f^6$
21	Sc	[Ar]$4s^2 3d^1$	58	Ce	[Xe]$6s^2 4f^1 5d^1$	95	Am	[Rn]$7s^2 5f^7$
22	Ti	[Ar]$4s^2 3d^2$	59	Pr	[Xe]$6s^2 4f^3$	96	Cm	[Rn]$7s^2 5f^7 6d^1$
23	V	[Ar]$4s^2 3d^3$	60	Nd	[Xe]$6s^2 4f^4$	97	Bk	[Rn]$7s^2 5f^9$
24	Cr	[Ar]$4s^1 3d^5$	61	Pm	[Xe]$6s^2 4f^5$	98	Cf	[Rn]$7s^2 5f^{10}$
25	Mn	[Ar]$4s^2 3d^5$	62	Sm	[Xe]$6s^2 4f^6$	99	Es	[Rn]$7s^2 5f^{11}$
26	Fe	[Ar]$4s^2 3d^6$	63	Eu	[Xe]$6s^2 4f^7$	100	Fm	[Rn]$7s^2 5f^{12}$
27	Co	[Ar]$4s^2 3d^7$	64	Gd	[Xe]$6s^2 4f^7 5d^1$	101	Md	[Rn]$7s^2 5f^{13}$
28	Ni	[Ar]$4s^2 3d^8$	65	Tb	[Xe]$6s^2 4f^9$	102	No	[Rn]$7s^2 5f^{14}$
29	Cu	[Ar]$4s^1 3d^{10}$	66	Dy	[Xe]$6s^2 4f^{10}$	103	Lr	[Rn]$7s^2 5f^{14} 6d^1$
30	Zn	[Ar]$4s^2 3d^{10}$	67	Ho	[Xe]$6s^2 4f^{11}$	104	Rf	[Rn]$7s^2 5f^{14} 6d^2$
31	Ga	[Ar]$4s^2 3d^{10} 4p^1$	68	Er	[Xe]$6s^2 4f^{12}$	105	Db	[Rn]$7s^2 5f^{14} 6d^3$
32	Ge	[Ar]$4s^2 3d^{10} 4p^2$	69	Tm	[Xe]$6s^2 4f^{13}$	106	Sg	[Rn]$7s^2 5f^{14} 6d^4$
33	As	[Ar]$4s^2 3d^{10} 4p^3$	70	Yb	[Xe]$6s^2 4f^{14}$	107	Bh	[Rn]$7s^2 5f^{14} 6d^5$
34	Se	[Ar]$4s^2 3d^{10} 4p^4$	71	Lu	[Xe]$6s^2 4f^{14} 5d^1$	108	Hs	[Rn]$7s^2 5f^{14} 6d^6$
35	Br	[Ar]$4s^2 3d^{10} 4p^5$	72	Hf	[Xe]$6s^2 4f^{14} 5d^2$	109	Mt	[Rn]$7s^2 5f^{14} 6d^7$
36	Kr	[Ar]$4s^2 3d^{10} 4p^6$	73	Ta	[Xe]$6s^2 4f^{14} 5d^3$	110	Ds	[Rn]$7s^2 5f^{14} 6d^8$
37	Rb	[Kr]$5s^1$	74	W	[Xe]$6s^2 4f^{14} 5d^4$	111	Rg	[Rn]$7s^2 5f^{14} 6d^9$

*The symbol [He] is called the helium core and represents $1s^2$. [Ne] is called the neon core and represents $1s^2 2s^2 2p^6$. [Ar] is called the argon core and represents [Ne]$3s^2 3p^6$. [Kr] is called the krypton core and represents [Ar]$4s^2 3d^{10} 4p^6$. [Xe] is called the xenon core and represents [Kr]$5s^2 4d^{10} 5p^6$. [Rn] is called the radon core and represents [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$.

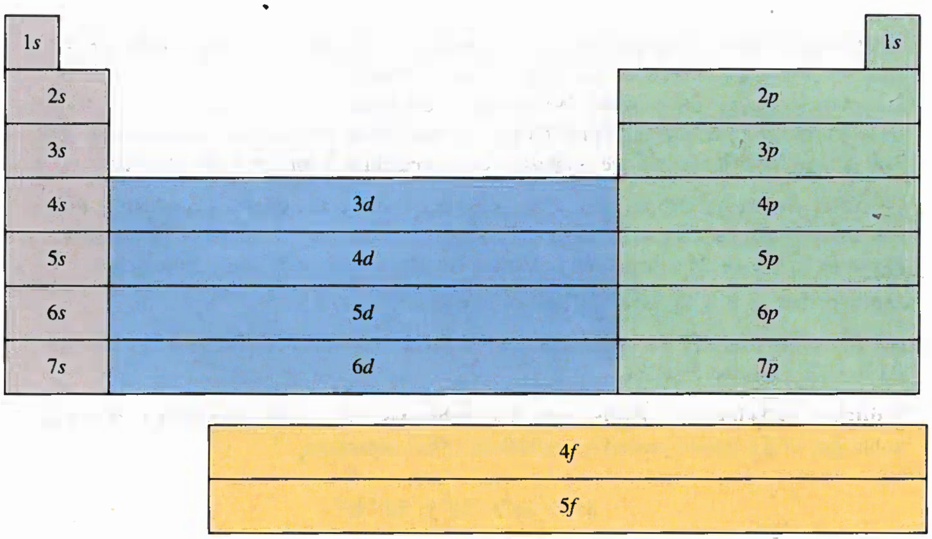


Figure 7.28 *Classification of groups of elements in the periodic table according to the type of subshell being filled with electrons.*

The electron configurations in the second transition metal series [yttrium ($Z = 39$) to silver ($Z = 47$)] are also irregular, but we will not be concerned with the details here.

The sixth period of the periodic table begins with cesium ($Z = 55$) and barium ($Z = 56$), whose electron configurations are $[\text{Xe}]6s^1$ and $[\text{Xe}]6s^2$, respectively. Next we come to lanthanum ($Z = 57$). From Figure 7.24 we would expect that after filling the $6s$ orbital we would place the additional electrons in $4f$ orbitals. In reality, the energies of the $5d$ and $4f$ orbitals are very close; in fact, for lanthanum $4f$ is slightly higher in energy than $5d$. Thus, lanthanum's electron configuration is $[\text{Xe}]6s^2 5d^1$ and not $[\text{Xe}]6s^2 4f^1$.

