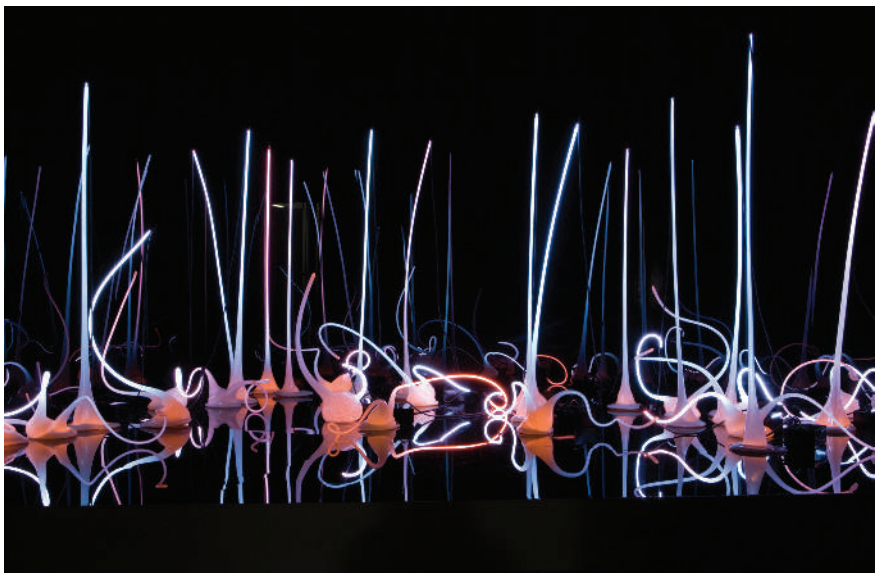
6 Electronic Structure and the Periodic Table

The tubes of glass in Dale Chihuly's *Glass Forest #3* are filled with neon gas. Neon light is obtained by electrifying the tubes or by placing them over an energized field.



Dale Chihuly, Glass Forest #3, 2007, 9x28x17', de Young Museum, San Francisco, installed 2008.

Not chaos-like crush'd and bruis'd
But, as the world, harmoniously
confus'd,
Where order in variety we see,
And where, though all things
differ, all agree.

—ALEXANDER POPE
Windsor Forest

Chapter Outline

In Chapter 2 we briefly considered the structure of the atom. You will recall that every atom has a tiny, positively charged nucleus, consisting of protons and neutrons. The nucleus is surrounded by negatively charged electrons. The number of protons in the nucleus is characteristic of the atoms of a particular element and is referred to as the atomic number. In a neutral atom, the number of electrons is equal to the number of protons and hence to the atomic number.

In this chapter, we focus on electron arrangements in atoms, paying particular attention to the relative energies of different electrons (*energy levels*) and their spatial locations (*orbitals*). Specifically, we consider the nature of the energy levels and orbitals available to

- the single electron in the hydrogen atom (Section 6-2).
- the several electrons in more complex atoms (Sections 6-3, 6-4).

With this background, we show how electron arrangements in multielectron atoms and the monatomic ions derived from them can be described in terms of

- ***electron configurations***, which show the number of electrons in each energy level (Sections 6-5, 6-7).
- ***orbital diagrams***, which show the arrangement of electrons within orbitals (Sections 6-6, 6-7).

The electron configuration or orbital diagram of an atom of an element can be deduced from its position in the periodic table. Beyond that, position in the table can predict (Section 6-8) the relative sizes of atoms and ions (*atomic radius, ionic radius*) and the relative tendencies of atoms to give up or acquire electrons (*ionization energy, electronegativity*).

Before dealing with electronic structures as such, it is helpful to examine briefly the experimental evidence on which such structures are based (Section 6-1). In particular, we need to look at the phenomenon of *atomic spectra*.

Figure 6.1 Fireworks. The different colors are created by the atomic spectra of different elements.

