THE QUANTUM MECHANICAL ATOM

7

Colorful fireworks such as this in Washington, D.C., on the fourth of July are popular events worldwide. Many of the fireworks displays resemble the flowers they are named after, such as chrysanthemum, peony, and palm. Each display is the result of two or more carefully timed chemical explosions. In this chapter we will see that the colors in a fireworks display are easily explained by modern quantum mechanics. *(Bill Ross/Corbis)*

CHAPTER OUTLINE

THIS CHAPTER IN CONTEXT Nature presents the observer with very complex and often large chemical structures that are essential for life and also make up the nonliving world around us. Understanding these structures starts at the atomic level. If we know how the atoms are put together and their properties we can understand how they bond to each other (Chapter 8) and then we will understand the basic three-dimensional geometries (Chapter 9) that then allow us to understand the larger structures and the interactions of matter. This chapter introduces us to the most modern concepts of the atom itself.

In previous chapters we have described how the structure of the atom was deduced from a variety of experimental evidence. Each experiment added more detail to the make-up of the atom. It started with the indivisible atom and grew to the nuclear model proposed by Rutherford where negatively charged electrons surrounded an extremely dense positively charged nucleus composed of protons and neutrons. This model explained the mass relationships between the elements and the nature of isotopes. However, there were many unanswered questions. Why do metals tend to form cations and why do nonmetals tend to form anions? Why are certain combinations of elements very common while other combinations are never observed? Why do two nonmetals combine to form compounds while no similar process exists for two metals to form a compound? Why are the noble gases virtually inert? Why does the periodic table have the arrangement and shape it has? Many more questions could also be posed, but there was one major question.

This fundamental question concerned the fact that classical physics predicted that atoms simply could not exist. The physics of the late 1800s predicted that electrons surrounding the nucleus must quickly lose energy and crash into the nucleus. We call this the **collapsing atom paradox.** At the same time other unsolvable problems arose for classical physics. Heated objects should have emitted vast quantities of ultraviolet (UV) light. In fact they emit very little UV radiation. This was known as the **ultraviolet catastrophe.** In addition, emerging studies of particles, such as electrons, passing through very small openings gave results (diffraction patterns) that could only be explained if we regarded particles as waves. This led to the concept of the **wave/particle duality** of matter and energy.

The above problems with classical physics made it clear that an entirely new set of concepts would be needed to define modern physics and chemistry. These concepts are commonly called **wave mechanics, quantum mechanics,** or **quantum theory** and they are now a cornerstone of modern chemistry.

Light emitted from atoms gives us clues about how electrons are arranged within an atom. At the same time an understanding of standing waves develops insights to explain why atoms do not collapse. Therefore we must begin our introduction to quantum mechanics by describing the nature of electromagnetic radiation.

7.1 ELECTROMAGNETIC RADIATION PROVIDES THE CLUE TO THE ELECTRONIC STRUCTURES OF ATOMS

Electromagnetic radiation can be described as a wave or as a stream of photons

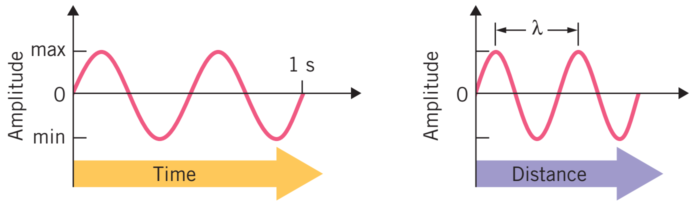
You've learned that objects can have energy in only two ways, as kinetic energy and as potential energy. You also learned that energy can be transferred between things, and in Chapter 6 our principal focus was on the transfer of heat. Energy can also be transferred between atoms and molecules in the form of light or electromagnetic energy. This is a very important form of energy in chemistry. For example, many chemical systems emit visible light as they react (see Figure 7.1).

Many experiments show that electromagnetic radiation carries energy through space by means of **waves.** Waves are an oscillation that moves outward from a disturbance (think of ripples moving away from a pebble dropped into a pond). In the case of electromagnetic radiation, the disturbance can be a vibrating electric charge. When the charge oscillates, it produces a pulse in the electric field around it. As the electric field pulses, it creates a pulse in the magnetic field. The magnetic field pulse gives rise to yet another electric field pulse

□ Electricity and magnetism are closely related to each other. A moving charge creates an electric current, which in turn creates a magnetic field around it. This is the fundamental idea behind electric motors. A moving magnetic field creates an electric field or current. This is the idea behind electrical generators and turbines.

(*a*) (*b*) (*c*)

FIG. 7.1 **Light is given off in a variety of chemical reactions.** (*a*) Combustion. (*b*) Cyalume light sticks. (*c*) A lightning bug. *(Peter Arnold, Inc.; IPA/The Image Works; Edward Degginger/Bruce Coleman, Inc.)*



(*a*) (*b*)

FIG. 7.2 **Two views of electromagnetic radiation.** (*a*) The frequency, *ν*, of a light wave is the number of complete oscillations each second. Here two cycles span a one-second time interval, so the frequency is 2 cycles per second, or 2 Hz. (*b*) Electromagnetic radiation frozen in time. This curve shows how the amplitude varies along the direction of travel. The distance between two peaks is the wavelength, λ, of the electromagnetic radiation.

▫ Electromagnetic waves don't need a medium to travel through, as water and sound waves do. They can cross empty space. The speed of the electromagnetic wave in a vacuum is the same no matter how the radiation is created (about 3.00×10^8 m/s).

further away from the disturbance. The process continues, with a pulse in one field giving rise to a pulse in the other, and the resulting train of pulses in the electric and magnetic fields is called an **electromagnetic wave.** This wave ripples away from the source at extremely high speeds.

An electromagnetic wave is often depicted as a sine wave that has an amplitude, wavelength, and frequency. Figure 7.2 shows how the amplitude or intensity of the wave varies with time and with distance as the wave travels through space. **Amplitude** of the wave is related to the intensity or brightness of the radiation. In Figure 7.2*a*, we see two complete oscillations or *cycles* of the wave during a one-second interval. The number of cycles per second is called the **frequency** of the electromagnetic radiation, and its symbol is $\boldsymbol{\nu}$ (the Greek letter *nu*, pronounced "new"). In the SI, the unit of time is the second (s), so frequency is given the unit "per second," which is $\frac{1}{\text{second}}$, or $(\text{second})^{-1}$. This unit is given the special name **hertz (Hz).**

▫ The SI symbol for the second is s.

$$s^{-1} = \frac{1}{s}$$

$$1 \text{ Hz} = 1 \text{ s}^{-1}$$

As electromagnetic radiation moves away from its source, the positions of maximum and minimum amplitude (peaks and troughs) are regularly spaced. The peak-to-peak distance is called the radiation's **wavelength,** symbolized by $\boldsymbol{\lambda}$ (the Greek letter *lambda*). See Figure 7.2*b*. Because wavelength is a distance, it has distance units (for example, meters).

If we multiply the wavelength by frequency, the result is the speed of the wave. We can see this if we analyze the units.

(In SI units)

$$\text{meters} \times \frac{1}{\text{second}} = \frac{\text{meters}}{\text{second}} = \text{speed}$$

$$\text{m} \times \frac{1}{\text{s}} = \frac{\text{m}}{\text{s}} = \text{m s}^{-1}$$

☐ For any wave, the product of its wavelength and its frequency equals the speed of the wave.

The speed of electromagnetic radiation in a vacuum is a constant and is commonly called the **speed of light.** Its value to three significant figures is 3.00×10^8 m/s (or m s^{-1}). This important physical constant is given the symbol ***c***.

$$c = 3.00 \times 10^8 \text{ m s}^{-1}$$

☐ The speed of light is one of our most carefully measured constants, because the meter is defined in terms of it. The precise value of the speed of light in a vacuum is 2.99792458×10^8 m/s, and a meter is defined as exactly the distance traveled by light in 1/299,792,458 of a second.

From the preceding discussion we obtain a very important relationship that allows us to convert between wavelength, λ and frequency, ν.

$$\lambda \times \nu = c = 3.00 \times 10^8 \text{ m s}^{-1} \tag{7.1}$$

TOOLS *Wavelength–frequency relationship*

EXAMPLE 7.1

Calculating Frequency from Wavelength

Mycobacterium tuberculosis, the organism that causes tuberculosis, can be completely destroyed by irradiation with ultraviolet light with a wavelength of 254 nm. What is the frequency of this radiation?

ANALYSIS: To convert between wavelength and frequency we use the tool expressed by Equation 7.1. However, we must be careful about the units.

SOLUTION: To calculate the frequency, we solve Equation 7.1 for ν.

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

Next, we substitute for c (3.00×10^8 m s^{-1}) and use 254 nm for the wavelength. However, to cancel units correctly, we must have the wavelength in meters. Recall from Chapter 1 that nm means nanometer and the prefix nano implies the factor "$\times 10^{-9}$."

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m}$$

Therefore, 254 nm equals 254×10^{-9} m. Substituting gives

$$\begin{aligned}\nu &= \frac{3.00 \times 10^8 \cancel{\text{m}}\,\text{s}^{-1}}{254 \times 10^{-9} \cancel{\text{m}}} \\ &= 1.18 \times 10^{15} \text{ s}^{-1} \\ &= 1.18 \times 10^{15} \text{ Hz}\end{aligned}$$

IS THE ANSWER REASONABLE? One way to test if our answer is correct is to see if the given wavelength, multiplied by our calculated frequency, gives us the speed of light. We will round the 254 nm to 250×10^{-9} m and round our answer to 1×10^{15} s^{-1}

$$(250 \times 10^{-9} \text{ m}) \times (1 \times 10^{15} \text{ s}^{-1}) = 250 \times 10^6 \text{ m s}^{-1} = 2.5 \times 10^8 \text{ m s}^{-1}$$

which is close to the actual speed of light, within one significant figure. Using the actual data and a calculator gives us the exact value for the speed of light.

EXAMPLE 7.2
Calculating Wavelength from Frequency

Radio station WGBB on Long Island, New York, broadcasts its AM signal, a form of electromagnetic radiation, at a frequency of 1240 kHz. What is the wavelength of the radio waves expressed in meters?

ANALYSIS: This question will utilize the same equation as Example 7.1. This time we solve for wavelength in the units asked for in the problem.

SOLUTION: Solving Equation 7.1 for the wavelength gives

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{1240 \text{ kHz}}$$

In order for the units to work out we recall that the prefix "k" in kHz means kilo and stands for "$\times\ 10^3$" and Hz means s^{-1}. Replacing k with $\times\ 10^3$ and Hz with s^{-1} results in the frequency written as $1240 \times 10^3\ s^{-1}$. Substituting gives

$$\begin{aligned}\lambda &= \frac{3.00 \times 10^8 \text{ m } \cancel{s^{-1}}}{1240 \times 10^3\ \cancel{s^{-1}}} \\ &= 242 \text{ m}\end{aligned}$$

IS THE ANSWER REASONABLE? If this wavelength is correct, we should be able to multiply it by the original frequency (in Hz) and get the speed of light, as we did in the previous example. Another approach is to test our answer by dividing the speed of light by the wavelength to get back the frequency. Rounding to one significant figure we get

$$\frac{3 \times 10^8\ \cancel{\text{m}}/\text{s}}{2 \times 10^2\ \cancel{\text{m}}} = 1.5 \times 10^6 \text{ Hz} = 1500 \text{ kHz}$$

which is reasonably close to the original frequency of 1240 kHz.

Practice Exercise 1: Helium derives it name from the Latin name for the sun. Helium was discovered when spectroscopists found that the 588 nm wavelength (among others) was missing from the sun's spectrum. What is the frequency of this radiation? (Hint: Recall the metric prefixes so units will cancel correctly.)

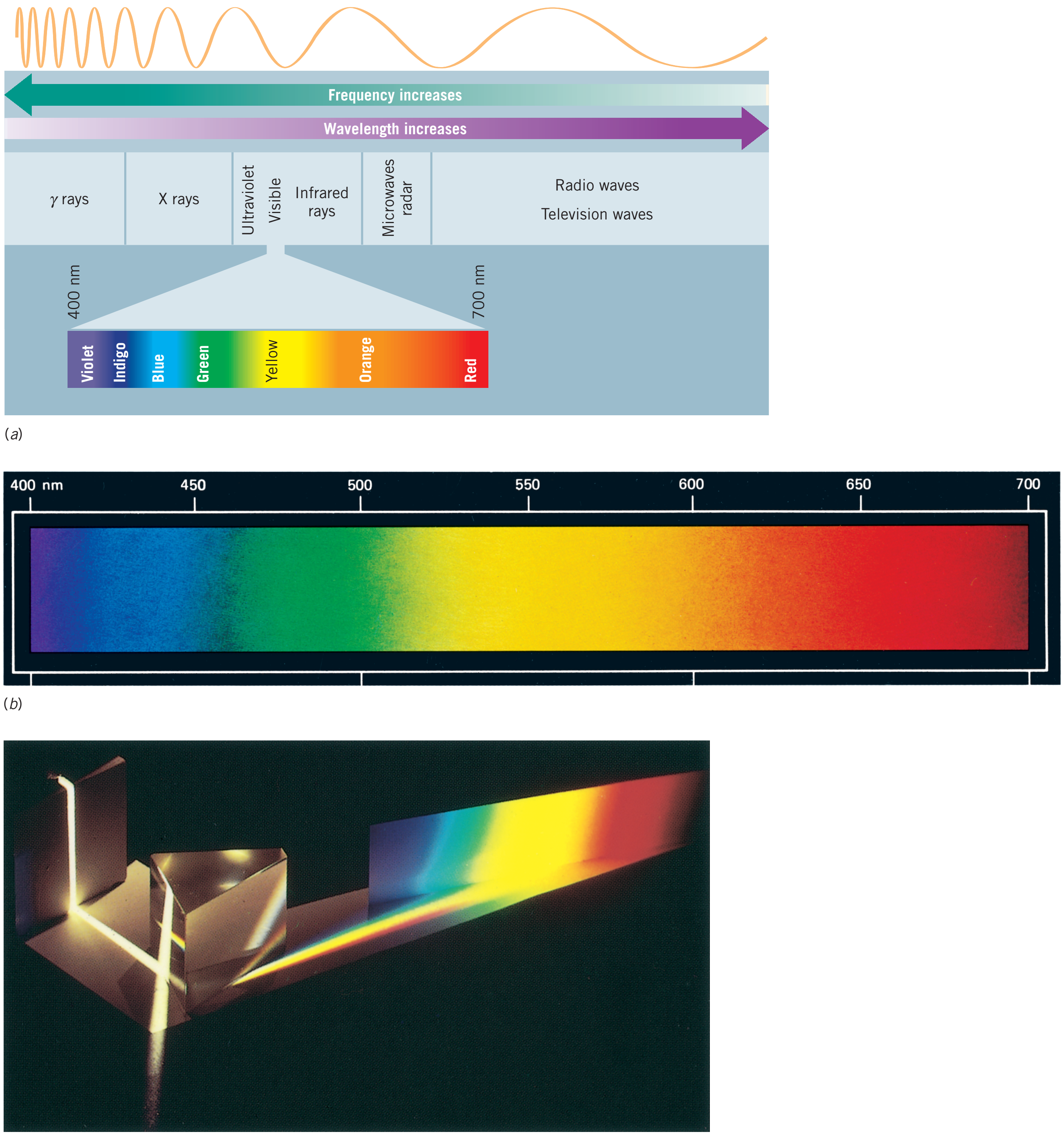
Practice Exercise 2: The most intense radiation emitted by the earth has a wavelength of about 10.0 μm. What is the frequency of this radiation in hertz?

Practice Exercise 3: An FM radio station in West Palm Beach, Florida, broadcasts electromagnetic radiation at a frequency of 104.3 MHz (megahertz). What is the wavelength of the radio waves, expressed in meters?

Electromagnetic waves are categorized by frequency

Electromagnetic radiation comes in a broad range of frequencies called the **electromagnetic spectrum,** illustrated in Figure 7.3. Some portions of the spectrum have popular names. For example, radio waves are electromagnetic radiations having very low frequencies (and therefore very long wavelengths). Microwaves, which also have low frequencies, are emitted by radar instruments such as those the police use to monitor the speeds of cars. In microwave ovens, similar radiation is used to heat water in foods, causing the food to cook quickly. Infrared radiation is emitted by hot objects and consists of the range of frequencies that can make molecules of most substances vibrate internally. You can't see infrared radiation, but you can feel how your body absorbs it by holding your hand near a hot radiator; the absorbed radiation makes your hand warm. Gamma rays (γ rays) are at the high-frequency end of the electromagnetic spectrum. They are produced by certain

□ Remember that there is an inverse relationship between wavelength and frequency. The lower the frequency, the longer the wavelength.



(*a*)

(*b*)

(*c*)

FIG. 7.3 **The electromagnetic spectrum.** (*a*) The electromagnetic spectrum is divided into regions according to the wavelengths of the radiation. (*b*) The visible spectrum is composed of wavelengths that range from about 400 to 700 nm. (*c*) The production of a visible spectrum by splitting white light into its rainbow of colors. (*From "The Gift of Color," Eastman Kodak Company.)*

elements that are radioactive. X rays are very much like gamma rays, but they are usually made by special equipment. Both X rays and gamma rays penetrate living things easily.

Most of the time, you are bombarded with electromagnetic radiation from all portions of the electromagnetic spectrum. Radio and TV signals pass through you; you feel infrared radiation when you sense the warmth of a radiator; X rays and gamma rays fall on you from space; and light from a lamp reflects into your eyes from the page you're reading. Of all these radiations, your eyes are able to sense only a very narrow band of wavelengths ranging from about 400 to 700 nm. This band is called the **visible spectrum** and consists of all the colors you can see, from red through orange, yellow, green, blue, and violet. White light is composed of all these colors and it can be separated into them by focusing a beam of white light through a prism, which spreads the various wavelengths apart. This is illustrated in Figure 7.3*b*. A photograph showing the production of a visible spectrum is given in Figure 7.3*c*.

The way substances absorb electromagnetic radiation often can help us characterize them. For example, each substance absorbs a uniquely different set of infrared frequencies. A plot of the wavelengths absorbed versus the intensities of absorption is called an infrared absorption spectrum. It can be used to identify a compound, because each infrared spectrum is as unique as a set of fingerprints. (See Figure 7.4.) Many substances absorb visible and ultraviolet radiations in unique ways, too, and they have visible and ultraviolet spectra (Figure 7.5).

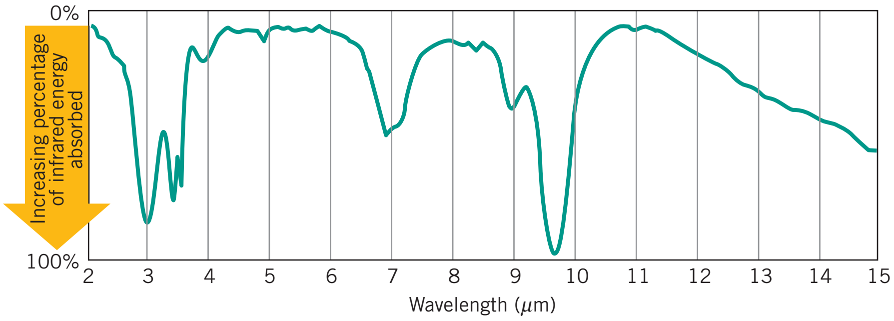
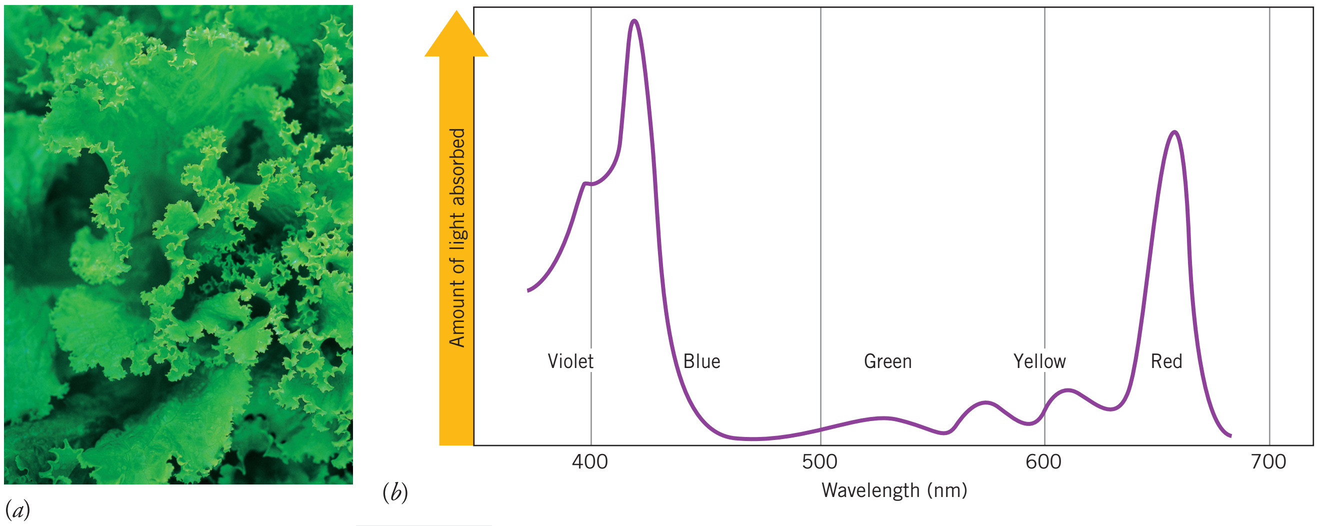


FIG. 7.4 Infrared absorption spectrum of methyl alcohol (also called wood alcohol), the fuel in "canned heat" products such as Sterno. In an infrared spectrum, the usual practice is to show the amount of light absorbed increasing from top to bottom in the graph. Thus, there is a peak in the percentage of light absorbed at about 3 μm. (Spectrum courtesy Sadtler Research Laboratories, Inc., Philadelphia, Pa.)



(*a*)

(*b*)

FIG. 7.5 Absorption of light by chlorophyll. (*a*) Chlorophyll is the green pigment plants use to harvest solar energy for photosynthesis. (*b*) In this visible absorption spectrum of chlorophyll, the percentage of light absorbed increases from bottom to top. Thus, there is a peak in the light absorbed at about 420 nm and another at about 660 nm. This means the pigment strongly absorbs blue-violet and red light. The green color we *see* is the light that's *not* absorbed. It's composed of the wavelengths of visible light that are reflected. (Our eyes are most sensitive to green, so we don't notice the yellow components of the reflected light.) *((a) Gary Braasch/Stone/Getty Images.)*

Electromagnetic radiation can be viewed as a stream of photons

When an electromagnetic wave passes an object, the oscillating electric and magnetic fields may interact with it, as ocean waves interact with a buoy in a harbor. A tiny charged particle placed in the path of the wave will be yanked back and forth by the oscillating electric and magnetic fields. For example, when a radio wave strikes an antenna, electrons within the antenna begin to bounce up and down, creating an alternating current which can be detected and decoded electronically. Because the wave exerts a force on the antenna's electrons and moves them through a distance, work is done. Thus, as energy is lost by the source of the wave (the radio transmitter) energy is gained by the electrons in the antenna.