Following lanthanum are the 14 elements known as the ***lanthanides,*** or ***rare earth series*** [cerium ($Z = 58$) to lutetium ($Z = 71$)]. The rare earth metals *have incompletely filled 4f subshells or readily give rise to cations that have incompletely filled 4f subshells.* In this series, the added electrons are placed in $4f$ orbitals. After the $4f$ subshell is completely filled, the next electron enters the $5d$ subshell of lutetium. Note that the electron configuration of gadolinium ($Z = 64$) is $[\text{Xe}]6s^2 4f^7 5d^1$ rather than $[\text{Xe}]6s^2 4f^8$. Like chromium, gadolinium gains extra stability by having a half-filled subshell ($4f^7$).

The third transition metal series, including lanthanum and hafnium ($Z = 72$) and extending through gold ($Z = 79$), is characterized by the filling of the $5d$ subshell. The $6s$ and $6p$ subshells are filled next, which takes us to radon ($Z = 86$).

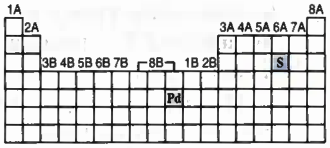
The *last row of elements* is the ***actinide series,*** which starts at thorium ($Z = 90$). *Most of these elements are not found in nature but have been synthesized.*

With few exceptions, you should be able to write the electron configuration of any element, using Figure 7.24 as a guide. Elements that require particular care are the transition metals, the lanthanides, and the actinides. As we noted earlier, at larger values of the principal quantum number n, the order of subshell filling may reverse from one element to the next. Figure 7.28 groups the elements according to the type of subshell in which the outermost electrons are placed.

Example 7.11

Write the ground-state electron configurations for (a) sulfur (S) and (b) palladium (Pd), which is diamagnetic.

(Continued)



(a) Strategy How many electrons are in the S ($Z = 16$) atom? We start with $n = 1$ and proceed to fill orbitals in the order shown in Figure 7.24. For each value of ℓ, we assign the possible values of m_ℓ. We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule and then write the electron configuration. The task is simplified if we use the noble-gas core preceding S for the inner electrons.

Solution Sulfur has 16 electrons. The noble gas core in this case is [Ne]. (Ne is the noble gas in the period preceding sulfur.) [Ne] represents $1s^22s^22p^6$. This leaves us 6 electrons to fill the 3s subshell and partially fill the 3p subshell. Thus, the electron configuration of S is $1s^22s^22p^63s^23p^4$ or $[\mathrm{Ne}]3s^23p^4$.

(b) Strategy We use the same approach as that in (a). What does it mean to say that Pd is a diamagnetic element?

Solution Palladium has 46 electrons. The noble-gas core in this case is [Kr]. (Kr is the noble gas in the period preceding palladium.) [Kr] represents

$$1s^22s^22p^63s^23p^64s^23d^{10}4p^6$$

The remaining 10 electrons are distributed among the 4d and 5s orbitals. The three choices are (1) $4d^{10}$, (2) $4d^95s^1$, and (3) $4d^85s^2$. Because palladium is diamagnetic, all the electrons are paired and its electron configuration must be

$$1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^{10}$$

or simply $[\mathrm{Kr}]4d^{10}$. The configurations in (2) and (3) both represent paramagnetic elements.

Check To confirm the answer, write the orbital diagrams for (1), (2), and (3).

Practice Exercise Write the ground-state electron configuration for phosphorus (P).

Similar problems: 7.87, 7.88.

Summary of Facts and Concepts

1. The quantum theory developed by Planck successfully explains the emission of radiation by heated solids. The quantum theory states that radiant energy is emitted by atoms and molecules in small discrete amounts (quanta), rather than over a continuous range. This behavior is governed by the relationship $E = h\nu$, where E is the energy of the radiation, h is Planck's constant, and ν is the frequency of the radiation. Energy is always emitted in whole-number multiples of $h\nu$ ($1\ h\nu$, $2\ h\nu$, $3\ h\nu, \ldots$).
2. Using quantum theory, Einstein solved another mystery of physics—the photoelectric effect. Einstein proposed that light can behave like a stream of particles (photons).
3. The line spectrum of hydrogen, yet another mystery to nineteenth-century physicists, was also explained by applying the quantum theory. Bohr developed a model of the hydrogen atom in which the energy of its single electron is quantized—limited to certain energy values determined by an integer, the principal quantum number.
4. An electron in its most stable energy state is said to be in the ground state, and an electron at an energy level higher than its most stable state is said to be in an excited state. In the Bohr model, an electron emits a photon when it drops from a higher-energy state (an excited state) to a lower-energy state (the ground state or another, less excited state). The release of specific amounts of energy in the form of photons accounts for the lines in the hydrogen emission spectrum.
5. De Broglie extended Einstein's wave-particle description of light to all matter in motion. The wavelength of a moving particle of mass m and velocity u is given by the de Broglie equation $\lambda = h/mu$.
6. The Schrödinger equation describes the motions and energies of submicroscopic particles. This equation launched quantum mechanics and a new era in physics.
7. The Schrödinger equation tells us the possible energy states of the electron in a hydrogen atom and the probability of its location in a particular region surrounding the nucleus. These results can be applied with reasonable accuracy to many-electron atoms.

8. An atomic orbital is a function (ψ) that defines the distribution of electron density (ψ^2) in space. Orbitals are represented by electron density diagrams or boundary surface diagrams.
9. Four quantum numbers characterize each electron in an atom: the principal quantum number n identifies the main energy level, or shell, of the orbital; the angular momentum quantum number ℓ indicates the shape of the orbital; the magnetic quantum number m_ℓ specifies the orientation of the orbital in space; and the electron spin quantum number m_s indicates the direction of the electron's spin on its own axis.
10. The single s orbital for each energy level is spherical and centered on the nucleus. The three p orbitals present at $n = 2$ and higher; each has two lobes, and the pairs of lobes are arranged at right angles to one another. Starting with $n = 3$, there are five d orbitals, with more complex shapes and orientations.
11. The energy of the electron in a hydrogen atom is determined solely by its principal quantum number. In many-electron atoms, the principal quantum number and the angular momentum quantum number together determine the energy of an electron.
12. No two electrons in the same atom can have the same four quantum numbers (the Pauli exclusion principle).
13. The most stable arrangement of electrons in a subshell is the one that has the greatest number of parallel spins (Hund's rule). Atoms with one or more unpaired electron spins are paramagnetic. Atoms in which all electrons are paired are diamagnetic.
14. The Aufbau principle provides the guideline for building up the elements. The periodic table classifies the elements according to their atomic numbers and thus also by the electronic configurations of their atoms.