6-1 Light, Photon Energies, and Atomic Spectra

Fireworks displays are fascinating to watch (Figure 6.1). Neon lights and sodium vapor lamps can transform the skyline of a city with their brilliant colors. The eerie phenomenon of the aurora borealis is an unforgettable experience when you see it for the first time. All of these events relate to the generation of light and its transmission through space.

The Wave Nature of Light: Wavelength and Frequency

Light travels through space as a wave, consisting of successive crests, which rise above the midline, and troughs, which sink below it. Waves have three primary characteristics (Figure 6.2), two of which are of particular interest at this point:

1. **Wavelength** (λ), the distance between two consecutive crests or troughs, most often measured in meters or nanometers (1 nm = 10^{-9} m).
2. **Frequency** (ν), the number of wave cycles (successive crests or troughs) that pass a given point in unit time. If 10^8 cycles pass a particular point in one second,

$$\nu = 10^8/\text{s} = 10^8 \text{ Hz}$$

The frequency unit **hertz** (Hz) represents one cycle per second.

The speed at which a wave moves through space can be found by multiplying the length of a wave cycle (λ) by the number of cycles passing a point in unit time (ν). For light,

$$\lambda\nu = c \qquad (6.1)$$

where c, the speed of light in a vacuum, is 2.998×10^8 m/s. To use this equation with this value of c—

- λ should be expressed in meters.
- ν should be expressed in reciprocal seconds (hertz).

λ is the Greek letter lambda; ν is the Greek letter nu.

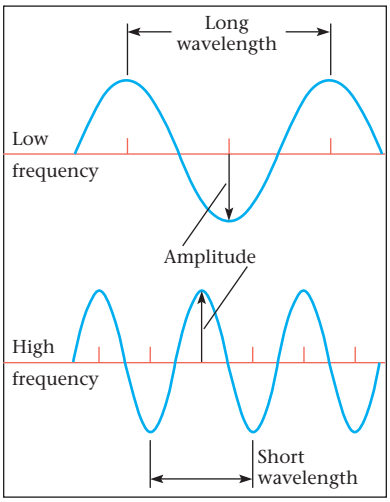


Figure 6.2 Characteristics of waves. The *amplitude* (Ψ) is the height of a crest or the depth of a trough. The *wavelength* (λ) is the distance between successive crests or troughs. The *frequency* (ν) is the number of wave cycles (successive crests or troughs) that pass a given point in a given time.

EXAMPLE 6.1

In a grocery store, a scanner uses a laser with a frequency of 4.62×10^{14} s^{-1} to scan the bar code on a power drink. The store pipes in music from an FM station with a frequency of 286 cm.

a What is the frequency of the FM station?

ANALYSIS

Information given:	wavelength of the station (286 cm)
Information implied:	speed of light (2.998×10^8 m/s) meter to centimeter conversion factor
Asked for:	frequency of the radio station

continued

STRATEGY

1. Recall the Greek letters used as symbols for frequency (ν) and wavelength (λ).
2. Use Equation 6.1 to relate frequency and wavelength.
3. Convert cm to m.

SOLUTION

Wavelength in meters	$286\ \text{cm} \times \dfrac{1\ \text{m}}{100\ \text{cm}} = 2.86\ \text{m}$
Frequency	$\nu = \dfrac{c}{\lambda} = \dfrac{2.998 \times 10^8\ \text{m/s}}{2.86\ \text{m}} = 1.05 \times 10^8\ \text{s}^{-1}$

b What is the wavelength of the laser in nm?

