Chapter 3

Electronic Structure and Periodic Properties of Elements

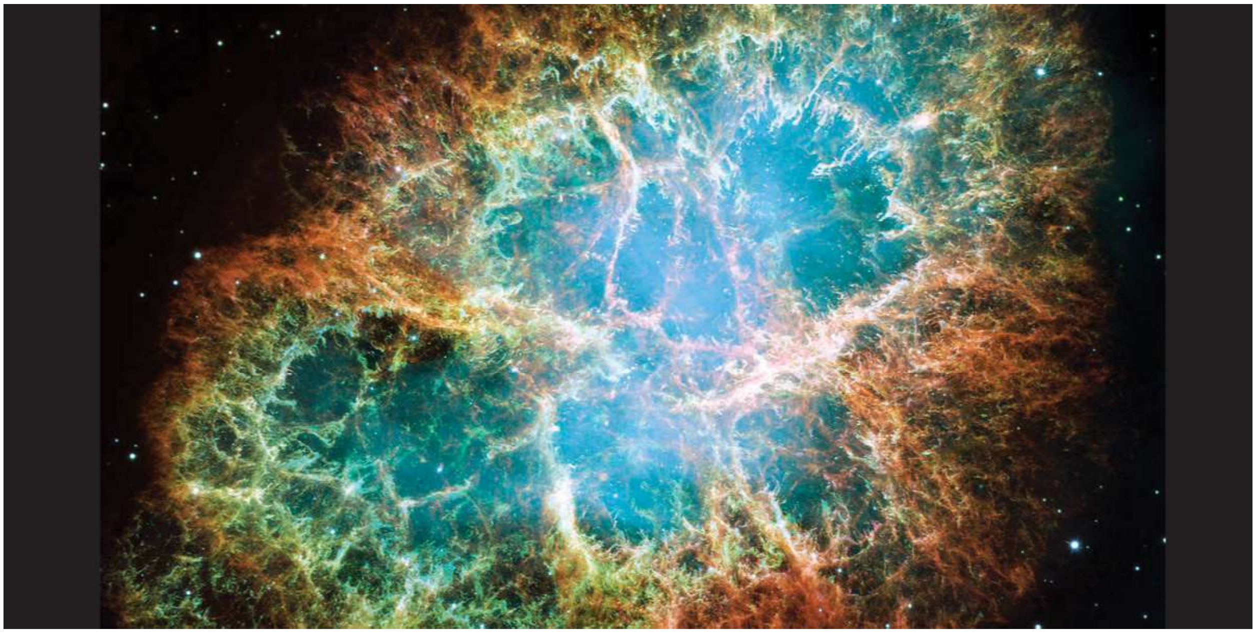


Figure 3.1 The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA's Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including S^+ (green filaments) and O^{2+} (red filaments). (credit: modification of work by NASA and ESA)

Chapter Outline

3.1 Electromagnetic Energy
3.2 The Bohr Model
3.3 Development of Quantum Theory
3.4 Electronic Structure of Atoms (Electron Configurations)
3.5 Periodic Variations in Element Properties
3.6 The Periodic Table
3.7 Molecular and Ionic Compounds

Introduction

In 1054, Chinese astronomers recorded the appearance of a "guest star" in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (**Figure 3.1**) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

3.1 Electromagnetic Energy

By the end of this section, you will be able to:

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in **Figure 3.2**, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz (Hz)**. Common multiples of this unit are megahertz, (1 MHz = 1×10^6 Hz) and gigahertz (1 GHz = 1×10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in **Figure 3.2**, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

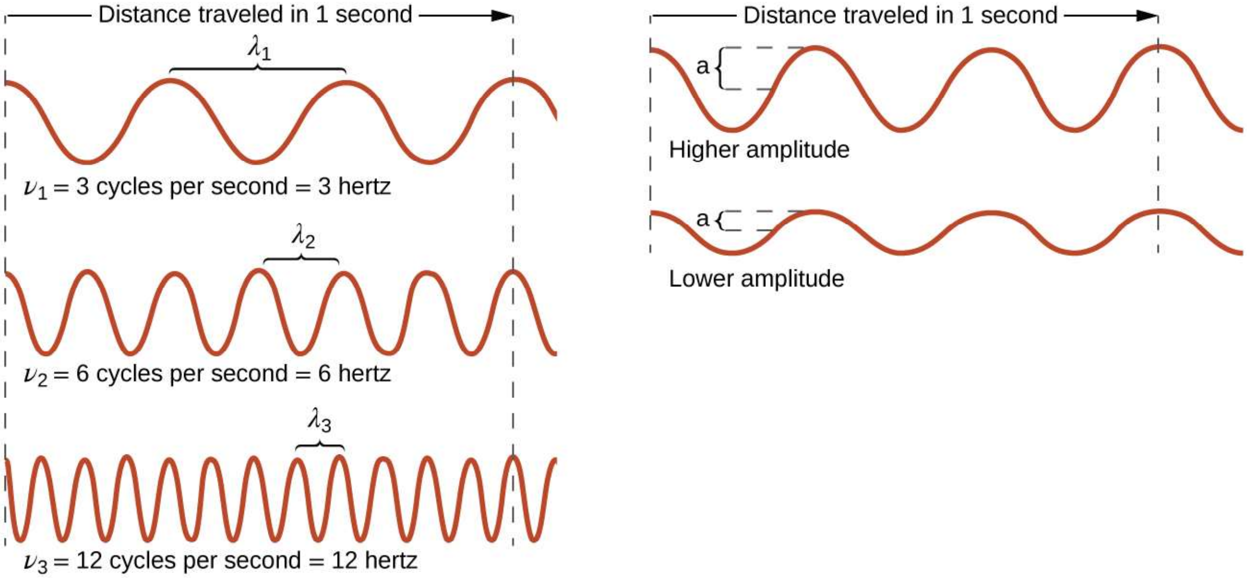


Figure 3.2 One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant, c:

$$c = 2.998 \times 10^8 \, \text{ms}^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in **Figure 3.3**. This figure also shows the **electromagnetic spectrum**, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

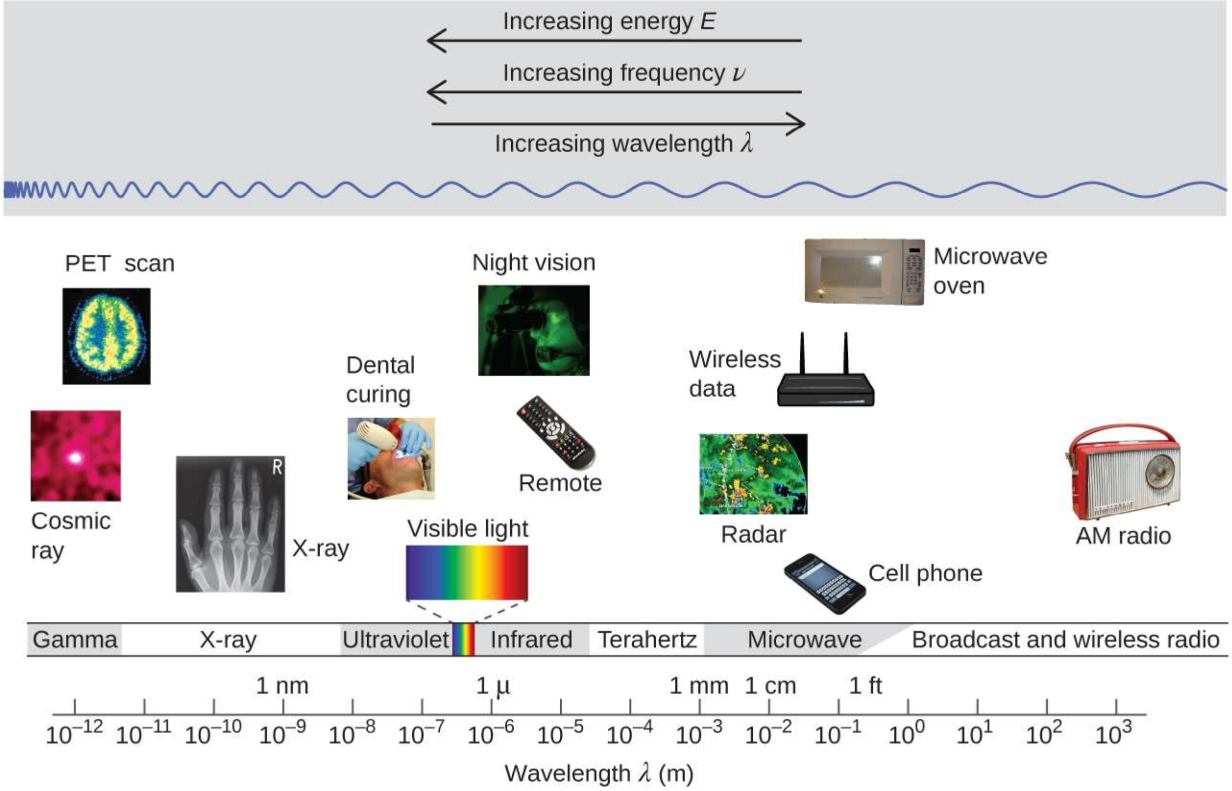


Figure 3.3 Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

Example 3.1

Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1 × 10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the equation $c = \lambda\nu$ to solve for the frequency:

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

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998\times10^{8}\,\cancel{\text{m}}\,\text{s}^{-1}}{589\,\cancel{\text{nm}}}\right)\left(\frac{1\times10^{9}\,\cancel{\text{nm}}}{1\,\cancel{\text{m}}}\right) = 5.09\times10^{14}\,\text{s}^{-1}$$

Check Your Learning

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer: 0.353 m = 35.3 cm

Chemistry in Everyday Life

Wireless Communication

Figure 3.4 Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (**Figure 3.5**). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

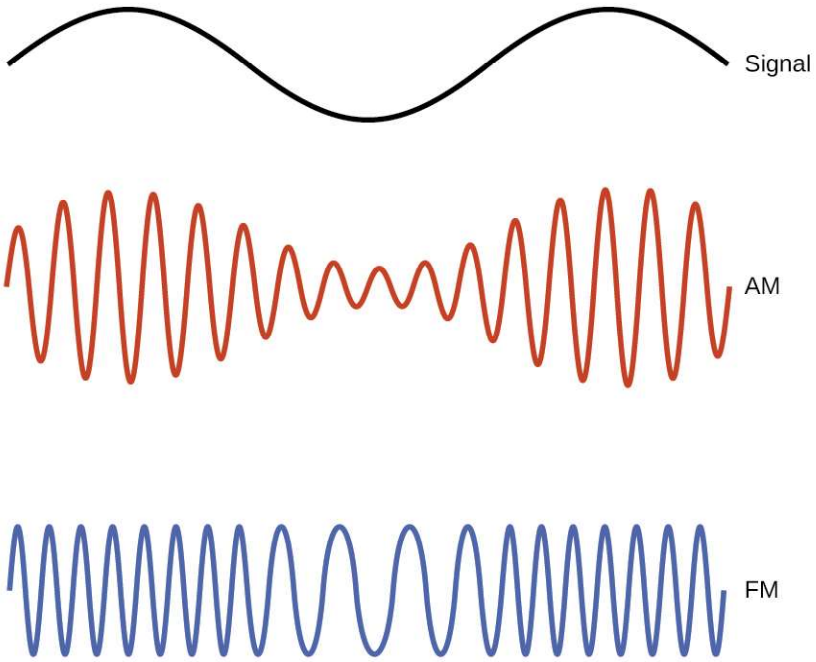


Figure 3.5 This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. **Figure 3.6** shows the **interference patterns** that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in **Figure 3.6** correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.

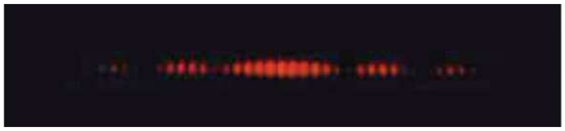


Figure 3.6 Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Portrait of a Chemist

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are travelling waves. **Standing waves** (also known as **stationary waves**) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. **Figure 3.7** shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in **Figure 3.7**. The key observation from the figure is *that only those waves having an integer number, n, of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths n. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

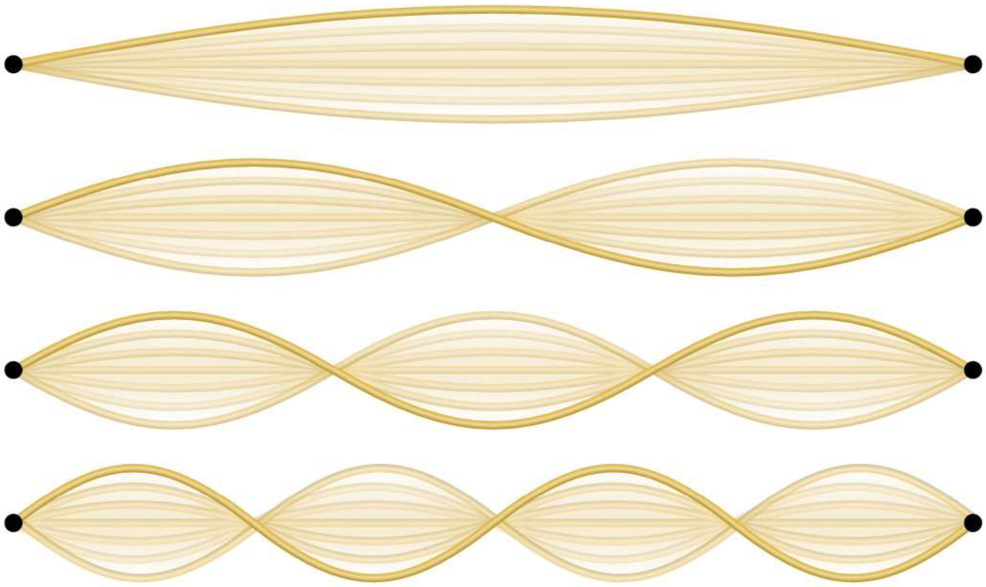


Figure 3.7 A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in **Figure 3.8**, which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume).

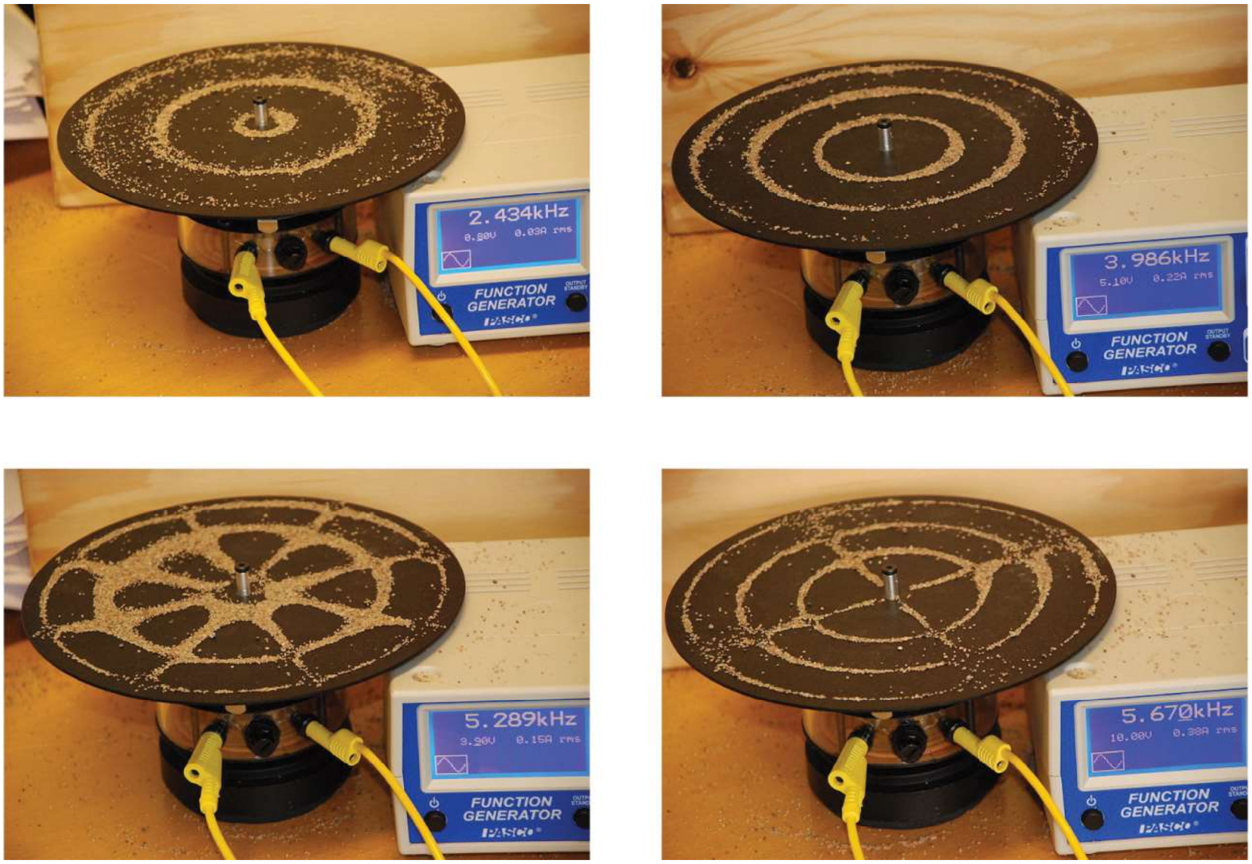


Figure 3.8 Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).