A series of groundbreaking experiments showed that classical physics does not correctly describe energy transfer by electromagnetic radiation. In 1900 a German physicist named Max Planck (1858–1947) proposed that electromagnetic radiation can be viewed as a stream of tiny packets or **quanta** of energy that were later called **photons.** Each photon travels at the speed of light. Planck proposed, and Albert Einstein (1879–1955) confirmed, that *the energy of a photon of electromagnetic radiation is proportional to the radiation's frequency,* not to its intensity or brightness as had been believed up to that time. (See Facets of Chemistry 7.1.)

□ The energy of one photon is called one **quantum** of energy.

$$\text{Energy of a photon} = E = h\nu \qquad (7.2)$$

TOOLS
Energy of a photon

In this expression, h is a proportionality constant that we now call **Planck's constant.** Note that Equation 7.2 relates two representations of electromagnetic radiation. The left-hand side of the equation deals with a property of particles (energy per photon); the right-hand side deals with a property of waves (the frequency). Quantum theory unites the two representations, so we can use whichever representation of electromagnetic radiation is convenient for describing experimental results. For example, in describing the photoelectric effect (Facets of Chemistry 7.1), we represent radiation as a stream of particles. When describing

□ The value of Planck's constant is 6.626×10^{-34} J s. It has units of energy (joules) multiplied by time (seconds).

FACETS OF CHEMISTRY **7.1**

Photoelectricity and Its Applications

One of the earliest clues to the relationship between the frequency of light and its energy was the discovery of the photoelectric effect. In the latter part of the nineteenth century, it was found that certain metals acquired a positive charge when they were illuminated by light. Apparently, light is capable of kicking electrons out of the surface of the metal.

When this phenomenon was studied in detail, it was discovered that electrons could be made to leave a metal's surface only if the frequency of the incident radiation was above some minimum value, which was named the threshold frequency. This threshold frequency differs for different metals, depending on how tightly the metal atom holds onto electrons. Above the threshold frequency, the kinetic energy of the emitted electron increases with increasing frequency of the light. Interestingly, however, its kinetic energy does not depend on the intensity of the light. In fact, if the frequency of the light is below the minimum frequency, no electrons are observed at all, no matter how bright the light is. To physicists of that time, this was very perplexing because they believed the energy of light was related to its brightness. The explanation of the phenomenon was finally given by Albert Einstein in the form of a very simple equation.

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

where KE is the kinetic energy of the electron that is emitted, $h\nu$ is the energy of the photon of frequency ν, and w is the minimum energy needed to eject the electron from the metal's surface. Stated another way, part of the energy of the photon is needed just to get the electron off the surface of the metal. This amount is w. Any energy left over ($h\nu - w$) appears as the electron's kinetic energy.

Besides its important theoretical implications, the photoelectric effect has many practical applications. For example, automatic "electric eye" door openers use this phenomenon by sensing the interruption of a light beam caused by the person wishing to use the door. The phenomenon is also responsible for photoconduction by certain substances that are used in light meters in cameras and other devices. The production of sound in motion pictures was first made possible by incorporating a strip along the edge of the film (called the sound track) that causes the light passing through it to fluctuate in intensity according to the frequency of the sound that's been recorded. A photocell converts this light to a varying electric current that is amplified and played through speakers in the theater. Even the sensitivity of photographic film to light is related to the release of photoelectrons within tiny grains of silver bromide that are suspended in a coating on the surface of the film.

FACETS OF CHEMISTRY 7.2

Electromagnetic Fields and Their Possible Physiological Effects

Over the past few years you may have heard reports of possible dangers associated with living near high-voltage power lines or operating electrical equipment. What has caused public concern is the fear that 60 Hz electromagnetic radiation emitted by electricity passing through wires might be affecting the health of those nearby. Such fears have been fueled by news media reports of increased cancer rates among groups receiving strong exposure to this radiation, although the actual evidence supporting a relationship between exposure and cancer is weak and even partly contradictory.

When an oscillating electric current with a certain frequency passes through a wire it emits radiation with that same frequency. In fact, that's how radio and TV stations broadcast their signals—by pulsing an electric current through a transmitting antenna. Ordinary household AC (alternating current) electricity has a frequency of 60 Hz, and weak electromagnetic signals are emitted by all wires that carry it. This radiation is most intense when the voltage is highest, as in the lines that carry electricity over long distances between power plants and cities.

High-voltage power lines such as these emit low levels of 60 Hz electromagnetic radiation (also called *ultralow frequency*, or ULF, radiation). *(Martin Heitner/Stock Connection Worldwide/NewsCom.)*

The energy possessed by photons of 60 Hz electromagnetic radiation is extremely small (you might try the calculation), so small that it cannot affect the bonds that hold molecules together or even cause heating effects the way microwaves do. How, then, can they affect the activities of cells? The answer might be in the weak pulsating electric and magnetic fields induced in the body by this radiation.

Strong electromagnetic fields have been shown to affect the rate of bone growth as well as the amounts of various proteins produced in cells. Experiments have also revealed that cells exposed to an electric field hold onto calcium ions more than cells not exposed. Other experiments have demonstrated that weak magnetic fields increase the uptake of calcium ions in cells that have been exposed to a substance that triggers cell division. It is believed that this additional calcium increases the tendency of these cells to divide. Since cancer growth depends on the rate of cell division, these results suggest one way cancers might be promoted by such radiation.

Despite laboratory evidence, the connection between electromagnetic radiation and cancer remains inconclusive. Although it is at least *possible* that cancer can be induced by electromagnetic fields, a lot of additional research will be necessary to pin down the answer.

how radiation can bend around small obstacles and fan out after passing through pinholes, we represent radiation as a wave phenomenon. Electromagnetic radiation is not a stream of particles, and it is not a wave, it's a combination of both that is difficult to describe. However, we can say that in some experiments radiation is best described as a wave and in other experiments the particle explanation works best.

Planck's and Einstein's discovery was really quite surprising. If a particular event requiring energy, such as photosynthesis in green plants, is initiated by the absorption of light, it is the frequency of the light that is important, not its intensity or brightness. This makes sense when we view light as a stream of photons, since "high frequency" is associated with higher energy of the photons, while higher intensity is associated with greater numbers of photons. But it makes no sense at all when we view radiation as a wave phenomenon.

■ Brighter light delivers more photons; higher frequency light delivers more energetic photons.

The idea that electromagnetic radiation can be represented as either a stream of photons or a wave is a cornerstone of the quantum theory. Physicists were able to use the concept of photons to understand many experimental results that classical physics simply had no explanation for. The success of the quantum theory in describing radiation paved the way for a second startling realization: electrons, like radiation, could be represented as either waves or particles. We now turn our attention to the first experimental evidence that led to our modern quantum mechanical model of atomic structure: the existence of discrete lines in atomic spectra.

7.2 ATOMIC LINE SPECTRA ARE EVIDENCE THAT ELECTRONS IN ATOMS HAVE QUANTIZED ENERGIES

Each spectrum described in Figure 7.3 is called a **continuous spectrum** because it contains a continuous unbroken distribution of light of *all* colors. It is formed when the light from an object that's been heated to a very high temperature (such as the filament in an electric lightbulb) is split by a prism and displayed on a screen. A rainbow after a summer shower appears as a continuous spectrum that most people have seen. In this case, tiny water droplets in the air spread out the colors contained in sunlight.

A rather different kind of spectrum is observed if we examine the light that is given off when an *electric discharge*, or spark, passes through a gas such as hydrogen. The electric discharge is an electric current that *excites,* or energizes, the atoms of the gas. More specifically, the electric current transfers energy to the electrons in the atoms raising them to **excited states.** The atoms then emit the absorbed energy in the form of light as the electrons return to lower energy states. When a narrow beam of this light is passed through a prism, as shown in Figure 7.6, we do *not* see a continuous spectrum. Instead, only a few colors are observed, displayed as a series of individual lines. This series of lines is called the element's **atomic spectrum** or **emission spectrum.** Figure 7.7 shows the visible portions of the atomic spectra of two common elements, sodium and hydrogen, and how they compare with a continuous spectrum. Notice that the spectra of these elements are quite different. In fact, each element has its own unique atomic spectrum that is as characteristic as a fingerprint, and can be used to produce fireworks as in the photo on page 250.

☐ Atoms of an element can also be excited by adding them to the flame of a Bunsen burner.

☐ An emission spectrum is also called a **line spectrum** because the light corresponding to the individual emissions appears as lines on the screen.

☐ Characteristic emissions from these substances add the color to modern fireworks: strontium for red; sodium for yellow; barium for green; copper for blue; charcoal for gold and burning titanium, aluminum or magnesium for silver and white.

A simple pattern of lines in the spectrum of hydrogen suggests a simple explanation for atomic spectra

The first success in explaining atomic spectra quantitatively came with the study of the spectrum of hydrogen. This is the simplest element, since its atoms have only one electron, and it produces the simplest spectrum with the fewest lines.

The atomic spectrum of hydrogen actually consists of several series of lines. One series is in the visible region of the electromagnetic spectrum and is shown in Figure 7.7*c*. Another series is in the ultraviolet region, and the rest are in the infrared. In 1885, J. J. Balmer found an equation that was able to give the wavelengths of the lines in the visible portion of the spectrum. This was soon extended to a more general equation, called the **Rydberg equation,** that could be used to calculate the wavelengths of *all* the spectral lines of hydrogen.

$$\text{Rydberg equation:} \qquad \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^{\,2}} - \frac{1}{n_2^{\,2}}\right)$$

The symbol λ stands for the wavelength, R_H is the Rydberg constant (109,678 cm^{-1}), and n_1 and n_2 are variables whose values are whole numbers that range from 1 to ∞. The only

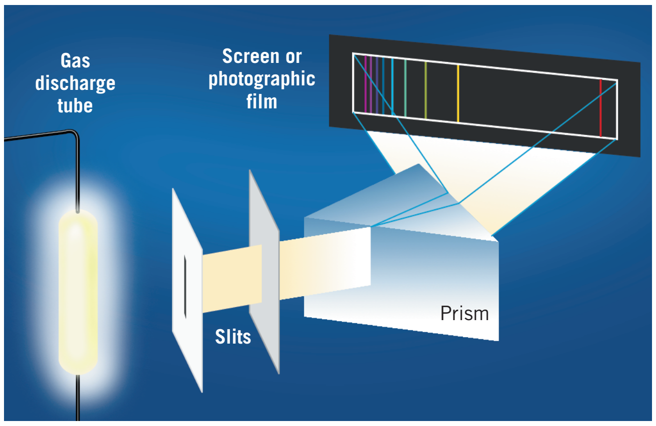


FIG. 7.6 Production and observation of an atomic spectrum. Light emitted by excited atoms is formed into a narrow beam by the slits. It then passes through a prism, which divides the light into relatively few narrow beams with frequencies that are characteristic of the particular element that's emitting the light. When these beams fall on a screen, a series of lines is observed, which is why the spectrum is also called a *line spectrum.*

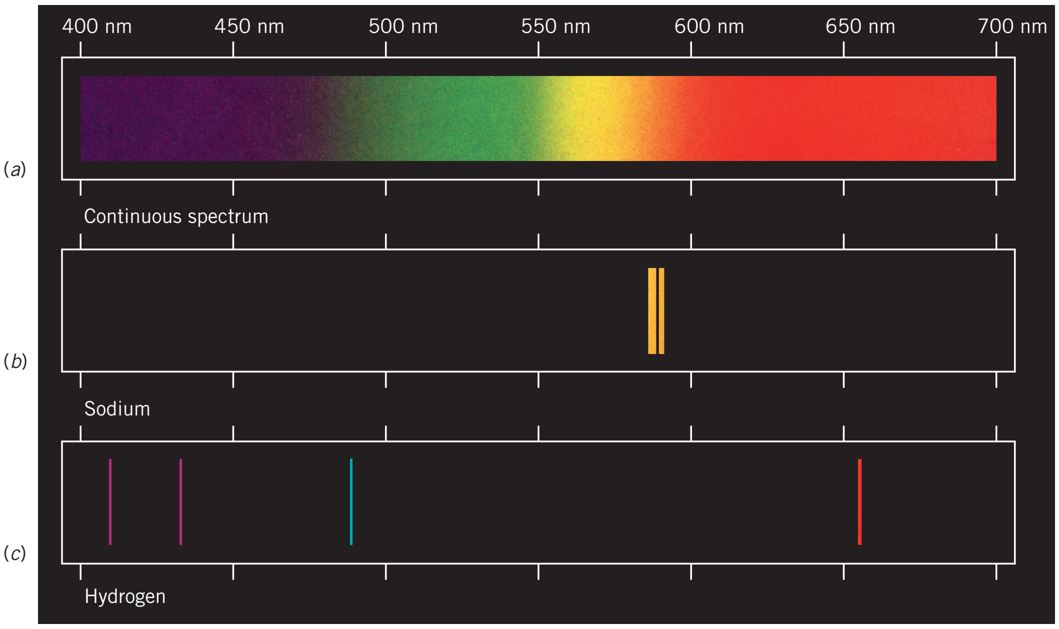


FIG. 7.7 **Continuous and atomic emission spectra.** (*a*) The continuous visible spectrum produced by the sun or an incandescent lamp. (*b*) The atomic spectrum emission produced by sodium. The emission spectrum of sodium actually contains more than 90 lines in the visible region. The two brightest lines are shown here. All the others are less than 1% as bright as these. (*c*) The atomic spectrum (line spectrum) produced by hydrogen. There are only four lines in this visible spectrum. They vary in brightness by only a factor of five, so they are all shown.

restriction is that the value of n_2 must be larger than n_1. (This assures that the calculated wavelength has a positive value.) Thus, if $n_1 = 1$, acceptable values of n_2 are 2, 3, 4, . . . , ∞. The Rydberg constant is an *empirical constant*, which means its value was chosen so that the equation gives values for λ that match the ones determined experimentally. The use of the Rydberg equation is straightforward, as illustrated in the following example.

EXAMPLE 7.3

Calculating the Wavelength of a Line in the Hydrogen Spectrum

The lines in the visible portion of the hydrogen spectrum are called the Balmer series, for which $n_1 = 2$ in the Rydberg equation. Calculate, to four significant figures, the wavelength in nanometers of the spectral line in this series for which $n_2 = 4$.

ANALYSIS: The Rydberg equation will be used for this calculation. The values for n_1 and n_2 are clearly given and the answer is calculated.

SOLUTION: To solve this problem, we substitute values into the Rydberg equation, which will give us $1/\lambda$. Taking the reciprocal will then give the wavelength. As usual, we must be careful with the units.

Substituting $n_1 = 2$ and $n_2 = 4$ into the Rydberg equation gives

$$\begin{aligned}\frac{1}{\lambda} &= 109{,}678\ \text{cm}^{-1}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)\\ &= 109{,}678\ \text{cm}^{-1}\left(\frac{1}{4} - \frac{1}{16}\right)\\ &= 109{,}678\ \text{cm}^{-1}\,(0.2500 - 0.0625)\\ &= 109{,}678\ \text{cm}^{-1}\,(0.1875)\\ &= 2.0565 \times 10^4\ \text{cm}^{-1}\end{aligned}$$

Taking the reciprocal gives the wavelength in centimeters.

$$\lambda = \frac{1}{2.0565 \times 10^4 \text{ cm}^{-1}}$$
$$= 4.8626 \times 10^{-5} \text{ cm}$$

Finally, we convert to nanometers.

$$\lambda = 4.8626 \times 10^{-5} \cancel{\text{cm}} \times \frac{10^{-2} \cancel{\text{m}}}{1 \cancel{\text{cm}}} \times \frac{1 \text{ nm}}{10^{-9} \cancel{\text{m}}}$$
$$= 486.3 \text{ nm}$$

Note that we kept one extra significant figure until the end and then rounded to the desired four significant figures.

IS THE ANSWER REASONABLE? Besides double-checking the arithmetic, we can note that the wavelength falls within the visible region of the spectrum, 400 to 700 nm. We can also check the answer against the experimental spectrum of hydrogen in Figure 7.7*c*. This wavelength corresponds to the turquoise line in the hydrogen spectrum.

Practice Exercise 4: Calculate the wavelength in micrometers, μm, of radiation expected when $n_1 = 4$ and $n_2 = 6$. Report your result to three significant figures. (Hint: The values of n_1 and n_2 are used to calculate the term in parentheses first.)

Practice Exercise 5: Calculate the wavelength in nanometers of the spectral line in the visible spectrum of hydrogen for which $n_1 = 2$ and $n_2 = 3$. What color is this line?

The discovery of the Rydberg equation was both exciting and perplexing. The fact that the wavelength of any line in the hydrogen spectrum can be calculated by a simple equation involving just one constant and the reciprocals of the squares of two whole numbers is remarkable. What is there about the behavior of the electron in the atom that could account for such simplicity?

The energy of electrons in atoms is quantized

Earlier you saw that there is a simple relationship between the frequency of light and its energy, $E = h\nu$. Because excited atoms emit light of only certain specific frequencies, it must be true that only certain characteristic energy changes are able to take place within the atoms. For instance, in the spectrum of hydrogen there is a red line (see Figure 7.7*c*) that has a wavelength of 656.4 nm and a frequency of 4.567×10^{14} Hz. The energy of a photon of this light is 3.026×10^{-19} J. Whenever a hydrogen atom emits red light, the frequency of the light is always precisely 4.567×10^{14} Hz and the energy of the atom decreases by *exactly* 3.026×10^{-19} J, never more and never less. Atomic spectra, then, tell us that *when an excited atom loses energy, not just any arbitrary amount can be lost*. The same is true if the atom gains energy.

How is it that atoms of a given element always undergo exactly the same specific energy changes? The answer seems to be that in an atom an electron can have only certain definite amounts of energy and no others. We say that the electron is restricted to certain **energy levels,** and that the energy of the electron is **quantized.**

The energy of an electron in an atom might be compared to the energy of the tortoise in the exhibit shown in Figure 7.8*b*. The tortoise trapped inside the zoo exhibit can only be "stable" on one of the ledges, so it has certain specific amounts of potential energy as determined by the "energy levels" of the various ledges. If the tortoise is raised to a higher ledge, its potential energy is increased. When it drops to a lower ledge, its potential energy decreases. If the tortoise tries to occupy heights between the ledges, it immediately falls to the lower ledge. Therefore, the energy changes for the tortoise are restricted to the differences in potential energy between the ledges.

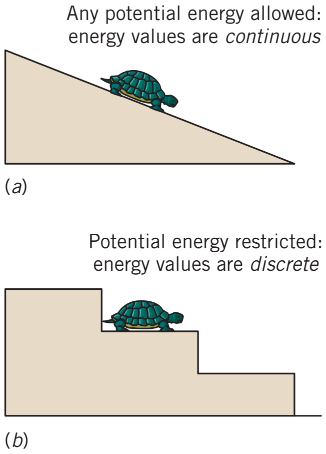


FIG. 7.8 Continuous and discrete energies. (*a*) The tortoise is free to move to any height less than the height of the hill. Its potential energy can take on any value between the maximum (at the hill top) and the minimum (at the bottom). Similarly, the energy of a free electron can take on any value. (*b*) The tortoise trapped inside a zoo exhibit is found only at three heights: at the bottom (the lowest, or *ground state*), middle, or top ledges. The potential energy of the tortoise at rest is quantized. Similarly, the energy of the electron trapped inside an atom is restricted to certain values, which correspond to the various energy levels in an atom.

So it is with an electron in an atom. The electron can only have energies corresponding to the set of electron energy levels in the atom. When the atom is supplied with energy (by an electric discharge, for example), an electron is raised from a low-energy level to a higher one. When the electron drops back, energy equal to the difference between the two levels is released and emitted as a photon. Because only certain energy jumps can occur, only certain frequencies of light can appear in the spectrum.

The existence of specific energy levels in atoms, as implied by atomic spectra, forms the foundation of all theories about electronic structure. Any model of the atom that attempts to describe the positions or motions of electrons must also account for atomic spectra.

The Bohr model explains the simple pattern of lines seen in the spectrum of hydrogen

The first theoretical model of the hydrogen atom that successfully accounted for the Rydberg equation was proposed in 1913 by Niels Bohr (1885–1962), a Danish physicist. In his model, Bohr likened the electron moving around the nucleus to a planet circling the sun. He suggested that the electron moves around the nucleus along fixed paths, or orbits. His model broke with the classical laws of physics by placing restrictions on the sizes of the orbits and the energy that the electron could have in a given orbit. This ultimately led Bohr to an equation that described the energy of the electron in the atom. The equation includes a number of physical constants such as the mass of the electron, its charge, and Planck's constant. It also contains an integer, n, that Bohr called a **quantum number.** Each of the orbits is identified by its value of n. When all the constants are combined, Bohr's equation becomes

- Niels Bohr won the 1922 Nobel Prize in Physics for his work on atomic structure.
- Classical physical laws, such as those discovered by Isaac Newton, place no restrictions on the sizes or energies of orbits.

$$E = \frac{-b}{n^2} \tag{7.3}$$

where E is the energy of the electron and b is the combined constant (its value is 2.18×10^{-18} J). The allowed values of n are whole numbers that range from 1 to ∞ (i.e., n could equal 1, 2, 3, 4, . . ., ∞). From this equation the energy of the electron in any particular orbit could be calculated.

- Bohr's equation for the energy actually is

$$E = -\frac{2\pi^2 me^4}{n^2h^2}$$

where m is the mass of the electron, e is the charge on the electron, n is the quantum number, and h is Planck's constant. Therefore, in Equation 7.3,

$$b = -\frac{2\pi^2 me^4}{h^2} = 2.18 \times 10^{-18}\text{ J.}$$

Because of the negative sign in Equation 7.3, the lowest (most negative) energy value occurs when $n = 1$, which corresponds to the *first Bohr orbit*. The lowest energy state of an atom is the most stable one and is called the **ground state.** For hydrogen, the ground state occurs when its electron has $n = 1$. According to Bohr's theory, this orbit brings the electron closest to the nucleus. Conversely, an atom with $n = \infty$ would correspond to an "unbound" electron that had escaped from the nucleus. Such an electron has an energy of zero in Bohr's theory. The negative sign in Equation 7.3 ensures that any electron with a finite value of n has a lower energy than an unbound electron. Thus, energy is released when a free electron is bound to a proton to form a hydrogen atom.

When a hydrogen atom absorbs energy, as it does when an electric discharge passes through it, the electron is raised from the orbit having $n = 1$ to a higher orbit, to $n = 2$ or $n = 3$ or even higher. The hydrogen atom is now in an excited state. These higher orbits are less stable than the lower ones, so the electron quickly drops to a lower orbit. When this happens, energy is emitted in the form of light (see Figure 7.9). Since the energy of the electron in a given orbit is fixed, a drop from one particular orbit to another, say, from $n = 2$ to $n = 1$, always releases the same amount of energy, and the frequency of the light emitted because of this change is always precisely the same.