Key Words

Actinide series, p. 301
Amplitude, p. 268
Atomic orbital, p. 285
Aufbau principle, p. 298
Boundary surface diagram, p. 288
Diamagnetic, p. 294
Electromagnetic radiation, p. 269
Electromagnetic wave, p. 269
Electron configuration, p. 293
Electron density, p. 285
Emission spectra, p. 274
Excited level (or state), p. 276
Frequency (ν), p. 268
Ground level (or state), p. 276
Ground state, p. 276
Heisenberg uncertainty principle, p. 284
Hund's rule, p. 296
Lanthanide (rare earth) series, p. 301
Line spectra, p. 274
Many-electron atom, p. 286
Noble gas core, p. 299
Node, p. 279
Paramagnetic, p. 294
Pauli exclusion principle, p. 293
Photoelectric effect, p. 272
Photon, p. 272
Quantum, p. 272
Quantum numbers, p. 286
Rare earth series, p. 301
Transition metals, p. 299
Wave, p. 268
Wavelength (λ), p. 268

Questions and Problems

Quantum Theory and Electromagnetic Radiation

Review Questions

7.1 What is a wave? Explain the following terms associated with waves: wavelength, frequency, amplitude.

7.2 What are the units for wavelength and frequency of electromagnetic waves? What is the speed of light in meters per second and miles per hour?

7.3 List the types of electromagnetic radiation, starting with the radiation having the longest wavelength and ending with the radiation having the shortest wavelength.

7.4 Give the high and low wavelength values that define the visible region of the electromagnetic spectrum.

7.5 Briefly explain Planck's quantum theory and explain what a quantum is. What are the units for Planck's constant?

7.6 Give two everyday examples that illustrate the concept of quantization.

Problems

7.7 (a) What is the wavelength (in nanometers) of light having a frequency of 8.6×10^{13} Hz? (b) What is the frequency (in Hz) of light having a wavelength of 566 nm?

7.8 (a) What is the frequency of light having a wavelength of 456 nm? (b) What is the wavelength (in nanometers) of radiation having a frequency of 2.45×10^9 Hz? (This is the type of radiation used in microwave ovens.)

7.9 The average distance between Mars and Earth is about 1.3×10^8 miles. How long would it take TV pictures transmitted from the *Viking* space vehicle on Mars' surface to reach Earth? (1 mile = 1.61 km.)

7.10 How many minutes would it take a radio wave to travel from the planet Venus to Earth? (Average distance from Venus to Earth = 28 million miles.)

7.11 The SI unit of time is the second, which is defined as 9,192,631,770 cycles of radiation associated with a certain emission process in the cesium atom. Calculate the wavelength of this radiation (to three significant figures). In which region of the electromagnetic spectrum is this wavelength found?

7.12 The SI unit of length is the meter, which is defined as the length equal to 1,650,763.73 wavelengths of the light emitted by a particular energy transition in krypton atoms. Calculate the frequency of the light to three significant figures.

The Photoelectric Effect

Review Questions

7.13 Explain what is meant by the photoelectric effect.

7.14 What are photons? What role did Einstein's explanation of the photoelectric effect play in the development of the particle-wave interpretation of the nature of electromagnetic radiation?

Problems

7.15 A photon has a wavelength of 624 nm. Calculate the energy of the photon in joules.

7.16 The blue color of the sky results from the scattering of sunlight by air molecules. The blue light has a frequency of about 7.5×10^{14} Hz. (a) Calculate the wavelength, in nm, associated with this radiation, and (b) calculate the energy, in joules, of a single photon associated with this frequency.

7.17 A photon has a frequency of 6.0×10^4 Hz. (a) Convert this frequency into wavelength (nm). Does this frequency fall in the visible region? (b) Calculate the energy (in joules) of this photon. (c) Calculate the energy (in joules) of 1 mole of photons all with this frequency.

7.18 What is the wavelength, in nm, of radiation that has an energy content of 1.0×10^3 kJ/mol? In which region of the electromagnetic spectrum is this radiation found?

7.19 When copper is bombarded with high-energy electrons, X rays are emitted. Calculate the energy (in joules) associated with the photons if the wavelength of the X rays is 0.154 nm.

7.20 A particular form of electromagnetic radiation has a frequency of 8.11×10^{14} Hz. (a) What is its wavelength in nanometers? In meters? (b) To what region of the electromagnetic spectrum would you assign it? (c) What is the energy (in joules) of one quantum of this radiation?

Bohr's Theory of the Hydrogen Atom

Review Questions

7.21 What are emission spectra? How do line spectra differ from continuous spectra?

7.22 What is an energy level? Explain the difference between ground state and excited state.

7.23 Briefly describe Bohr's theory of the hydrogen atom and how it explains the appearance of an emission spectrum. How does Bohr's theory differ from concepts of classical physics?

7.24 Explain the meaning of the negative sign in Equation (7.5).

Problems

7.25 Explain why elements produce their own characteristic colors when they emit photons?

7.26 Some copper compounds emit green light when they are heated in a flame. How would you determine whether the light is of one wavelength or a mixture of two or more wavelengths?

7.27 Is it possible for a fluorescent material to emit radiation in the ultraviolet region after absorbing visible light? Explain your answer.

7.28 Explain how astronomers are able to tell which elements are present in distant stars by analyzing the electromagnetic radiation emitted by the stars.

7.29 Consider the following energy levels of a hypothetical atom:

E_4 ________ -1.0×10^{-19} J
E_3 ________ -5.0×10^{-19} J
E_2 ________ -10×10^{-19} J
E_1 ________ -15×10^{-19} J

(a) What is the wavelength of the photon needed to excite an electron from E_1 to E_4? (b) What is the energy (in joules) a photon must have in order to excite an electron from E_2 to E_3? (c) When an electron drops from the E_3 level to the E_1 level, the atom is said to undergo emission. Calculate the wavelength of the photon emitted in this process.

7.30 The first line of the Balmer series occurs at a wavelength of 656.3 nm. What is the energy difference between the two energy levels involved in the emission that results in this spectral line?

7.31 Calculate the wavelength (in nanometers) of a photon emitted by a hydrogen atom when its electron drops from the $n = 5$ state to the $n = 3$ state.