Link to Learning

You can watch the formation of various radial nodes here (http://openstax.org/l/16radnodes) as singer Imogen Heap projects her voice across a kettle drum.

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. Figure 3.9 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

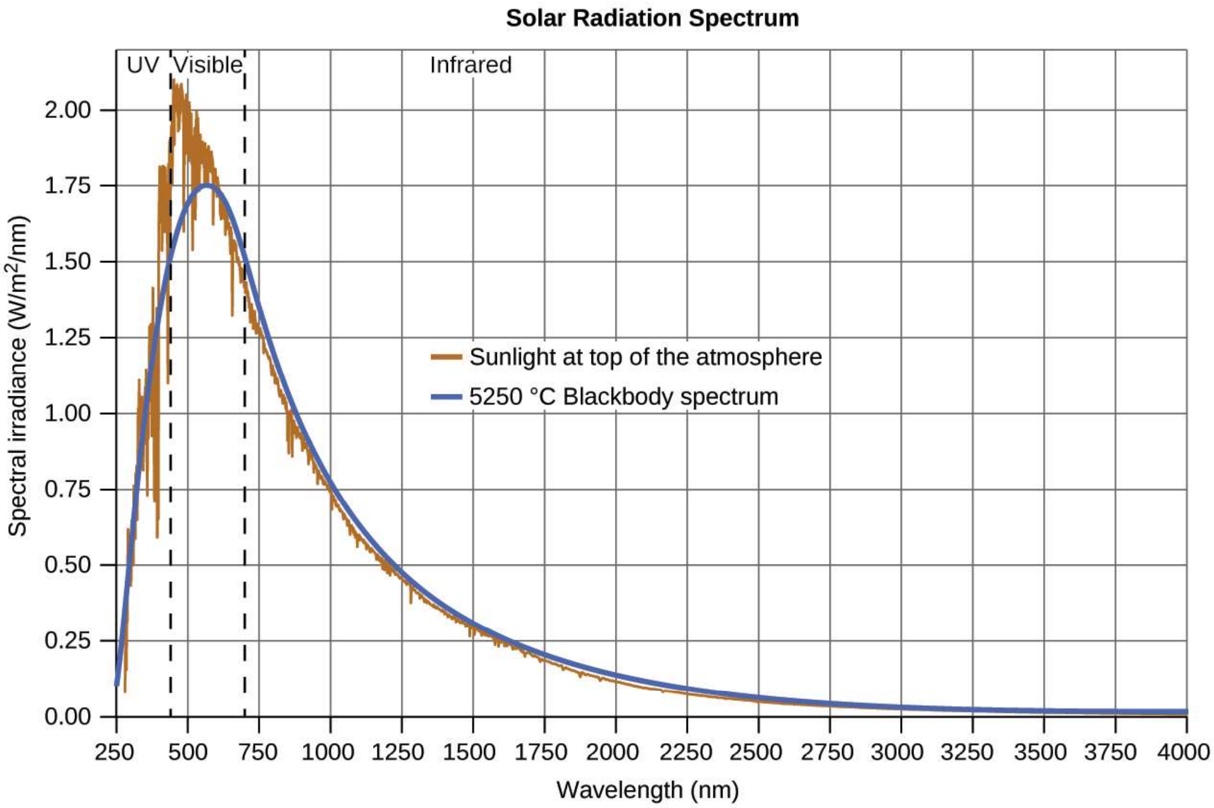


Figure 3.9 The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In **Figure 3.9**, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A **blackbody** is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. **Figure 3.10** shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu, \quad n = 1, \ 2, \ 3, \ \ldots$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

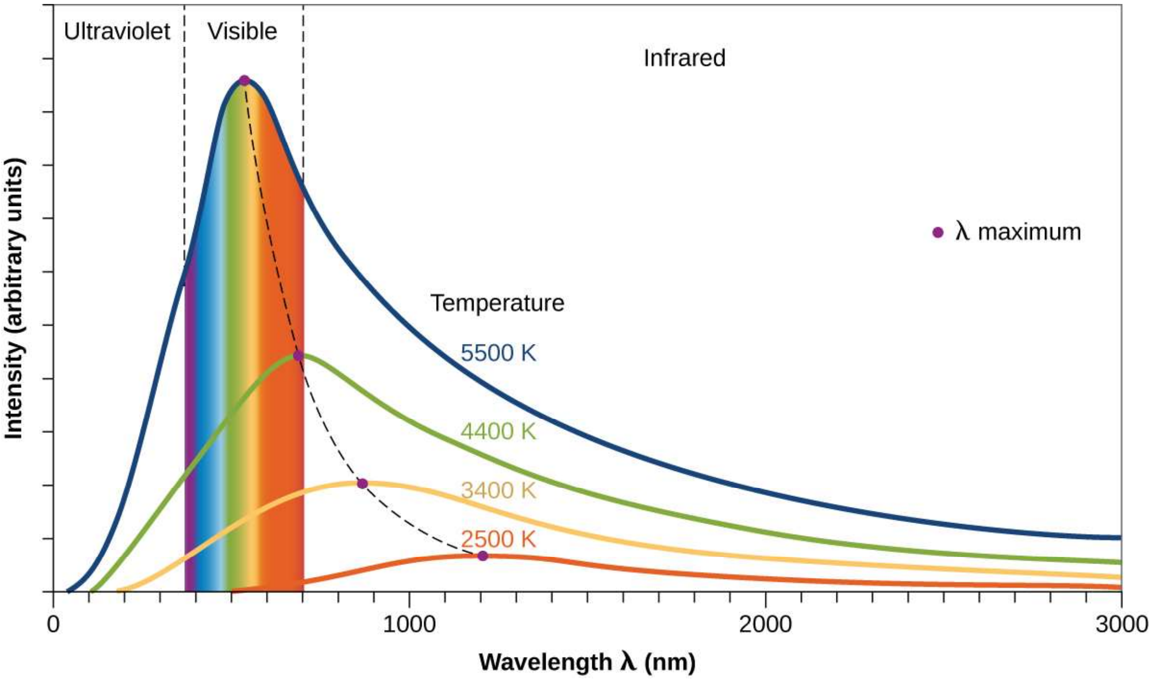


Figure 3.10 Blackbody spectral distribution curves are shown for some representative temperatures.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (**Figure 3.11**). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Processes that increase the energy of an atom involve the absorption of light and are called **endothermic**. Processes that decrease the energy involve emission of light and are called **exothermic**. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.

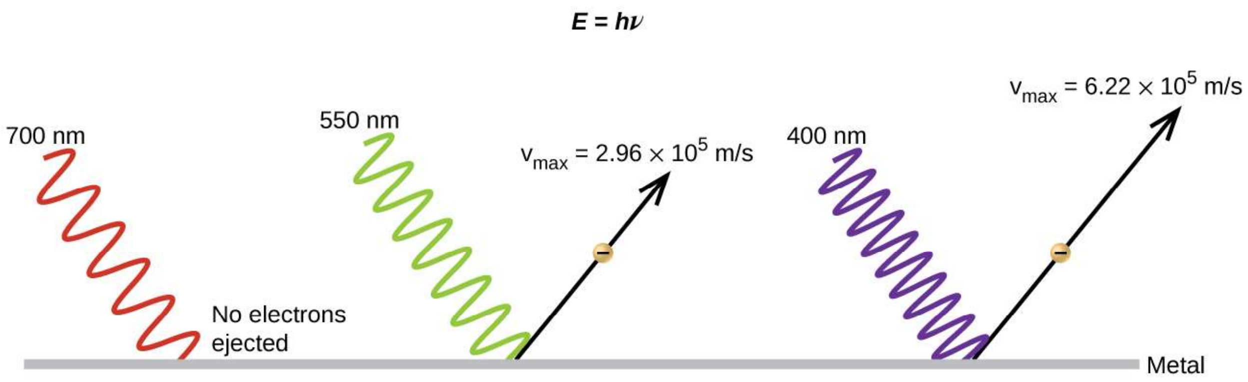


Figure 3.11 Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example 3.2

Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$E = \frac{hc}{\lambda}$$

$$E = \frac{(6.626 \times 10^{-34}\ \text{J}\cancel{\text{s}})(2.998 \times 10^{8}\ \text{m}\cancel{\text{s}}^{-1})}{(640\ \cancel{\text{nm}})\left(\frac{1\ \text{m}}{10^{9}\ \cancel{\text{nm}}}\right)}$$

$$E = 3.10 \times 10^{-19}\ \text{J}$$

Check Your Learning

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer: 2×10^{-24} J

Link to Learning

Use this simulation program (http://openstax.org/l/16photelec) to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

Example 3.3

Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

(a) Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.

(b) Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.

(c) Increasing the brightness of incoming light *increases* the number of ejected electrons.

(d) Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

(a) False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.

(b) False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.

(c) True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.

(d) True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Check Your Learning

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87×10^{14} Hz.

Answer: 394

Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in **Figure 3.9**, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in **Figure 3.10**.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in **Figure 3.13**. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (**Figure 3.12**). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.

Figure 3.12 Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in **Figure 3.13**.

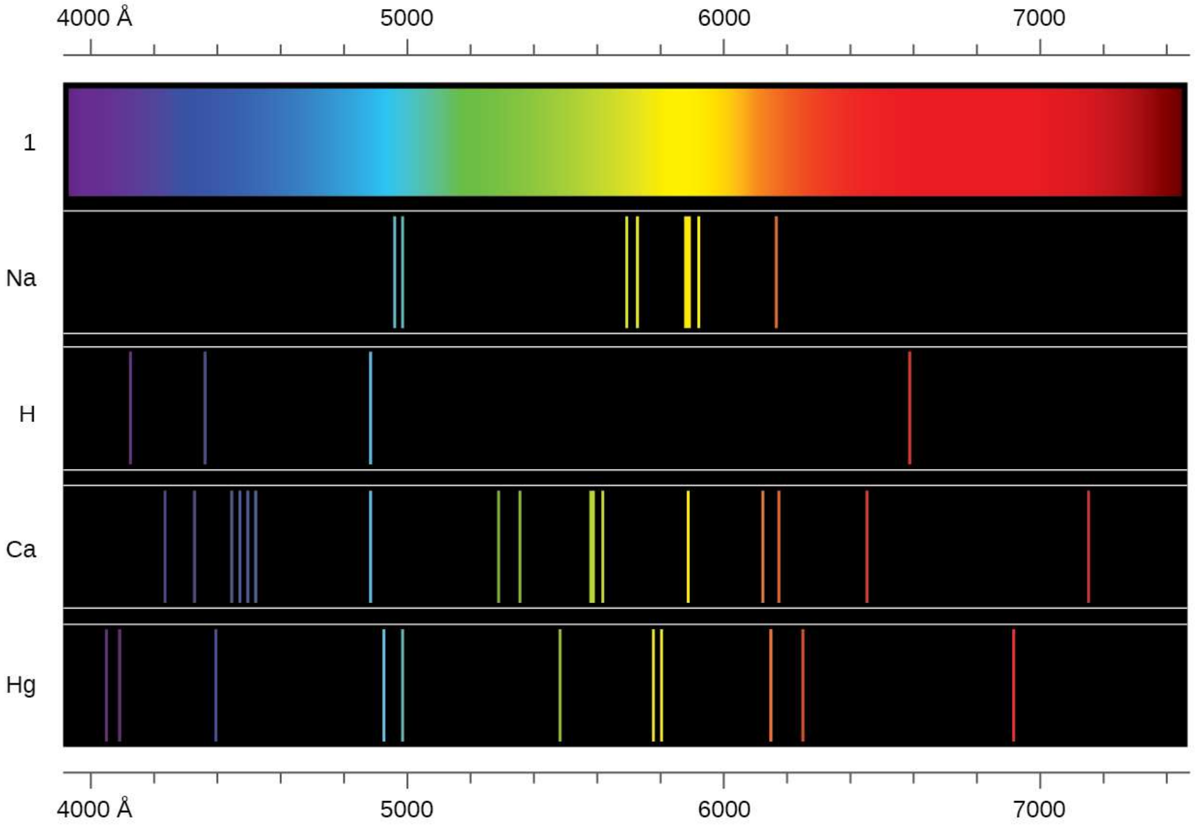


Figure 3.13 Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

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

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant (1.097×10^7 m^{-1}).

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

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

3.2 The Bohr Model

By the end of this section, you will be able to:

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature “solar system” with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron’s orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism’s prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck’s ideas of quantization and Einstein’s finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\,\Delta E\,| \;=\; |\,E_{\mathrm{f}} - E_{\mathrm{i}}\,| \;= h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck’s constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were quantized:

$$E_n = -\frac{k}{n^2},\quad n = 1,\; 2,\; 3,\quad \ldots$$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck’s constant. Inserting the expression for the orbit energies into the equation for ΔE gives

$$\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda}$$

or

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

which is identical to the Rydberg equation in which $R_\infty = \frac{k}{hc}$. When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr’s model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in **Figure 3.14**. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its **ground electronic state** (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher *n* value and the atom is now in an **excited electronic state** (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (**Figure 3.15**).