The success of Bohr's theory was in its ability to account for the Rydberg equation. When the atom emits a photon, an electron drops from a higher initial energy E_{high} to a lower final energy E_{low}. If the initial quantum number of the electron is n_{high} and the final quantum number is n_{low}, then the energy change, calculated as a positive quantity, is

$$\Delta E = E_{\text{high}} - E_{\text{low}} = \left(\frac{-b}{{n_{\text{high}}}^2}\right) - \left(\frac{-b}{{n_{\text{low}}}^2}\right)$$

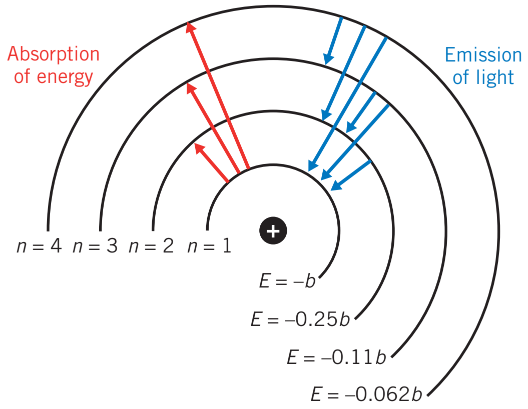


FIG. 7.9 **Absorption of energy and emission of light by the hydrogen atom.** When the atom absorbs energy, the electron is raised to a higher energy level. When the electron falls to a lower energy level, light of a particular energy and frequency is emitted.

This can be rearranged to give

$$\Delta E = b\left(\frac{1}{{n_{\text{low}}}^2} - \frac{1}{{n_{\text{high}}}^2}\right) \qquad \text{with } n_{\text{high}} > n_{\text{low}}$$

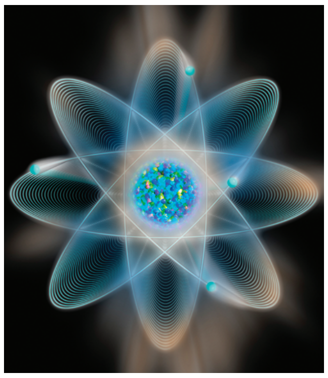
By combining Equations 7.1 and 7.2, the relationship between the energy "ΔE" of a photon and its wavelength λ is

$$\Delta E = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right)$$

Substituting and solving for $1/\lambda$ give

$$\frac{1}{\lambda} = \frac{b}{hc}\left(\frac{1}{{n_{\text{low}}}^2} - \frac{1}{{n_{\text{high}}}^2}\right) \qquad \text{with } n_{\text{high}} > n_{\text{low}}$$

Notice how closely this equation derived from Bohr's theory matches the Rydberg equation, which was obtained solely from the experimentally measured atomic spectrum of hydrogen. Equally satisfying is that the combination of constants, b/hc, has a value of 109,730 cm^{-1}, which differs by only 0.05% from the experimentally derived value of R_H in the Rydberg equation.



The solar system model of the atom was the way that Niels Bohr's model was presented to the public. Today this simple picture of the atom makes a nice corporate logo, but the idea of an atom with electrons orbiting a nucleus as planets orbit a sun has been replaced by the wave mechanical model.

The Bohr model fails for atoms with more than one electron

Bohr's model of the atom was both a success and a failure. By calculating the energy changes that occur between energy levels, Bohr was able to account for the Rydberg equation and, therefore, for the atomic spectrum of hydrogen. However, the theory was not able to explain quantitatively the spectra of atoms with more than one electron, and all attempts to modify the theory to make it work met with failure. Gradually, it became clear that Bohr's picture of the atom was flawed and that another theory would have to be found. Nevertheless, the concepts of quantum numbers and fixed energy levels were important steps forward.

7.3 ELECTRONS HAVE PROPERTIES OF BOTH PARTICLES AND WAVES

Bohr's efforts to develop a theory of electronic structure were doomed from the very beginning because the classical laws of physics—those known in his day—simply do not apply to objects as small as the electron. Classical physics fails for atomic particles because matter is not really as our physical senses perceive it. When bound inside an atom, electrons behave not like solid particles, but instead like waves. This idea was proposed in 1924 by a young French graduate student, Louis de Broglie.

- All the objects that had been studied by scientists until the time of Bohr were large and massive in comparison with the electron, so no one had detected the limits of classical physics.

- De Broglie was awarded a Nobel prize in 1929.

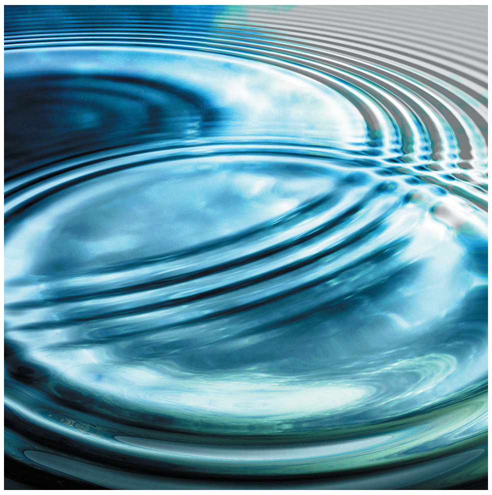


FIG. 7.10 Diffraction of water waves on the surface of a pond. As the waves cross, the amplitudes increase where the waves are in phase and cancel where they are out of phase. *(Mandy Collins/Alamy Images.)*

Gigantic waves, called rogue waves, with heights up to 100 ft have been observed in the ocean and are believed to be formed when a number of wave sets moving across the sea become in phase simultaneously.

In Section 7.1 you learned that light waves are characterized by their wavelengths and their frequencies. The same is true of matter waves. De Broglie suggested that the wavelength of a matter wave, λ is given by the equation

$$\lambda = \frac{h}{mv} \tag{7.4}$$

where h is Planck's constant, m is the particle's mass, and v is its velocity. Notice that this equation allows us to connect a wave property, wavelength, with particle properties, mass and velocity. We may describe the electron either as a particle or a wave, and the de Broglie relationship provides a link between the two descriptions.

When first encountered, the concept of a particle of matter behaving as a wave rather than as a solid object is difficult to comprehend. This book certainly seems solid enough, especially if you drop it on your toe! The reason for the book's apparent solidity is that in de Broglie's equation (Equation 7.4) the mass appears in the denominator. This means that heavy objects have extremely short wavelengths. The peaks of the matter waves for heavy objects are so close together that the wave properties go unnoticed and can't even be measured experimentally. But tiny particles with very small masses have much longer wavelengths, so their wave properties become an important part of their overall behavior.

Diffraction provides evidence that electrons have wave properties

Perhaps by now you've begun to wonder if there is any way to *prove* that matter has wave properties. Actually, these properties can be demonstrated by a phenomenon that you have probably witnessed. When raindrops fall on a quiet pond, ripples spread out from where the drops strike the water, as shown in Figure 7.10. When two sets of ripples cross, there are places where the waves are *in phase*, which means that the peak of one wave coincides with the peak of the other. At these points the intensities of the waves add and the height of the water is equal to the sum of the heights of the two crossing waves. At other places the crossing waves are *out of phase*, which means the peak of one wave occurs at the trough of the other. In these places the intensities of the waves cancel. This reinforcement and cancellation of wave intensities, referred to, respectively, as *constructive* and *destructive interference*, is a phenomenon called **diffraction.** It is examined more closely in Figure 7.11. Note how diffraction creates characteristic **interference fringes** when waves pass through adjacent pinholes or reflect off closely spaced grooves. You have seen interference fringes yourself if you've ever noticed the rainbow of colors that shine from the surface of a compact disc (Figure 7.12). When white light, which contains all the visible wavelengths,

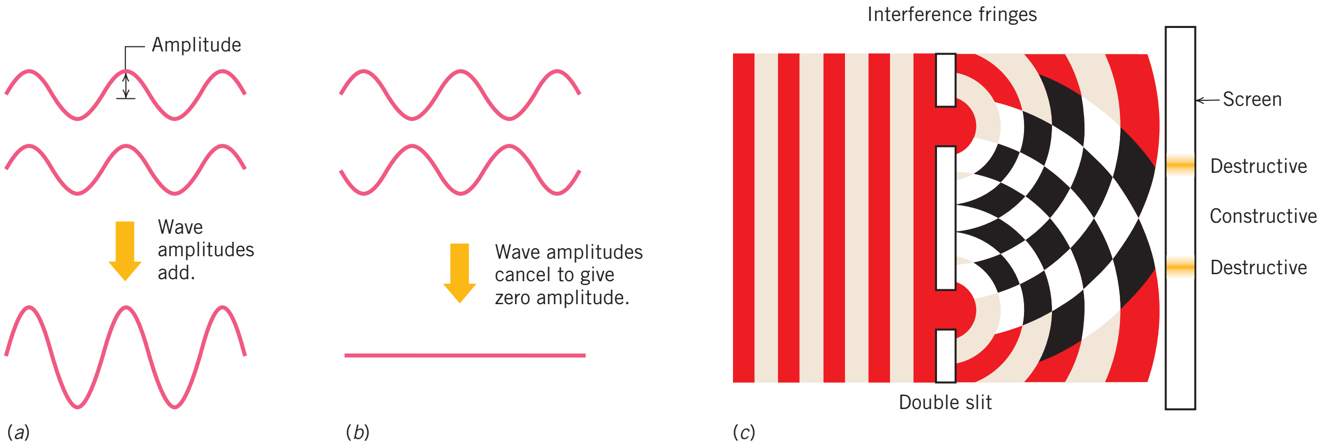


FIG. 7.11 Constructive and destructive interference. (*a*) Waves in phase produce constructive interference and an increase in intensity. (*b*) Waves out of phase produce destructive interference and yield cancellation of intensity. (*c*) Light waves passing through two pinholes fan out and interfere with each other, producing an interference pattern characteristic of waves.

FIG. 7.12 Diffraction of light from a compact disc. Colored interference fringes are produced by the diffraction of reflected light from the closely spaced grooves on the surface of a compact disc. *(John Paul Endress/Corbis Stock Market.)*

is reflected from the closely spaced "grooves" on the CD, it is divided into many individual light beams. For a given angle between the incoming and reflected light, the light waves experience interference with each other for all wavelengths (colors) except for one wavelength which is reinforced. Our eye sees the wavelength of light that is reinforced and as the angle changes the wavelengths that are reinforced change. The result is a rainbow of colors reflected from the CD.

Diffraction is a phenomenon that can only be explained as a property of waves, and we have seen how it can be demonstrated with water waves and light waves. Experiments can also be done to show that electrons, protons, and neutrons experience diffraction, which demonstrates their wave nature (see Figure 7.13). In fact, electron diffraction is the principle on which the electron microscope is based (see Facets of Chemistry 7.3).

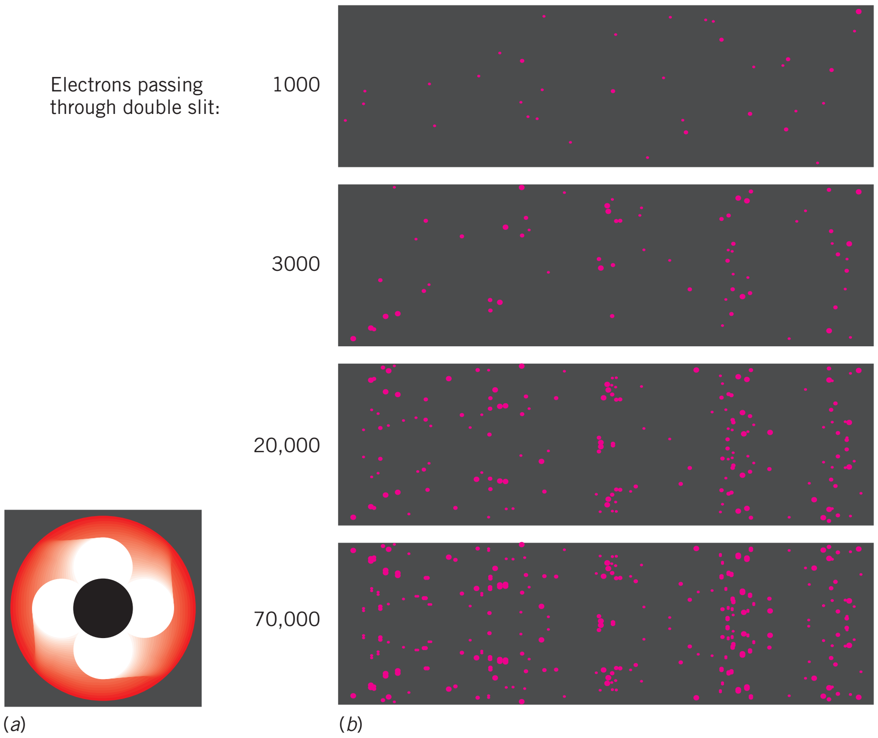


FIG. 7.13 Experimental evidence of wave behavior in electrons. (*a*) An electron diffraction pattern collected by reflecting a beam of electrons from crystalline silicon. (Semiconductor Surface Physics Group, Queens University.) (*b*) Electrons passing *one at a time* through a double slit. Each spot shows an electron impact on a detector. As more and more electrons are passed through the slits, interference fringes are observed.

Bound electrons have quantized energies because they behave like standing waves

Before we can discuss how electron waves behave in atoms, we need to know a little more about waves in general. There are basically two kinds of waves, **traveling waves** and **standing waves**. On a lake or ocean the wind produces waves whose crests and troughs

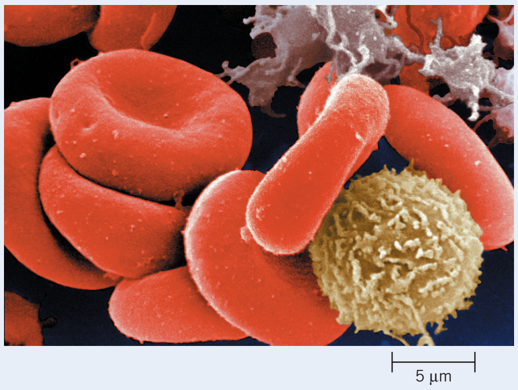
FACETS OF CHEMISTRY 7.3

The Electron Microscope

The usefulness of a microscope in studying small specimens is limited by its ability to distinguish between closely spaced objects. We call this ability the *resolving power* of the microscope. Through optics, it is possible to increase the magnification and thereby increase the resolving power, but only within limits. These limits depend on the wavelength of the light that is used. Objects with diameters less than the wavelength of the light cannot be seen in detail. Since the smallest wavelength of visible light is about 400 nm, objects smaller than this can't be clearly seen with a microscope that uses visible light.

The electron microscope uses electron waves to "see" very small objects.

De Broglie's equation, $\lambda = h/mv$, suggests that if an electron, proton, or neutron has a very high velocity, its wavelength will be very small. In the electron microscope, electrons are accelerated to high speeds across high-voltage electrodes. This gives electron waves with typical wavelengths of about 0.006 to 0.001 nm that strike the sample and are then focused magnetically (using "magnetic lenses") onto a fluorescent screen where they form a visible image. Because of certain difficulties, the actual resolving power of the instrument is quite a bit less than the wavelength of the electron waves—generally on the order of 6 to 1 nm. Some high resolution electron microscopes, however, are able to reveal the shadows of individual atoms in very thin specimens through which the electron beam passes.



A modern electron microscope operated by trained technicians is used to obtain electron-micrographs such as the one shown here depicting red and white blood cells. *(Brand X/Superstock; Yorgos Nikas/Stone/Getty Images.)*

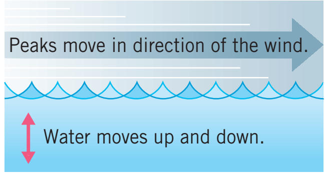


FIG. 7.14 Traveling waves.

move across the water's surface, as shown in Figure 7.14. The water moves up and down while the crests and troughs travel horizontally in the direction of the wind. These are examples of **traveling waves.**

A more important kind of wave for us is the standing wave. An example is the vibrating string of a guitar. When the string is plucked, its center vibrates up and down while the ends, of course, remain fixed. The crest, or point of maximum amplitude of the wave, occurs at one position. At the ends of the string are points of zero amplitude, called **nodes,** and their positions are also fixed. A **standing wave,** then, is one in which the crests and nodes do not change position. One of the interesting things about standing waves is that they lead naturally to "quantum numbers." Let's see how this works using the guitar as an example.

As you know, many notes can be played on a guitar string by shortening its effective length with a finger placed at frets along the neck of the instrument. But even without shortening the string, we can play a variety of notes. For instance, if the string is touched momentarily at its midpoint at the same time it is plucked, the string vibrates as shown in Figure 7.15 and produces a tone an octave higher. The wave that produces this higher tone has a wavelength exactly half of that formed when the untouched string is plucked. In Figure 7.15 we see that other wavelengths are possible, too, and each gives a different note.

Notes played this way are called harmonics.

If you examine Figure 7.15, you will see that there are some restrictions on the wavelengths that can exist. Not just any wavelength is possible because the nodes at either end of the string are in fixed positions. The only waves that can occur are those for which a half-wavelength is repeated *exactly* a whole number of times. Expressed another way, the

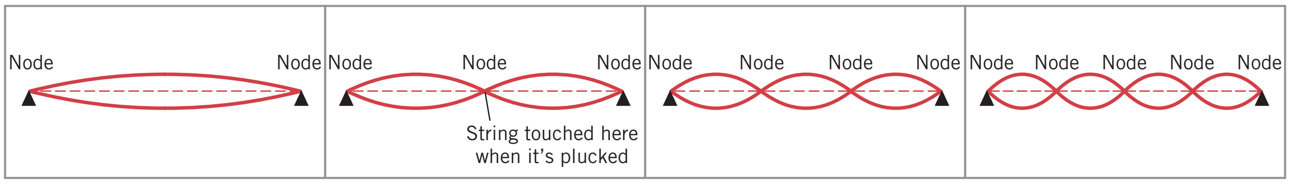


FIG. 7.15 **Standing waves on a guitar string.**

length of the string is a whole-number multiple of half-wavelengths. In a mathematical form we could write this as

$$L = n\left(\frac{\lambda}{2}\right)$$

where L is the length of the string, λ is a wavelength (therefore, $\lambda/2$ is half the wavelength), and n is an integer. Rearranging this to solve for the wavelength gives

$$\lambda = \frac{2L}{n} \tag{7.5}$$

We see that the waves that are possible are determined quite naturally by a set of whole numbers (similar to quantum numbers).

We are now in a position to demonstrate how quantum theory unites wave and particle descriptions to build a simple but accurate model of a bound electron. Let's look at an electron that is confined to a wire of length L. To keep things simple, let's assume that the wire is infinitely thin, so that the electron can only move in straight lines along the wire. The wire is clamped in place at either end, and its ends cannot move up or down.

First, let's consider a classical particle model: the "bead on a wire" model shown in Figure 7.16*a*. The bead can slide in either direction along the wire, like a bead on an abacus. If the electron's mass is m and its velocity is v, its kinetic energy is given by

$$E = \frac{1}{2}mv^2$$

The bead can have any velocity, even zero, so the energy E can have any value, even zero. No position on the wire is any more favorable than any other, and the bead is equally likely to be found anywhere on the wire. There is no reason why the bead's position and velocity cannot be known simultaneously.

Now consider a classical wave along the wire, Figure 7.16*b*. It is exactly like the guitar string we looked at in Figure 7.15. The ends of the wire are clamped in place, so there *must* be a whole number of peaks and troughs along the wire. The wavelength is restricted to values calculated by Equation 7.5. We can see that the quantum number, n, is just the number of peaks and troughs along the wave. It has integer values (1, 2, 3, . . .) because you can't have half a peak or half a trough.

Notes played on a guitar rely on standing waves. The ends of the strings correspond to nodes of the standing waves. Different notes can be played by shortening the effective lengths of the strings with fingers placed along the neck of the instrument. *(© Index Stock.)*

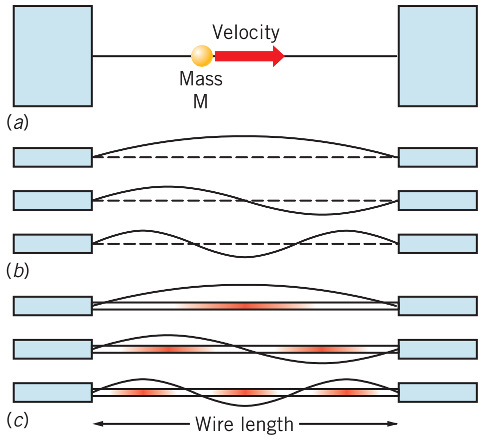


FIG. 7.16 **Three models of an electron on an infinitely thin wire of length L.** (*a*) A classical model of the electron as a bead that can slide along the wire. Any energy is possible, even zero, and the exact position and velocity of the bead can be known simultaneously. (*b*) A classical model of the electron as a standing wave on a wire. An integer number of peaks and troughs (n) is required. The wavelength is restricted to values given by Equation 7.5. (*c*) A quantum mechanical model of the electron on a wire obtained by uniting model (*a*) with model (*b*), using the de Broglie relationship (Equation 7.4). The shaded areas indicate most probable positions for the electron. Energy is quantized and is never zero.

Now let's use the de Broglie relation, Equation 7.4, to unite these two classical models. Our goal is to derive an expression for the energy of an electron trapped on the wire. Notice that to calculate the kinetic energy of the bead on a wire, we need to know its velocity, a particle property. The de Broglie relation lets us relate particle velocities with wavelengths. Rearranging Equation 7.4, we have

$$v = \frac{h}{m\lambda}$$

and inserting this into the equation for kinetic energy gives

$$\begin{aligned} E &= \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 \\ &= \frac{h^2}{2m\lambda^2} \end{aligned}$$

This equation will give us the energy of the electron from its wavelength. If we substitute in Equation 7.5, which gives the wavelength of the standing wave in terms of the wire length L and the quantum number n, we have

$$E = \frac{n^2h^2}{8mL^2} \tag{7.6}$$

This equation has a number of profound implications. The fact that the electron's energy depends on an integer, n, means that *only certain energy states are allowed.* The allowed states are plotted on the energy level diagram shown in Figure 7.17. The lowest value of n is 1, so the lowest energy level (the ground state) is $E_1 = h^2/8mL^2$. Energies lower than this are not allowed, so the energy cannot be zero! This indicates that the electron will always have some residual kinetic energy. The electron is never at rest. This is true for the electron trapped in a wire and it is also true for an electron trapped in an atom. Thus, *quantum theory resolves the collapsing atom paradox.*

Note that the spacing between energy levels is proportional to $1/L^2$. This means that when the wire is made longer, the energy levels become more closely spaced. In general, *the more room an electron has to move in, the smaller the spacings between its energy levels.* Chemical reactions sometimes change the way that electrons are confined in molecules. This causes changes in the wavelengths of light the reacting mixture absorbs. This is why color changes sometimes occur during chemical changes.