7.32 Calculate the frequency (Hz) and wavelength (nm) of the emitted photon when an electron drops from the $n = 4$ to the $n = 2$ level in a hydrogen atom.

7.33 Careful spectral analysis shows that the familiar yellow light of sodium lamps (such as street lamps) is made up of photons of two wavelengths, 589.0 nm and 589.6 nm. What is the difference in energy (in joules) between photons with these wavelengths?

7.34 An electron in the hydrogen atom makes a transition from an energy state of principal quantum numbers n_i to the $n = 2$ state. If the photon emitted has a wavelength of 434 nm, what is the value of n_i?

Particle-Wave Duality

Review Questions

7.35 Explain the statement, Matter and radiation have a "dual nature."

7.36 How does de Broglie's hypothesis account for the fact that the energies of the electron in a hydrogen atom are quantized?

7.37 Why is Equation (7.8) meaningful only for submicroscopic particles, such as electrons and atoms, and not for macroscopic objects?

7.38 Does a baseball in flight possess wave properties? If so, why can we not determine its wave properties?

Problems

7.39 Thermal neutrons are neutrons that move at speeds comparable to those of air molecules at room temperature. These neutrons are most effective in initiating a nuclear chain reaction among ^{235}U isotopes. Calculate the wavelength (in nm) associated with a beam of neutrons moving at 7.00×10^2 m/s. (Mass of a neutron = 1.675×10^{-27} kg.)

7.40 Protons can be accelerated to speeds near that of light in particle accelerators. Estimate the wavelength (in nm) of such a proton moving at 2.90×10^8 m/s. (Mass of a proton = 1.673×10^{-27} kg.)

7.41 What is the de Broglie wavelength, in cm, of a 12.4-g hummingbird flying at 1.20×10^2 mph? (1 mile = 1.61 km.)

7.42 What is the de Broglie wavelength (in nm) associated with a 2.5-g Ping-Pong ball traveling 35 mph?

Quantum Mechanics

Review Questions

7.43 What are the inadequacies of Bohr's theory?

7.44 What is the Heisenberg uncertainty principle? What is the Schrödinger equation?

7.45 What is the physical significance of the wave function?

7.46 How is the concept of electron density used to describe the position of an electron in the quantum mechanical treatment of an atom?

7.47 What is an atomic orbital? How does an atomic orbital differ from an orbit?

Atomic Orbitals

Review Questions

7.48 Describe the shapes of *s*, *p*, and *d* orbitals. How are these orbitals related to the quantum numbers n, ℓ, and m_ℓ?

7.49 List the hydrogen orbitals in increasing order of energy.

7.50 Describe the characteristics of an *s* orbital, a *p* orbital, and a *d* orbital. Which of the following orbitals do not exist: 1*p*, 2*s*, 2*d*, 3*p*, 3*d*, 3*f*, 4*g*?

7.51 Why is a boundary surface diagram useful in representing an atomic orbital?

7.52 Describe the four quantum numbers used to characterize an electron in an atom.

7.53 Which quantum number defines a shell? Which quantum numbers define a subshell?

7.54 Which of the four quantum numbers (n, ℓ, m_ℓ, m_s) determine (a) the energy of an electron in a hydrogen atom and in a many-electron atom, (b) the size of an orbital, (c) the shape of an orbital, (d) the orientation of an orbital in space?

Problems

7.55 An electron in a certain atom is in the $n = 2$ quantum level. List the possible values of ℓ and m_ℓ that it can have.

7.56 An electron in an atom is in the $n = 3$ quantum level. List the possible values of ℓ and m_ℓ that it can have.

7.57 Give the values of the quantum numbers associated with the following orbitals: (a) 2*p*, (b) 3*s*, (c) 5*d*.

7.58 Give the values of the four quantum numbers of an electron in the following orbitals: (a) 3*s*, (b) 4*p*, (c) 3*d*.

7.59 Discuss the similarities and differences between a 1*s* and a 2*s* orbital.

7.60 What is the difference between a $2p_x$ and a $2p_y$ orbital?

7.61 List all the possible subshells and orbitals associated with the principal quantum number n, if $n = 5$.

7.62 List all the possible subshells and orbitals associated with the principal quantum number n, if $n = 6$.

7.63 Calculate the total number of electrons that can occupy (a) one *s* orbital, (b) three *p* orbitals, (c) five *d* orbitals, (d) seven *f* orbitals.

7.64 What is the total number of electrons that can be held in all orbitals having the same principal quantum number n?

7.65 Determine the maximum number of electrons that can be found in each of the following subshells: 3*s*, 3*d*, 4*p*, 4*f*, 5*f*.

7.66 Indicate the total number of (a) *p* electrons in N ($Z = 7$); (b) *s* electrons in Si ($Z = 14$); and (c) 3*d* electrons in S ($Z = 16$).

7.67 Make a chart of all allowable orbitals in the first four principal energy levels of the hydrogen atom. Designate each by type (for example, *s*, *p*) and indicate how many orbitals of each type there are.

7.68 Why do the $3s$, $3p$, and $3d$ orbitals have the same energy in a hydrogen atom but different energies in a many-electron atom?

7.69 For each of the following pairs of hydrogen orbitals, indicate which is higher in energy: (a) $1s$, $2s$; (b) $2p$, $3p$; (c) $3d_{xy}$, $3d_{yz}$; (d) $3s$, $3d$; (e) $4f$, $5s$.

7.70 Which orbital in each of the following pairs is lower in energy in a many-electron atom? (a) $2s$, $2p$; (b) $3p$, $3d$; (c) $3s$, $4s$; (d) $4d$, $5f$.

Electron Configuration

Review Questions

7.71 What is electron configuration? Describe the roles that the Pauli exclusion principle and Hund's rule play in writing the electron configuration of elements.

7.72 Explain the meaning of the symbol $4d^6$.

7.73 Explain the meaning of diamagnetic and paramagnetic. Give an example of an element that is diamagnetic and one that is paramagnetic. What does it mean when we say that electrons are paired?

7.74 What is meant by the term "shielding of electrons" in an atom? Using the Li atom as an example, describe the effect of shielding on the energy of electrons in an atom.

Problems

7.75 Indicate which of the following sets of quantum numbers in an atom are unacceptable and explain why: (a) $(1, 0, \frac{1}{2}, \frac{1}{2})$, (b) $(3, 0, 0, +\frac{1}{2})$, (c) $(2, 2, 1, +\frac{1}{2})$, (d) $(4, 3, -2, +\frac{1}{2})$, (e) $(3, 2, 1, 1)$.