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^+, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of 2.179×10^{-18} J.

$$E_n = -\frac{kZ^2}{n^2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which α_0 is a constant called the Bohr radius, with a value of 5.292×10^{-11} m:

$$r = \frac{n^2}{Z} a_0$$

The equation also shows us that as the electron's energy increases (as *n* increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence of electrostatic attraction on distance, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases and it is held less tightly in the atom. Note that as *n* gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \longrightarrow \infty$ and $r \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_{n \longrightarrow \infty} - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

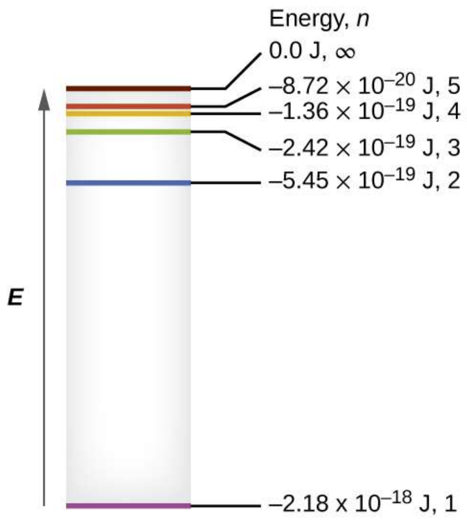


Figure 3.14 Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

Example 3.4

Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by this equation:

$$E = \frac{-kZ^2}{n^2}$$

The atomic number, Z, of hydrogen is 1; $k = 2.179 \times 10^{-18}$ J; and the electron is characterized by an n value of 3. Thus,

$$E = \frac{-(2.179 \times 10^{-18}\ \text{J}) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19}\ \text{J}$$

Check Your Learning

The electron in **Figure 3.15** is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer: -6.053×10^{-20} J

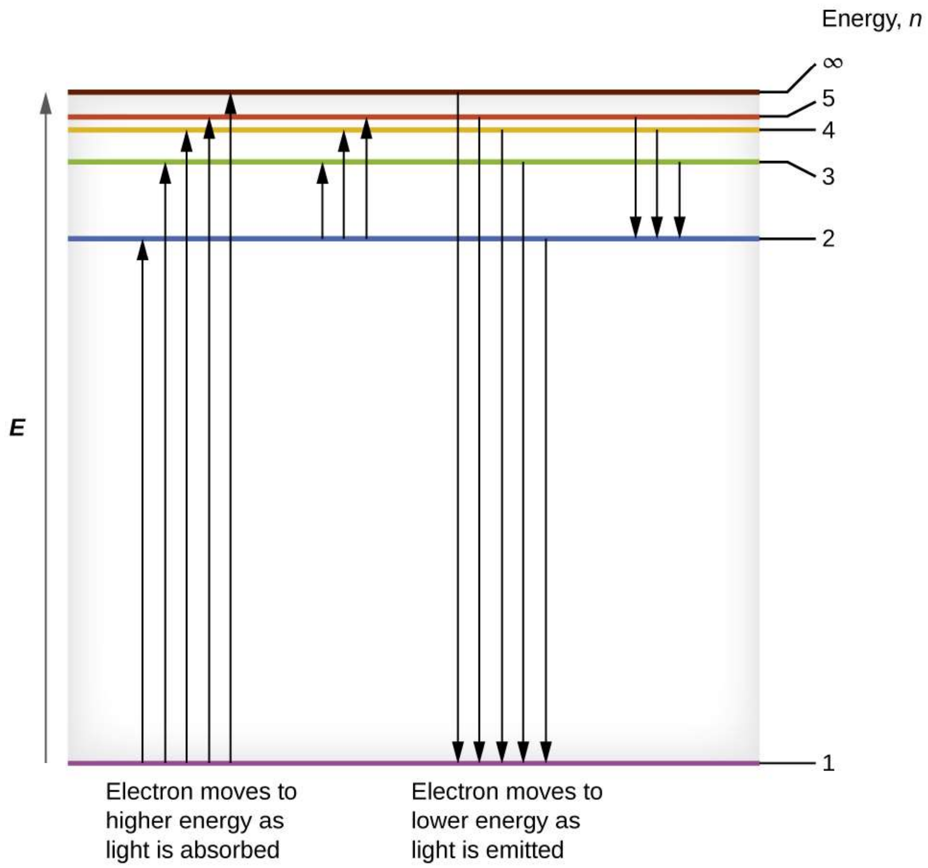


Figure 3.15 The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Example 3.5

Calculating the Energy and Wavelength of Electron Transitions in a One–electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = 2.179 \times 10^{-18}\left(\frac{1}{4^2} - \frac{1}{6^2}\right)\text{J}$$

$$\Delta E = 2.179 \times 10^{-18}\left(\frac{1}{16} - \frac{1}{36}\right)\text{J}$$

$$\Delta E = 7.566 \times 10^{-20}\ \text{J}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the $n = 4$ orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives:

$$\begin{aligned} \lambda &= \frac{hc}{E} \\ &= \left(6.626 \times 10^{-34}\ \cancel{\text{J}}\ \cancel{\text{s}}\right) \times \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{\text{s}}^{-1}}{7.566 \times 10^{-20}\ \cancel{\text{J}}} \\ &= 2.626 \times 10^{-6}\ \text{m} \end{aligned}$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Check Your Learning

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^{+} ion ($Z = 2$ for He^{+})?

Answer: 6.198×10^{-19} J; 3.205×10^{-7} m

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

3.3 Development of Quantum Theory

By the end of this section, you will be able to:

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patters similar to those shown on **Figure 3.16**. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

Figure 3.16 An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the *de Broglie wavelength*. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (**Figure 3.17**).

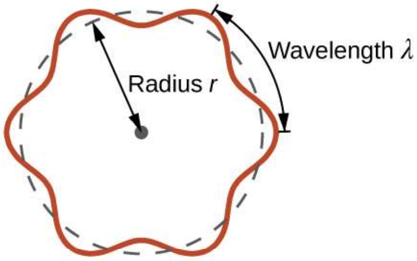


Figure 3.17 If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius r, the circumference is $2\pi r$, and so de Broglie's condition is:

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

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. **Figure 3.18** shows an interference pattern. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. The wave–particle duality of matter can be seen in **Figure 3.18** by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

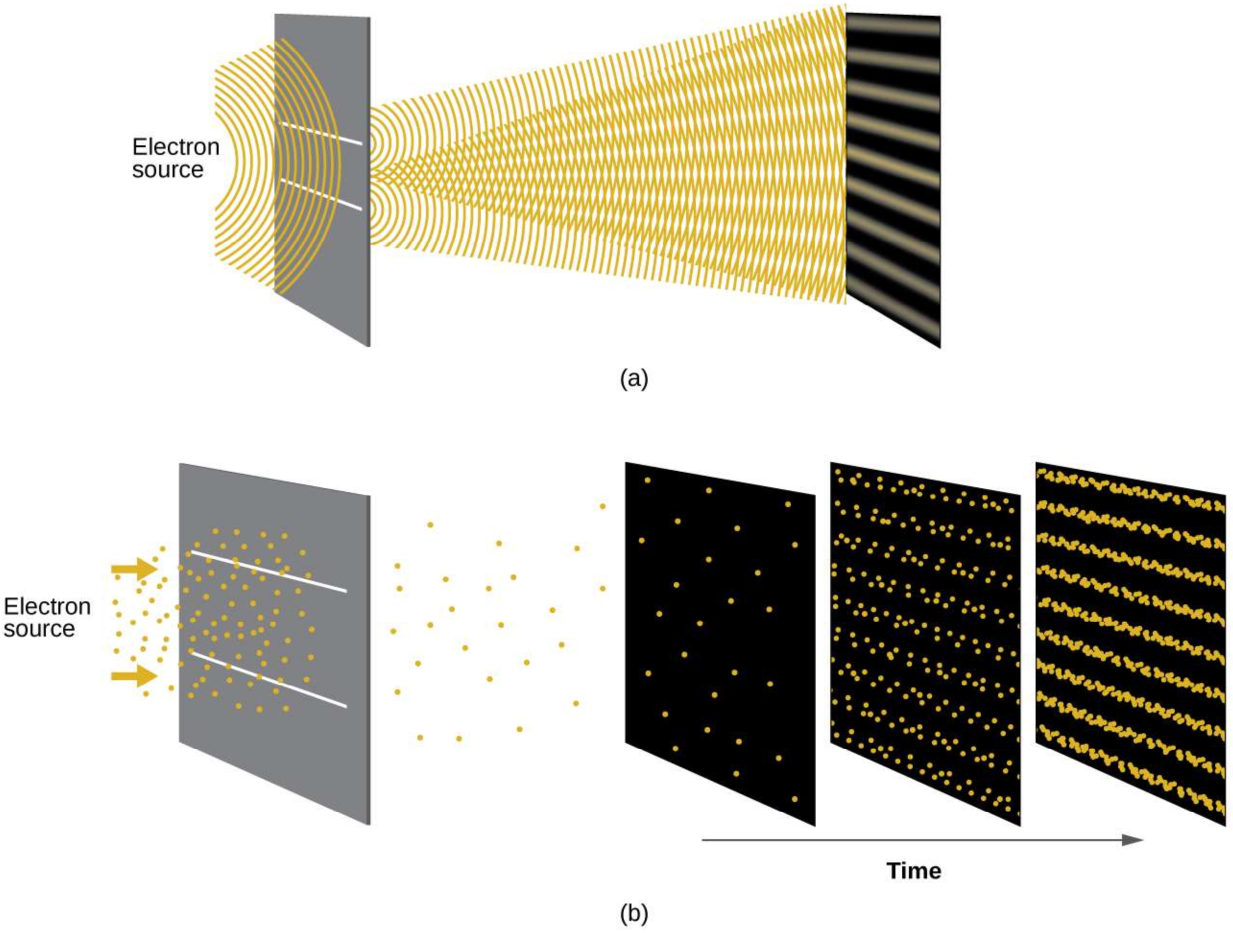


Figure 3.18 (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

Link to Learning

View the Dr. Quantum – Double Slit Experiment cartoon (http://openstaxcollege.org/l/16duality) for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 3.6

Calculating the Wavelength of a Particle

If an electron travels at a velocity of 1.000×10^7 m s^{-1} and has a mass of 9.109×10^{-28} g, what is its wavelength?

Solution

We can use de Broglie’s equation to solve this problem, but we first must do a unit conversion of Planck’s constant. You learned earlier that 1 J = 1 kg m^2/s^2. Thus, we can write $h = 6.626 \times 10^{-34}$ J s as 6.626 ×

10^{-34} kg m^2/s.

$$\begin{aligned}\lambda &= \frac{h}{mv}\\ &= \frac{6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}}{\left(9.109 \times 10^{-31}\ \text{kg}\right)\left(1.000 \times 10^{7}\ \text{m/s}\right)}\\ &= 7.274 \times 10^{-11}\ \text{m}\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Check Your Learning

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer: 1.9×10^{-34} m. We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass m moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x , must be greater than or equal to $\frac{\hbar}{2}$ (where $\hbar = \frac{h}{2\pi}$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\left[\Delta p = m\Delta v = \frac{h}{(2\Delta x)}\right] = \frac{\left(1.055 \times 10^{-34}\ \text{kg m}^2/\text{s}\right)}{\left(2 \times 1 \times 10^{-12}\ \text{m}\right)} = 5 \times 10^{-23}\ \text{kg m/s.}$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as $\Delta E\ \Delta t \geq \frac{\hbar}{2}$.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

Link to Learning

Read this **article (http://openstaxcollege.org/l/16uncertainty)** that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie’s work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr’s expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron’s density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

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

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger’s work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

Link to Learning

You may also have heard of Schrödinger because of his famous thought experiment. **This story (http://openstaxcollege.org/l/16superpos)** explains the concepts of superposition and entanglement as related to a cat in a box with poison.

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where n = 1, 2, 3, …. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The **principal quantum number** defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The **shells** of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (**Figure 3.19**). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

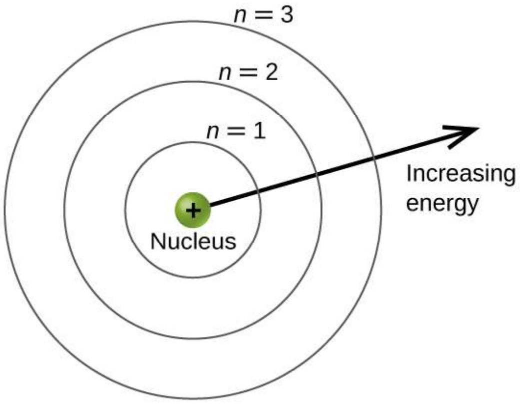


Figure 3.19 Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

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

The values n_{f} and n_{i} are the final and initial energy states of the electron. **Example 3.5** in the previous section of the chapter demonstrates calculations of such energy changes.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n - 1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called ***s* orbitals** and they make up the *s* subshells. The value $l = 1$ corresponds to the *p* orbitals. For a given *n*, ***p* orbitals** constitute a *p* subshell (e.g., 3*p* if $n = 3$). The orbitals with $l = 2$ are called the ***d* orbitals**, followed by the *f-*, *g-, and h-*orbitals for $l = 3$, 4, and 5.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node. The number of radial nodes in an orbital is $n - l - 1$.

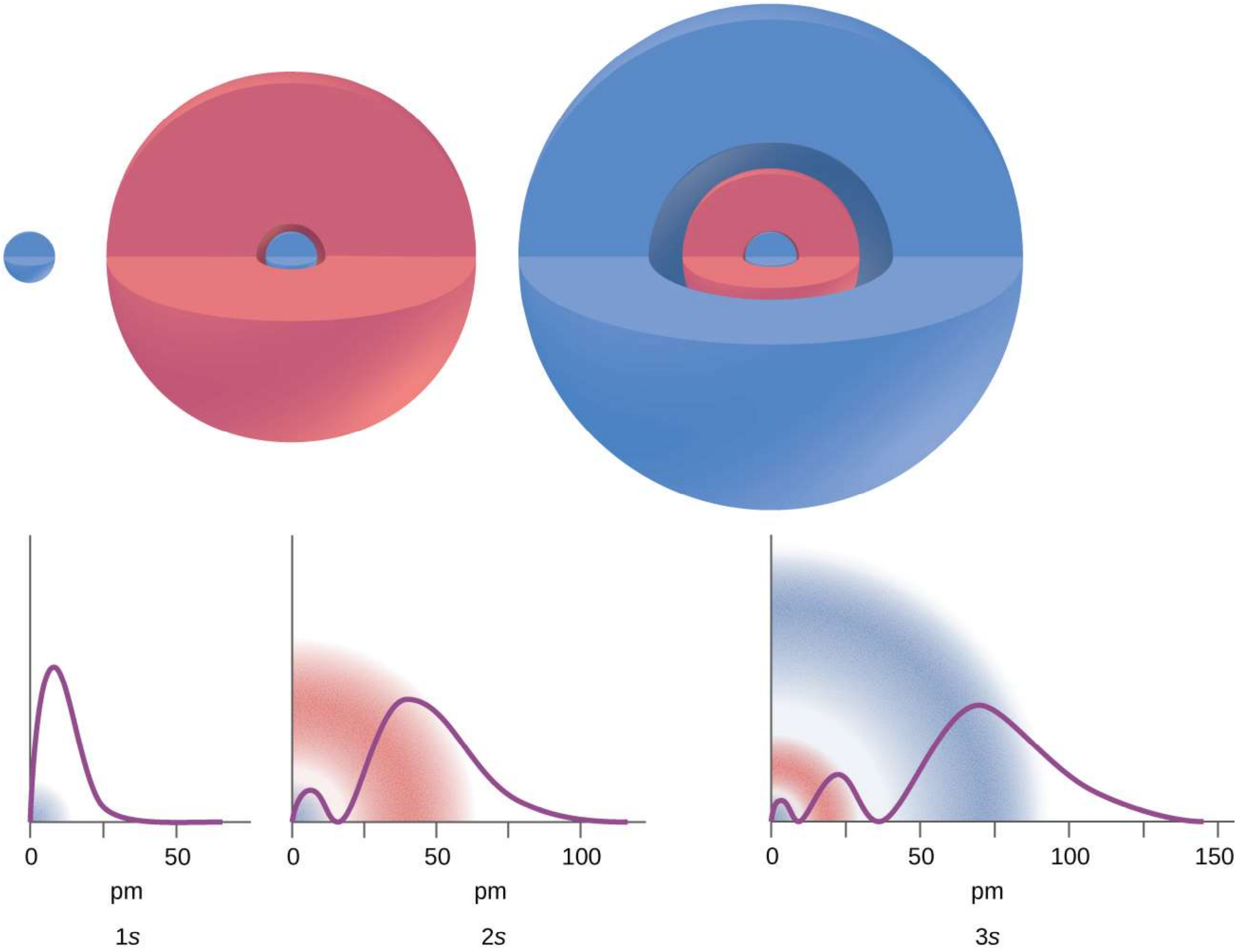


Figure 3.20 The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus.