Electron waves are represented by wave functions

The wave that corresponds to the electron is called a **wave function.** The wave function is usually represented by the symbol ψ (Greek letter psi). The wave function can be used to describe the shape of the electron wave and its energy. The wave function is not an

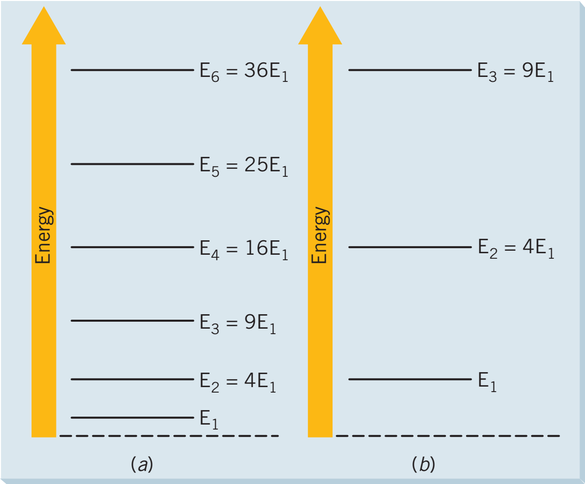


FIG. 7.17 Energy level diagram for the electron on a wire model. (*a*) A long wire, with $L = 2$ nm, and (*b*) a short wire, with $L = 1$ nm. Notice how the energy levels become more closely spaced when the electron has more room to move. Also notice that the energy in the ground state is not zero.

oscillation of the wire, like a guitar wave, nor is it an electromagnetic wave. The wave's amplitude at any given point can be related to the probability of finding the electron there.

The electron waves shown in Figure 7.16*c* show that, unlike the bead on a wire model, the electron is more likely to be found at some places on the wire than others. For the ground state, with $n = 1$, the electron is most likely to be found in the center of the wire. Where the amplitude is zero, for example, at the ends of the wire or the center of the wire in the $n = 2$ state, there is a zero probability of finding the electron! Points where the amplitude of the electron wave is zero are called **nodes.** Notice that the higher the quantum number n, the more nodes the electron wave has and, from Equation 7.6, the more energy the electron has. It is generally true that *the more nodes an electron wave has, the higher its energy.*

- The probability of finding an electron at a given point is proportional to the amplitude of the electron wave squared. Thus, peaks and troughs in the electron wave indicate places where there is the greatest buildup of negative charge.

Electron waves in atoms are called orbitals

In 1926 Erwin Schrödinger (1887–1961), an Austrian physicist, became the first scientist to successfully apply the concept of the wave nature of matter to an explanation of electronic structure. His work and the theory that developed from it are highly mathematical. Fortunately, we need only a qualitative understanding of electronic structure, and the main points of the theory can be understood without all the math.

- Schrödinger won a Nobel prize in 1933 for his work. The equation he developed that gives electronic wave functions and energies is known as *Schrödinger's equation.* The equation is extremely difficult to solve. Even an approximate solution of the equation for large molecules can require hours or days of supercomputer time.

Schrödinger developed an equation that can be solved to give wave functions and energy levels for electrons trapped inside atoms. Wave functions for electrons in atoms are called **orbitals.** Not all of the energies of the waves are different, but most are. *Energy changes within an atom are simply the result of an electron changing from a wave pattern with one energy to a wave pattern with a different energy.*

- Electron waves are described by the term *orbital* to differentiate them from the notion of *orbits,* which was part of the Bohr model of the atom.

We will be interested in two properties of orbitals, their energies and their shapes. Their energies are important because when an atom is in its most stable state (its *ground state*), the atom's electrons have waveforms with the lowest possible energies. The shapes of the wave patterns (i.e., where their amplitudes are large and where they are small) are important because the theory tells us that the amplitude of a wave at any particular place is related to the likelihood of finding the electron there. This will be important when we study how and why atoms form chemical bonds to each other.

- "Most stable" almost always means "lowest energy."

In much the same way that the characteristics of a wave on a one-dimensional guitar string can be related to a single integer, wave mechanics tells us that the three-dimensional electron waves (orbitals) can be characterized by a set of *three* integer quantum numbers, n, ℓ, and m_ℓ. In discussing the energies of the orbitals, it is usually most convenient to sort the orbitals into groups according to these quantum numbers.

The principal quantum number, *n*

The quantum number $\boldsymbol{n}$ is called the **principal quantum number,** and all orbitals that have the same value of n are said to be in the same **shell.** The values of n can range from $n = 1$ to $n = \infty$. The shell with $n = 1$ is called the *first shell,* the shell with $n = 2$ is the *second shell,* and so forth. The various shells are also sometimes identified by letters, beginning (for no significant reason) with K for the first shell ($n = 1$).

- The term shell comes from an early notion that atoms could be thought of as similar to onions, with the electrons being arranged in layers around the nucleus.

The principal quantum number is related to the size of the electron wave (i.e., how far the wave effectively extends from the nucleus). The higher the value of n, the larger is the electron's average distance from the nucleus. This quantum number is also related to the energy of the orbital. As n increases, the energies of the orbitals also increase.

Bohr's theory took into account only the principal quantum number n. His theory worked fine for hydrogen because hydrogen just happens to be the one element in which all orbitals having the same value of n also have the same energy. Bohr's theory failed for atoms other than hydrogen, however, because when the atom has more than one electron, orbitals with the same value of n can have different energies.

- Bohr was fortunate to have used the element hydrogen to develop his model of the atom. If he had chosen a different element, his model would not have worked.

The secondary quantum number, ℓ

The **secondary quantum number, $\boldsymbol{\ell}$,** divides the shells into smaller groups of orbitals called **subshells.** The value of n determines which values of ℓ are allowed. For a given n, ℓ can range from $\ell = 0$ to $\ell = (n - 1)$. Thus, when $n = 1$, $(n - 1) = 0$, so the only value of ℓ that's allowed is zero. This means that when $n = 1$, there is only one subshell (the shell and subshell are really identical). When $n = 2$, ℓ can have values of 0 or 1. (The maximum value

- ℓ is also called the **azimuthal quantum number** and the **orbital angular momentum number.**

of $\ell = n - 1 = 2 - 1 = 1$.) This means that when $n = 2$, there are two subshells. One has $n = 2$ and $\ell = 0$, and the other has $n = 2$ and $\ell = 1$. The relationship between n and the allowed values of ℓ are summarized in the table in the margin.

Relationship between n and ℓ

Value of n	Values of ℓ
1	0
2	0, 1
3	0, 1, 2
4	0, 1, 2, 3
5	0, 1, 2, 3, 4
n	0, 1, 2, ..., $(n - 1)$

Subshells could be identified by their value of ℓ. However, to avoid confusing numerical values of n with those of ℓ, a letter code is normally used to specify the value of ℓ.

Value of ℓ	0	1	2	3	4	5	...
Letter designation	*s*	*p*	*d*	*f*	*g*	*h*	...

To designate a particular subshell, we write the value of its principal quantum number followed by the letter code for the subshell. For example, the subshell with $n = 2$ and $\ell = 1$ is the 2*p* subshell; the subshell with $n = 4$ and $\ell = 0$ is the 4*s* subshell. Notice that because of the relationship between n and ℓ, every shell has an *s* subshell (1*s*, 2*s*, 3*s*, etc.). All the shells except the first have a *p* subshell (2*p*, 3*p*, 4*p*, etc.). All but the first and second shells have a *d* subshell (3*d*, 4*d*, etc.); and so forth.

☐ The number of subshells in a given shell equals the value of n for that shell. For example, when $n = 3$, there are three subshells.

Practice Exercise 6: How many subshells are there in each of the first six shells of an atom? (Hint: Count the subshells based on sets of groups representing *s*, *p*, *d*, and *f* orbitals.)

Practice Exercise 7: What subshells would be found in the shells with $n = 3$ and $n = 4$?

The secondary quantum number determines the shape of the orbital, which we will examine more closely later. Except for the special case of hydrogen, which has only one electron, the value of ℓ also affects the energy. This means that in atoms with two or more electrons, the subshells within a given shell differ slightly in energy, with the energy of the subshell increasing with increasing ℓ. Therefore, within a given shell, the *s* subshell is lowest in energy, *p* is the next lowest, followed by *d*, then *f*, and so on. For example,

$$\underset{\text{— increasing energy} \rightarrow}{4s < 4p < 4d < 4f}$$

The magnetic quantum number, m_ℓ

The third quantum number, $\boldsymbol{m_\ell}$, is known as the **magnetic quantum number.** Its value indicates individual orbitals within a subshell. Also, its values are related to the way the individual orbitals are oriented relative to each other in space. As with ℓ, there are restrictions as to the possible values of m_ℓ, which can range from $+\ell$ to $-\ell$. When $\ell = 0$, m_ℓ can have only the value 0 because $+0$ and -0 are the same. An *s* subshell, then, has just a single orbital. When $\ell = 1$, the possible values of m_ℓ are $+1$, 0, and -1. A *p* subshell therefore has three orbitals: one with $\ell = 1$ and $m_\ell = 1$, another with $\ell = 1$ and $m_\ell = 0$, and a third with $\ell = 1$ and $m_\ell = -1$. Similarly, we find that a *d* subshell has five orbitals and an *f* subshell has seven orbitals. The numbers of orbitals in the subshells are easy to remember because they follow a simple arithmetic progression.

☐ Spectroscopists used m_ℓ to explain additional lines that appear in atomic spectra when atoms emit light while in a magnetic field, which explains how this quantum number got its name.

s	*p*	*d*	*f*	. . .
1	3	5	7	. . .

The whole picture

The relationships among all three quantum numbers are summarized in Table 7.1. In addition, the relative energies of the subshells in an atom containing two or more electrons are depicted in Figure 7.18. Several important features should be noted. First, observe that each orbital on this energy diagram is indicated by a separate circle—one for an *s* subshell, three for a *p* subshell, and so forth. Second, notice that all the orbitals of a given subshell have the *same* energy. Third, note that, in going upward on the energy scale, the spacing between successive shells decreases as the number of subshells increases. This leads to some overlapping of shells having different values of *n*. For instance, the 4*s* subshell is lower in energy than the 3*d* subshell, 5*s* is lower than 4*d*, and 6*s* is lower than 5*d*. In addition, the 4*f* subshell is below the 5*d* subshell and 5*f* is below 6*d*.

TABLE 7.1 **Summary of Relationships among the Quantum Numbers n, ℓ, and m_ℓ**

Value of n	Value of ℓ	Values of m_ℓ	Subshell	Number of Orbitals
1	0	0	1*s*	1
2	0	0	2*s*	1
	1	−1, 0, 1	2*p*	3
3	0	0	3*s*	1
	1	−1, 0, 1	3*p*	3
	2	−2, −1, 0, 1, 2	3*d*	5
4	0	0	4*s*	1
	1	−1, 0, 1	4*p*	3
	2	−2, −1, 0, 1, 2	4*d*	5
	3	−3, −2, −1, 0, 1, 2, 3	4*f*	7

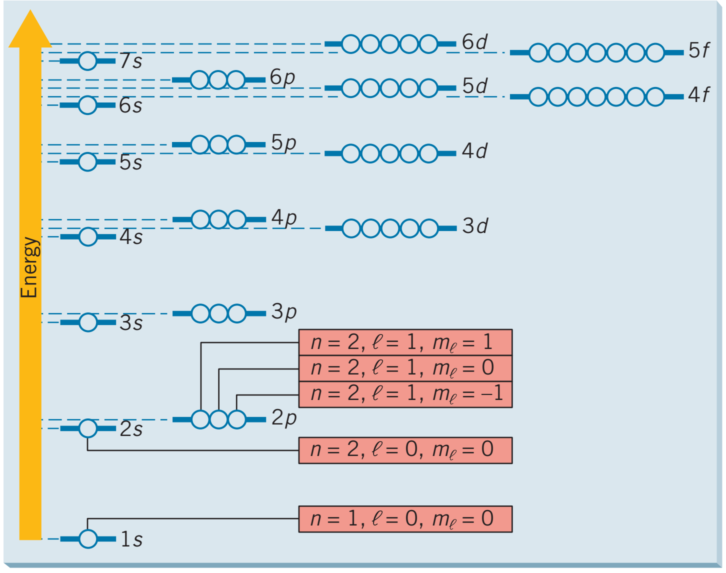


FIG. 7.18 **Approximate energy level diagram for atoms with two or more electrons.** The quantum numbers associated with the orbitals in the first two shells are also shown.

We will see shortly that Figure 7.18 is very useful for predicting the electronic structures of atoms. Before discussing this, however, we must study another very important property of the electron, a property called spin. Electron spin gives rise to a fourth quantum number.

In an atom, an electron can take on many different energies and waveshapes, each of which is called an orbital that is identified by a set of values for n, ℓ, and m_ℓ. When the electron wave possesses a given set of n, ℓ, and m_ℓ, we say the electron "occupies the orbital" with that set of quantum numbers.

7.4 ELECTRON SPIN AFFECTS THE DISTRIBUTION OF ELECTRONS AMONG ORBITALS IN ATOMS

Earlier it was stated that an atom is in its most stable state (its ground state) when its electrons have the lowest possible energies. This occurs when the electrons "occupy" the lowest energy orbitals that are available. But what determines how the electrons "fill" these orbitals? Fortunately, there are some simple rules that can help. These govern both the maximum number of electrons that can be in a particular orbital and how orbitals with the same energy become filled. One important factor that influences the distribution of electrons is the phenomenon known as *electron spin*.

Electrons behave like tiny charges that can spin in one of two directions

When a beam of atoms with an odd number of electrons is passed through an uneven magnetic field, the beam is split in two, as shown in Figure 7.19. The splitting occurs because the electrons within the atoms interact with the magnetic field in two different ways. The electrons behave like tiny magnets, and they are attracted to one or the other of the poles depending on their orientation. This can be explained by imagining that an electron spins around its axis, like a toy top. A moving charge creates a moving electric field, which in

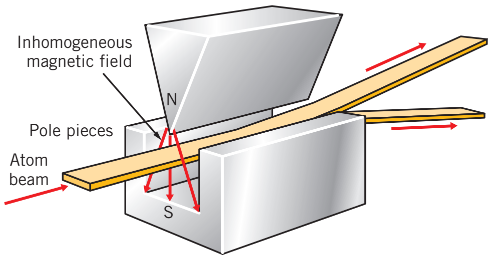


FIG. 7.19 **The discovery of electron spin.** In this classic experiment by Stern and Gerlach, a beam of atoms with an odd number of electrons is passed through an uneven magnetic field, created by magnet pole faces of different shapes. The beam splits in two, indicating that the electrons in the atoms behave as tiny magnets, which are attracted to one or the other of the poles depending on their orientation. "Electron spin" was proposed to account for the two possible orientations for the electron's magnetic field.

turn creates a magnetic field. The spinning electrical charge of the electron creates its own magnetic field. This **electron spin** could occur in two possible directions, which accounted for the two beams.

Electron spin gives us a fourth quantum number for the electron, called the **spin quantum number, m_s,** which can take on two possible values: $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$, corresponding to the two beams in Figure 7.19. The actual values of m_s and the reason they are not integers aren't very important to us, but the fact that there are *only* two values is very significant.

▫ Electrons don't actually spin. We've seen that electrons are not simply particles. But the magnetic properties of electrons are just what we'd see if the electron were a spinning charged particle, and it is useful to picture the electron as spinning.

No two electrons in an atom have identical sets of quantum numbers

In 1925 an Austrian physicist, Wolfgang Pauli (1900–1958), expressed the importance of electron spin in determining electronic structure. The **Pauli exclusion principle** states that *no two electrons in the same atom can have identical values for all four of their quantum numbers.* To understand the significance of this, suppose two electrons were to occupy the 1*s* orbital of an atom. Each electron would have $n = 1$, $\ell = 0$, and $m_\ell = 0$. Since these three quantum numbers are the same for both electrons, the exclusion principle requires that their fourth quantum numbers (their spin quantum numbers) be different; one electron must have $m_s = +\frac{1}{2}$ and the other, $m_s = -\frac{1}{2}$. No more than two electrons can occupy the 1*s* orbital of the atom simultaneously because there are only two possible values of m_s. Thus the Pauli exclusion principle is really telling us that *the maximum number of electrons in any orbital is two*, and that *when two electrons are in the same orbital, they must have opposite spins.*

▫ Pauli received the 1945 Nobel Prize in Physics for his discovery of the exclusion principle.

The limit of two electrons per orbital also limits the maximum electron populations of the shells and subshells. For the subshells we have

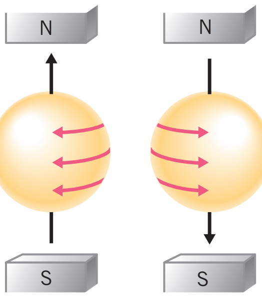
Subshell	Number of Orbitals	Maximum Number of Electrons
s	1	2
p	3	6
d	5	10
f	7	14

▫ Remember that a shell is a group of orbitals with the same value of *n*. A subshell is a group of orbitals with the same values of *n* and ℓ.

The maximum electron population per shell is shown below.

Shell	Subshells	Maximum Shell Population	
1	1*s*	2	
2	2*s* 2*p*	8	(2 + 6)
3	3*s* 3*p* 3*d*	18	(2 + 6 + 10)
4	4*s* 4*p* 4*d* 4*f*	32	(2 + 6 + 10 + 14)

This trend shows that the maximum electron population of a shell is $2n^2$.



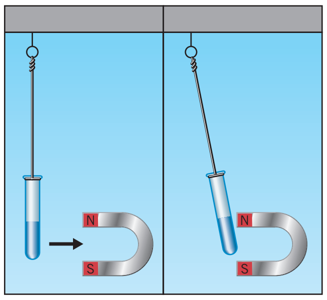
The electron can spin in either of two directions in the presence of an external magnetic field.

Atoms with unpaired electrons are weakly attracted to magnets

We have seen that when two electrons occupy the same orbital they must have different values of m_s. When this occurs, we say that the spins of the electrons are *paired*, or simply that the electrons are *paired*. Such pairing leads to the cancellation of the magnetic effects of the electrons because the north pole of one electron magnet is opposite the south pole of the other. Atoms with more electrons that spin in one direction than in the other are said to contain *unpaired* electrons. For these atoms, the magnetic effects do not cancel and the atoms themselves become tiny magnets that can be attracted to an external magnetic field. This weak attraction of a substance containing unpaired electrons to a magnet indicates that the material is **paramagnetic.** Substances in which all the electrons are paired are not attracted to a magnet and are said to be **diamagnetic.**

□ Diamagnetic substances are actually weakly repelled by a magnetic field.

Paramagnetism and diamagnetism are measurable properties that provide experimental verification of the presence or absence of unpaired electrons in substances. In addition, the quantitative measurement of the strength of the attraction of a paramagnetic substance toward a magnetic field permits the calculation of the number of unpaired electrons in its atoms, molecules, or ions.



A paramagnetic substance is attracted to a magnetic field.

7.5 THE GROUND STATE ELECTRON CONFIGURATION IS THE LOWEST ENERGY DISTRIBUTION OF ELECTRONS AMONG ORBITALS

The distribution of electrons among the orbitals of an atom is called the atom's **electronic structure** or **electron configuration.** This is something very useful to know about an element because the arrangement of electrons in the outer parts of an atom, which is determined by its electron configuration, controls the chemical properties of the element.

We are interested in the ground state electron configurations of the elements. This is the configuration that yields the lowest energy for an atom and can be predicted for many of the elements by the use of the energy level diagram in Figure 7.18 and application of the Pauli exclusion principle. To see how we go about this, let's begin with the simplest atom of all, hydrogen.

Hydrogen has an atomic number, Z, equal to 1, so a neutral hydrogen atom has one electron. In its ground state this electron occupies the lowest energy orbital that's available, which is the $1s$ orbital. To indicate symbolically the electron configuration we list the subshells that contain electrons and indicate their electron populations by appropriate superscripts. Thus the electron configuration of hydrogen is written as

$$\text{H} \qquad 1s^1$$

Another way of expressing electron configurations that we will sometimes find useful is the **orbital diagram.** In it, a circle will represent each orbital and arrows will be used to indicate the individual electrons, head up for spin in one direction and head down for spin in the other. The orbital diagram for hydrogen is simply

$$\text{H} \qquad \underset{1s}{\textcircled{\uparrow}}$$

□ It doesn't matter whether the arrow points up or down. The energy of the electron is the same whether it has one spin or the other. For consistency, when an orbital is half-filled, we will show the electron with an arrow that points up.

Electron configurations are built up by filling lowest energy orbitals first

To arrive at the electron configuration of an atom of another element, we imagine that we begin with a hydrogen atom and then add one proton after another (plus whatever neutrons are also needed) until we obtain the nucleus of the atom of interest. As we proceed, we also must add electrons, one at a time to the lowest available orbital, until we have added enough electrons to give the neutral atom of the element in question. This process for obtaining the electronic structure of an atom is known as the **aufbau principle,** the word *aufbau* being German for "building up."

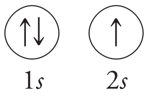
How *s* orbitals fill

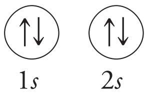
Let's look at the way this works for helium, which has $Z = 2$. This atom has two electrons, both of which are permitted to occupy the $1s$ orbital. The electron configuration and orbital diagram of helium can now be written as

$$\text{He} \qquad 1s^2 \qquad \text{or} \qquad \text{He} \qquad \underset{1s}{\textcircled{\uparrow\downarrow}}$$

Notice that the orbital diagram shows that both electrons in the $1s$ orbital are paired.

We can proceed in the same fashion to predict successfully the electron configurations of most of the elements in the periodic table. For example, the next two elements in the table are lithium, Li ($Z = 3$), and beryllium, Be ($Z = 4$), which have three and four electrons, respectively. For each of these, the first two electrons enter the 1*s* orbital with their spins paired. The Pauli exclusion principle tells us that the 1*s* subshell is filled with two electrons, and Figure 7.18 shows that the orbital of next lowest energy is the 2*s*, which can also hold up to two electrons. Therefore, the third electron of lithium and the third and fourth electrons of beryllium enter the 2*s*. We can represent the electronic structures of lithium and beryllium as

Li $1s^22s^1$ or Li 

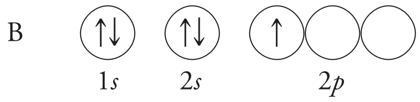
Be $1s^22s^2$ or Be 

Filling *p* orbitals

After beryllium comes boron, B ($Z = 5$). Referring to Figure 7.18, we see that the first four electrons of this atom complete the 1*s* and 2*s* subshells, so the fifth electron must be placed into the 2*p* subshell.

B $1s^22s^22p^1$

In the orbital diagram for boron, the fifth electron can be put into any one of the 2*p* orbitals—which one doesn't matter because they are all of equal energy.



Notice, however, that when we give this orbital diagram we show *all* of the orbitals of the 2*p* subshell even though two of them are empty.

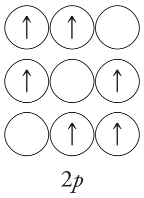
Next we come to carbon, which has six electrons. As before, the first four electrons complete the 1*s* and 2*s* orbitals. The remaining two electrons go in the 2*p* subshell to give

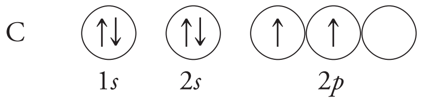
C $1s^2\,2s^2\,2p^2$

Now, however, to write the orbital diagram we have to make a decision as to where to put the two *p* electrons. (At this point you may have an unprintable suggestion! But try to bear up. It's really not all that bad.) To make this decision, we apply **Hund's rule,** which states that *when electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible*. Both theory and experiment have shown that if we follow this rule, we obtain the electron configuration with the lowest energy. For carbon, it means that the two *p* electrons are in separate orbitals and their spins are in the same direction.[1]

- Spread them out and then line them up.