7.76 The ground-state electron configurations listed here are incorrect. Explain what mistakes have been made in each and write the correct electron configurations.

Al: $1s^22s^22p^43s^23p^3$

B: $1s^22s^22p^5$

F: $1s^22s^22p^6$

7.77 The atomic number of an element is 73. Is this element diamagnetic or paramagnetic?

7.78 Indicate the number of unpaired electrons present in each of the following atoms: B, Ne, P, Sc, Mn, Se, Kr, Fe, Cd, I, Pb.

The Building-Up Principle

Review Questions

7.79 State the Aufbau principle and explain the role it plays in classifying the elements in the periodic table.

7.80 Describe the characteristics of the following groups of elements: transition metals, lanthanides, actinides.

7.81 What is the noble gas core? How does it simplify the writing of electron configurations?

7.82 What are the group and period of the element osmium?

7.83 Define the following terms and give an example of each: transition metals, lanthanides, actinides.

7.84 Explain why the ground-state electron configurations of Cr and Cu are different from what we might expect.

7.85 Explain what is meant by a noble gas core. Write the electron configuration of a xenon core.

7.86 Comment on the correctness of the following statement: The probability of finding two electrons with the same four quantum numbers in an atom is zero.

Problems

7.87 Use the Aufbau principle to obtain the ground-state electron configuration of selenium.

7.88 Use the Aufbau principle to obtain the ground-state electron configuration of technetium.

7.89 Write the ground-state electron configurations for the following elements: B, V, Ni, As, I, Au.

7.90 Write the ground-state electron configurations for the following elements: Ge, Fe, Zn, Ni, W, Tl.

7.91 The electron configuration of a neutral atom is $1s^22s^22p^63s^2$. Write a complete set of quantum numbers for each of the electrons. Name the element.

7.92 Which of the following species has the most unpaired electrons? S^+, S, or S^-. Explain how you arrive at your answer.

Additional Problems

7.93 When a compound containing cesium ion is heated in a Bunsen burner flame, photons with an energy of 4.30×10^{-19} J are emitted. What color is the cesium flame?

7.94 Discuss the current view of the correctness of the following statements. (a) The electron in the hydrogen atom is in an orbit that never brings it closer than 100 pm to the nucleus. (b) Atomic absorption spectra result from transitions of electrons from lower to higher energy levels. (c) A many-electron atom behaves somewhat like a solar system that has a number of planets.

7.95 Distinguish carefully between the following terms: (a) wavelength and frequency, (b) wave properties and particle properties, (c) quantization of energy and continuous variation in energy.

7.96 What is the maximum number of electrons in an atom that can have the following quantum numbers? Specify the orbitals in which the electrons would be found. (a) $n = 2, m_s = +\frac{1}{2}$; (b) $n = 4, m_\ell = +1$; (c) $n = 3, \ell = 2$; (d) $n = 2, \ell = 0, m_s = -\frac{1}{2}$; (e) $n = 4, \ell = 3, m_\ell = -2$.

7.97 Identify the following individuals and their contributions to the development of quantum theory: Bohr, de Broglie, Einstein, Planck, Heisenberg, Schrödinger.

7.98 What properties of electrons are used in the operation of an electron microscope?

7.99 In a photoelectric experiment a student uses a light source whose frequency is greater than that needed to eject electrons from a certain metal. However, after continuously shining the light on the same area of the metal for a long period of time the student notices that the maximum kinetic energy of ejected electrons begins to decrease, even though the frequency of the light is held constant. How would you account for this behavior?

7.100 A certain pitcher's fastballs have been clocked at about 100 mph. (a) Calculate the wavelength of a 0.141-kg baseball (in nm) at this speed. (b) What is the wavelength of a hydrogen atom at the same speed? (1 mile = 1609 m.)

7.101 Considering only the ground-state electron configuration, are there more diamagnetic or paramagnetic elements? Explain.

7.102 A ruby laser produces radiation of wavelength 633 nm in pulses whose duration is 1.00×10^{-9} s. (a) If the laser produces 0.376 J of energy per pulse, how many photons are produced in each pulse? (b) Calculate the power (in watts) delivered by the laser per pulse. (1 W = 1 J/s.)

7.103 A 368-g sample of water absorbs infrared radiation at 1.06×10^4 nm from a carbon dioxide laser. Suppose all the absorbed radiation is converted to heat. Calculate the number of photons at this wavelength required to raise the temperature of the water by 5.00°C.

7.104 Photodissociation of water

$$H_2O(l) + h\nu \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

has been suggested as a source of hydrogen. The $\Delta H^\circ_{\text{rxn}}$ for the reaction, calculated from thermochemical data, is 285.8 kJ per mole of water decomposed. Calculate the maximum wavelength (in nm) that would provide the necessary energy. In principle, is it feasible to use sunlight as a source of energy for this process?

7.105 Spectral lines of the Lyman and Balmer series do not overlap. Verify this statement by calculating the longest wavelength associated with the Lyman series and the shortest wavelength associated with the Balmer series (in nm).

7.106 Only a fraction of the electrical energy supplied to a tungsten lightbulb is converted to visible light. The rest of the energy shows up as infrared radiation (that is, heat). A 75-W lightbulb converts 15.0 percent of the energy supplied to it into visible light (assume the wavelength to be 550 nm). How many photons are emitted by the lightbulb per second? (1 W = 1 J/s.)

7.107 Certain sunglasses have small crystals of silver chloride (AgCl) incorporated in the lenses. When the lenses are exposed to light of the appropriate wavelength, the following reaction occurs:

$$AgCl \longrightarrow Ag + Cl$$

The Ag atoms formed produce a uniform gray color that reduces the glare. If ΔH for the preceding reaction is 248 kJ/mol, calculate the maximum wavelength of light that can induce this process.

7.108 The He^+ ion contains only one electron and is therefore a hydrogenlike ion. Calculate the wavelengths, in increasing order, of the first four transitions in the Balmer series of the He^+ ion. Compare these wavelengths with the same transitions in a H atom. Comment on the differences. (The Rydberg constant for He^+ is 8.72×10^{-18} J.)

7.109 Ozone (O_3) in the stratosphere absorbs the harmful radiation from the sun by undergoing decomposition: $O_3 \longrightarrow O + O_2$. (a) Referring to Table 6.3, calculate the ΔH° for this process. (b) Calculate the maximum wavelength of photons (in nm) that possess this energy to cause the decomposition of ozone photochemically.