Consider the examples in **Figure 3.20**. The orbitals depicted are of the *s* type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are $1 - 0 - 1 = 0$ places where the density is zero (nodes) for 1*s* ($n = 1$), $2 - 0 - 1 = 1$ node for 2*s*, and $3 - 0 - 1 = 2$ nodes for the 3*s* orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and ***f* orbitals** are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

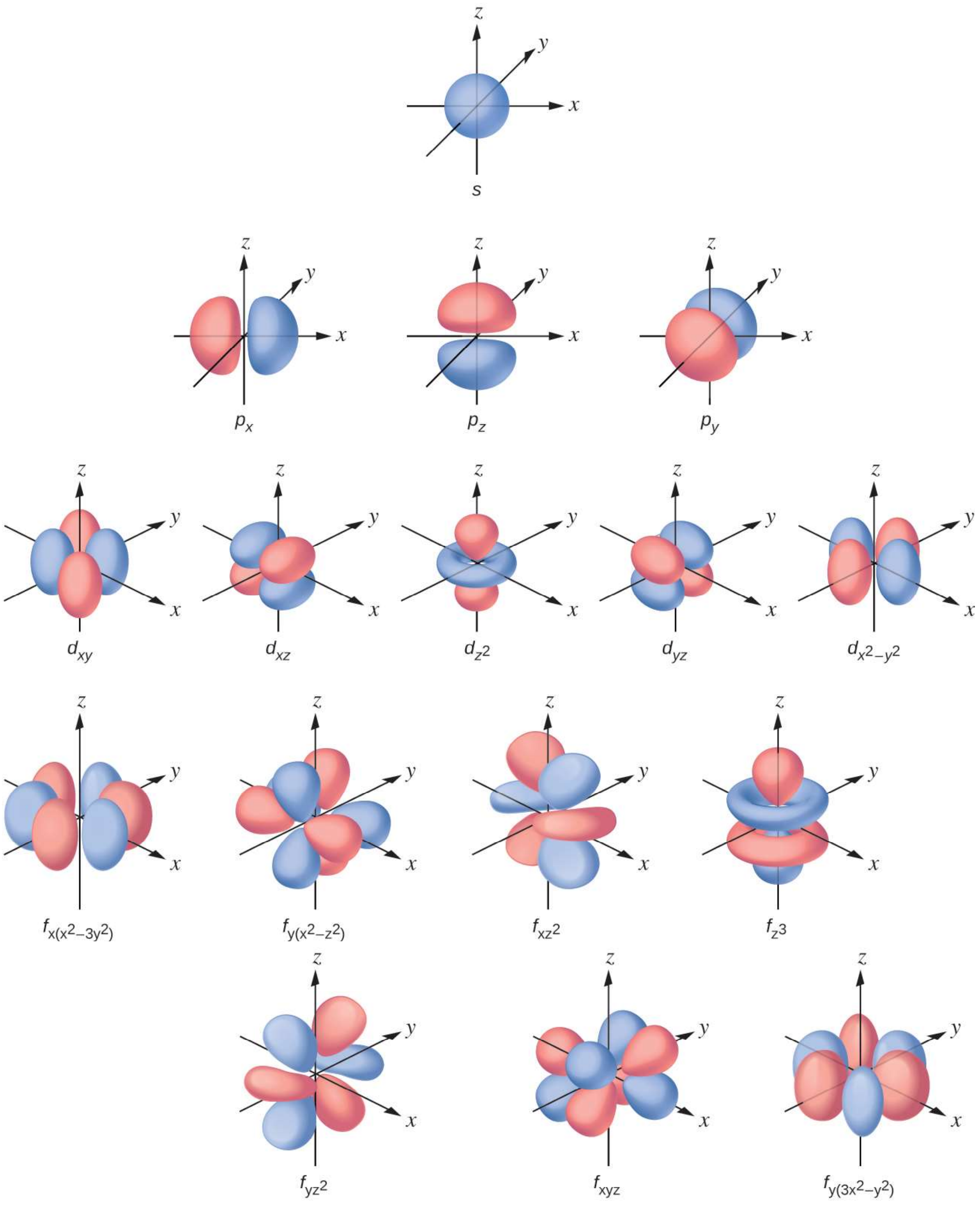


Figure 3.21 Shapes of *s*, *p*, *d*, and *f* orbitals.

The **magnetic quantum number**, m_l, specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l can be equal to $-l, -(l-1), \ldots, 0, \ldots, (l-1), l$. The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l + 1$. Thus, there is one *s*-orbital in an *s* subshell ($l = 0$), there are three *p*-orbitals in a *p* subshell ($l = 1$), five *d*-orbitals in a *d* subshell ($l = 2$), seven *f*-orbitals in an *f* subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 3.21.

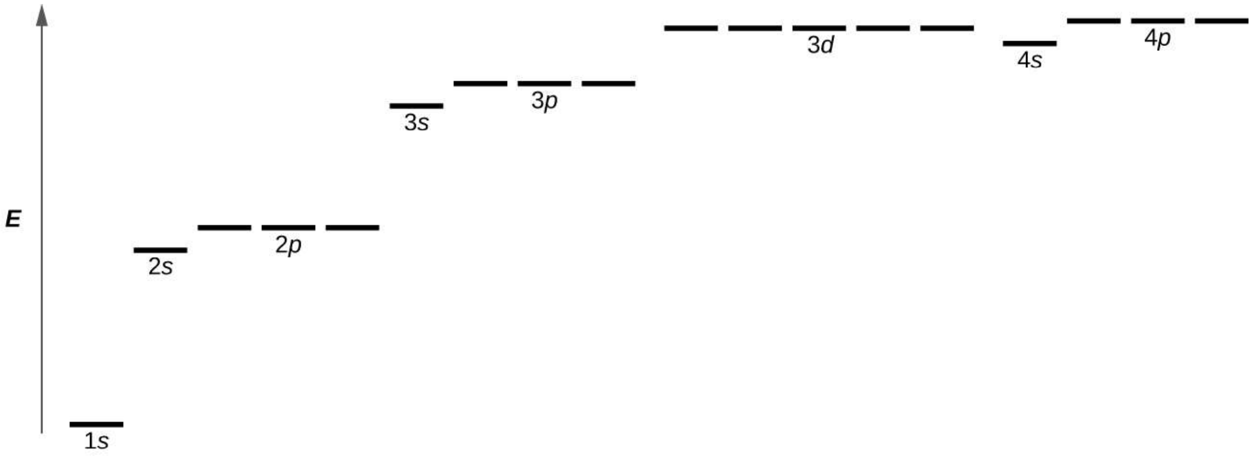


Figure 3.22 The chart shows the energies of electron orbitals in a multi-electron atom.

Figure 3.22 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number $l = 0$ for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called **degenerate orbitals**. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure 3.22. Orbitals within the same subshell are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or $\boldsymbol{m_s}$.

The other three quantum numbers, *n*, *l*, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the *z* component of the spin being in the positive direction of the *z* axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the *z* component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.

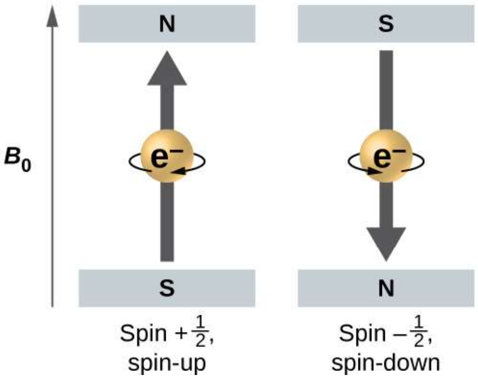


Figure 3.23 Electrons with spin values $\pm\frac{1}{2}$ in an external magnetic field.

Figure 3.23 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $\frac{1}{2}$ spin quantum number and down (in the negative *z* direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on **Figure 3.23**) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \frac{1}{2}$ has a slightly lower energy in an external field in the positive *z* direction, and an electron with $m_s = -\frac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers n, l, and m_l) only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(\pm\frac{1}{2}\right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in **Table 3.1**.

Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \le l \le n - 1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$-l \le m_l \le l$	orientation of the orbital
spin quantum number	m_s	$\frac{1}{2},\ -\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

Table 3.1

Example 3.7

Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, *s*, *p*, *d*, and *f* subshells are found in the $n = 4$ shell of an atom. For $l = 0$ (the *s* subshell), m_l can only be 0. Thus, there is only one 4*s* orbital. For $l = 1$ (*p*-type orbitals), m can have values of –1, 0, +1, so we find three 4*p* orbitals. For $l = 2$ (*d*-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4*d* orbitals. When $l = 3$ (*f*-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4*f* orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

Check Your Learning

Identify the subshell in which electrons with the following quantum numbers are found: (a) $n = 3$, $l = 1$; (b) $n = 5$, $l = 3$; (c) $n = 2$, $l = 0$.

Answer: (a) 3*p* (b) 5*f* (c) 2s

Example 3.8

Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) $n = 2$, (b) $n = 5$, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When $n = 2$, there are four orbitals (a single 2*s* orbital, and three orbitals labeled 2*p*). These four orbitals can contain eight electrons.

(b) When $n = 5$, there are five subshells of orbitals that we need to sum:

1 orbital labeled 5*s*
3 orbitals labeled 5*p*
5 orbitals labeled 5*d*
7 orbitals labeled 5*f*

+9 orbitals labeled 5*g*
25 orbitals total

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell *n* will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

Check Your Learning

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Answer: $n = 4$

Example 3.9

Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is *nl*, where *l* = 0, 1, 2, 3, 4, 5, … is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, …,
- The m_l degeneracy is the number of orbitals within an *l* subshell, and so is $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to $n - l - 1$.

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Check Your Learning

How many orbitals have $l = 2$ and $n = 3$?

Answer: The five degenerate 3*d* orbitals

3.4 Electronic Structure of Atoms (Electron Configurations)

By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, *n*, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. **Figure 3.24** depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

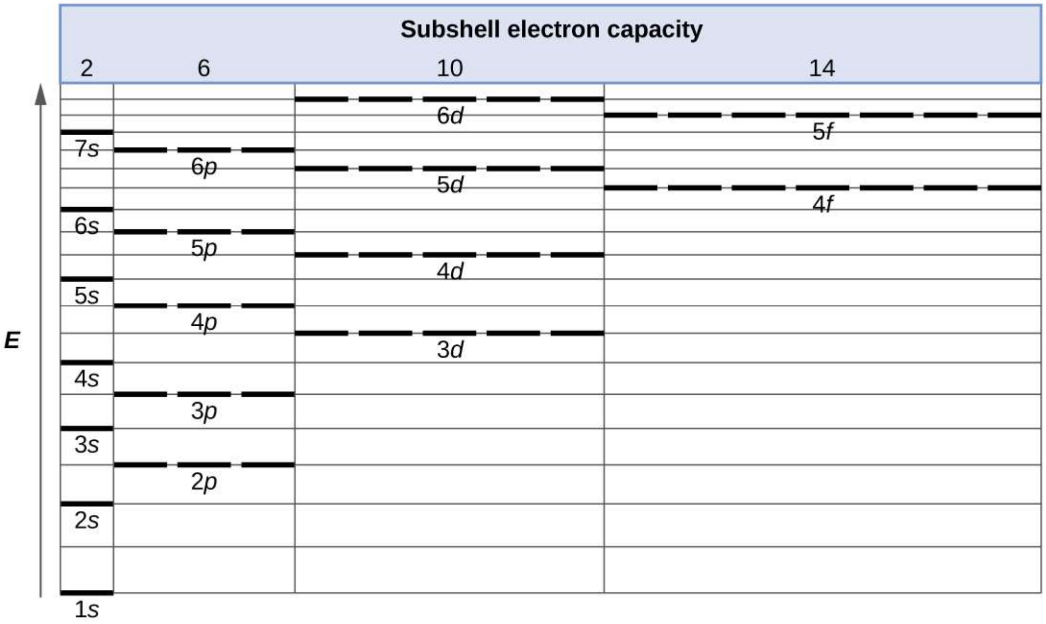


Figure 3.24 Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order $s > p > d > f$. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (**Figure 3.25**):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

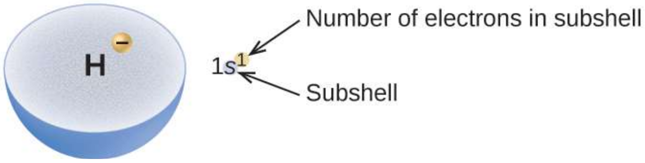


Figure 3.25 The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in **Figure 3.24**), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. **Figure 3.26** illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, **Figure 3.27** provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

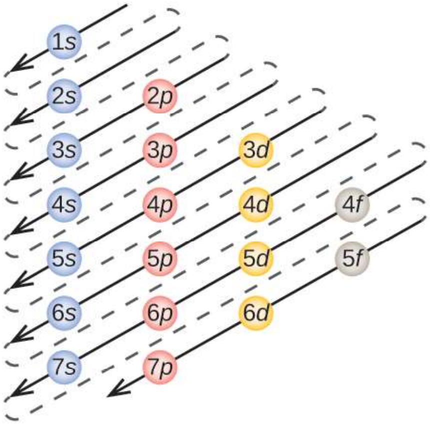


Figure 3.26 This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

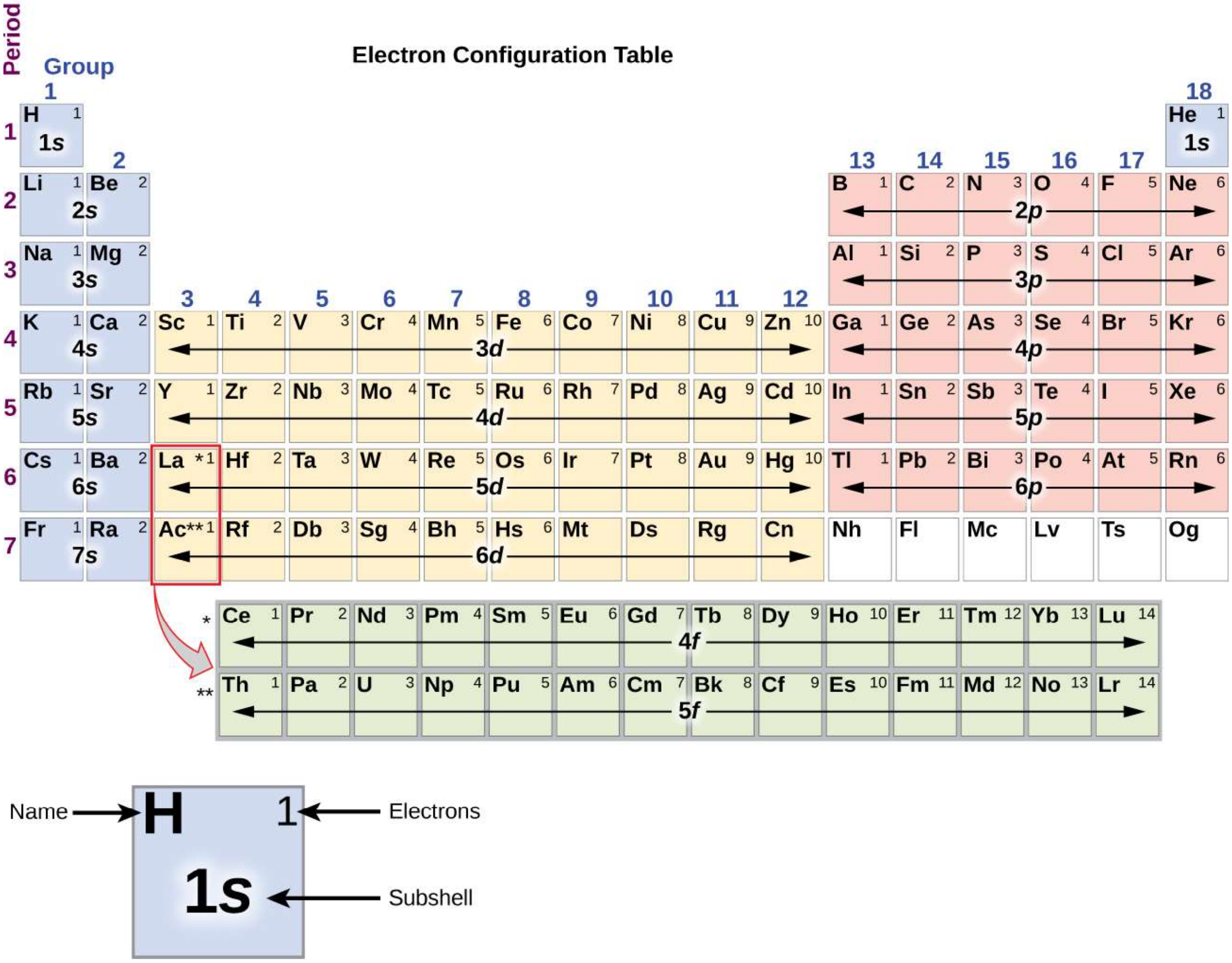
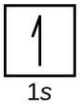


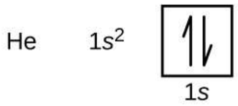
Figure 3.27 This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 3.26 or Figure 3.27, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

H $1s^1$

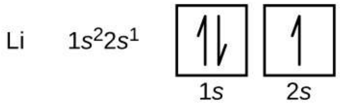


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

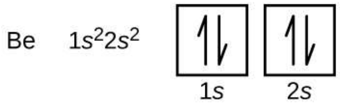


The *n* = 1 shell is completely filled in a helium atom.