- It doesn't matter which two orbitals are shown as occupied. Any of these are okay for the ground state of carbon.





Applying the Pauli exclusion principle and Hund's rule, we can now complete the electron configurations and orbital diagrams for the rest of the elements of the second period.

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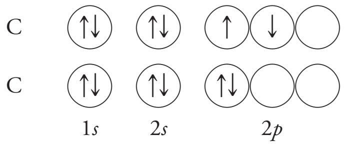
[1] Hund's rule gives us the *lowest* energy (ground state) distribution of electrons among the orbitals. However, configurations such as



are not impossible; it is just that neither of them corresponds to the lowest energy distribution of electrons in the carbon atom.

		$1s$	$2s$	$2p$
N	$1s^22s^22p^3$	↑↓	↑↓	↑ ↑ ↑
O	$1s^22s^22p^4$	↑↓	↑↓	↑↓ ↑ ↑
F	$1s^22s^22p^5$	↑↓	↑↓	↑↓ ↑↓ ↑
Ne	$1s^22s^22p^6$	↑↓	↑↓	↑↓ ↑↓ ↑↓

We can continue to predict electron configurations in this way, using Figure 7.18 as a guide to tell us which subshells become occupied and in what order. For instance, after completing the $2p$ subshell at neon, Figure 7.18 predicts that the next two electrons enter the $3s$, followed by the filling of the $3p$. Then we find the $4s$ is lower in energy than the $3d$, so it is filled first. Next, the $3d$ is completed before we go on to fill the $4p$, and so forth.

You might be thinking that you'll have to consult Figure 7.18 whenever you need to write down the ground state electron configuration of an element. However, as you will see in the next section, all the information contained in that figure is also contained in the periodic table.

7.6 ELECTRON CONFIGURATIONS EXPLAIN THE STRUCTURE OF THE PERIODIC TABLE

In Chapter 2 you learned that when Mendeleev constructed his periodic table, elements with similar chemical properties were arranged in vertical columns called groups. Later work led to the expanded version of the periodic table we use today. The basic structure of this table is one of the strongest empirical supports for the quantum theory, which we have been using to predict electron configurations, and it also permits us to use the periodic table itself as a device for predicting electron configurations.

The periodic table is a guide for predicting electron configurations

TOOLS
Periodic table and electron configurations

Consider, for example, the way the table is laid out (Figure 7.20). On the left there is a block of *two* columns shown in blue; on the right there is a block of *six* columns shown in pink; in the center there is a block of *ten* columns shown in yellow, and below the table there are two rows consisting of *fourteen* elements each shown in gray. These numbers—2, 6, 10, and 14—are *precisely* the numbers of electrons that the quantum theory tells us can occupy *s*, *p*, *d*, and *f* subshells, respectively. In fact, *we can use the structure of the periodic table to predict the filling order of the subshells when we write the electron configuration of an element*.

☐ This would be an amazing coincidence if the theory were wrong!

To use the periodic table to predict electron configurations, we follow the aufbau principle as before. We start with hydrogen and then move through the table row after row

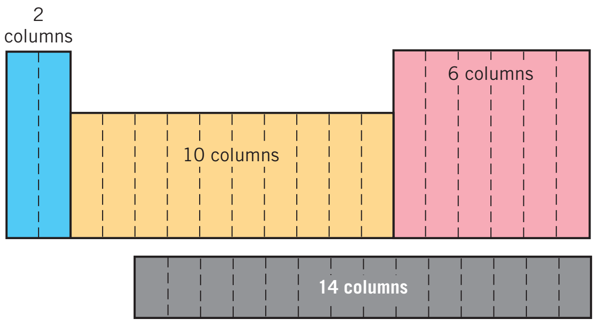


FIG. 7.20 The overall column structure of the periodic table. The table is naturally divided into regions of 2, 6, 10, and 14 columns, which are the numbers of electrons that can occupy *s*, *p*, *d*, and *f* subshells.

until we reach the element of interest, noting as we go along which regions of the table we pass through. For example, consider the element calcium. Using Figure 7.20, we obtain the electron configuration

$$\text{Ca} \qquad 1s^22s^22p^63s^23p^64s^2$$

To see how this configuration relates to the periodic table, refer to the inside front cover of the book.

Filling periods 1, 2, and 3

Notice that the first period has just two elements, H and He. Starting with hydrogen and passing through this period, two electrons are added to the atom. These enter the 1*s* subshell and are written as $1s^2$. Next we move across the second period, where the first two elements, Li and Be, are in the block of two columns. The two electrons for Li and Be enter the 2*s* subshell and are written as $2s^2$. Then we move to the block of six columns, and as we move across this region in the second row we fill the 2*p* subshell with six electrons, writing $2p^6$. Now we go to the third period where we first pass through the block of two columns, filling the 3*s* subshell with two electrons ($3s^2$), and then through the block of six columns, filling the 3*p* with six electrons ($3p^6$).

Filling periods 4 and 5

Next, we move to the fourth period. To get to calcium in the example above we step through two elements in the two-column block, filling the 4*s* subshell with two more electrons. Up to calcium we have only filled *s* and *p* subshells. Figure 7.21 shows that after calcium the 3*d* subshell will be filled. Ten electrons are then added for the ten elements in the first row of the transition elements. After the 3*d* subshell we complete the fourth period by filling the 4*p* subshell with six electrons. The fifth period fills the 5*s*, 4*d*, and 5*p* subshells in sequence with 2, 10, and 6 electrons, respectively.

Filling periods 6 and 7

The inner transition elements (*f* subshells) begin to fill in the sixth and seventh periods. Period 6 fills the 6*s*, 4*f*, 5*d*, and 6*p* subshells with 2, 14, 10, and 6 electrons, respectively. The reason for this sequence is that, in general, the 6*s* subshell has the lowest energy. Subshells 4*f*, 5*d*, and 6*p* have increasingly greater energies in this period. There are many irregularities in this sequence, however, and Appendix A should be consulted for the correct electron configurations. The seventh period fills the 7*s*, 5*f*, 6*d*, and 7*p* subshells. Once again, the sequence is based on the energies of the subshells and there are many irregularities that make it advisable to consult Appendix A for the correct electron configurations.

Notice that in the above patterns the *s* and *p* subshells always have the same number as the period they are in. The *d* subshells always have a number that is one less than the period they are in. Finally, the *f* subshells are always two less than the period in which they reside.

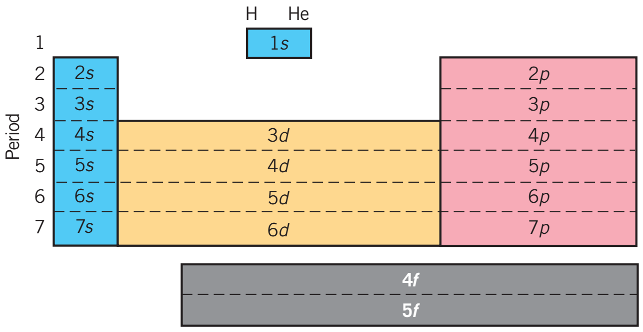


FIG. 7.21 **Arrangement of subshells in the periodic table.** This format illustrates the sequence for filling subshells.

EXAMPLE 7.4
Predicting Electron Configurations

What is the electron configuration of (a) Mn and (b) Bi?

ANALYSIS: We use the periodic table as a tool to tell us which subshells become filled. It is best if you can do this without referring to Figure 7.21.

SOLUTION: (a) To get to manganese, we cross the following regions of the table, with the results indicated.

Period 1	Fill the 1*s* subshell
Period 2	Fill the 2*s* and 2*p* subshells
Period 3	Fill the 3*s* and 3*p* subshells
Period 4	Fill the 4*s* and then move five places in the 3*d* region

The electron configuration of Mn is therefore

$$\text{Mn} \qquad 1s^22s^22p^63s^23p^64s^23d^5$$

This configuration is correct as is. In elements with electrons in *d* and *f* orbitals, we can also group all subshells of the same shell together. For manganese, this gives

$$\text{Mn} \qquad 1s^22s^22p^63s^23p^63d^54s^2$$

We'll see later that writing the configuration with this way is convenient when working out ground state electronic configurations for ions.

(b) To get to bismuth, we fill the following subshells:

Period 1	Fill the 1*s*
Period 2	Fill the 2*s* and 2*p*
Period 3	Fill the 3*s* and 3*p*
Period 4	Fill the 4*s*, 3*d*, and 4*p*
Period 5	Fill the 5*s*, 4*d*, and 5*p*
Period 6	Fill the 6*s*, 4*f*, 5*d*, and then add three electrons to the 6*p*

This gives

$$\text{Bi} \qquad 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^3$$

Grouping subshells with the same value of *n* gives

$$\text{Bi} \qquad 1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^3$$

Again, either of these configurations is correct.

IS THE ANSWER REASONABLE? We can count the number of electrons to be sure we have 25 for Mn and 83 for Bi and none have been left out or added. If the textbook is available we can look at Appendix A to check our configurations.

Practice Exercise 8: Use the periodic table to predict the electron configurations of (a) Mg, (b) Ge, (c) Cd, and (d) Gd. Group subshells of the same shell together. (Hint: Recall which areas of the periodic table represent *s, p, d,* and *f* electrons.)

Practice Exercise 9: Describe in your own words how to use the periodic table to write the electron configuration of an element.

Practice Exercise 10: Use the periodic table to predict the electron configurations of (a) O, S, Se and (b) P, N, Sb. What is the same about all the elements in part (a), and the elements in part (b)?

Practice Exercise 11: Draw orbital diagrams for (a) Na, (b) S, and (c) Fe. (Hint: Recall how we indicate paired electron spins.)

Practice Exercise 12: Use orbital diagrams to determine how many unpaired electrons are in each of these elements: (a) Mg, (b) Ge, (c) Cd, and (d) Gd.

Electron configurations can be abbreviated using noble gas core configurations

When we consider the chemical reactions of atoms, our attention is usually focused on the distribution of electrons in the **outer shell** of the atom (the occupied shell with the largest value of n). This is because the **outer electrons** (those in the outer shell) are the ones that are exposed to other atoms when the atoms react. The inner electrons of an atom, called the **core electrons,** are buried deep within the atom and normally do not play a role when chemical bonds are formed.

Because we are interested primarily in the electrons of the outer shell, we often write electron configurations in an abbreviated, or shorthand, form. To illustrate, let's consider the elements sodium and magnesium. Their full electron configurations are

$$\begin{array}{ll} \text{Na} & 1s^22s^22p^63s^1 \\ \text{Mg} & 1s^22s^22p^63s^2 \end{array}$$

The outer electrons of both atoms are in the $3s$ subshell and each has the core configuration $1s^22s^22p^6$, which is the same as that of the noble gas neon.

To write the *shorthand configuration* for an element we indicate what the core is by placing in brackets the symbol of the noble gas whose electron configuration is the same as the core configuration. This is followed by the configuration of the outer electrons for the particular element. The noble gas used is almost always the one that occurs at the end of the period preceding the period containing the element whose configuration we wish to represent. Thus, for sodium and magnesium we write

$$\begin{array}{ll} \text{Na} & [\text{Ne}]\ 3s^1 \\ \text{Mg} & [\text{Ne}]\ 3s^2 \end{array}$$

Even with the transition elements, we need only concern ourselves with the outermost shell and the d subshell just below. For example, iron has the configuration

$$\text{Fe} \qquad 1s^22s^22p^63s^23p^63d^64s^2$$

Only the $4s$ and $3d$ electrons play a role in the chemistry of iron. In general, the electrons below the outer s and d subshells of a transition element—the *core* electrons—are relatively unimportant. In every case these core electrons have the electron configuration of a noble gas. Therefore, for iron the core is $1s^22s^22p^63s^23p^6$, which is the same as the electron configuration of argon. The abbreviated configuration of iron is therefore written as

$$\text{Fe} \qquad [\text{Ar}]\ 3d^64s^2$$

EXAMPLE 7.5

Writing Shorthand Electron Configurations

What is the shorthand electron configuration of manganese? Draw the orbital diagram for manganese using the shorthand configuration.

ANALYSIS: As usual, the periodic table serves as our tool for deriving the electron configuration. For the shorthand configuration of an element, we write, in brackets, the symbol for the noble gas that is at the end of the preceding period, followed by the electron configuration of the occupied subshells that exist beyond the noble gas core. For the orbital diagram, we use a circle to represent each of the orbitals in a populated subshell. The orbitals are then populated with the required number of electrons, using arrows as appropriate, following Hund's rule.

SOLUTION: Manganese is in Period 4. The preceding noble gas is argon, Ar, so to write the abbreviated configuration we write the symbol for argon in brackets followed by the electron configuration that exists beyond the argon core. We can obtain this by noting that to get to Mn in Period 4, we first cross the "*s* region" by adding two electrons to the 4*s* subshell, and then go five steps into the "*d* region" where we add five electrons to the 3*d* subshell. Therefore, the shorthand electron configuration for Mn is

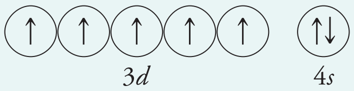
$$\text{Mn} \qquad [\text{Ar}]\ 4s^2 3d^5$$

Placing the electrons that are in the highest shell farthest to the right gives

$$\text{Mn} \qquad [\text{Ar}]\ 3d^5 4s^2$$

To draw the orbital diagram, we simply distribute the electrons in the 3*d* and 4*s* orbitals following Hund's rule. This gives

Mn [Ar]



Notice that each of the 3*d* orbitals is half-filled. The atom contains five unpaired electrons and is paramagnetic.

IS THE ANSWER REASONABLE? From the left, count the groups needed to reach Mn. These should equal seven, the number of electrons in the orbitals beyond Ar as written above. The orbital diagram must have seven electrons and must obey Hund's rule.

Practice Exercise 13: Can an element with an even atomic number be paramagnetic? (Hint: Try writing the orbital diagrams of a few of the transition elements in Period 4.)

Practice Exercise 14: Write shorthand configurations and abbreviated orbital diagrams for (a) P and (b) Sn. Where appropriate, place the electrons that are in the highest shell farthest to the right. How many unpaired electrons does each of these atoms have?

Chemical properties of the representative elements depend on valence shell electron configurations

You learned that Mendeleev constructed the periodic table by placing elements with similar properties in the same group. We are now ready to understand the reason for these similarities in terms of the electronic structures of atoms. It seems reasonable, therefore, that elements with similar properties should have similar outer shell electron configurations. This is, in fact, exactly what we observe. For example, let's look at the alkali metals of Group IA. Going by our rules, we obtain the following configurations.

Li	$[\text{He}]\ \mathbf{2s^1}$	or	$1s^2\mathbf{2s^1}$
Na	$[\text{Ne}]\ \mathbf{3s^1}$	or	$1s^22s^22p^6\mathbf{3s^1}$
K	$[\text{Ar}]\ \mathbf{4s^1}$	or	$1s^22s^22p^63s^23p^6\mathbf{4s^1}$
Rb	$[\text{Kr}]\ \mathbf{5s^1}$	or	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6\mathbf{5s^1}$
Cs	$[\text{Xe}]\ \mathbf{6s^1}$	or	$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6\mathbf{6s^1}$

Each of these elements has just one outer shell electron that is in an *s* subshell. We know that when they react, the alkali metals each lose one electron to form ions with a charge of 1+. For each, the electron that is lost is this outer *s* electron, and the electron configuration of the ion that is formed is the same as that of the preceding noble gas.

Li^+	$1s^2$	He	$1s^2$
Na^+	$1s^22s^22p^6$	Ne	$1s^22s^22p^6$
K^+	$1s^22s^22p^63s^23p^6$	Ar	$1s^22s^22p^63s^23p^6$

etc.

If you write the electron configurations of the members of any of the groups in the periodic table, you will find the same kind of similarity among the configurations of the outer shell electrons. The differences are in the value of the principal quantum number of the outer electrons.

TOOLS
Periodic table and similarities in chemical properties

For the representative elements (those in the longer columns), the only electrons that are normally important in controlling chemical properties are the ones in the outer shell. This outer shell is known as the **valence shell,** and it is always the occupied shell with the largest value of *n*. The electrons in the valence shell are called **valence electrons.** (The term *valence* comes from the study of chemical bonding and relates to the combining capacity of an element, but that's not important here.)

For the representative elements it is very easy to determine the electron configuration of the valence shell by using the periodic table. *The valence shell always consists of just the s and p subshells that we encounter crossing the period that contains the element in question.* Thus, to determine the valence shell configuration of sulfur, a Period 3 element, we note that to reach sulfur in Period 3 we place two electrons into the 3*s* and four electrons into the 3*p*. The valence shell configuration of sulfur is therefore

$$\text{S} \qquad 3s^2 3p^4$$

EXAMPLE 7.6
Writing Valence Shell Configurations

Predict the electron configuration of the valence shell of arsenic ($Z = 33$).

ANALYSIS: To determine the number of *s* and *p* electrons in the highest shell we write the electron configuration grouping the subshells in each shell together. The last subshell must be either an *s* or *p* subshell. If it is an *s* subshell, the valence shell consists of the *s* electrons. If the last subshell is a *p* subshell, the valence shell includes both the *s* and *p* electrons in that shell.

SOLUTION: To reach arsenic in Period 4, we add electrons to the 4*s,* 3*d,* and 4*p* subshells. But the 3*d* is not part of the fourth shell and therefore not part of the valence shell, so all we need be concerned with are the electrons in the 4*s* and 4*p* subshells. This gives us the valence shell configuration of arsenic,

$$\text{As} \qquad 4s^2 4p^3$$

IS THE ANSWER REASONABLE? First of all, only *s* and *p* electrons can be valence electrons. We can then count backward from As to the start of the period counting only the *p* and then *s* electrons. These add up to the numbers above, indicating the answer is correct.

Practice Exercise 15: Give an example of a valence shell with more than eight electrons. If that is not possible, explain why. (Hint: Are there any elements where *d* shell electrons are valence shell electrons?)

Practice Exercise 16: What is the valence shell electron configuration of (a) Se, (b) Sn, and (c) I?

Configurations for transition and rare earth elements are sometimes unexpected

The rules you've learned for predicting electron configurations work most of the time, but not always. Appendix A gives the electron configurations of all of the elements as determined experimentally. Close examination reveals that there are quite a few exceptions to the rules. Some of these exceptions are significant for us because they occur with common elements.

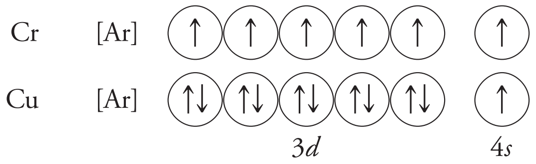
Two important exceptions are for chromium and copper. Following the rules, we would expect the configurations to be

$$\text{Cr} \qquad [\text{Ar}]\ 3d^4 4s^2$$
$$\text{Cu} \qquad [\text{Ar}]\ 3d^9 4s^2$$

However, the actual electron configurations, determined experimentally, are

$$\begin{array}{ll} \text{Cr} & [\text{Ar}]\ 3d^5 4s^1 \\ \text{Cu} & [\text{Ar}]\ 3d^{10} 4s^1 \end{array}$$

The corresponding orbital diagrams are



Notice that for chromium, an electron is "borrowed" from the 4*s* subshell to give a 3*d* subshell that is exactly half-filled. For copper the 4*s* electron is borrowed to give a completely filled 3*d* subshell. A similar thing happens with silver and gold, which have filled 4*d* and 5*d* subshells, respectively.

$$\begin{array}{ll} \text{Ag} & [\text{Kr}]\ 4d^{10} 5s^1 \\ \text{Au} & [\text{Xe}]\ 4f^{14} 5d^{10} 6s^1 \end{array}$$

Apparently, half-filled and filled subshells (particularly the latter) have some special stability that makes such borrowing energetically favorable. This subtle but nevertheless important phenomenon affects not only the ground state configurations of atoms but also the relative stabilities of some of the ions formed by the transition elements. Similar irregularities occur among the lanthanide and the actinide elements.

7.7

QUANTUM THEORY PREDICTS THE SHAPES OF ATOMIC ORBITALS

To picture what electrons are doing within the atom, we are faced with imagining an object that behaves like a particle in some experiments and like a wave in others. There is nothing in our experience that is comparable. Fortunately we can still think of the electron as a particle in the usual sense by using the statistical probability of the electron being found at a particular place. We can then use quantum mechanics to mathematically connect the particle and wave representations of the electron. Even though we may have trouble imagining an object that can be represented both ways, mathematics describes its behavior very accurately.

Describing the electron's position in terms of statistical probability is based on more than simple convenience. The German physicist Werner Heisenberg showed mathematically that it is impossible to measure with complete precision both a particle's velocity and position at the same instant. To measure an electron's position or velocity, we have to bounce another particle off it. Thus, the very act of making the measurement changes the electron's position and velocity. We cannot determine both exact position and exact velocity simultaneously, no matter how cleverly we make the measurements. This was Heisenberg's famous **uncertainty principle.** The theoretical limitations on measuring speed and position are not significant for large objects. For small particles such as the electron, however, these limitations prevent us from ever knowing or predicting where in an atom an electron will be at a particular instant, so we speak of probabilities instead.

▫ The uncertainty principle is often stated mathematically as

$$\Delta x = \frac{h}{4\pi m}\left(\frac{1}{\Delta v}\right)$$

where Δx is the minimum uncertainty in the particle's location, h is Planck's constant, m is the mass of the particle, and Δv is the minimum uncertainty in the particle's velocity. Notice that we can generally measure the particle's location more precisely if the particle is heavier. Notice also that the greater the uncertainty in the velocity, the smaller the uncertainty in the particle's location.

Wave mechanics views the probability of finding an electron at a given point in space as equal to the square of the amplitude of the electron wave (given by the square of the wave function, ψ^2) at that point. It seems quite reasonable to relate probability to amplitude, or intensity, because where a wave is intense its presence is strongly felt. The amplitude is squared because, mathematically, the amplitude can be either positive or negative, but probability only makes sense if it is positive. Squaring the amplitude assures us that the probabilities will be positive. We need not be very concerned about this point, however.

The notion of electron probability leads to two very important and frequently used concepts. One is that an electron behaves as if it were spread out around the nucleus in a sort of **electron cloud**. Figure 7.22*a* is a *dot-density diagram* that illustrates the way

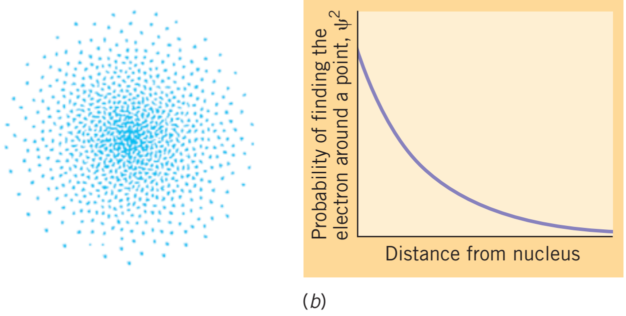


FIG. 7.22 **Electron distribution in a 1*s* orbital.** (*a*) A dot-density diagram that illustrates the electron probability distribution for a 1*s* electron. (*b*) A graph that shows how the probability of finding the 1*s* electron around a given point, ψ^2, decreases as the distance from the nucleus increases.