ANALYSIS

Information given:	frequency of the laser ($4.62 \times 10^{14}\ \text{s}^{-1}$)
Information implied:	speed of light (2.998×10^8 m/s) meter to nanometer conversion factor
Asked for:	wavelength of the laser

STRATEGY

1. Use Equation 6.1 to relate frequency and wavelength.
2. Convert m to nm.

SOLUTION

Wavelength	$\lambda = \dfrac{c}{\nu} = \dfrac{2.998 \times 10^8\ \text{m/s}}{4.62 \times 10^{14}\ \text{s}^{-1}} = 6.49 \times 10^{-7}\ \text{m}$
Wavelength in nm	$6.49 \times 10^{-7}\ \text{m} \times \dfrac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 649\ \text{nm}$

Light visible to the eye is only a tiny portion of the entire electromagnetic spectrum (Figure 6.3) covering only the narrow wavelength region from 400 to 700 nm. For a substance to be colored, it must absorb somewhere within this region. Ozone in the upper atmosphere absorbs harmful, high-energy **ultraviolet (UV)**

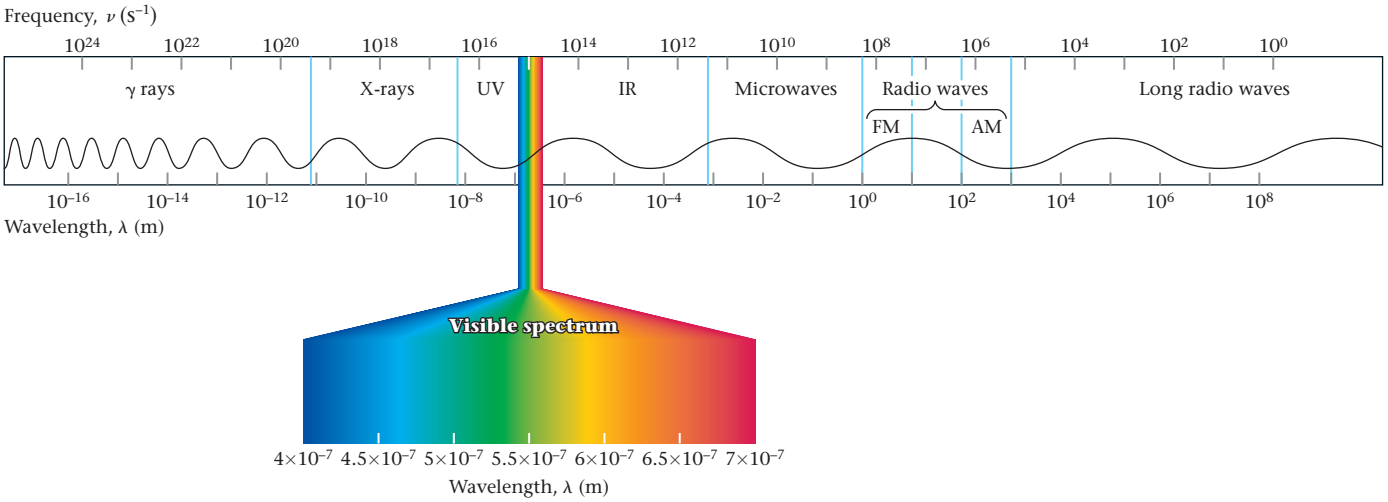


Figure 6.3 The electromagnetic spectrum. Note that only a small fraction is visible to the human eye.

Table 6.1 Relation Between Color and Wavelength

Wavelength (nanometers)	Color Absorbed	Color Transmitted
<400 nm	Ultraviolet	Colorless
400–450 nm	Violet	Red, orange, yellow
450–500 nm	Blue	
500–550 nm	Green	Purple
550–580 nm	Yellow	
580–650 nm	Orange	Blue, green
650–700 nm	Red	
>700 nm	Infrared	Colorless

Figure 6.4 Crystals of potassium permanganate falling into water. The purple color of the solution results from absorption at approximately 550 nm.

radiation from the sun. Carbon dioxide absorbs **infrared (IR) radiation** given off by the earth's surface, preventing it from escaping into the outer atmosphere, thereby contributing to global warming. Microwave ovens produce radiation at wavelengths longer than infrared radiation, whereas x-rays have wavelengths shorter than UV radiation (Figure 6.3).