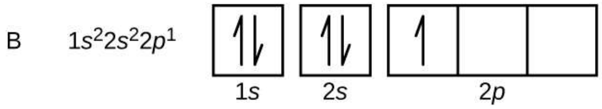
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital (**Figure 3.26** or **Figure 3.27**). Thus, the electron configuration and orbital diagram of lithium are:



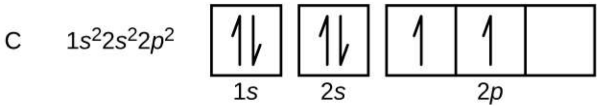
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.



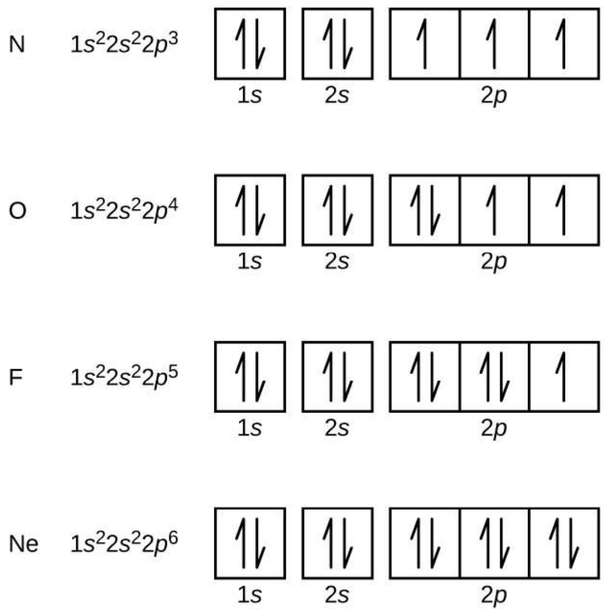
An atom of boron (atomic number 5) contains five electrons. The *n* = 1 shell is filled with two electrons and three electrons will occupy the *n* = 2 shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = −1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.



Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the *n* = 1 and the *n* = 2 shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (**Figure 3.28**). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[\text{Ne}]3s^1$.

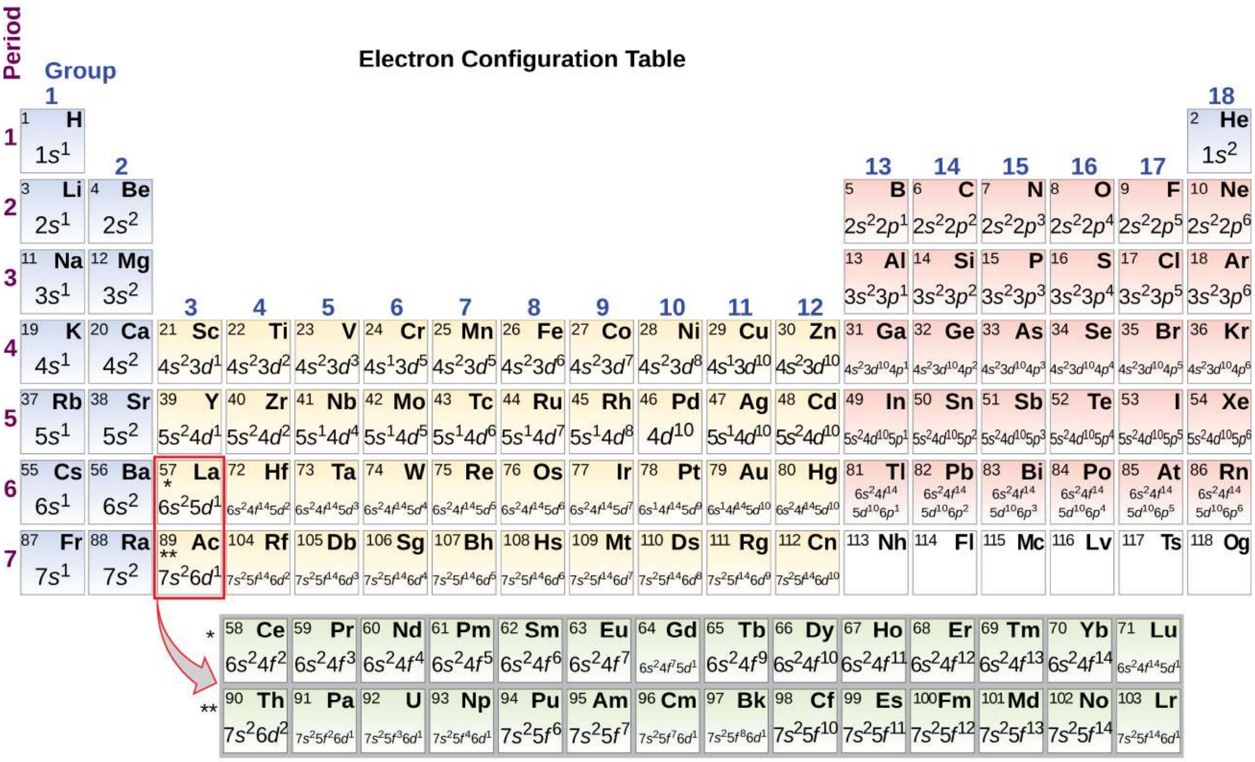
Figure 3.28 A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[\text{He}]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\text{Li: }[\text{He}]2s^1$$
$$\text{Na: }[\text{Ne}]3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[\text{Ne}]3s^2$ configuration, is analogous to its family member beryllium, $[\text{He}]2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[\text{Ne}]3s^2 3p^1$, is analogous to its family member boron, $[\text{He}]2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. **Figure 3.29** shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.



Electron Configuration Table

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^23d^{10}4p^1$	32 **Ge** $4s^23d^{10}4p^2$	33 **As** $4s^23d^{10}4p^3$	34 **Se** $4s^23d^{10}4p^4$	35 **Br** $4s^23d^{10}4p^5$	36 **Kr** $4s^23d^{10}4p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^14d^6$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^24d^{10}5p^1$	50 **Sn** $5s^24d^{10}5p^2$	51 **Sb** $5s^24d^{10}5p^3$	52 **Te** $5s^24d^{10}5p^4$	53 **I** $5s^24d^{10}5p^5$	54 **Xe** $5s^24d^{10}5p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** * $6s^25d^1$	72 **Hf** $6s^24f^{14}5d^2$	73 **Ta** $6s^24f^{14}5d^3$	74 **W** $6s^24f^{14}5d^4$	75 **Re** $6s^24f^{14}5d^5$	76 **Os** $6s^24f^{14}5d^6$	77 **Ir** $6s^24f^{14}5d^7$	78 **Pt** $6s^14f^{14}5d^9$	79 **Au** $6s^14f^{14}5d^{10}$	80 **Hg** $6s^24f^{14}5d^{10}$	81 **Tl** $6s^24f^{14}5d^{10}6p^1$	82 **Pb** $6s^24f^{14}5d^{10}6p^2$	83 **Bi** $6s^24f^{14}5d^{10}6p^3$	84 **Po** $6s^24f^{14}5d^{10}6p^4$	85 **At** $6s^24f^{14}5d^{10}6p^5$	86 **Rn** $6s^24f^{14}5d^{10}6p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** ** $7s^26d^1$	104 **Rf** $7s^25f^{14}6d^2$	105 **Db** $7s^25f^{14}6d^3$	106 **Sg** $7s^25f^{14}6d^4$	107 **Bh** $7s^25f^{14}6d^5$	108 **Hs** $7s^25f^{14}6d^6$	109 **Mt** $7s^25f^{14}6d^7$	110 **Ds** $7s^25f^{14}6d^8$	111 **Rg** $7s^25f^{14}6d^9$	112 **Cn** $7s^25f^{14}6d^{10}$	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**
*				58 **Ce** $6s^24f^2$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}5d^1$	
**				90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^86d^1$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$	

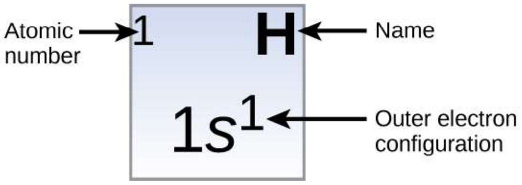


Figure 3.29 This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (**Figure 3.29**). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

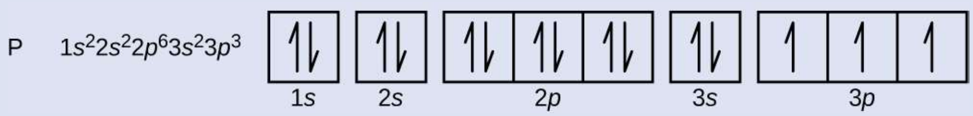
Example 3.10

Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Check Your Learning

Identify the atoms from the electron configurations given:

(a) $[Ar]4s^23d^5$

(b) $[Kr]5s^24d^{10}5p^6$

Answer: (a) Mn (b) Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in **Figure 3.26** or **Figure 3.27**. For instance, the electron configurations (shown in **Figure 3.29**) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^24d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^14d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (**Figure 3.29**), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in **Figure 3.29**, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of **Figure 3.29** show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in **Figure 3.29**. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration $[\text{Ar}]\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in **Figure 3.29**) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in **Figure 3.29**), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in **Figure 3.29**. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the *ns* subshells. There are two inner transition series:
    a. The lanthanide series: lanthanide (La) through lutetium (Lu)
    b. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n-1)d$ or $(n-2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 3.11

Predicting Electron Configurations of Ions

What is the electron configuration of:

(a) Na^+

(b) P^{3-}

(c) Al^{2+}

(d) Fe^{2+}

(e) Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

(a) Na: $1s^22s^22p^63s^1$. Sodium cation loses one electron, so Na^+: $1s^22s^22p^63s^1$ = Na^+: $1s^22s^22p^6$.

(b) P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^22s^22p^63s^23p^6$.

(c) Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^22s^22p^63s^23p^1$ =

Al^{2+}: $1s^22s^22p^63s^1$.

(d) Fe: $1s^22s^22p^63s^23p^64s^23d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^22s^22p^63s^23p^64s^23d^6 = 1s^22s^22p^63s^23p^63d^6$.

(e). Sm: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6 = 1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^5$.

Check Your Learning

Which ion with a +2 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^5$? Which ion with a +3 charge has this configuration?

Answer: Tc^{2+}, Ru^{3+}

3.5 Periodic Variations in Element Properties

By the end of this section, you will be able to:

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Link to Learning

Explore **visualizations (http://openstaxcollege.org/l/16pertrends)** of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** (**Figure 3.30**), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in **Table 3.2** and **Figure 3.30**. The trends for the entire periodic table can be seen in **Figure 3.30**.

Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53

Table 3.2

Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
At	148	+85

Table 3.2

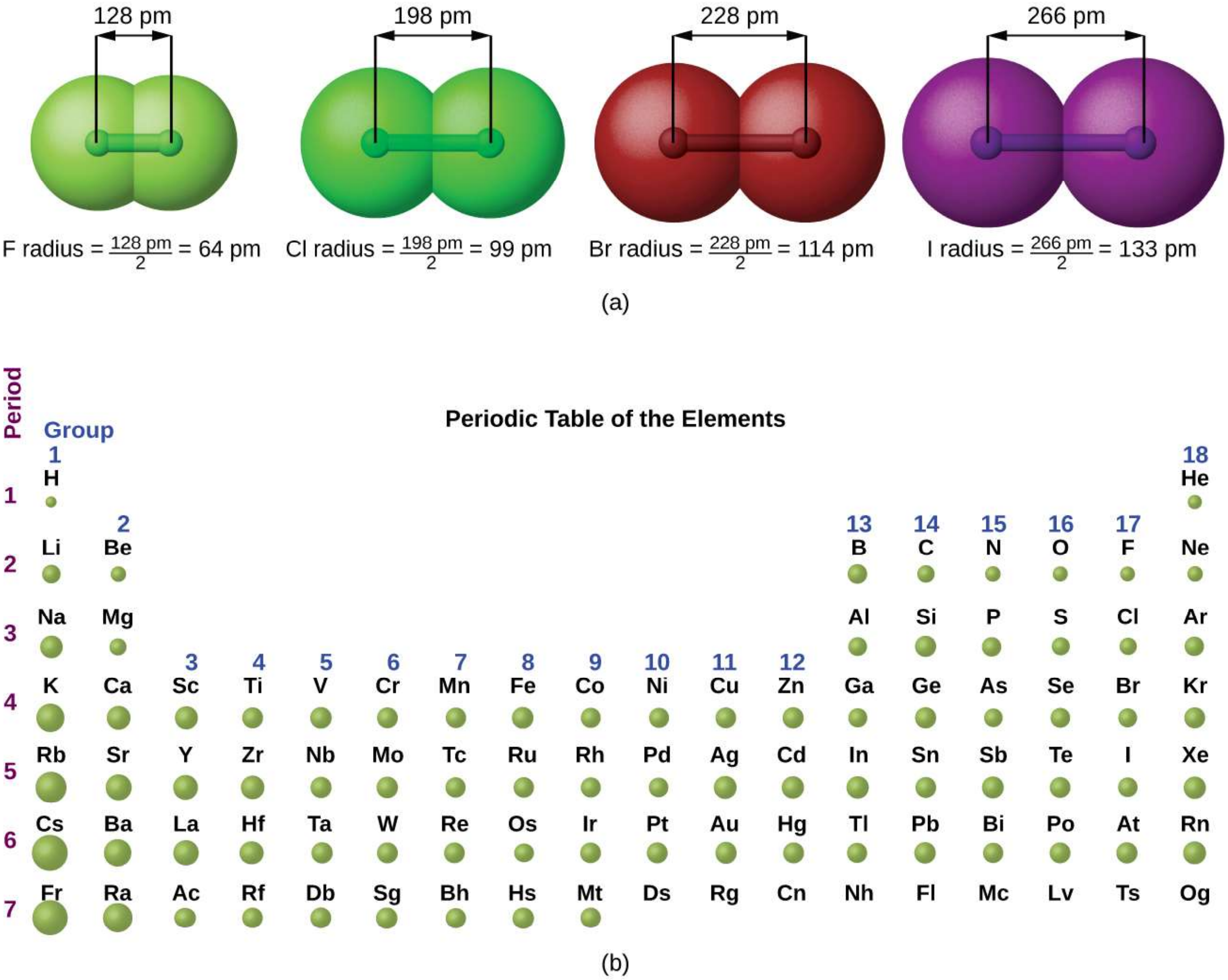


Figure 3.30 (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

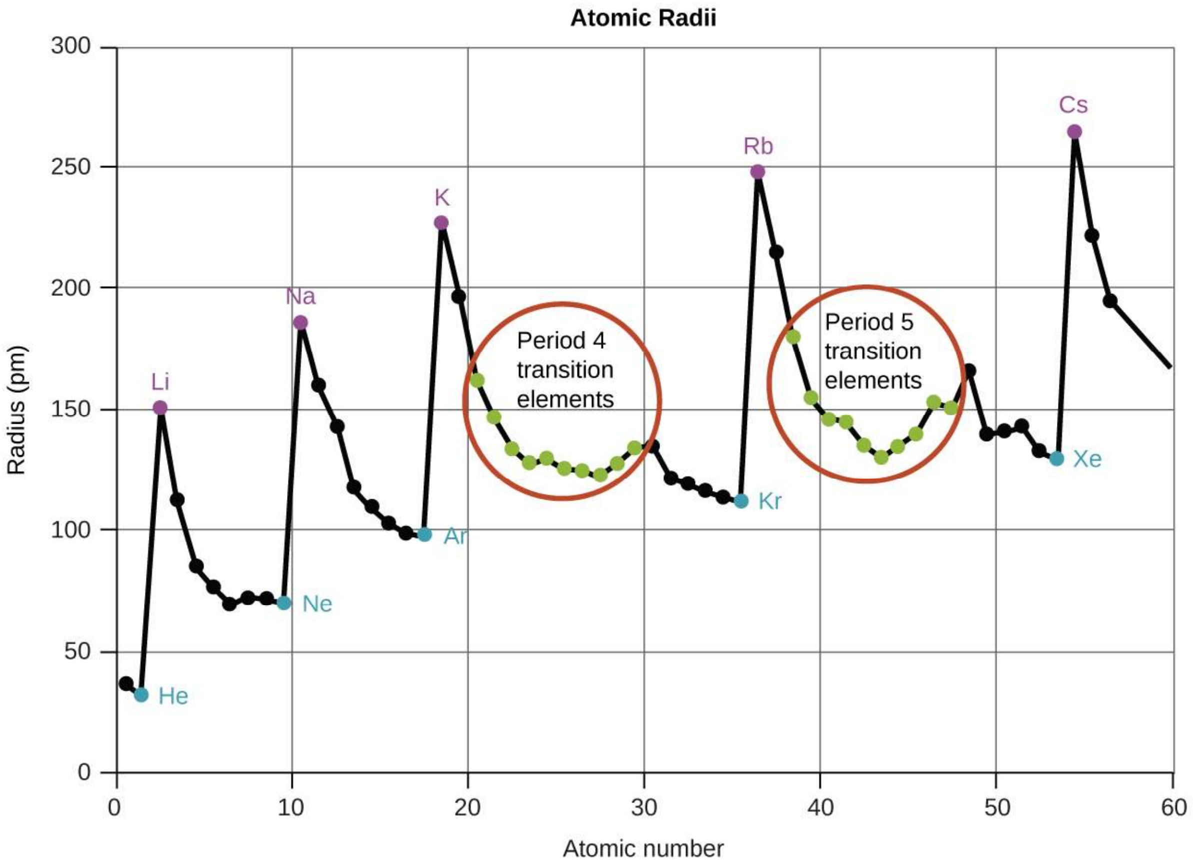


Figure 3.31 Within each period, the trend in atomic radius decreases as *Z* increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as *Z* increases.