□ The amplitude of an electron wave is described by a *wave function,* which is usually given the symbol ψ (the Greek letter psi). The probability of finding the electron in a given location is given by ψ^2.

the probability of finding the electron varies in space for a 1*s* orbital. In those places where the dot density is large (i.e., where there are large numbers of dots per unit volume), the amplitude of the wave is large and the probability of finding the electron is also large. Figure 7.22*b* shows how the electron probability for a 1*s* orbital varies as we move away from the nucleus. As you might expect, the probability of finding the electron close to the nucleus is large and decreases with increasing distance from the nucleus.

The other important concept that stems from the notion that the electron probability varies from place to place is **electron density,** which relates to how much of the electron's charge is packed into a given volume. In regions of high probability there is a high concentration of electrical charge (and mass) and the electron density is large; in regions of low probability, the electron density is small.

Remember that an electron confined to a tiny space no longer behaves much like a particle. It's more like a cloud of negative charge. Like clouds made of water vapor, the density of the cloud varies from place to place. In some places the cloud is dense; in others the cloud is thinner and may be entirely absent. This is a useful picture to keep in mind as you try to visualize the shapes of atomic orbitals.

s orbitals are spherical; *p* orbitals have two lobes

In looking at the way the electron density distributes itself in atomic orbitals, we are interested in three things: the *shape* of the orbital, its *size,* and its *orientation* in space relative to other orbitals.

The electron density in an orbital doesn't end abruptly at some particular distance from the nucleus. It gradually fades away. Therefore, to define the size and shape of an orbital, it is useful to picture some imaginary surface enclosing, say, 90% of the electron density of the orbital, and on which the probability of finding the electron is everywhere the same. For the 1*s* orbital in Figure 7.22, we find that if we go out a given distance from the nucleus in *any* direction, the probability of finding the electron is the same. This means that all the points of equal probability lie on the surface of a sphere, so we can say that the shape of the orbital is spherical. In fact, all *s* orbitals are spherical. As suggested earlier, their sizes increase with increasing *n*. This is illustrated in Figure 7.23. Notice that beginning with the 2*s* orbital, there are certain places where the electron density drops to zero. These are spherical shaped nodes of the *s* orbital electron waves. It is interesting that electron waves have nodes just like the waves on a guitar string. For *s* orbital electron waves, however, the nodes consist of imaginary spherical *surfaces* on which the electron density is zero.

The *p* orbitals are quite different from *s* orbitals, as shown in Figure 7.24. Notice that the electron density is equally distributed in two regions on opposite sides of the nucleus. Figure 7.24*a* illustrates the two "lobes" of *one* 2*p* orbital. Between the lobes is a **nodal plane**—an imaginary flat surface on which every point has an electron density of zero. The size of the *p* orbitals also increases with increasing *n* as illustrated by the cross section

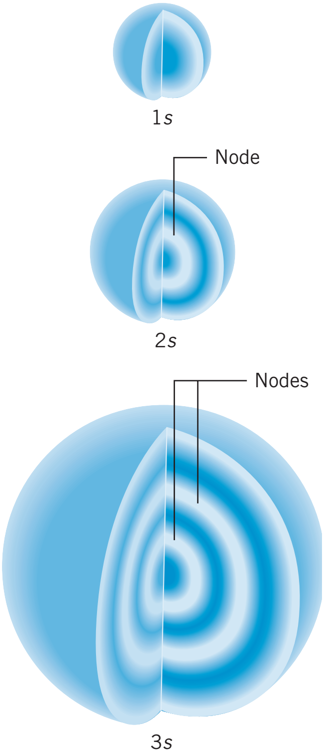


FIG. 7.23 **Size variations among *s* orbitals.** The orbitals become larger as the principal quantum number, *n*, becomes larger.

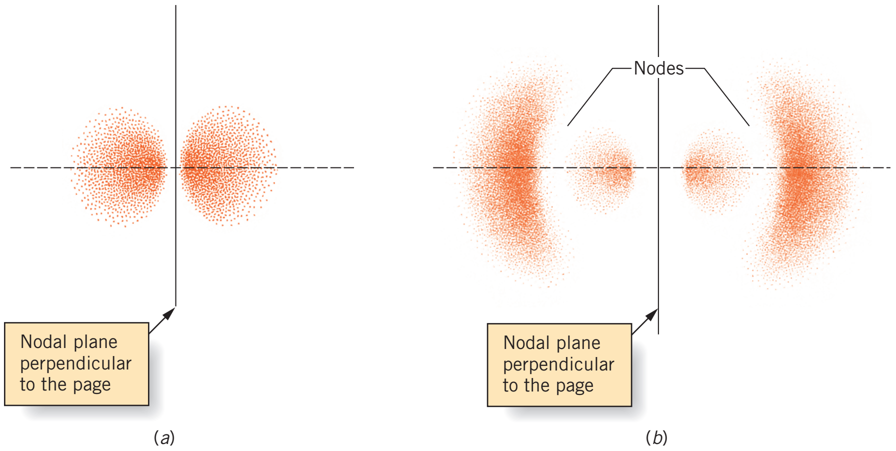


FIG. 7.24 Distribution of electron density in p orbitals. (*a*) Dot-density diagram that represents a cross section of the probability distribution in a $2p$ orbital. There is a nodal plane between the two lobes of the orbital. (*b*) Cross section of a $3p$ orbital. Note the nodes in the electron density that are in addition to the nodal plane passing through the nucleus.

of a $3p$ orbital in Figure 7.24*b*. The $3p$ and higher p orbitals have additional nodes besides the nodal plane that passes through the nucleus.

Figure 7.25*a* illustrates the shape of a surface of constant probability for a $2p$ orbital. Often chemists will simplify this shape by drawing two "balloons" connected at the nucleus and pointing in opposite directions as shown in Figure 7.25*b*. Both representations emphasize the point that a p orbital has two equal-sized lobes that extend in opposite directions along a line that passes through the nucleus.

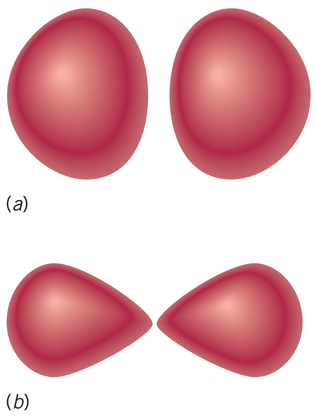


FIG. 7.25 Representations of the shapes of p orbitals. (*a*) Shape of a surface of constant probability for a $2p$ orbital. (*b*) A simplified representation of a p orbital that emphasizes the directional nature of the orbital.

Orbitals in a *p* subshell are oriented at 90° to each other

As you've learned, a p subshell consists of three orbitals of equal energy. Wave mechanics tells us that the lines along which the orbitals have their maximum electron densities are oriented at 90° angles to each other, corresponding to the axes of an imaginary xyz coordinate system (Figure 7.26). For convenience in referring to the individual p orbitals they are often labeled according to the axis along which they lie. The p orbital concentrated along the x axis is labeled p_x, and so forth.

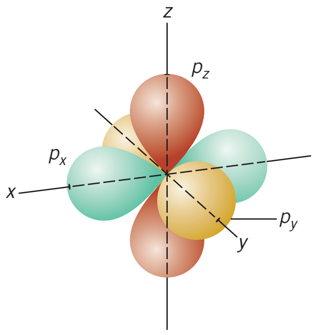


FIG. 7.26 The orientations of the three p orbitals in a p subshell. Because the directions of maximum electron density lie along lines that are mutually perpendicular, like the axes of an xyz coordinate system, it is convenient to label the orbitals p_x, p_y, and p_z.

Four of the five *d* orbitals in a *d* subshell have the same shape

The shapes of the d orbitals, illustrated in Figure 7.27, are a bit more complex than are those of the p orbitals. Because of this, and because there are five orbitals in a d subshell, we haven't attempted to draw all of them at the same time on the same set of coordinate axes. Notice that four of the five d orbitals have the same shape and consist of four lobes

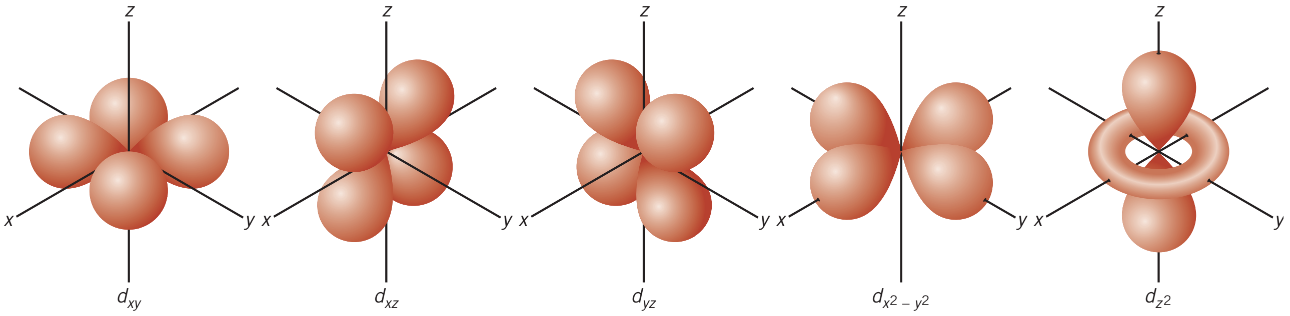


FIG. 7.27 The shapes and directional properties of the five d orbitals of a d subshell.

of electron density. These four *d* orbitals each have two perpendicular nodal planes that intersect the nucleus. These orbitals differ only in their orientations around the nucleus (their labels come from the mathematics of wave mechanics). The fifth *d* orbital, labeled d_{z^2}, has two lobes that point in opposite directions along the *z* axis plus a doughnut-shaped ring of electron density around the center that lies in the x–y plane. The two nodes for the d_{z^2} orbital are conic surfaces whose peaks meet at the nucleus. We will see that the *d* orbitals are important in the formation of chemical bonds in certain molecules, and that their shapes and orientations are important in understanding the properties of the transition metals, which will be discussed in Chapter 21.

The shapes of the *f* orbitals are more complex than those of the *d* orbitals, having more lobes and a variety of shapes. Use of *f* orbitals for bonding is not important for this course. However, we should note that each *f* orbital has three nodal planes or surfaces.

▫ The *f* orbitals are even more complex than the *d* orbitals, but we will have no need to discuss their shapes.

7.8 ATOMIC PROPERTIES CORRELATE WITH AN ATOM'S ELECTRON CONFIGURATION

There are many chemical and physical properties that vary in a more or less systematic way according to an element's position in the periodic table. For example, in Chapter 2 we noted that the metallic character of the elements increases from top to bottom in a group and decreases from left to right across a period. In this section we discuss several physical properties of the elements that have an important influence on chemical properties. We will see how these properties correlate with an atom's electron configuration, and because electron configuration is also related to the location of an element in the periodic table, we will study their periodic variations as well.

Effective nuclear charge is the positive charge "felt" by outer electrons

Many of an atom's properties are determined by the amount of positive charge felt by the atom's outer electrons. Except for hydrogen, this positive charge is always *less* than the full nuclear charge, because the negative charge of the electrons in inner shells partially offsets, or "neutralizes," the positive charge of the nucleus.

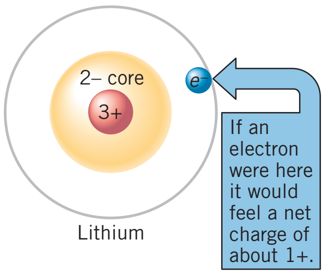


FIG. 7.28 Effective nuclear charge. If the 2− charge of the $1s^2$ core of lithium were 100% effective at shielding the 2*s* electron from the nucleus, the valence electron would feel an effective nuclear charge of only about 1+.

To gain a better understanding of this, consider the element lithium, which has the electron configuration $1s^22s^1$. The core electrons ($1s^2$), which lie beneath the valence shell ($2s^1$), are tightly packed around the nucleus and for the most part lie between the nucleus and the electron in the outer shell. This core has a charge of 2− and it surrounds a nucleus that has a charge of 3+. When the outer 2*s* electron "looks toward" the center of the atom, it "sees" the 3+ charge of the nucleus reduced to only about 1+ because of the intervening 2− charge of the core. In other words, the 2− charge of the core effectively neutralizes two of the positive charges of the nucleus, so the net charge that the outer electron feels, which we call the **effective nuclear charge,** is only about 1+. This is illustrated in an overly simplified way in Figure 7.28.

Although electrons in inner shells shield the electrons in outer shells quite effectively from the nuclear charge, electrons in the *same* shell are much less effective at shielding each other. For example, in the element beryllium ($1s^22s^2$) each of the electrons in the outer 2*s* orbital is shielded quite well from the nuclear charge by the inner $1s^2$ core, but one 2*s* electron doesn't shield the other 2*s* electron very well at all. This is because electrons in the same shell are at about the same average distance from the nucleus, and in attempting to stay away from each other they only spend a very small amount of time one below the other, which is what's needed to provide shielding. Since electrons in the same shell hardly shield each other at all from the nuclear charge, *the effective nuclear charge felt by the outer electrons is determined primarily by the difference between the charge on the nucleus and the charge on the core.* With this as background, let's examine some properties controlled by the effective nuclear charge.

▫ An electron spends very little time between the nucleus and another electron in the same shell, so it shields that other electron poorly.

Atomic and ionic sizes increase with increasing *n* and decreasing effective nuclear charge

The wave nature of the electron makes it difficult to define exactly what we mean by the "size" of an atom or ion. As we've seen, the electron cloud doesn't simply stop at some particular distance from the nucleus; instead it gradually fades away. Nevertheless, atoms and ions do behave in many ways as though they have characteristic sizes. For example, in a whole host of hydrocarbons, ranging from methane (CH_4, natural gas) to octane (C_8H_{18}, in gasoline) to many others, the distance between the nuclei of carbon and hydrogen atoms is virtually the same. This would suggest that carbon and hydrogen have the same relative sizes in each of these compounds.

☐ The C—H distance in most hydrocarbons is about 110 pm (110×10^{-12} m).

Experimental measurements reveal that the diameters of atoms range from about 1.4×10^{-10} to 5.7×10^{-10} m. Their radii, which is the usual way that size is specified, range from about 7.0×10^{-11} to 2.9×10^{-10} m. Such small numbers are difficult to comprehend. A million carbon atoms placed side by side in a line would extend a little less than 0.2 mm, or about the diameter of the period at the end of this sentence.

The sizes of atoms and ions are rarely expressed in meters because the numbers are so cumbersome. Instead, a unit is chosen that makes the values easier to comprehend. A unit that scientists have traditionally used is called the **angstrom** (symbolized **Å**), which is defined as

$$1\ \text{Å} = 1 \times 10^{-10}\ \text{m}$$

☐ The angstrom is named after Anders Jonas Ångström (1814–1874), a Swedish physicist who was the first to measure the wavelengths of the four most prominent lines of the hydrogen spectrum.

However, the angstrom is not an SI unit, and in many current scientific journals, atomic dimensions are in picometers, or sometimes in nanometers ($1\ \text{pm} = 10^{-12}$ m and $1\ \text{nm} = 10^{-9}$ m). In this book, we will normally express atomic dimensions in picometers, but because much of the scientific literature has these quantities in angstroms, you may someday find it useful to remember the conversions:

$$1\ \text{Å} = 100\ \text{pm}$$
$$1\ \text{Å} = 0.1\ \text{nm}$$

Atomic size varies periodically

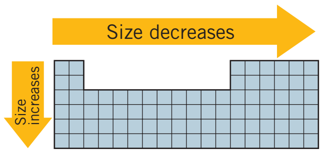
The variations in atomic radii within the periodic table are illustrated in Figure 7.29. Here we see that atoms generally become larger going from top to bottom in a group, and they become smaller going from left to right across a period. To understand these variations we must consider two factors. One is the value of the principal quantum number of the valence electrons, and the other is the effective nuclear charge felt by the valence electrons.

☐ Large atoms are found in the lower left of the periodic table, and small atoms are found in the upper right.

TOOLS *Periodic trends in atomic size*

Going from top to bottom within a group, the effective nuclear charge felt by the outer electrons remains nearly constant, while the principal quantum number of the valence shell increases. For example, consider the elements of Group IA. For lithium, the valence shell configuration is $2s^1$; for sodium, it is $3s^1$; for potassium, it is $4s^1$; and so forth. For each of these elements, the core has a negative charge that is one less than the nuclear charge, so the valence electron of each experiences a nearly constant effective nuclear charge of about 1+. However, as we descend the group, the value of *n* for the valence shell increases, and as you learned earlier, the larger the value of *n*, the larger is the orbital. Therefore, the atoms become larger as we go down a group simply because the orbitals containing the valence electrons become larger. This same argument applies whether the valence shell orbitals are *s* or *p*.

Moving from left to right across a period, electrons are added to the same shell. The orbitals holding the valence electrons all have the *same* value of *n*. In this case we have to examine the variation in the effective nuclear charge felt by the valence electrons.



As we move from left to right across a period, the nuclear charge increases; the outer shells of the atoms become more populated, but the inner core remains the same. For example, from lithium to fluorine the nuclear charge increases from 3+ to 9+. The core ($1s^2$) stays the same, however. As a result, the outer electrons feel an increase in positive charge (i.e., effective nuclear charge) that causes them to be drawn inward, and thereby causes the sizes of the atoms to decrease.

Across a row of transition elements or inner transition elements, the size variations are less pronounced than among the representative elements. This is because the outer shell

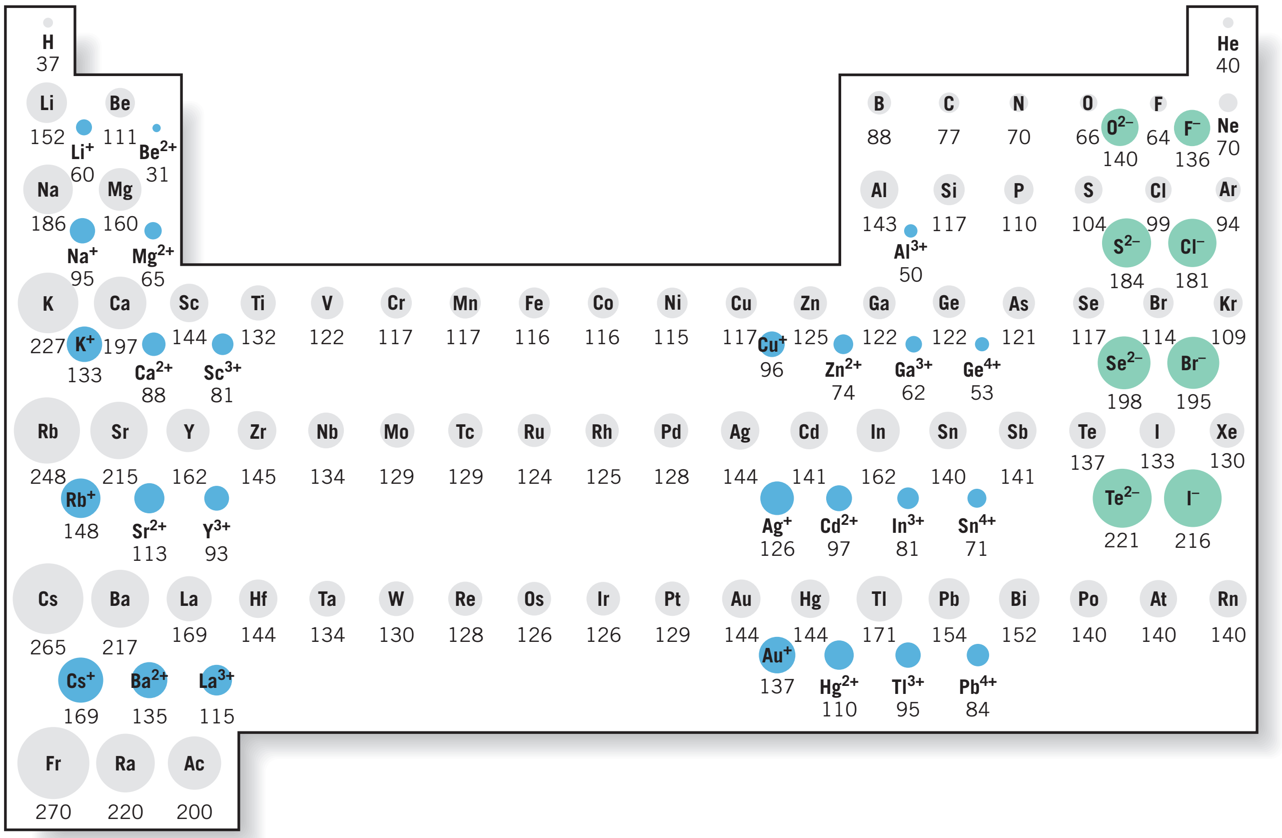


FIG. 7.29 **Variation in atomic and ionic radii in the periodic table.** Values are in picometers.

configuration remains essentially the same while an inner shell is filled. From atomic numbers 21 to 30, for example, the outer electrons occupy the 4*s* subshell while the underlying 3*d* subshell is gradually completed. The amount of shielding provided by the addition of electrons to this inner 3*d* level is greater than the amount of shielding that would occur if the electrons were added to the outer shell, so the effective nuclear charge felt by the outer electrons increases more gradually. As a result, the decrease in size with increasing atomic number is also more gradual.

TOOLS
Trends in ionic size

Ion sizes show the same trends as atom sizes, but anions are larger and cations are smaller than their parent atoms

Figure 7.29 also illustrates how sizes of the ions compare with those of the neutral atoms. As you can see, when atoms gain or lose electrons to form ions, rather significant size changes take place. The reasons are easy to understand and remember.

When electrons are added to an atom, the mutual repulsions between them increase. This causes the electrons to push apart and occupy a larger volume. Therefore, *negative ions are always about 1.5 to 2 times larger than the atoms from which they are formed* (Figure 7.30).

- Adding electrons creates an ion that is larger than the neutral atom; removing electrons produces an ion that is smaller than the neutral atom.

When electrons are removed from an atom, the electron–electron repulsions decrease, which allows the remaining electrons to be pulled closer together around the nucleus. Therefore, *positive ions are always smaller than the atoms from which they are formed.* As Figure 7.29 shows, cations often are only 1/2 to 2/3 the size of their parent atom. This is also illustrated in Figure 7.30 for the elements lithium and iron. For lithium, removal of the outer 2*s* electron completely empties the valence shell and exposes the smaller $1s^2$ core. When a metal is able to form more than one positive ion, the sizes of the ions decrease as the amount of positive charge on the ion increases. To form the Fe^{2+} ion, an iron atom loses its outer 4*s* electrons. To form the Fe^{3+} ion, an additional electron is lost from the 3*d* subshell that lies beneath the 4*s*. Comparing sizes, we see that the radius of an iron atom

Li	$1s^22s^1$
Li^+	$1s^2$
Fe	[Ar] $3d^64s^2$
Fe^{2+}	[Ar] $3d^6$
Fe^{3+}	[Ar] $3d^5$

is 116 pm whereas the radius of the Fe^{2+} ion is 76 pm. Removing yet another electron to give Fe^{3+} decreases electron–electron repulsions in the *d* subshell and gives the Fe^{3+} ion a radius of 64 pm.