7.110 The retina of a human eye can detect light when radiant energy incident on it is at least 4.0×10^{-17} J. For light of 600-nm wavelength, how many photons does this correspond to?

7.111 An electron in an excited state in a hydrogen atom can return to the ground state in two different ways: (a) via a direct transition in which a photon of wavelength λ_1 is emitted and (b) via an intermediate excited state reached by the emission of a photon of wavelength λ_2. This intermediate excited state then decays to the ground state by emitting another photon of wavelength λ_3. Derive an equation that relates λ_1 to λ_2 and λ_3.

7.112 A photoelectric experiment was performed by separately shining a laser at 450 nm (blue light) and a laser at 560 nm (yellow light) on a clean metal surface and measuring the number and kinetic energy of the ejected electrons. Which light would generate more electrons? Which light would eject electrons with greater kinetic energy? Assume that the same amount of energy is delivered to the metal surface by each laser and that the frequencies of the laser lights exceed the threshold frequency.

7.113 Draw the shapes (boundary surfaces) of the following orbitals: (a) $2p_y$, (b) $3d_{z^2}$, (c) $3d_{x^2-y^2}$. (Show coordinate axes in your sketches.)

7.114 The electron configurations described in this chapter all refer to gaseous atoms in their ground states. An atom may absorb a quantum of energy and promote one of its electrons to a higher-energy orbital. When this happens, we say that the atom is in an excited state. The electron configurations of some excited atoms are given. Identify these atoms and write their ground-state configurations:

(a) $1s^1 2s^1$
(b) $1s^2 2s^2 2p^2 3d^1$
(c) $1s^2 2s^2 2p^6 4s^1$
(d) $[Ar]4s^1 3d^{10} 4p^4$
(e) $[Ne]3s^2 3p^4 3d^1$

7.115 Draw orbital diagrams for atoms with the following electron configurations:

(a) $1s^22s^22p^5$

(b) $1s^22s^22p^63s^23p^3$

(c) $1s^22s^22p^63s^23p^64s^23d^7$

7.116 If Rutherford and his coworkers had used electrons instead of alpha particles to probe the structure of the nucleus as described in Section 2.2, what might they have discovered?

7.117 Scientists have found interstellar hydrogen atoms with quantum number n in the hundreds. Calculate the wavelength of light emitted when a hydrogen atom undergoes a transition from $n = 236$ to $n = 235$. In what region of the electromagnetic spectrum does this wavelength fall?

7.118 Calculate the wavelength of a helium atom whose speed is equal to the root-mean-square speed at 20°C.

7.119 Ionization energy is the minimum energy required to remove an electron from an atom. It is usually expressed in units of kJ/mol, that is, the energy in kilojoules required to remove one mole of electrons from one mole of atoms. (a) Calculate the ionization energy for the hydrogen atom. (b) Repeat the calculation, assuming in this second case that the electrons are removed from the $n = 2$ state.

7.120 An electron in a hydrogen atom is excited from the ground state to the $n = 4$ state. Comment on the correctness of the following statements (true or false).

(a) $n = 4$ is the first excited state.

(b) It takes more energy to ionize (remove) the electron from $n = 4$ than from the ground state.

(c) The electron is farther from the nucleus (on average) in $n = 4$ than in the ground state.

(d) The wavelength of light emitted when the electron drops from $n = 4$ to $n = 1$ is longer than that from $n = 4$ to $n = 2$.

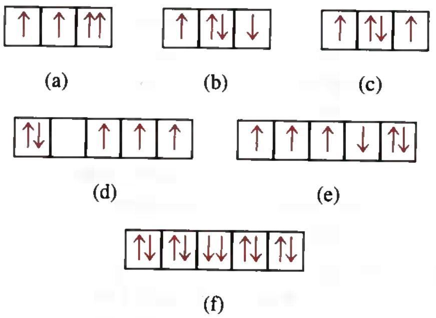
(e) The wavelength the atom absorbs in going from $n = 1$ to $n = 4$ is the same as that emitted as it goes from $n = 4$ to $n = 1$.

7.121 The ionization energy of a certain element is 412 kJ/mol (see Problem 7.119). However, when the atoms of this element are in the first excited state, the ionization energy is only 126 kJ/mol. Based on this information, calculate the wavelength of light emitted in a transition from the first excited state to the ground state.

7.122 Alveoli are the tiny sacs of air in the lungs (see Problem 5.132) whose average diameter is 5.0×10^{-5} m. Consider an oxygen molecule (5.3×10^{-26} kg) trapped within a sac. Calculate the uncertainty in the velocity of the oxygen molecule. (*Hint:* The maximum uncertainty in the position of the molecule is given by the diameter of the sac.)

7.123 How many photons at 660 nm must be absorbed to melt 5.0×10^2 g of ice? On average, how many H_2O molecules does one photon convert from ice to water? (*Hint:* It takes 334 J to melt 1 g of ice at 0°C.)

7.124 Shown below are portions of orbital diagrams representing the ground-state electron configurations of certain elements. Which of them violate the Pauli exclusion principle? Hund's rule?



7.125 The UV light that is responsible for tanning the skin falls in the 320- to 400-nm region. Calculate the total energy (in joules) absorbed by a person exposed to this radiation for 2.0 h, given that there are 2.0×10^{16} photons hitting Earth's surface per square centimeter per second over a 80-nm (320 nm to 400 nm) range and that the exposed body area is 0.45 m^2. Assume that only half of the radiation is absorbed and the other half is reflected by the body. (*Hint:* Use an average wavelength of 360 nm in calculating the energy of a photon.)

7.126 The sun is surrounded by a white circle of gaseous material called the corona, which becomes visible during a total eclipse of the sun. The temperature of the corona is in the millions of degrees Celsius, which is high enough to break up molecules and remove some or all of the electrons from atoms. One way astronomers have been able to estimate the temperature of the corona is by studying the emission lines of ions of certain elements. For example, the emission spectrum of Fe^{14+} ions has been recorded and analyzed. Knowing that it takes 3.5×10^4 kJ/mol to convert Fe^{13+} to Fe^{14+}, estimate the temperature of the sun's corona. (*Hint:* The average kinetic energy of one mole of a gas is $\frac{3}{2}RT$.)