As shown in **Figure 3.31**, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge, Z_{eff}**. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{eff} = Z - shielding$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n-1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 3.12

Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Check Your Learning

Give an example of an atom whose size is smaller than fluorine.

Answer: Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (**Figure 3.32**). For example, the covalent radius of an aluminum atom ($1s^22s^22p^63s^23p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^22s^22p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

Figure 3.32 The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (**Figure 3.32**). For example, a sulfur atom ($[Ne]3s^23p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^23p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^22s^22p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^23p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X}(g) \longrightarrow \mathrm{X}^{+}(g) + \mathrm{e}^{-} \qquad \mathrm{IE}_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X}^{+}(g) \longrightarrow \mathrm{X}^{2+}(g) + \mathrm{e}^{-} \qquad \mathrm{IE}_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 3.33 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in **Figure 3.34**. Within a period, the IE_1 generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[\mathrm{He}]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[\mathrm{He}]2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

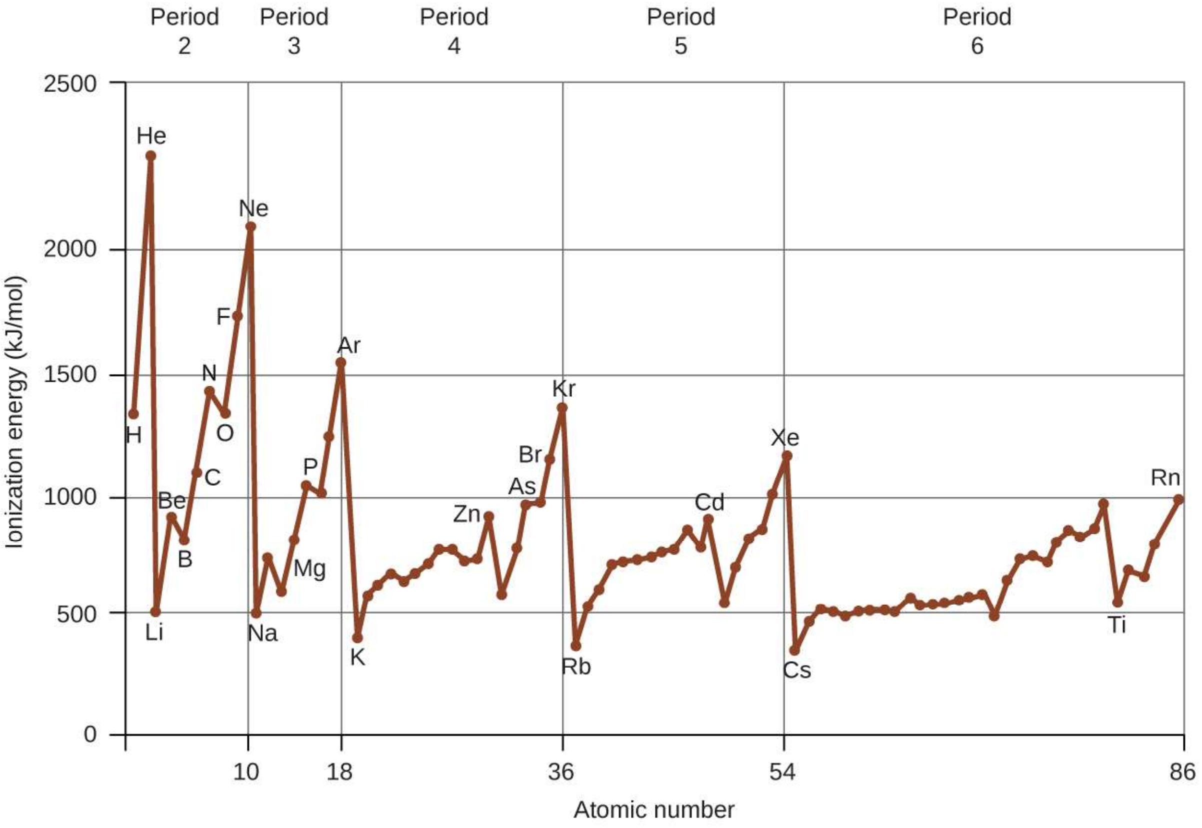
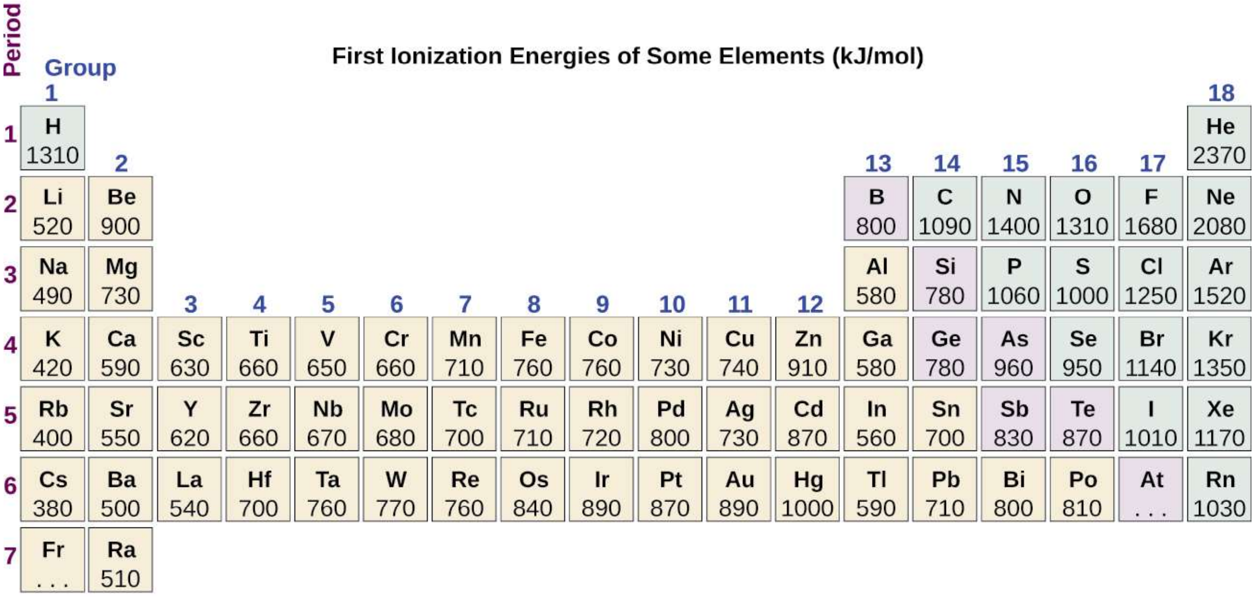


Figure 3.33 The first ionization energy of the elements in the first five periods are plotted against their atomic number.

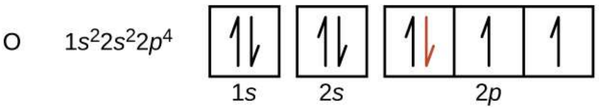


First Ionization Energies of Some Elements (kJ/mol)

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1310																	He 2370
2	Li 520	Be 900											B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 490	Mg 730											Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At . . .	Rn 1030
7	Fr . . .	Ra 510																

Figure 3.34 This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in **Figure 3.34**).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in **Table 3.3**, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available

Table 3.3

Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Table 3.3

Example 3.13

Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al $(Al^{2+} \longrightarrow Al^{3+} + e^-)$ requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

Check Your Learning

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer: Ba

Variation in Electron Affinities

The **electron affinity** (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

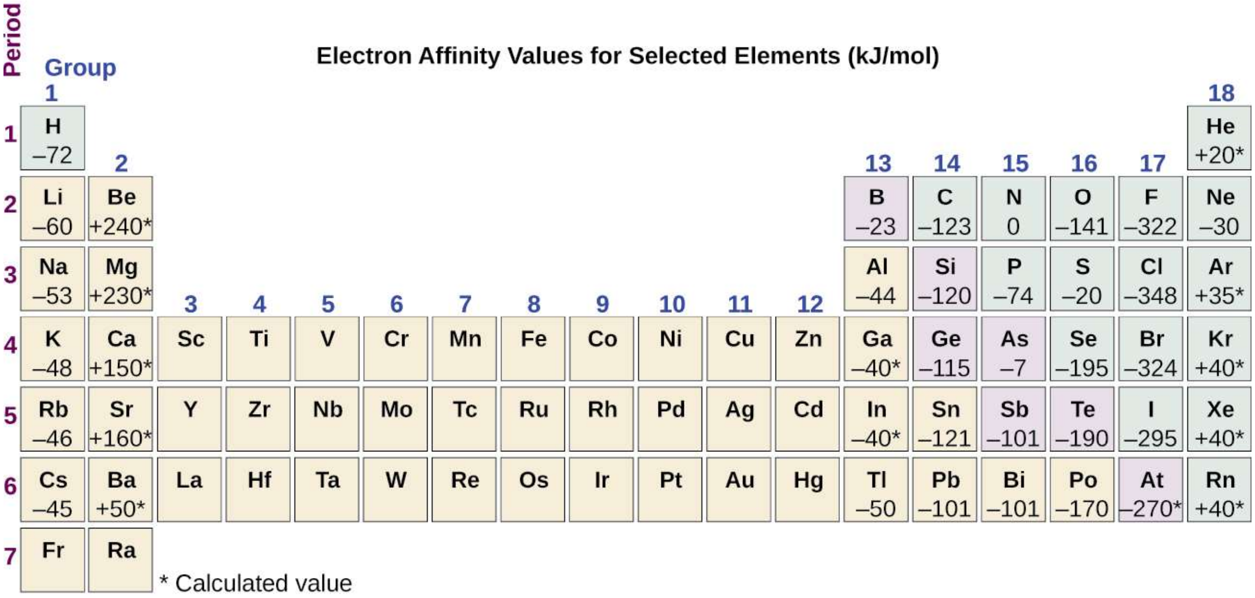
$$X(g) + e^- \longrightarrow X^-(g) \qquad EA_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 3.35. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the most negative EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the *second* element in the group most often has the most negative EA. This can be attributed to the small size of the

$n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily, resulting in a more negative EA.


Electron Affinity Values for Selected Elements (kJ/mol)

Period / Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –20	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 3.35 This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

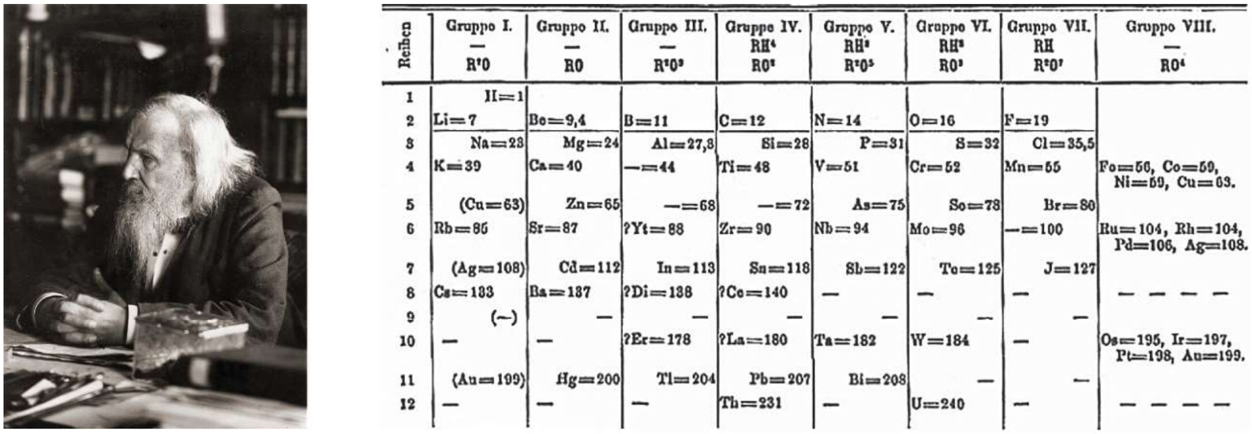
3.6 The Periodic Table

By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (**Figure 3.36**).

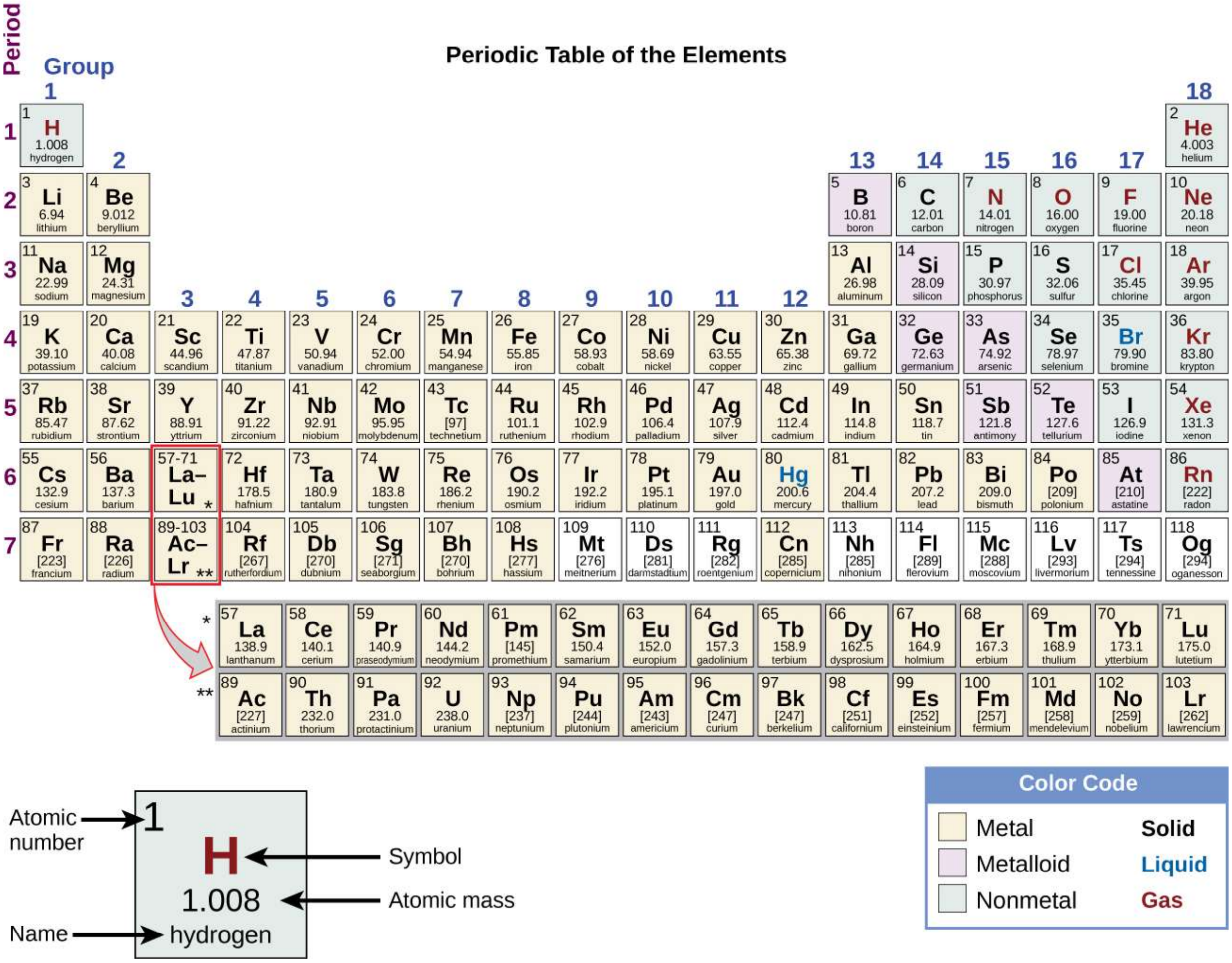


(a) (b)

Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

Figure 3.36 (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (**Figure 3.37**). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.