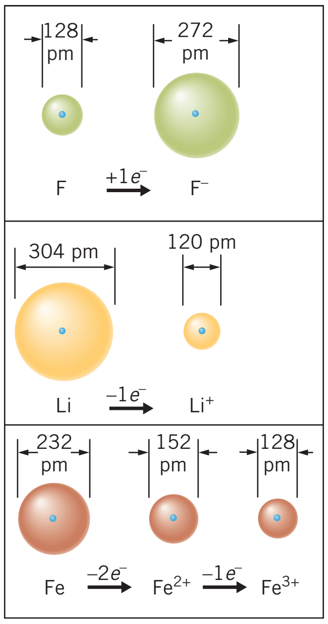


FIG. 7.30 **Changes in size when atoms gain or lose electrons to form ions.** Adding electrons leads to an increase in the size of the particle, as illustrated for fluorine. Removing electrons leads to a decrease in the size of the particle, as shown for lithium and iron.

Practice Exercise 17: Use the periodic table to choose the largest atom or ion in each set. (Hint: Recall that electrons repel each other.)

(a) Ge, Te, Se, Sn (c) Cr, Cr^{2+}, Cr^{3+}
(b) C, F, Br, Ga (d) O, O^{2-}, S, S^{2-}

Practice Exercise 18: Use the periodic table to determine the smallest atom or ion in each group.

(a) Si, Ge, As, P (c) Db, W, Tc, Fe
(b) Fe^{2+}, Fe^{3+}, Fe (d) Br^-, I^-, Cl^-

Energy changes are associated with the gain or loss of electrons by atoms

The ionization energy is the energy required to remove an electron from an atom or ion

The **ionization energy** (abbreviated **IE**) *is the energy required to remove an electron from an isolated, gaseous atom or ion in its ground state.* For an atom of an element *X*, it is the increase in potential energy associated with the change

$$X(g) \longrightarrow X^+(g) + e^-$$

In effect, the ionization energy is a measure of how much work is required to pull an electron from an atom, so it reflects how tightly the electron is held by the atom. Usually, the ionization energy is expressed in units of kilojoules per mole (kJ/mol), so we can also view it as the energy needed to remove one mole of electrons from one mole of gaseous atoms.

Table 7.2 gives the ionization energies of the first 12 elements. As you can see, atoms with more than one electron have more than one ionization energy. These correspond to the stepwise removal of electrons, one after the other. Lithium, for example, has three ionization energies because it has three electrons. Removing the outer 2s electrons from

TABLE 7.2 Successive Ionization Energies for Hydrogen through Magnesium (kJ/mol)[a]

	1st	2nd	3rd	4th	5th	6th	7th	8th
H	1312							
He	2372	5250						
Li	520	7297	11,810					
Be	899	1757	14,845	21,000				
B	800	2426	3659	25,020	32,820			
C	1086	2352	4619	6221	37,820	47,260		
N	1402	2855	4576	7473	9442	53,250	64,340	
O	1314	3388	5296	7467	10,987	13,320	71,320	84,070
F	1680	3375	6045	8408	11,020	15,160	17,860	92,010
Ne	2080	3963	6130	9361	12,180	15,240	—	—
Na	496	4563	6913	9541	13,350	16,600	20,113	25,666
Mg	737	1450	7731	10,545	13,627	17,995	21,700	25,662

[a] Note the sharp increase in ionization energy when crossing the "staircase," indicating that the last of the valence electrons has been removed.

one mole of isolated lithium atoms to give one mole of gaseous lithium ions, Li^+, requires 520 kJ; so the *first ionization energy* of lithium is 520 kJ/mol. The second IE of lithium is 7297 kJ/mol, and corresponds to the process

$$Li^+(g) \longrightarrow Li^{2+}(g) + e^-$$

This involves the removal of an electron from the now-exposed 1*s* core of lithium. Removal of the third (and last) electron requires the third IE, which is 11,810 kJ/mol. In general, successive ionization energies always increase because each subsequent electron is being pulled away from an increasingly more positive ion, and that requires more work.

☐ Ionization energies are additive. For example,

$$Li(g) \longrightarrow Li^+(g) + e^- \qquad IE_1 = 520\text{ kJ}$$
$$Li^+(g) \longrightarrow Li^{2+}(g) + e^- \qquad IE_2 = 7297\text{ kJ}$$
$$Li(g) \longrightarrow Li^{2+}(g) + 2e^- \qquad IE_{total} = IE_1 + IE_2 = 7817\text{ kJ}$$

Larger atoms have lower ionization energies

Within the periodic table there are trends in the way IE varies that are useful to know and to which we will refer in later discussions. We can see these by examining a graph that shows how the first ionization energy varies with an element's position in the table, which is shown in Figure 7.31. Notice that the elements with the largest ionization energies are the nonmetals in the upper right of the periodic table, and that those with the smallest ionization energies are the metals in the lower left of the table. In general, then, the following trends are observed.

☐ It is often helpful to remember that the trends in IE are just the opposite of the trends in atomic size within the periodic table; when size increases, IE decreases.

TOOLS
Periodic trends in ionization energy

Ionization energy generally increases from bottom to top within a group and increases from left to right within a period. Overall the ionization energy increases from the lower left corner of the periodic table to the upper right corner. This is usually referred to as a **diagonal relationship.**

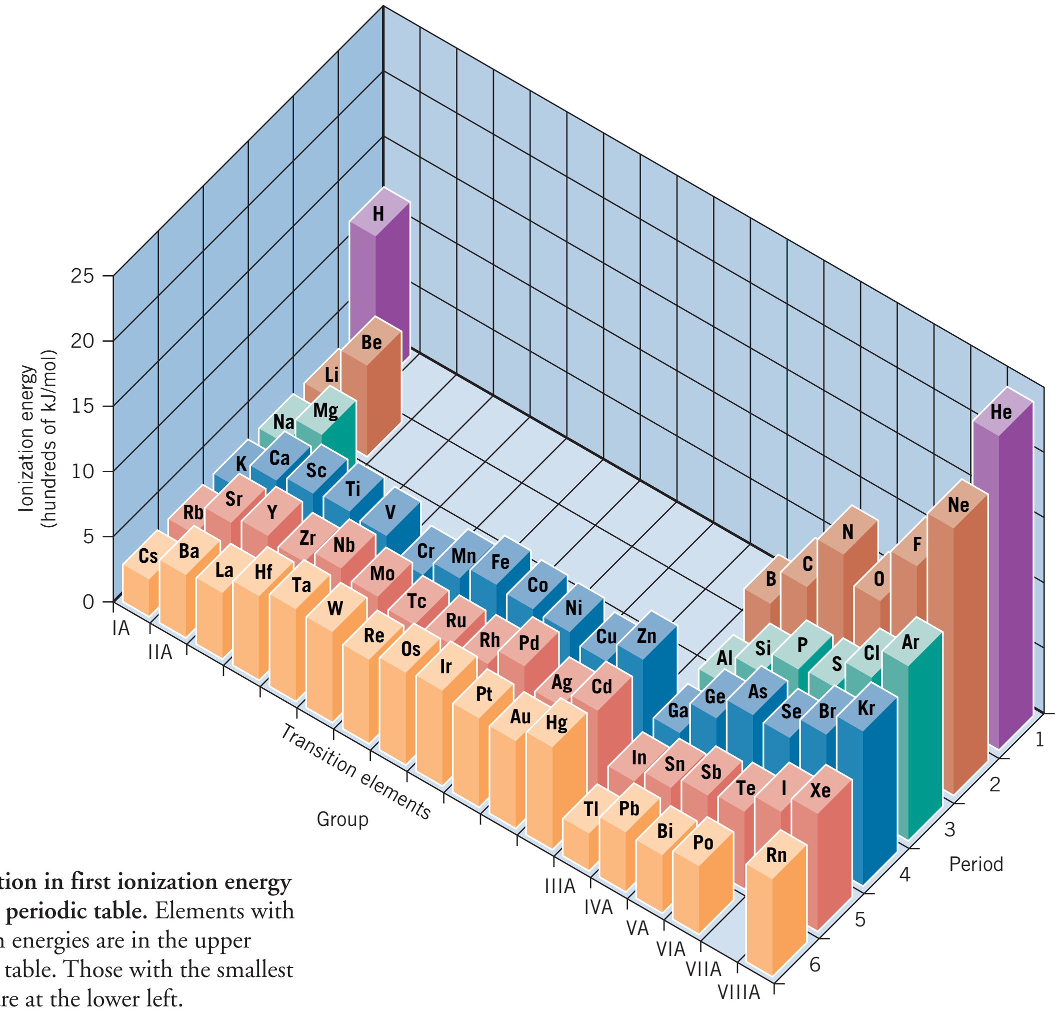
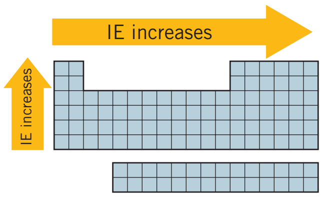


FIG. 7.31 Variation in first ionization energy with location in the periodic table. Elements with the largest ionization energies are in the upper right of the periodic table. Those with the smallest ionization energies are at the lower left.

The same factors that affect atomic size also affect ionization energy. As the value of *n* increases going down a group, the orbitals become larger and the outer electrons are farther from the nucleus. Electrons farther from the nucleus are bound less tightly, so IE decreases from top to bottom. Of course, this is just the same as saying that it increases from bottom to top.



As you can see, there is a gradual overall increase in IE as we move from left to right across a period, although the horizontal variation of IE is somewhat irregular (see Facets of Chemistry 7.4). The reason for the overall trend is the increase in effective nuclear charge felt by the valence electrons as we move across a period. As we've seen, this draws the valence electrons closer to the nucleus and leads to a decrease in atomic size as we move from left to right. But the increasing effective nuclear charge also causes the valence electrons to be held more tightly, which makes it more difficult to remove them.

The results of these trends place elements with the largest IE in the upper right-hand corner of the periodic table. It is very difficult to cause these atoms to lose electrons. In the lower left-hand corner of the table are elements that have loosely held valence electrons. These elements form positive ions relatively easily, as you learned in Chapter 2.

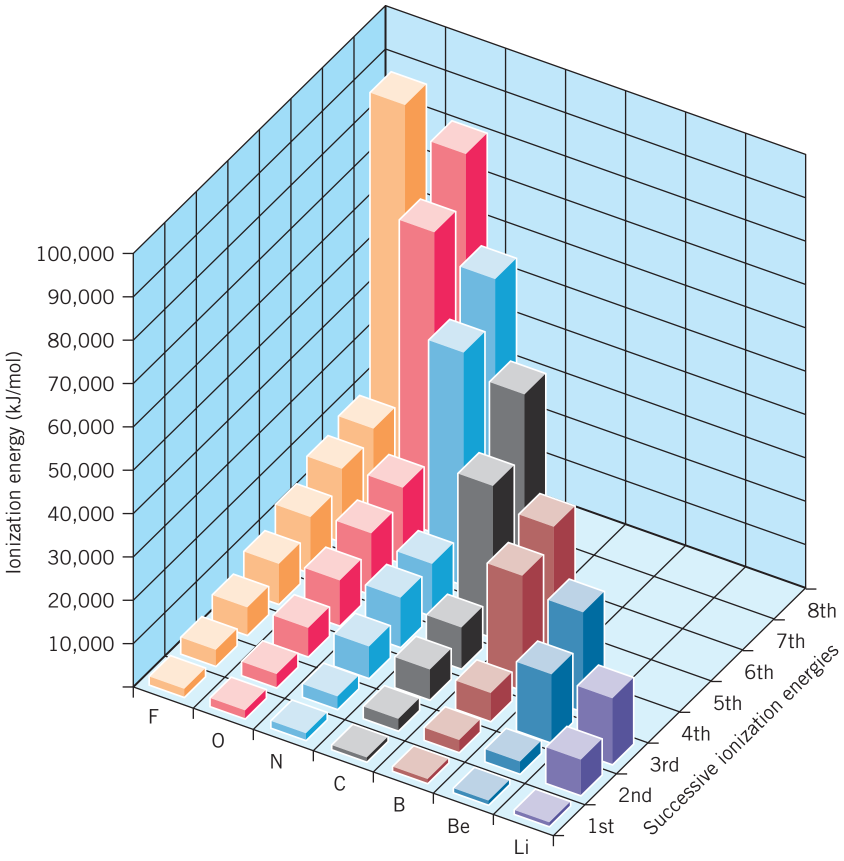


FIG. 7.32 **Variations in successive ionization energies for the elements lithium through fluorine.**

Noble gas configurations are extremely stable

Table 7.2 shows that, for a given element, successive ionization energies increase gradually until the valence shell is emptied. Then a very much larger increase in IE occurs when core electrons are removed. This is illustrated graphically in Figure 7.32 for the Period 2 elements lithium through fluorine. For lithium, we see that the first electron (the 2*s* electron) is removed rather easily, but the second and third electrons, which come from the 1*s* core, are much more difficult to dislodge. For beryllium, the large jump in IE occurs after two electrons (the two 2*s* electrons) are removed. In fact, for all of these elements, the big jump in IE happens when the core electrons are removed.

The data displayed in Figure 7.32 suggest that although it may be moderately difficult to empty the valence shell of an atom, it is *extremely* difficult to remove the core electrons that have the noble gas configuration. As you will learn, this is one of the factors that influences the number of positive charges on ions formed by the representative metals.

Practice Exercise 19: Use the periodic table to select the atom with the most positive value for its first ionization energy, IE: (a) Na, Sr, Be, Rb; (b) B, Al, C, Si. (Hint: Use the diagonal relationships of the IE values within the periodic table.)

Practice Exercise 20: Use Table 7.2 to determine which of the following is expected to have the most positive ionization energy, IE: (a) Na^+, Mg^+, H, C^{2+}; (b) Ne, F, Mg^{2+}, Li^+.

Electron affinity is energy released or absorbed when a particle gains an electron

The **electron affinity** (abbreviated **EA**) *is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state.* For an element *X*, it is the change in potential energy associated with the process

$$X(g) + e^- \longrightarrow X^-(g)$$

As with ionization energy, electron affinities are usually expressed in units of kilojoules per mole, so we can also view the EA as the energy change associated with adding one mole of electrons to one mole of gaseous atoms or ions.

For nearly all the elements, the addition of one electron to the neutral atom is exothermic, and the EA is given as a negative value. This is because the incoming electron experiences an attraction to the nucleus that causes the potential energy to be lowered as the electron approaches the atom. However, when a second electron must be added, as in the formation of the oxide ion, O^{2-}, work must be done to force the electron into an already negative ion. This is an endothermic process where energy must be added and the EA has a positive value.

Change	EA (kJ/mol)
$O(g) + e^- \longrightarrow O^-(g)$	−141
$O^-(g) + e^- \longrightarrow O^{2-}(g)$	+844
$O(g) + 2e^- \longrightarrow O^{2-}(g)$	+703 (net)

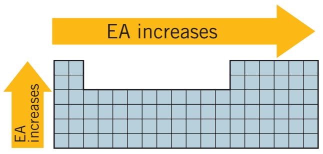


FIG. 7.33 Variation of electron affinity (as an exothermic quantity) within the periodic table.

Notice that more energy is absorbed adding an electron to the O^- ion than is released by adding an electron to the O atom. Overall, the formation of an isolated oxide ion leads to a net increase in potential energy (so we say its formation is *endothermic*). The same applies to the formation of *any* negative ion with a charge larger than 1−.

The electron affinities of the representative elements are given in Table 7.3, and we see that periodic trends in electron affinity roughly parallel those for ionization energy. (See Facets of Chemistry 7.4 for a discussion of some of the irregularities in the trends.)

TOOLS
Periodic trends in electron affinity

Although there are some irregularities, overall, the electron affinities of the elements become more *exothermic* going from left to right across a period and from bottom to top in a group (Figure 7.33).

This shouldn't be surprising, because a valence shell that loses electrons easily (low IE) will have little attraction for additional electrons (small EA). On the other hand, a valence shell that holds its electrons tightly will also tend to bind an additional electron tightly.

TABLE 7.3 Electron Affinities of the Representative Elements (kJ/mol)

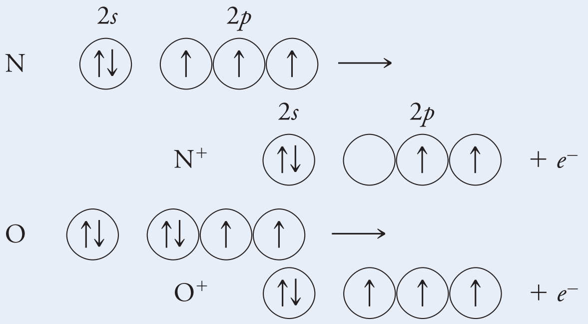
IA	IIA	IIIA	IVA	VA	VIA	VIIA
H						
−73						
Li	Be	B	C	N	O	F
−60	+238	−27	−122	~ +9	−141	−328
Na	Mg	Al	Si	P	S	Cl
−53	+230	−44	−134	−72	−200	−348
K	Ca	Ga	Ge	As	Se	Br
−48	+155	−30	−120	−77	−195	−325
Rb	Sr	In	Sn	Sb	Te	I
−47	+167	−30	−121	−101	−190	−295
Cs	Ba	Tl	Pb	Bi	Po	At
−45	+50	−30	−110	−110	−183	−270

FACETS OF CHEMISTRY 7.4

Irregularities in the Periodic Variations in Ionization Energy and Electron Affinity

The variation in first ionization energy across a period is not a smooth one, as seen in the graph for the elements in period 2. The first irregularity occurs between Be and B, where the IE increases from Li to Be but then decreases from Be to B. This happens because there is a change in the nature of the subshell from which the electron is being removed. For Li and Be, the electron is removed from the 2*s* subshell, but at boron the first electron comes from the higher energy 2*p* subshell where it is not bound so tightly.

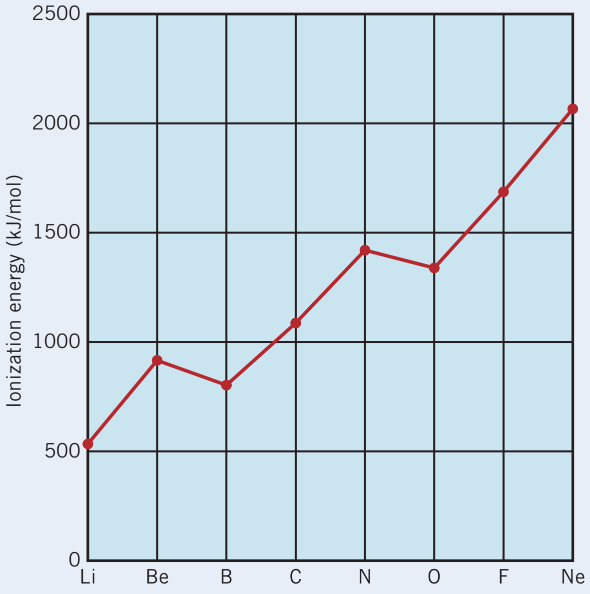
Another irregularity occurs between nitrogen and oxygen. For nitrogen, the electron that's removed comes from a singly occupied orbital. For oxygen, the electron is taken from an orbital that already contains an electron. We can diagram this as follows:



For oxygen, repulsions between the two electrons in the *p* orbital that's about to lose an electron help the electron leave. This "help" is absent for the electron that's about to leave the *p* orbital of nitrogen. As a result, it is not as difficult to remove one electron from an oxygen atom as it is to remove one electron from a nitrogen atom.

As with ionization energy, there are irregularities in the periodic trends for electron affinity. For example, the Group IIA elements have little tendency to acquire electrons because their outer shell *s* orbitals are filled. The incoming electron must enter a higher energy *p* orbital. We also see that the EA for elements in Group VA are either endothermic or only slightly exothermic. This is because the incoming electron must enter an orbital already occupied by an electron.

One of the most interesting irregularities occurs between periods 2 and 3 among the nonmetals. In any group, the element in period 2 has a less exothermic electron affinity than the element below it. The reason seems to be the small size of the nonmetal atoms of period 2, which are among the smallest elements in the periodic table. Repulsions between the many electrons in the small valence shells of these atoms leads to a lower than expected attraction for an incoming electron and a less exothermic electron affinity than the element below in period 3.



Variation in IE for the Period 2 elements, Li through Ne.

SUMMARY

Electromagnetic Radiation. Electromagnetic radiation, or light energy, travels through space at a constant speed of 3.00×10^8 m s^{-1} in the form of waves. The **wavelength,** λ, and **frequency,** ν, of the wave are related by the equation $\lambda\nu = c$, where c is the **speed of light.** The SI unit for frequency is the **hertz** (**Hz,** 1 Hz = 1 s^{-1}). Light also behaves as if it consists of small packets of energy called **photons** or **quanta.** The energy delivered by a photon is proportional to the frequency of the light, and is given by the equation $E = h\nu$, where h is **Planck's constant.** White light is composed of all the frequencies visible to the eye and can be split into a **continuous spectrum.** Visible light represents only a small portion of the entire **electromagnetic spectrum,** which also includes **X rays, ultraviolet, infrared, microwaves,** and **radio** and **TV** waves.

Atomic Spectra. The occurrence of **line spectra** tells us that atoms can emit energy only in discrete amounts and suggests that the energy of the electron is **quantized;** that is, the electron is restricted to certain specific **energy levels** in an atom. Niels Bohr recognized this and, although his theory was later shown to be incorrect, he was the first to propose a model that was able to account for the **Rydberg equation.** Bohr was the first to introduce the idea of **quantum numbers.**

Matter Waves. The wave behavior of electrons and other tiny particles, which can be demonstrated by **diffraction** experiments, was suggested by de Broglie. Schrödinger applied wave theory to the atom and launched the theory we call **wave mechanics** or **quantum mechanics.** This theory tells us that electron waves in atoms are **standing waves** whose crests and **nodes** are stationary. Each standing wave, or **orbital,** is characterized by three quantum numbers, n, ℓ, and m_ℓ (**principal, secondary,** and **magnetic quantum numbers,** respectively). **Shells** are designated by n (which can range from 1 to ∞), **subshells** by ℓ (which can range from 0 to $n - 1$), and orbitals within subshells by m_ℓ (which can range from $-\ell$ to $+\ell$).

Electron Configurations. The electron has magnetic properties that are explained in terms of spin. The **spin quantum number,** m_s, can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$. The **Pauli exclusion principle** limits orbitals to a maximum population of two electrons with **paired spins.** Substances with unpaired electrons are **paramagnetic** and are attracted weakly to a magnetic field. Substances with only paired electrons are **diamagnetic** and are slightly repelled by a magnetic field. The **electron configuration** of an element in its **ground state** is obtained by filling orbitals beginning with the 1s subshell and following the Pauli exclusion principle and **Hund's rule** (which states that electrons spread out as much as possible in orbitals of equal energy). The periodic table serves as a guide in predicting electron configurations. **Abbreviated configurations** show subshell populations outside a noble gas **core. Valence shell configurations** show the populations of subshells in the **outer shell** of an atom of the representative elements. Sometimes we represent electron configurations using **orbital diagrams.** Unexpected configurations occur for chromium and copper because of the extra stability of half-filled and filled subshells, respectively.