7.127 In 1996 physicists created an anti-atom of hydrogen. In such an atom, which is the antimatter equivalent of an ordinary atom, the electrical charges of all the component particles are reversed. Thus, the nucleus of an anti-atom is made of an anti-proton, which has the same mass as a proton but bears a negative charge, while the electron is replaced by an anti-electron (also called positron) with the same mass as an electron, but bearing a positive charge. Would you expect the energy levels, emission spectra, and atomic orbitals of an antihydrogen atom to be different from those of a hydrogen atom? What would happen if an anti-atom of hydrogen collided with a hydrogen atom?

7.128 Use Equation (5.16) to calculate the de Broglie wavelength of a N_2 molecule at 300 K.

7.129 When an electron makes a transition between energy levels of a hydrogen atom, there are no restrictions on the initial and final values of the principal quantum number n. However, there is a quantum mechanical rule that restricts the initial and final values of the orbital angular momentum ℓ. This is the *selection rule*, which states that $\Delta\ell = \pm 1$, that is, in a transition, the value of ℓ can only increase or decrease by one. According to this rule, which of the following transitions are allowed: (a) $1s \longrightarrow 2s$, (b) $2p \longrightarrow 1s$, (c) $1s \longrightarrow 3d$, (d) $3d \longrightarrow 4f$, (e) $4d \longrightarrow 3s$?

7.130 In an electron microscope, electrons are accelerated by passing them through a voltage difference. The kinetic energy thus acquired by the electrons is equal to the voltage times the charge on the electron. Thus, a voltage difference of 1 volt imparts a kinetic energy of 1.602×10^{-19} volt-coulomb or 1.602×10^{-19} J. Calculate the wavelength associated with electrons accelerated by 5.00×10^3 volts.

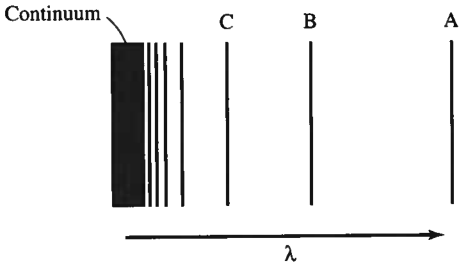
7.131 A microwave oven operating at 1.22×10^8 nm is used to heat 150 mL of water (roughly the volume of a tea cup) from 20°C to 100°C. Calculate the number of photons needed if 92.0 percent of microwave energy is converted to the thermal energy of water.

7.132 The radioactive Co-60 isotope is used in nuclear medicine to treat certain types of cancer. Calculate the wavelength and frequency of an emitted gamma particle having the energy of 1.29×10^{11} J/mol.

7.133 (a) An electron in the ground state of the hydrogen atom moves at an average speed of 5×10^6 m/s. If the speed is known to an uncertainty of 1 percent, what is the uncertainty in knowing its position? Given that the radius of the hydrogen atom in the ground state is 5.29×10^{-11} m, comment on your result. The mass of an electron is 9.1094×10^{-31} kg. (b) A 0.15-kg baseball thrown at 100 mph has a momentum of 6.7 kg · m/s. If the uncertainty in measuring the momentum is 1.0×10^{-7} of the momentum, calculate the uncertainty in the baseball's position.

Special Problems

7.134 For hydrogenlike ions, that is, ions containing only one electron, Equation (7.5) is modified as follows: $E_n = -R_H Z^2(1/n^2)$, where Z is the atomic number of the parent atom. The figure here represents the emission spectrum of such a hydrogenlike ion in the gas phase. All the lines result from the electronic transitions from the excited states to the $n = 2$ state. (a) What electronic transitions correspond to lines B and C? (b) If the wavelength of line C is 27.1 nm, calculate the wavelengths of lines A and B. (c) Calculate the energy needed to remove the electron from the ion in the $n = 4$ state. (d) What is the physical significance of the continuum?



7.135 When two atoms collide, some of their kinetic energy may be converted into electronic energy in one or both atoms. If the average kinetic energy is about equal to the energy for some allowed electronic transition, an appreciable number of atoms can absorb enough energy through an inelastic collision to be raised to an excited electronic state. (a) Calculate the average kinetic energy per atom in a gas sample at 298 K. (b) Calculate the energy difference between the $n = 1$ and $n = 2$ levels in hydrogen. (c) At what temperature is it possible to excite a hydrogen atom from the $n = 1$ level to $n = 2$ level by collision? [The average kinetic energy of 1 mole of an ideal gas is $(\frac{3}{2})RT$].

7.136 Calculate the energies needed to remove an electron from the $n = 1$ state and the $n = 5$ state in the Li^{2+} ion. What is the wavelength (in nm) of the emitted photon in a transition from $n = 5$ to $n = 1$? The Rydberg constant for hydrogen-like ions is $(2.18 \times 10^{-18}\ \text{J})Z^2$, where Z is the atomic number.

7.137 According to Einstein's special theory of relativity, the mass of a moving particle, m_{moving}, is related to its mass at rest, m_{rest}, by the following equation

$$m_{\text{moving}} = \frac{m_{\text{rest}}}{\sqrt{1 - \left(\frac{u}{c}\right)^2}}$$

where u and c are the speeds of the particle and light, respectively. (a) In particle accelerators, protons, electrons, and other charged particles are often accelerated to speeds close to the speed of light. Calculate the wavelength (in nm) of a proton moving at 50.0 percent the speed of light. The mass of a proton is 1.673×10^{-27} kg. (b) Calculate the mass of a 6.0×10^{-2} kg tennis ball moving at 63 m/s. Comment on your results.

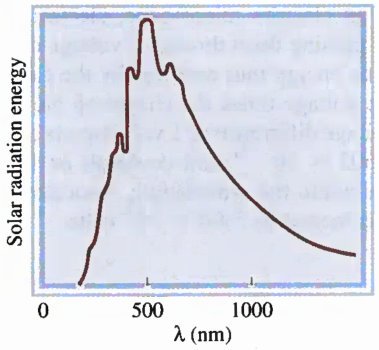
7.138 The mathematical equation for studying the photoelectric effect is

$$h\nu = W + \tfrac{1}{2}m_e u^2$$

where ν is the frequency of light shining on the metal, W is the energy needed to remove an electron from the metal [same as BE in Equation (7.4)], m_e and u are the mass and speed of the ejected electron. In an experiment, a student found that a maximum wavelength of 351 nm is needed to just dislodge electrons from a zinc metal surface. Calculate the velocity (in m/s) of an ejected electron when she employed light with a wavelength of 313 nm.