Some of the substances you work with in general chemistry can be identified at least tentatively by their color. Gaseous nitrogen dioxide has a brown color; vapors of bromine and iodine are red and violet, respectively. A water solution of copper sulfate is blue, and a solution of potassium permanganate is purple (Figure 6.4).

The colors of gases and liquids are due to the selective absorption of certain components of visible light. Bromine, for example, absorbs in the violet and blue regions of the spectrum (Table 6.1). The subtraction of these components from visible light accounts for the red color of bromine liquid or vapor. The purple (blue-red) color of a potassium permanganate solution results from absorption in the green region (Figure 6.5).

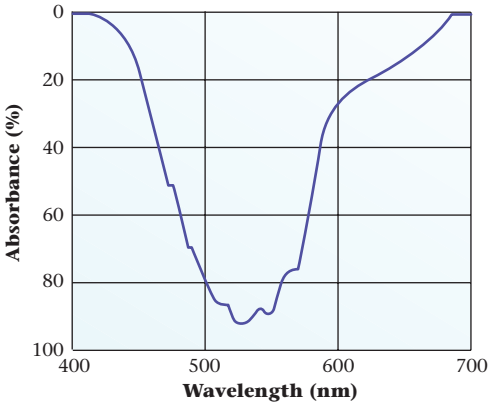


Figure 6.5 Absorption spectrum of potassium permanganate.

The Particle Nature of Light; Photon Energies

A hundred years ago it was generally supposed that all the properties of light could be explained in terms of its wave nature. A series of investigations carried out between 1900 and 1910 by Max Planck (1858–1947) (blackbody radiation) and Albert Einstein (1879–1955) (photoelectric effect) discredited that notion. Today we consider light to be generated as a stream of particles called **photons,** whose energy E (Figure 6.6) is given by the equation

$$E = h\nu = hc/\lambda \qquad (6.2)$$

Throughout this text, we will use the SI unit **joule** (J), 1 kg · m^2/s^2, to express energy. A joule is a rather small quantity. One joule of electrical energy would keep a 10-W lightbulb burning for only a tenth of a second. For that reason, we will often express energies in *kilojoules* (1 kJ = 10^3 J). The quantity h appearing in Planck's equation is referred to as *Planck's constant*.

$$h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$$

Notice from this equation that energy is *inversely* related to wavelength. This explains why you put on sunscreen to protect yourself from UV solar radiation (<400 nm) and a "lead apron" when dental x-rays (<10 nm) are being taken. Conversely, IR (>700 nm) and microwave photons (>80,000 nm) are of relatively low energy (but don't try walking on hot coals).

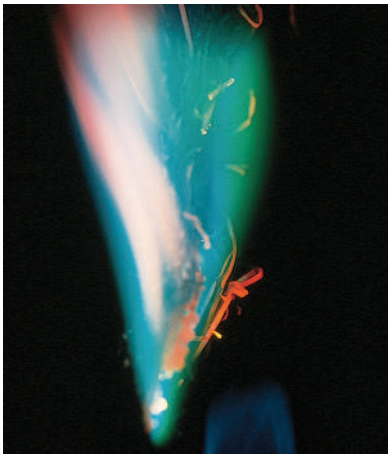


Figure 6.6 Energy and wavelength. A copper wire held in a flame colors the flame green. The energy of the photons of this light can be calculated from its wavelength.

EXAMPLE 6.2 GRADED

Sodium vapor lamps are commonly used to illuminate highways because of their intense yellow-orange emissions at 589 nm.

a Calculate the energy, in joules, of one photon of this light.

ANALYSIS

Information given:	wavelength of sodium vapor (589 nm)
Information implied:	speed of light (2.998×10^8 m/s); Planck's constant (6.626×10^{-34} J · s)
Asked for:	energy of one photon in J

STRATEGY

Use Equation 6.2 to relate energy to wavelength.