Orbital Shapes. The **Heisenberg uncertainty principle** says we cannot know exactly the position and velocity of an electron both at the same instant. Consequently, wave mechanics describes the probable locations of electrons in atoms. In each orbital the electron is conveniently viewed as an **electron cloud** with a varying **electron density.** All s orbitals are spherical; each p orbital consists of two lobes with a **nodal plane** between them. A p subshell has three p orbitals whose axes are mutually perpendicular and point along the x, y, and z axes of an imaginary coordinate system centered at the nucleus. Four of the five d orbitals in a d subshell have the same shape, with four lobes of electron density each. The fifth has two lobes of electron density pointing in opposite directions along the z axis and a ring of electron density in the x–y plane.

Atomic Properties. The amount of positive charge felt by the valence electrons of an atom is the **effective nuclear charge.** This is less than the actual nuclear charge because core electrons partially shield the valence electrons from the full positive charge of the nucleus. **Atomic radii** depend on the value of n of the valence shell orbitals and the effective nuclear charge experienced by the valence electrons. These radii are expressed in units of picometers or nanometers, or an older unit called the **angstrom (Å),** where 1 Å = 100 pm = 0.1 nm. Atomic radii decrease from left to right in a period and from bottom to top in a group in the periodic table. Negative ions are larger than the atoms from which they are formed; positive ions are smaller than the atoms from which they are formed.

Ionization energy (IE) is the energy needed to remove an electron from an isolated gaseous atom, molecule, or ion in its ground state; it is endothermic. The first ionization energies of the elements increase from left to right in a period and from bottom to top in a group. (Irregularities occur in a period when the nature of the orbital from which the electron is removed changes and when the electron removed is first taken from a doubly occupied p orbital.) Successive ionization energies become larger, but there is a very large jump when the next electron must come from the noble gas core beneath the valence shell.

Electron affinity (EA) is the potential energy change associated with the addition of an electron to a gaseous atom or ion in its ground state. For atoms, the first EA is usually exothermic. When more than one electron is added to an atom, the overall potential energy change is endothermic. In general, electron affinity becomes more exothermic from left to right in a period and from bottom to top in a group. (However, the EA of second period nonmetals is less exothermic than for the nonmetals of the third period. Irregularities across a period occur when the electron being added must enter the next higher energy subshell and when it must enter a half-filled p subshell.)

TOOLS FOR PROBLEM SOLVING

Below we list the tools you have learned in this chapter. Notice that only two of them are related to numerical calculations. The others are conceptual tools that we use in analyzing properties of substances in terms of the underlying structure of matter. Review all these tools and refer to them, if necessary, when working on the Review Questions and Problems that follow.

Wavelength–frequency relationship *(page 253)* Use this equation to convert between frequency and wavelength.

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

Energy of a photon *(page 257)* Use the following equation to calculate the energy carried by a photon of frequency ν. Also, ν can be calculated if E is known.

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

Periodic table We will use the periodic table as a tool for many purposes. In this chapter you learned to use the periodic table as an aid in writing electron configurations (page *275*) of the elements and as a tool to correlate an element's location in the table to similarities in chemical properties (page 280).

Periodic trends in atomic and ionic size *(pages 285, 286)* The periodic table helps us predict relative sizes of atoms and ions.

Periodic trends in ionization energy *(page 288)* Trends are used to compare the ease with which atoms of the elements lose electrons.

Periodic trends in electron affinity *(page 290)* Trends help to compare the tendency of atoms or ions to gain electrons.

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at www.wiley.com/college/brady. OH = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Electromagnetic Radiation

7.1 In general terms, why do we call light *electromagnetic radiation*?

7.2 In general, what does the term *frequency* imply? What is meant by the term *frequency of light*? What symbol is used for it, and what is the SI unit (and symbol) for frequency?

7.3 What is meant by the term *wavelength* of light? What symbol is used for it?

7.4 Sketch a picture of a wave and label its wavelength and its amplitude.

7.5 Which property of light waves is a measure of the brightness of the light? Which specifies the color of the light? Which is related to the energy of the light?

7.6 Arrange the following regions of the electromagnetic spectrum in order of increasing wavelength (i.e., shortest wavelength → longest wavelength): microwaves, TV, X rays, ultraviolet, visible, infrared, gamma rays.

7.7 What wavelength range is covered by the *visible spectrum*?

7.8 Arrange the following colors of visible light in order of increasing wavelength: orange, green, blue, yellow, violet, red.

7.9 Write the equation that relates the wavelength and frequency of a light wave. (Define all symbols used.)

7.10 How is the frequency of a particular type of radiation related to the energy associated with it? (Give an equation, defining all symbols.)

7.11 What is a photon?

7.12 Show that the energy of a photon is given by the equation $E = hc/\lambda$.

7.13 Examine each of the following pairs and state which of the two has the higher *energy.*
(a) microwaves and infrared
(b) visible light and infrared
(c) ultraviolet light and X rays
(d) visible light and ultraviolet light

7.14 What is a quantum of energy?

Atomic Spectra

7.15 What is an atomic spectrum? How does it differ from a continuous spectrum?

7.16 What fundamental fact is implied by the existence of atomic spectra?

Bohr Atom and the Hydrogen Spectrum

7.17 Describe Niels Bohr's model of the structure of the hydrogen atom.

7.18 In qualitative terms, how did Bohr's model account for the atomic spectrum of hydrogen?

7.19 What is the "ground state"?

7.20 In what way was Bohr's theory a success? How was it a failure?

Wave Nature of Matter

7.21 How does the behavior of very small particles differ from that of the larger, more massive objects that we meet in everyday life? Why don't we notice this same behavior for the larger, more massive objects?

7.22 Describe the phenomenon called diffraction. How can this be used to demonstrate that de Broglie's theory was correct?

7.23 What experiment could you perform to determine whether a beam was behaving as a wave or as a stream of particles?

7.24 What is *wave/particle duality*?

7.25 What is the difference between a *traveling wave* and a *standing wave*?

7.26 What is the collapsing atom paradox?

7.27 How does quantum mechanics resolve the collapsing atom paradox?

Electron Waves in Atoms

7.28 What are the names used to refer to the theories that apply the matter–wave concept to electrons in atoms?

7.29 What is the term used to describe a particular waveform of a standing wave for an electron?

7.30 What are the two properties of orbitals in which we are most interested? Why?

Quantum Numbers

7.31 What are the allowed values of the principal quantum number?

7.32 What is the value for n for (a) the K shell and (b) the M shell?

7.33 Why does every shell contain an s subshell?

7.34 How many orbitals are found in (a) an s subshell, (b) a p subshell, (c) a d subshell, and (d) an f subshell?

7.35 If the value of m_ℓ for an electron in an atom is 2, could another electron in the same subshell have $m_\ell = -3$?

7.36 Suppose an electron in an atom has the following set of quantum numbers: $n = 2$, $\ell = 1$, $m_\ell = 1$, $m_s = +\frac{1}{2}$. What set of quantum numbers is impossible for another electron in this same atom?

Electron Spin

7.37 What physical property of electrons leads us to propose that they spin like a toy top?

7.38 What is the name of the magnetic property exhibited by atoms that contain unpaired electrons?

7.39 What is the Pauli exclusion principle? What effect does it have on the populating of orbitals by electrons?

7.40 What are the possible values of the spin quantum number?

Electron Configuration of Atoms

7.41 What do we mean by the term *electronic structure?*

7.42 Within any given shell, how do the energies of the *s, p, d,* and *f* subshells compare?

7.43 What fact about the energies of subshells was responsible for the apparent success of Bohr's theory about electronic structure?

7.44 How do the energies of the orbitals belonging to a given subshell compare?

7.45 Give the electron configurations of the elements in Period 2 of the periodic table.

7.46 Give the correct electron configurations of (a) Cr and (b) Cu.

7.47 What is the correct electron configuration of silver?

7.48 How are the electron configurations of the elements in a given group similar? Illustrate your answer by writing shorthand configurations for the elements in Group VIA.

7.49 Define the terms *valence shell* and *valence electrons.*

Shapes of Atomic Orbitals

7.50 Why do we use probabilities when we discuss the position of an electron in the space surrounding the nucleus of an atom?

7.51 Sketch the approximate shape of (a) a $1s$ orbital and (b) a $2p$ orbital.

7.52 How does the size of a given type of orbital vary with n?

7.53 How are the p orbitals of a given p subshell oriented relative to each other?

7.54 What is a *nodal plane*?

7.55 What is a spherical node?

7.56 How many nodal planes does a p orbital have? How many does a d orbital have?

7.57 On appropriate coordinate axes, sketch the shape of the following d orbitals: (a) d_{xy}, (b) $d_{x^2-y^2}$, and (c) d_{z^2}.

Atomic and Ionic Size

7.58 What is the meaning of *effective nuclear charge?* How does the effective nuclear charge felt by the outer electrons vary going down a group? How does it change as we go from left to right across a period?

7.59 In what region of the periodic table are the largest atoms found? Where are the smallest atoms found?

7.60 Going from left to right in the periodic table, why are the size changes among the transition elements more gradual than those among the representative elements?

Ionization Energy

7.61 Define ionization energy. Why are ionization energies of atoms and positive ions endothermic quantities?

7.62 For oxygen, write a reaction for the change associated with (a) its first ionization energy and (b) its third ionization energy.

7.63 Explain why ionization energy increases from left to right in a period and decreases from top to bottom in a group.

7.64 Why is an atom's second ionization energy always larger than its first ionization energy?

7.65 Why is the fifth ionization energy of carbon so much larger than its fourth?

7.66 Why is the first ionization energy of aluminum less than the first ionization energy of magnesium?

7.67 Why does phosphorus have a larger first ionization energy than sulfur?

Electron Affinity

7.68 Define *electron affinity*.

7.69 For sulfur, write an equation for the change associated with (a) its first electron affinity and (b) its second electron affinity. How should they compare?

7.70 Why does Cl have a more exothermic electron affinity than F? Why does Br have a less exothermic electron affinity than Cl?

7.71 Why is the second electron affinity of an atom always endothermic?

7.72 How is electron affinity related to effective nuclear charge? On this basis, explain the relative magnitudes of the electron affinities of oxygen and fluorine.

REVIEW PROBLEMS

Electromagnetic Radiation

7.73 What is the frequency in hertz of blue light having a wavelength of 430 nm?

OH **7.74** Ultraviolet light with a wavelength of more than 280 nm has little germicidal value. What is the frequency that corresponds to this wavelength?

7.75 A certain substance strongly absorbs infrared light having a wavelength of 6.85 μm. What is the frequency of this light in hertz?

7.76 The sun emits many wavelengths of light. The brightest light is emitted at about 0.48 μm. What frequency does this correspond to?

7.77 Ozone protects the earth's inhabitants from the harmful effects of ultraviolet light arriving from the sun. This shielding is a maximum for UV light having a wavelength of 295 nm. What is the frequency in hertz of this light?

7.78 The meter is defined as the length of the path light travels in a vacuum during the time interval of 1/299,792,458 of a second. The standards body recommends use of light from a helium–neon laser for realizing the meter. The light from the laser has a wavelength of 632.99139822 nm. What is the frequency of this light, in hertz?

7.79 In New York City, radio station WCBS broadcasts its FM signal at a frequency of 101.1 megahertz (MHz). What is the wavelength of this signal in meters?

7.80 Sodium vapor lamps are often used in residential street lighting. They give off a yellow light having a frequency of 5.09×10^{14} Hz. What is the wavelength of this light in nanometers?

7.81 There has been some concern in recent times about possible hazards to people who live very close to high-voltage electric power lines. The electricity in these wires oscillates at a frequency of 60 Hz, which is the frequency of any electromagnetic radiation that they emit. What is the wavelength of this radiation in meters? What is it in kilometers?

7.82 An X-ray beam has a frequency of 1.50×10^{18} Hz. What is the wavelength of this light in nanometers and in picometers?

7.83 Calculate the energy in joules of a photon of red light having a frequency of 4.0×10^{14} Hz. What is the energy of one mole of these photons?

7.84 Calculate the energy in joules of a photon of green light having a wavelength of 560 nm.

Atomic Spectra

7.85 In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. (a) What color is this line? (b) What is its frequency? (c) What is the energy of each of its photons?

7.86 In the spectrum of sodium, there is a line with a wavelength of 589 nm. (a) What color is this line? (b) What is its frequency? (c) What is the energy of each of its photons?

OH **7.87** Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which $n_2 = 6$ and $n_1 = 3$. Would we be expected to see the light corresponding to this spectral line? Explain your answer.

7.88 Use the Rydberg equation to calculate the wavelength in nanometers of the spectral line of hydrogen for which $n_2 = 5$ and $n_1 = 2$. Would we be expected to see the light corresponding to this spectral line? Explain your answer.

7.89 Calculate the wavelength of the spectral line produced in the hydrogen spectrum when an electron falls from the tenth Bohr orbit to the fourth. In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?

7.90 Calculate the energy in joules and the wavelength in nanometers of the spectral line produced in the hydrogen spectrum when an electron falls from the fourth Bohr orbit to the first. In which region of the electromagnetic spectrum (UV, visible, or infrared) is the line?

Quantum Numbers

7.91 What is the letter code for a subshell with (a) $\ell = 1$ and (b) $\ell = 3$?

7.92 What is the value of ℓ for (a) an *f* orbital and (b) a *d* orbital?

7.93 Give the values of n and ℓ for the following subshells: (a) 3*s* and (b) 5*d*.

7.94 Give the values of n and ℓ for the following subshells: (a) 4*p* and (b) 6*f*.

7.95 For the shell with $n = 6$, what are the possible values of ℓ?

7.96 In a particular shell, the largest value of ℓ is 7. What is the value of n for this shell?

7.97 What are the possible values of m_ℓ for a subshell with (a) $\ell = 1$ and (b) $\ell = 3$?

7.98 If the value of ℓ for an electron in an atom is 5, what are the possible values of m_ℓ that this electron could have?

7.99 If the value of m_ℓ for an electron in an atom is -4, what is the smallest value of ℓ that the electron could have? What is the smallest value of n that the electron could have?

7.100 How many orbitals are there in an h subshell ($\ell = 5$)? What are their values of m_ℓ?

OH **7.101** Give the complete set of quantum numbers for all of the electrons that could populate the $2p$ subshell of an atom.

7.102 Give the complete set of quantum numbers for all of the electrons that could populate the $3d$ subshell of an atom.

7.103 In an antimony atom, how many electrons have $\ell = 1$? How many electrons have $\ell = 2$ in an antimony atom?

7.104 In an atom of barium, how many electrons have (a) $\ell = 0$ and (b) $m_\ell = 1$?

Electron Configurations of Atoms

7.105 Give the electron configurations of (a) S, (b) K, (c) Ti, and (d) Sn.

7.106 Write the electron configurations of (a) As, (b) Cl, (c) Ni, and (d) Si.

7.107 Which of the following atoms in their ground states are expected to be paramagnetic: (a) Mn, (b) As, (c) S, (d) Sr, and (e) Ar?

7.108 Which of the following atoms in their ground states are expected to be diamagnetic: (a) Ba, (b) Se, (c) Zn, and (d) Si?

ILW OH **7.109** How many unpaired electrons would be found in the ground state of (a) Mg, (b) P, and (c) V?

7.110 How many unpaired electrons would be found in the ground state of (a) Cs, (b) S, and (c) Ni?

7.111 Write the shorthand electron configurations for (a) Ni, (b) Cs, (c) Ge, (d) Br, and (e) Bi.

7.112 Write the shorthand electron configurations for (a) Al, (b) Se, (c) Ba, (d) Sb, and (e) Gd.

7.113 Draw complete orbital diagrams for (a) Mg and (b) Ti.

7.114 Draw complete orbital diagrams for (a) As and (b) Ni.

7.115 Draw orbital diagrams for the shorthand configurations of (a) Ni, (b) Cs, (c) Ge, and (d) Br.

7.116 Draw orbital diagrams for the shorthand configurations of (a) Al, (b) Se, (c) Ba, and (d) Sb.

7.117 What is the value of n for the valence shells of (a) Sn, (b) K, (c) Br, and (d) Bi?

7.118 What is the value of n for the valence shells of (a) Al, (b) Se, (c) Ba, and (d) Sb?

7.119 Give the configuration of the valence shell for (a) Na, (b) Al, (c) Ge, and (d) P.

7.120 Give the configuration of the valence shell for (a) Mg, (b) Br, (c) Ga, and (d) Pb.

7.121 Draw the orbital diagram for the valence shell for (a) Na, (b) Al, (c) Ge, and (d) P.

7.122 Draw the orbital diagram for the valence shell of (a) Mg, (b) Br, (c) Ga, and (d) Pb.

Atomic Properties

7.123 If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in (a) Na, (b) S, and (c) Cl?

7.124 If the core electrons were 100% effective at shielding the valence electrons from the nuclear charge and the valence electrons provided no shielding for each other, what would be the effective nuclear charge felt by a valence electron in (a) Mg, (b) Si, and (c) Br?

7.125 Choose the larger atom in each pair: (a) Mg or S; (b) As or Bi.

7.126 Choose the larger atom in each pair: (a) Al or Ar; (b) Tl or In.

7.127 Choose the largest atom among the following: Ge, As, Sn, and Sb.

7.128 Place the following in order of increasing size: N^{3-}, Mg^{2+}, Na^{+}, Ne, F^{-}, and O^{2-}.

7.129 Choose the larger particle in each pair: (a) Na or Na^{+}; (b) Co^{3+} or Co^{2+}; (c) Cl or Cl^{-}.

OH **7.130** Choose the larger particle in each pair: (a) S or S^{2-}; (b) Al^{3+} or Al; (c) Au^{+} or Au^{3+}.

7.131 Choose the atom with the larger first ionization energy in each pair: (a) B or N; (b) Se or S; (c) Cl or Ge.

7.132 Choose the atom with the larger first ionization energy in each pair: (a) Li or Rb ; (b) Al or F; (c) F or C.

7.133 Choose the atom with the more exothermic electron affinity in each pair: (a) I or Br; (b) Ga or As.

7.134 Choose the atom with the more exothermic electron affinity in each pair: (a) S or As; (b) Si or N.

7.135 Use the periodic table to select the element in the following list for which there is the largest difference between the second and third ionization energies: Na, Mg, Al, Si, P, Se, and Cl.

7.136 Use the periodic table to select the element in the following list for which there is the largest difference between the fourth and fifth ionization energies: Na, Mg, Al, Si, P, Se, and Cl.

ADDITIONAL EXERCISES

7.137 The human ear is sensitive to sound ranging from 20 to 20,000 Hz. The speed of sound is 330 m/s in air, and 1500 m/s under water. What is the longest and the shortest wavelength that can be heard (a) in air and (b) under water?

7.138 Microwaves are used to heat food in microwave ovens. The microwave radiation is absorbed by moisture in the food. This heats the water, and as the water becomes hot, so does the food. How many photons having a wavelength of 3.00 mm would have to be absorbed by 1.00 g of water to raise its temperature by 1.00 °C?

7.139 In the spectrum of hydrogen, there is a line with a wavelength of 410.3 nm. Use the Rydberg equation to calculate the value of n for the higher energy Bohr orbit involved in the emission of this light. Assume the value of n for the lower energy orbit equals 2.

7.140 Calculate the wavelength in nanometers of the shortest wavelength of light emitted by a hydrogen atom.

7.141 Which of the following electronic transitions could lead to the emission of light from an atom?

$$1s \longrightarrow 4p \longrightarrow 3d \longrightarrow 5f \longrightarrow 4d \longrightarrow 2p$$

7.142 A neon sign is a gas discharge tube in which electrons traveling from the cathode to the anode collide with neon atoms in the tube and knock electrons off of them. As electrons return to the neon ions and drop to lower energy levels, light is given off. How fast would an electron have to be moving to eject an electron from an atom of neon, which has a first ionization energy equal to 2080 kJ mol^{-1}?

OH ***7.143** How many grams of water could have its temperature raised by 5.0 °C by a mole of photons that have a wavelength of (a) 600 nm and (b) 300 nm?

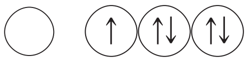
OH ***7.144** It has been found that when the chemical bond between chlorine atoms in Cl_2 is formed, 328 kJ is released per mole of Cl_2 formed. What is the wavelength of light that would be required to break chemical bonds between chlorine atoms?

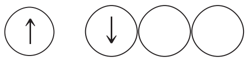
7.145 Calculate the wavelengths of the lines in the spectrum of hydrogen that result when an electron falls from a Bohr orbit with (a) $n = 5$ to $n = 1$, (b) $n = 4$ to $n = 2$, and (c) $n = 6$ to $n = 4$. In which regions of the electromagnetic spectrum are these lines?

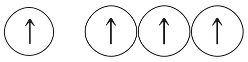
OH **7.146** What, if anything, is wrong with the following electron configurations for atoms in their ground states?

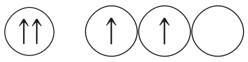
(a) $1s^2 2s^1 2p^3$ (c) $1s^2 2s^2 2p^4$
(b) [Kr] $3d^7 4s^2$ (d) [Xe] $4f^{14} 5d^8 6s^1$

7.147 Suppose students gave the following orbital diagrams for the $2s$ and $2p$ subshell in the ground state of an atom. What, if anything, is wrong with them? Are any of these electron distributions impossible?

(a)


(b)


(c)


(d)


7.148 How many electrons are in p orbitals in an atom of germanium?

7.149 What are the quantum numbers of the electrons that are lost by an atom of iron when it forms the ion Fe^{2+}?

***7.150** The removal of an electron from the hydrogen atom corresponds to raising the electron to the Bohr orbit that has $n = \infty$. On the basis of this statement, calculate the ionization energy of hydrogen in units of (a) joules per atom and (b) kilojoules per mole.

7.151 Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. On the basis of what you have learned about electron affinities and electron configurations, why is it extremely difficult to place a third electron on the oxygen atom?

7.152 From the data available in this chapter, determine the ionization energy of (a) F^-, (b) O^-, and (c) O^{2-}. Are any of these energies exothermic?

7.153 For an oxygen atom, which requires more energy, the addition of two electrons or the removal of one electron?

EXERCISES IN CRITICAL THINKING

7.154 Our understanding of the quantum mechanical atom has been developing since the early 1900s. Has quantum mechanics had any effect on the daily lives of people?

7.155 When a copper atom loses an electron to become a Cu^+ ion, what are the possible quantum numbers of the electron that was lost?

7.156 The "red shift" of spectral features of distant stars is used to estimate their relative velocity compared to the earth. Using the information in this chapter, and other reference sources, explain how this is done.

7.157 Placing a small piece of an element from Group IA in water results in increasingly rapid and violently spectacular reactions as we progress from lithium down to cesium. What information in this chapter makes this behavior understandable?

7.158 In this chapter we saw that atoms in an excited state emit light when their electrons relax to lower energy levels. Lasers also emit certain wavelengths of light. What are the similarities and differences in how laser light is produced compared to atomic spectra?

7.159 In this chapter we saw that atoms in an excited state emit light when their electrons relax to lower energy levels. Light emitting diodes, LEDs, can be designed to emit light of different colors. How does the way light is produced in an LED differ from an excited state atom?