Periodic Table of the Elements

Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008 hydrogen																	2 He 4.003 helium
2	3 Li 6.94 lithium	4 Be 9.012 beryllium											5 B 10.81 boron	6 C 12.01 carbon	7 N 14.01 nitrogen	8 O 16.00 oxygen	9 F 19.00 fluorine	10 Ne 20.18 neon
3	11 Na 22.99 sodium	12 Mg 24.31 magnesium											13 Al 26.98 aluminum	14 Si 28.09 silicon	15 P 30.97 phosphorus	16 S 32.06 sulfur	17 Cl 35.45 chlorine	18 Ar 39.95 argon
4	19 K 39.10 potassium	20 Ca 40.08 calcium	21 Sc 44.96 scandium	22 Ti 47.87 titanium	23 V 50.94 vanadium	24 Cr 52.00 chromium	25 Mn 54.94 manganese	26 Fe 55.85 iron	27 Co 58.93 cobalt	28 Ni 58.69 nickel	29 Cu 63.55 copper	30 Zn 65.38 zinc	31 Ga 69.72 gallium	32 Ge 72.63 germanium	33 As 74.92 arsenic	34 Se 78.97 selenium	35 Br 79.90 bromine	36 Kr 83.80 krypton
5	37 Rb 85.47 rubidium	38 Sr 87.62 strontium	39 Y 88.91 yttrium	40 Zr 91.22 zirconium	41 Nb 92.91 niobium	42 Mo 95.95 molybdenum	43 Tc [97] technetium	44 Ru 101.1 ruthenium	45 Rh 102.9 rhodium	46 Pd 106.4 palladium	47 Ag 107.9 silver	48 Cd 112.4 cadmium	49 In 114.8 indium	50 Sn 118.7 tin	51 Sb 121.8 antimony	52 Te 127.6 tellurium	53 I 126.9 iodine	54 Xe 131.3 xenon
6	55 Cs 132.9 cesium	56 Ba 137.3 barium	57-71 La–Lu *	72 Hf 178.5 hafnium	73 Ta 180.9 tantalum	74 W 183.8 tungsten	75 Re 186.2 rhenium	76 Os 190.2 osmium	77 Ir 192.2 iridium	78 Pt 195.1 platinum	79 Au 197.0 gold	80 Hg 200.6 mercury	81 Tl 204.4 thallium	82 Pb 207.2 lead	83 Bi 209.0 bismuth	84 Po [209] polonium	85 At [210] astatine	86 Rn [222] radon
7	87 Fr [223] francium	88 Ra [226] radium	89-103 Ac–Lr **	104 Rf [267] rutherfordium	105 Db [270] dubnium	106 Sg [271] seaborgium	107 Bh [270] bohrium	108 Hs [277] hassium	109 Mt [276] meitnerium	110 Ds [281] darmstadtium	111 Rg [282] roentgenium	112 Cn [285] copernicium	113 Nh [285] nihonium	114 Fl [289] flerovium	115 Mc [288] moscovium	116 Lv [293] livermorium	117 Ts [294] tennessine	118 Og [294] oganesson
			*	57 La 138.9 lanthanum	58 Ce 140.1 cerium	59 Pr 140.9 praseodymium	60 Nd 144.2 neodymium	61 Pm [145] promethium	62 Sm 150.4 samarium	63 Eu 152.0 europium	64 Gd 157.3 gadolinium	65 Tb 158.9 terbium	66 Dy 162.5 dysprosium	67 Ho 164.9 holmium	68 Er 167.3 erbium	69 Tm 168.9 thulium	70 Yb 173.1 ytterbium	71 Lu 175.0 lutetium
			**	89 Ac [227] actinium	90 Th 232.0 thorium	91 Pa 231.0 protactinium	92 U 238.0 uranium	93 Np [237] neptunium	94 Pu [244] plutonium	95 Am [243] americium	96 Cm [247] curium	97 Bk [247] berkelium	98 Cf [251] californium	99 Es [252] einsteinium	100 Fm [257] fermium	101 Md [258] mendelevium	102 No [259] nobelium	103 Lr [262] lawrencium

Color Code	
▨ Metal	Solid
▨ Metalloid	Liquid
▨ Nonmetal	Gas

Figure 3.37 Elements in the periodic table are organized according to their properties.

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity—shaded green); and **metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the **main-group elements** (or **representative elements**) in the columns labeled 1, 2, and 13–18; the **transition metals** in the columns labeled 3–12; [1] and **inner transition metals** in the two rows at the bottom of the table (the top-row elements are called **lanthanides** and the bottom-row elements are **actinides**; Figure 3.38). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with

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[1] Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.

similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), **halogens** (group 17), and the **noble gases** (group 18, also known as **inert gases**). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

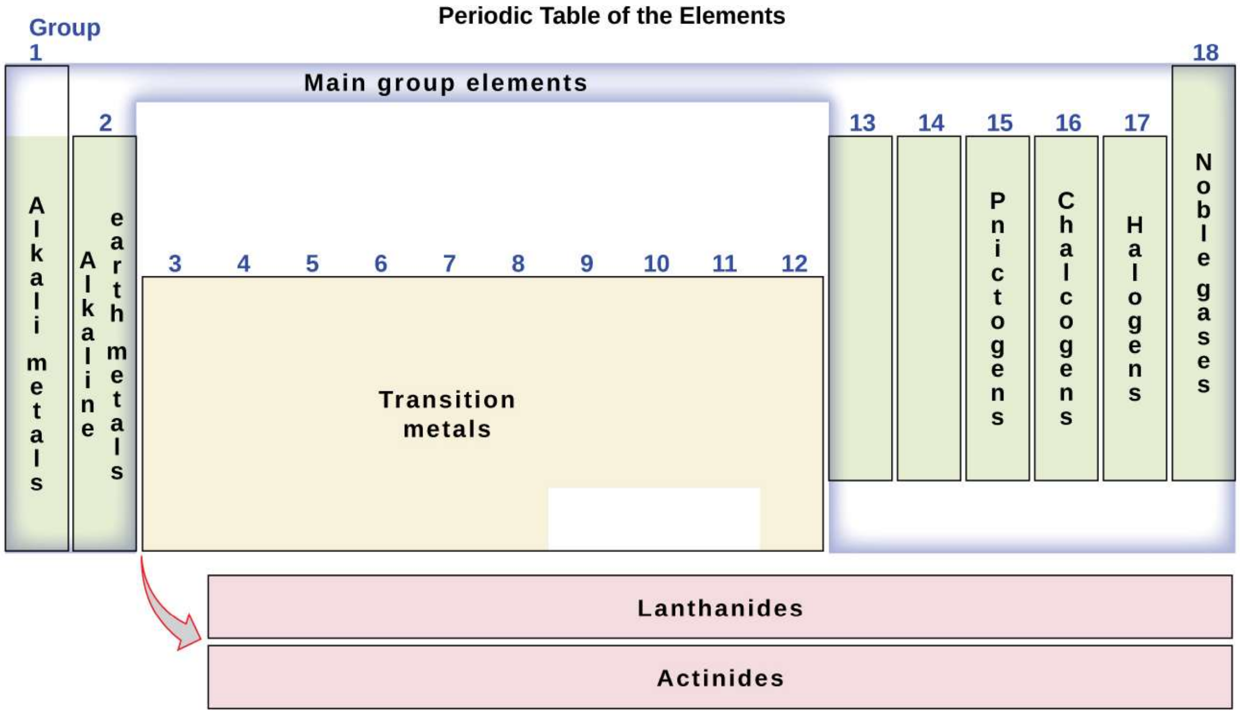


Figure 3.38 The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this link (http://openstax.org/l/16Periodic) for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one (http://openstax.org/l/16Periodic2) that shows photos of all the elements.

Example 3.14

Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

(a) chlorine

(b) calcium

(c) sodium

(d) sulfur

Solution

The family names are as follows:

(a) halogen

(b) alkaline earth metal

(c) alkali metal

(d) chalcogen

Check Your Learning

Give the group name for each of the following elements:

(a) krypton

(b) selenium

(c) barium

(d) lithium

Answer: (a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

3.7 Molecular and Ionic Compounds

By the end of this section, you will be able to:

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (**Figure 3.39**).

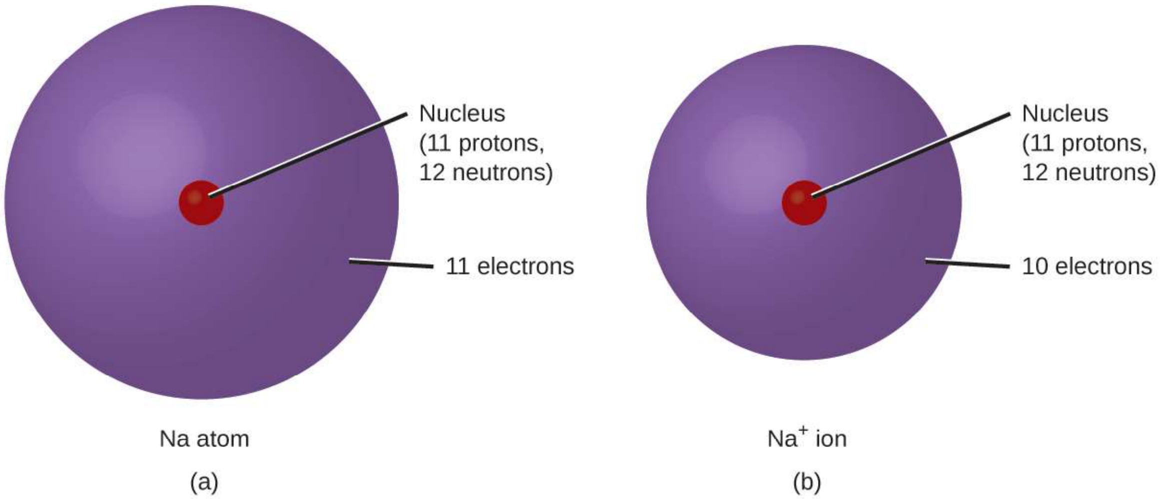


Figure 3.39 (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (**Figure 3.40**). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

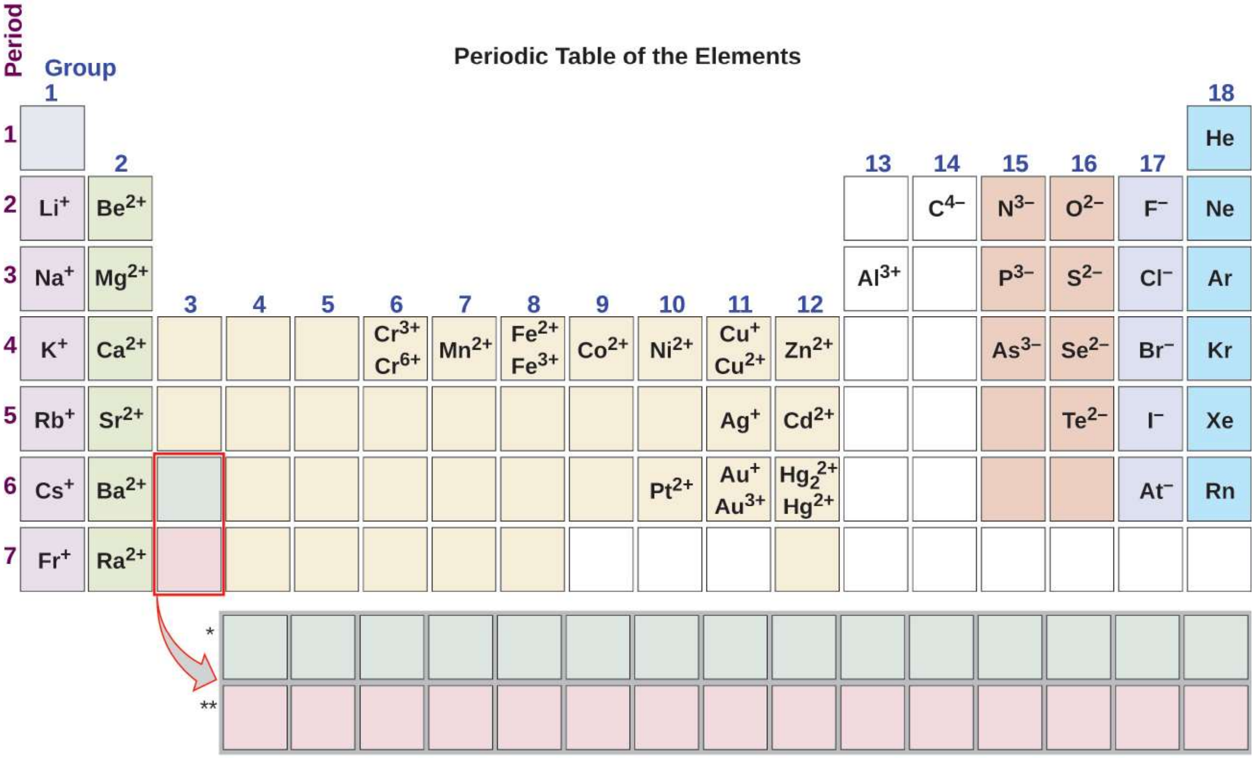


Figure 3.40 Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 3.15

Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Check Your Learning

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer: Se^{2-}, the selenide ion

Example 3.16

Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium’s position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen’s position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Check Your Learning

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer: Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called **monatomic ions**, that is, they are ions formed from only one atom. We also find many **polyatomic ions**. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 3.4. **Oxyanions** are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfiric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		

Table 3.4

Common Polyatomic Ions

Name	Formula	Related Acid	Formula
sulfite	$SO_3{}^{2-}$	sulfurous acid	H_2SO_3
hydrogen sulfite	$HSO_3{}^{-}$		
phosphate	$PO_4{}^{3-}$	phosphoric acid	H_3PO_4
hydrogen phosphate	$HPO_4{}^{2-}$		
dihydrogen phosphate	$H_2PO_4{}^{-}$		
perchlorate	$ClO_4{}^{-}$	perchloric acid	$HClO_4$
chlorate	$ClO_3{}^{-}$	chloric acid	$HClO_3$
chlorite	$ClO_2{}^{-}$	chlorous acid	$HClO_2$
hypochlorite	ClO^{-}	hypochlorous acid	$HClO$
chromate	$CrO_4{}^{2-}$	chromic acid	$H_2Cr_2O_4$
dichromate	$Cr_2O_7{}^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	$MnO_4{}^{-}$	permanganic acid	$HMnO_4$

Table 3.4

Note that there is a system for naming some polyatomic ions; -*ate* and -*ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per*- (short for "hyper") and *hypo*- (meaning "under") are prefixes meaning more oxygen atoms than -*ate* and fewer oxygen atoms than -*ite*, respectively. For example, perchlorate is $ClO_4{}^{-}$, chlorate is $ClO_3{}^{-}$, chlorite is $ClO_2{}^{-}$ and hypochlorite is ClO^{-}. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is $NO_3{}^{-}$ while sulfate is $SO_4{}^{2-}$. This will be covered in more detail later in the module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, **ionic bonds** result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, **covalent bonds** result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^{+}, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^{-}, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^{+} ion for each Cl^{-} ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an **ionic compound**. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (**Figure 3.41**).