7.139 In the beginning of the twentieth century, some scientists thought that a nucleus may contain both electrons and protons. Use the Heisenberg uncertainty principle to show that an electron cannot be confined within a nucleus. Repeat the calculation for a proton. Comment on your results. Assume the radius of a nucleus to be 1.0×10^{-15} m. The masses of an electron and a proton are 9.109×10^{-31} kg and 1.673×10^{-27} kg, respectively. (*Hint*: Treat the radius of the nucleus as the uncertainty in position.)

7.140 Blackbody radiation is the term used to describe the dependence of the radiation energy emitted by an object on wavelength at a certain temperature. Planck proposed the quantum theory to account for this dependence. Shown in the figure is a plot of the radiation energy emitted by our sun versus wavelength. This curve is characteristic of objects at about 6000 K, which is the temperature at the surface of the sun. At a higher temperature, the curve has a similar shape but the maximum will shift to a shorter wavelength. (a) What does this curve reveal about two consequences of great biological significance on Earth? (b) How are astronomers able to determine the temperature at the surface of stars in general?



Answers to Practice Exercises

7.1 625 Hz. **7.2** 8.24 m. **7.3** 3.39×10^3 nm. **7.4** 2.63×10^3 nm. **7.5** 56.6 nm. **7.6** $n = 3, \ell = 1, m_\ell = -1, 0, 1$. **7.7** 16. **7.8** $(5, 1, -1, +\frac{1}{2})$, $(5, 1, 0, +\frac{1}{2})$, $(5, 1, 1, +\frac{1}{2})$, $(5, 1, -1, -\frac{1}{2})$, $(5, 1, 0, -\frac{1}{2})$, $(5, 1, 1, -\frac{1}{2})$. **7.9** 32. **7.10** $(1, 0, 0, +\frac{1}{2})$, $(1, 0, 0, -\frac{1}{2})$, $(2, 0, 0, +\frac{1}{2})$, $(2, 0, 0, -\frac{1}{2})$, $(2, 1, -1, -\frac{1}{2})$. There are 5 other acceptable ways to write the quantum numbers for the last electron. **7.11** $[\mathrm{Ne}]3s^23p^3$.

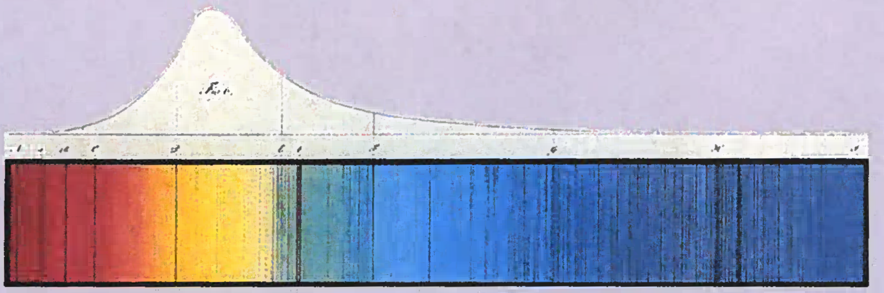
CHEMICAL Mystery

Discovery of Helium and the Rise and Fall of Coronium

Scientists know that our sun and other stars contain certain elements. How was this information obtained?

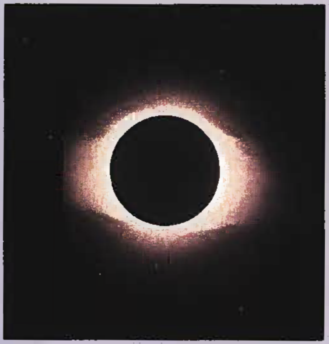
In the early nineteenth century, the German physicist Josef Fraunhofer studied the emission spectrum of the sun and noticed certain dark lines at specific wavelengths. We interpret the appearance of these lines by supposing that originally a continuous band of color was radiated and that, as the emitted light moves outward from the sun, some of the radiation is reabsorbed at those wavelengths by the atoms in space. These dark lines are therefore absorption lines. For atoms, the emission and absorption of light occur at the same wavelengths. By matching the absorption lines in the emission spectra of a star with the emission spectra of known elements in the laboratory, scientists have been able to deduce the types of elements present in the star.

Another way to study the sun spectroscopically is during its eclipse. In 1868 the French physicist Pierre Janssen observed a bright yellow line (see Figure 7.8) in the emission spectrum of the sun's corona during the totality of the eclipse. (The corona is the pearly white crown of light visible around the sun during a total eclipse.) This line did not match the emission lines of known elements, but did match one of the dark lines in the spectrum sketched by Fraunhofer. The name helium (from Helios, the sun god in Greek mythology) was given to the element responsible for the emission line. Twenty-seven years later, helium was discovered on Earth by the British chemist William Ramsay in a mineral of uranium. On Earth, the only source of helium is through radioactive decay processes—α particles emitted during nuclear decay are eventually converted to helium atoms.



Fraunhofer's original drawing, in 1814, showing the dark absorption lines in the sun's emission spectrum. The top of the diagram shows the overall brightness of the sun at different colors.

The search for new elements from the sun did not end with helium. Around the time of Janssen's work, scientists also detected a bright green line in the spectrum from the corona. They did not know the identity of the element giving rise to the line, so they called it coronium because it was only found in the corona. Over the following years, additional mystery coronal emission lines were found. The coronium problem proved much harder to solve than the helium case because no matchings were found with the emission lines of known elements. It was not until the late 1930s that the Swedish physicist Bengt Edlén identified these lines as coming from partially ionized atoms of iron, calcium, and nickel. At very high temperatures (over a million degrees Celsius), many atoms become ionized by losing one or more electrons. Therefore, the mystery emission lines come from the resulting ions of the metals and not from a new element. So, after some 70 years the coronium problem was finally solved. There is no such element as coronium after all!



During the total eclipse of the sun, which lasts for only a few seconds, the corona becomes visible.

Chemical Clues

1. Sketch a two-energy-level system (E_1 and E_2) to illustrate the absorption and emission processes.
2. Explain why the sun's spectrum provides only absorption lines (the dark lines), whereas the corona spectrum provides only emission lines.
3. Why is it difficult to detect helium on Earth?
4. How are scientists able to determine the abundances of elements in stars?
5. Knowing the identity of an ion of an element giving rise to a coronal emission line, describe in qualitative terms how you can estimate the temperature of the corona.