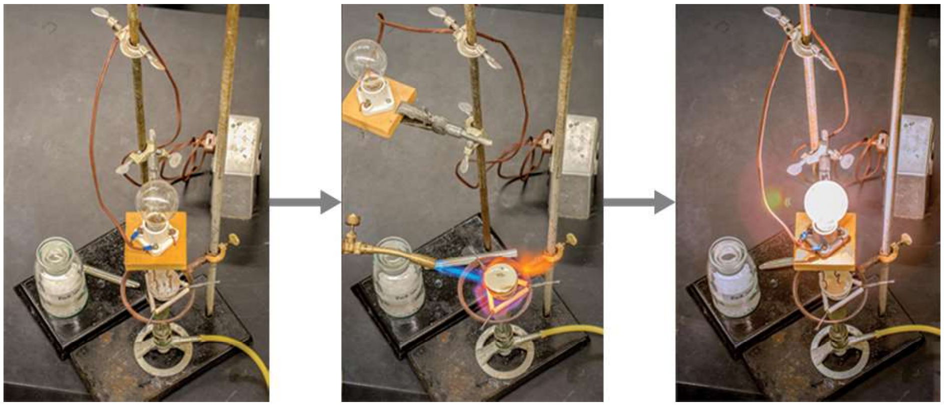


Figure 3.41 Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this **video (http://openstax.org/l/16moltensalt)** to see a mixture of salts melt and conduct electricity.

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example 3.17

Predicting the Formula of an Ionic Compound

The gemstone sapphire (**Figure 3.42**) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Figure 3.42 Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

Check Your Learning

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer: Na_2S

Many ionic compounds contain polyatomic ions (**Table 3.4**) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $(PO_4{}^{3-})$ groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 3.18

Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4{}^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4{}^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Check Your Learning

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, $O_2{}^{2-}$ (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer: Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4{}^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4{}^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These **molecular compounds** (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example 3.19

Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

(a) KI, the compound used as a source of iodine in table salt

(b) H_2O_2, the bleach and disinfectant hydrogen peroxide

(c) $CHCl_3$, the anesthetic chloroform

(d) Li_2CO_3, a source of lithium in antidepressants

Solution

(a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.

(b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.

(c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.

(d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

Check Your Learning

Using the periodic table, predict whether the following compounds are ionic or covalent:

(a) SO_2

(b) CaF_2

(c) N_2H_4

(d) $Al_2(SO_4)_3$

Answer: (a) molecular; (b) ionic; (c) molecular; (d) ionic

Key Terms

actinide inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal element in group 1

alkaline earth metal element in group 2

amplitude extent of the displacement caused by a wave

atomic orbital mathematical function that describes the behavior of an electron in an atom (also called the wavefunction)

Aufbau principle procedure in which the electron configuration of the elements is determined by “building” them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

blackbody idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Bohr’s model of the hydrogen atom structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius

chalcogen element in group 16

continuous spectrum electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

core electron electron in an atom that occupies the orbitals of the inner shells

covalent bond attractive force between the nuclei of a molecule’s atoms and pairs of electrons between the atoms

covalent compound (also, molecular compound) composed of molecules formed by atoms of two or more different elements

covalent radius one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

***d* orbital** region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$.

degenerate orbitals orbitals that have the same energy

effective nuclear charge charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electromagnetic radiation energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays

electron affinity energy change associated with addition of an electron to a gaseous atom or ion

electron configuration listing that identifies the electron occupancy of an atom’s shells and subshells

electron density a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

endothermic processes that increase the energy of an atom and involve the absorption of light

excited state state having an energy greater than the ground-state energy

exothermic processes that decrease the energy of an atom and involve the emission of light

***f* orbital** multilobed region of space with high electron density, describes orbitals with $l = 3$

frequency (ν) number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

ground state state in which the electrons in an atom, ion, or molecule have the lowest energy possible

group vertical column of the periodic table

halogen element in group 17

Heisenberg uncertainty principle rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

hertz (Hz) the unit of frequency, which is the number of cycles per second, s^{-1}

Hund's rule every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

inert gas (also, noble gas) element in group 18

inner transition metal (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

intensity property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

ionic bond electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

ionization energy energy required to remove an electron from a gaseous atom or ion

isoelectronic group of ions or atoms that have identical electron configurations

lanthanide inner transition metal in the top of the bottom two rows of the periodic table

line spectrum electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

magnetic quantum number (m_l) quantum number signifying the orientation of an atomic orbital around the nucleus

main-group element (also, representative element) element in groups 1, 2, and 13–18

metal element that is shiny, malleable, good conductor of heat and electricity

metalloid element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

molecular compound (also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion ion composed of a single atom

noble gas (also, inert gas) element in group 18

node any point of a standing wave with zero amplitude

nonmetal element that appears dull, poor conductor of heat and electricity

orbital diagram pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

oxyanion polyatomic anion composed of a central atom bonded to oxygen atoms

***p* orbital** dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$

Pauli exclusion principle specifies that no two electrons in an atom can have the same value for all four quantum numbers

period (also, series) horizontal row of the periodic table

periodic law properties of the elements are periodic function of their atomic numbers

periodic table table of the elements that places elements with similar chemical properties close together

photon smallest possible packet of electromagnetic radiation, a particle of light

pnictogen element in group 15

polyatomic ion ion composed of more than one atom

principal quantum number (n) quantum number specifying the shell an electron occupies in an atom

quantization limitation of some property to specific discrete values, not continuous

quantum mechanics field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

quantum number number having only specific allowed values and used to characterize the arrangement of electrons in an atom

representative element (also, main-group element) element in columns 1, 2, and 12–18

***s* orbital** spherical region of space with high electron density, describes orbitals with $l = 0$

secondary (angular momentum) quantum number (l) quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

series (also, period) horizontal row of the period table

shell atomic orbitals with the same principal quantum number, n

spin quantum number (m_s) number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

standing wave (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

subshell atomic orbitals with the same values of *n* and *l*

transition metal element in groups 3–12 (more strictly defined, 3–11; see chapter on transition metals and coordination chemistry)

valence electrons electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom

valence shell outermost shell of electrons in a ground-state atom

wave oscillation of a property over time or space; can transport energy from one point to another

wave-particle duality observation that elementary particles can exhibit both wave-like and particle-like properties

wavefunction (ψ) mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

wavelength (λ) distance between two consecutive peaks or troughs in a wave

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34}$ J s
- $\frac{1}{\lambda} = R_\infty\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$
- $E_n = -\frac{kZ^2}{n^2},\ n = 1,\ 2,\ 3,\ \ldots$
- $\Delta E = kZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$
- $r = \frac{n^2}{Z}a_0$

Summary

3.1 Electromagnetic Energy

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, *c*, of 2.998×10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E = \frac{hc}{\lambda}$), where *h* is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

3.2 The Bohr Model

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

3.3 Development of Quantum Theory

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The secondary (angular momentum) quantum number, l, can have any integer value from 0 to $n – 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $–l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

3.4 Electronic Structure of Atoms (Electron Configurations)

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

3.5 Periodic Variations in Element Properties

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

3.6 The Periodic Table

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

3.7 Molecular and Ionic Compounds

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

Exercises

3.1 Electromagnetic Energy

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

2. An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of 1.031×10^8 s^{-1} (103.1 MHz). What is the wavelength of these radio waves in meters?

3. FM-95, an FM radio station, broadcasts at a frequency of 9.51×10^7 s^{-1} (95.1 MHz). What is the wavelength of these radio waves in meters?

4. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

5. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?

6. Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

7. A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

8. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

9. The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

10. Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

11. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

12. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

13. RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

14. Answer the following questions about a Blu-ray laser:

(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

(b) A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

(c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = $0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

(d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^{7} bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

15. What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects an electron with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

3.2 The Bohr Model

16. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

17. What does it mean to say that the energy of the electrons in an atom is quantized?

18. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

19. The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

20. Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

21. Using the Bohr model, determine the lowest possible energy for the electron in the He^{+} ion.

22. Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

23. Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

24. How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

25. What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

26. Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

27. Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

28. Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1, 2, 3,$ and 4 orbits.

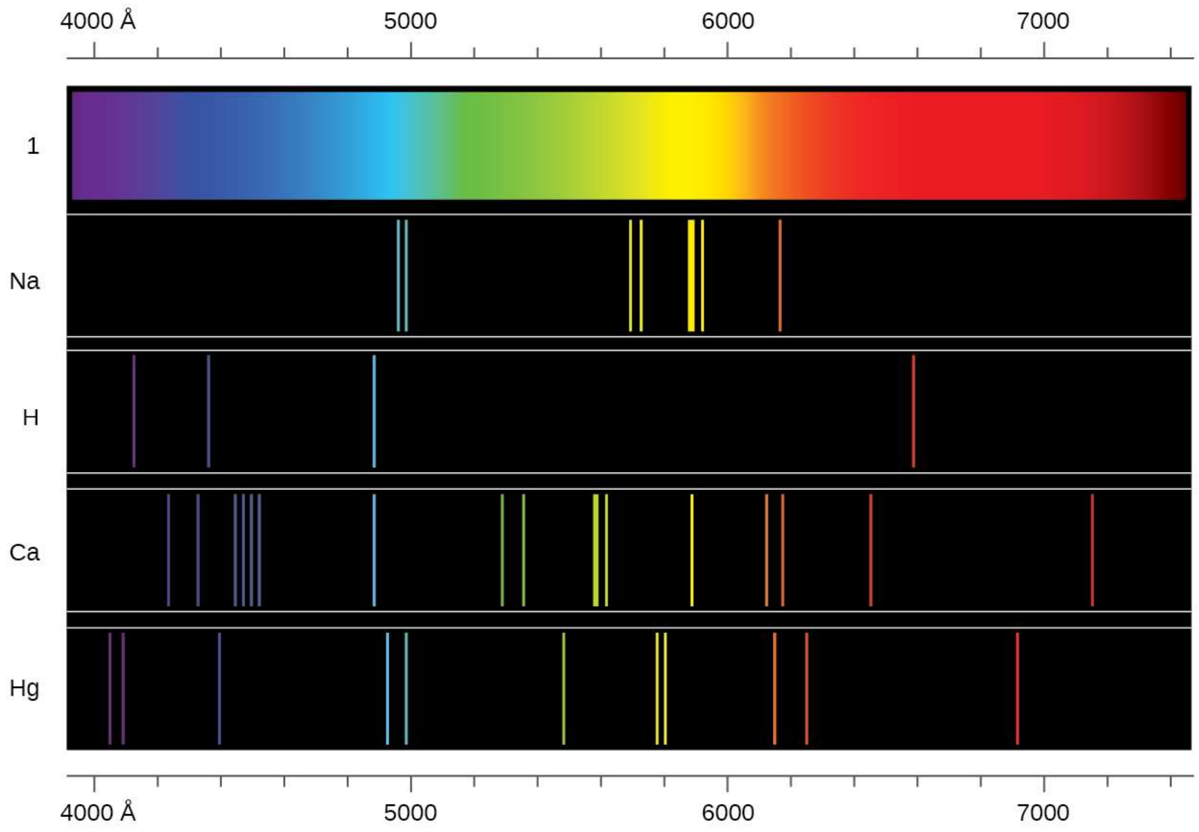
(a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbitals?

(b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).

(c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

29. How are the Bohr model and the Rutherford model of the atom similar? How are they different?

30. The spectra of hydrogen and of calcium are shown here.



What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

3.3 Development of Quantum Theory

31. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

32. What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

33. Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

34. Answer the following questions:

(a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.

(b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

35. Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 2$, $l = 1$

(b) $n = 4$, $l = 2$

(c) $n = 6$, $l = 0$

36. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

37. Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 3$, $l = 2$

(b) $n = 1$, $l = 0$

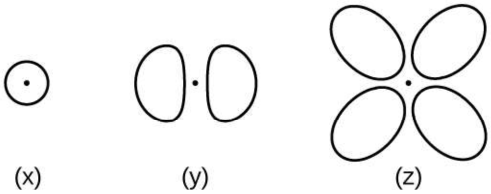
(c) $n = 4$, $l = 3$

38. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

39. Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

40. Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

41. Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?

(b) How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?

(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with $n = 4$. Of an orbital of type (y) in a shell with $n = 2$. Of an orbital of type (z) in a shell with $n = 3$.

(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?

(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

42. State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

43. How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

44. Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda \nu$

(b) $E = \frac{m\nu^2}{2}$

(c) $r = \frac{n^2 a_0}{Z}$

(d) $E = h\nu$

(e) $\lambda = \frac{h}{m\nu}$

45. Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

3.4 Electronic Structure of Atoms (Electron Configurations)

46. Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

47. Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

48. Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Sm

49. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Tb

50. Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

51. What additional information do we need to answer the question “Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$”?

52. Draw the orbital diagram for the valence shell of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Ru

53. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Mo

54. Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

(a) N^{3-}

(b) Ca^{2+}

(c) S^{-}

(d) Cs^{2+}

(e) Cr^{2+}

(f) Gd^{3+}

55. Which atom has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$?

56. Which atom has the electron configuration $1s^22s^22p^63s^23p^63d^74s^2$?

57. Which ion with a +1 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$? Which ion with a –2 charge has this configuration?

58. Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

59. Which of the following has two unpaired electrons?

(a) Mg

(b) Si

(c) S

(d) Both Mg and S

(e) Both Si and S.

60. Which atom would be expected to have a half-filled 6*p* subshell?

61. Which atom would be expected to have a half-filled 4*s* subshell?

62. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

63. Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

64. Write the electron configurations for the following atoms or ions:

(a) B^{3+}

(b) O^-

(c) Cl^{3+}

(d) Ca^{2+}

(e) Ti

65. Cobalt–60 and iodine–131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

66. Write a set of quantum numbers for each of the electrons with an *n* of 3 in a Sc atom.

3.5 Periodic Variations in Element Properties

67. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

68. Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

69. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

70. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

71. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

72. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si

73. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

74. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

75. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

76. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

77. Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

78. List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

79. Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

80. Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

81. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

82. Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: Note the process depicted does *not* correspond to electron affinity.)

$$\text{E}^+(g) + \text{e}^- \longrightarrow \text{E}(g)$$

83. Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$$\text{E}(g) \longrightarrow \text{E}^+(g) + \text{e}^-$$

84. The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

85. Which main group atom would be expected to have the lowest second ionization energy?

86. Explain why Al is a member of group 13 rather than group 3?

3.6 The Periodic Table

87. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) uranium

(b) bromine

(c) strontium

(d) neon

(e) gold

(f) americium

(g) rhodium

(h) sulfur

(i) carbon

(j) potassium

88. Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

(a) cobalt

(b) europium

(c) iodine

(d) indium

(e) lithium

(f) oxygen

(g) cadmium

(h) terbium

(i) rhenium

89. Using the periodic table, identify the lightest member of each of the following groups:

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

90. Using the periodic table, identify the heaviest member of each of the following groups:

(a) alkali metals

(b) chalcogens

(c) noble gases

(d) alkaline earth metals

91. Use the periodic table to give the name and symbol for each of the following elements:

(a) the noble gas in the same period as germanium

(b) the alkaline earth metal in the same period as selenium

(c) the halogen in the same period as lithium

(d) the chalcogen in the same period as cadmium

92. Use the periodic table to give the name and symbol for each of the following elements:

(a) the halogen in the same period as the alkali metal with 11 protons

(b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons

(c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons

(d) the noble gas in the same period as gold

93. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the alkali metal with 11 protons and a mass number of 23

(b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom

(c) the isotope with 33 protons and 40 neutrons in its nucleus

(d) the alkaline earth metal with 88 electrons and 138 neutrons

94. Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

(a) the chalcogen with a mass number of 125

(b) the halogen whose longest-lived isotope is radioactive

(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

3.7 Molecular and Ionic Compounds

95. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

96. Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

97. For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

(a) NF_3

(b) BaO,

(c) $(NH_4)_2CO_3$

(d) $Sr(H_2PO_4)_2$

(e) IBr

(f) Na_2O

98. For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

(a) $KClO_4$

(b) $MgC_2H_3O_2$

(c) H_2S

(d) Ag_2S

(e) N_2Cl_4

(f) $Co(NO_3)_2$

99. For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

(a) Ca^{2+}, S^{2-}

(b) $NH_4{}^{+}$, $SO_4{}^{2-}$

(c) Al^{3+}, Br^{-}

(d) Na^{+}, $HPO_4{}^{2-}$

(e) Mg^{2+}, $PO_4{}^{3-}$

100. For each of the following pairs of ions, write the symbol for the formula of the compound they will form.

(a) K^+, O^{2-}

(b) $NH_4{}^+$, $PO_4{}^{3-}$

(c) Al^{3+}, O^{2-}

(d) Na^+, $CO_3{}^{2-}$

(e) Ba^{2+}, $PO_4{}^{3-}$