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

SOLUTION

Energy for one photon

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J} \cdot \text{s})(2.998 \times 10^{8}\ \text{m/s})}{589 \times 10^{-9}\ \text{m}} = 3.37 \times 10^{-19}\ \text{J}$$

b Calculate the energy, in kilojoules, of one mole of such photons.

ANALYSIS

Information given:	From part (a), the energy of one photon (3.37×10^{-19} J)
Information implied:	Avogadro's number (6.022×10^{23} units/mol)
Asked for:	energy of one mole of photons in kJ

STRATEGY

Use the appropriate conversion factors to change nm to m, J to kJ, and one photon to one mole of photons.

SOLUTION

E/mol of photons

$$E = 1\ \text{mol photons} \times \frac{3.37 \times 10^{-19}\ \text{J}}{1\ \text{photon}} \times \frac{6.022 \times 10^{23}\ \text{photons}}{1\ \text{mol photons}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = 203\ \text{kJ}$$

c To sense visible light, the optic nerve needs at least 2.0×10^{-17} J of energy to trigger impulses that reach the brain. How many photons of the sodium lamp emissions are needed to "see" the yellow light?

ANALYSIS

Information given:	Energy required by the optic nerve (2.0×10^{-17} J) From part (a), the energy of one photon (3.37×10^{-19} J)
Asked for:	number of photons needed to "see" yellow light

STRATEGY

Use the energy per photon for yellow light found in part (a) as a conversion factor.

$$\frac{3.37 \times 10^{-19}\ \text{J}}{1\ \text{photon}}$$

SOLUTION

Photons needed

$$2.0 \times 10^{-17}\ \text{J} \times \frac{1\ \text{photon}}{3.37 \times 10^{-19}\ \text{J}} = 59\ \text{photons}$$

continued

END POINTS

1. In part (a), 3.37×10^{-19} J may seem like a tiny amount of energy, but bear in mind that it comes from a single photon.
2. In part (b), the energy calculated for one mole of photons, 203 kJ, is roughly comparable to the energy effects in chemical reactions. About 240 kJ of heat is evolved when a mole of hydrogen gas burns (more on this in Chapter 8).
3. In part (c), note that not too many photons are needed to sense light.

Atomic Spectra

In the seventeenth century, Sir Isaac Newton showed that visible (white) light from the Sun can be broken down into its various color components by a prism. The **atomic spectrum** obtained is continuous; it contains essentially all wavelengths between 400 and 700 nm.

The situation with high-energy atoms of gaseous elements is quite different (Figure 6.7). Here the spectrum consists of discrete lines given off at specific wavelengths. Each element has a characteristic spectrum that can be used to identify it. In the case of sodium, there are two strong lines in the yellow region at 589.0 nm and 589.6 nm. These lines account for the yellow color of sodium vapor lamps used to illuminate highways.

The fact that the photons making up atomic spectra have only certain discrete wavelengths implies that they can have only certain discrete energies, because

$$E = h\nu = hc/\lambda$$

Since these photons are produced when an electron moves from one energy level to another, the electronic energy levels in an atom must be *quantized,* that is, limited to particular values. Moreover, it would seem that by measuring the spectrum of an element it should be possible to unravel its electronic energy levels. This is indeed possible, but it isn't easy. Gaseous atoms typically give off hundreds, even thousands, of spectral lines.

Atomic spectroscopy can identify metals at concentrations as low as 10^{-7} mol/L.

One of the simplest of atomic spectra, and the most important from a theoretical standpoint, is that of hydrogen. When energized by a high-voltage discharge, gaseous hydrogen atoms emit radiation at wavelengths that can be grouped into several different series (Table 6.2). The first of these to be discovered, the Balmer series, lies partly in the visible region. It consists of a strong line at 656.28 nm followed by successively weaker lines, closer and closer together, at lower wavelengths.

Balmer was a Swiss high-school teacher.

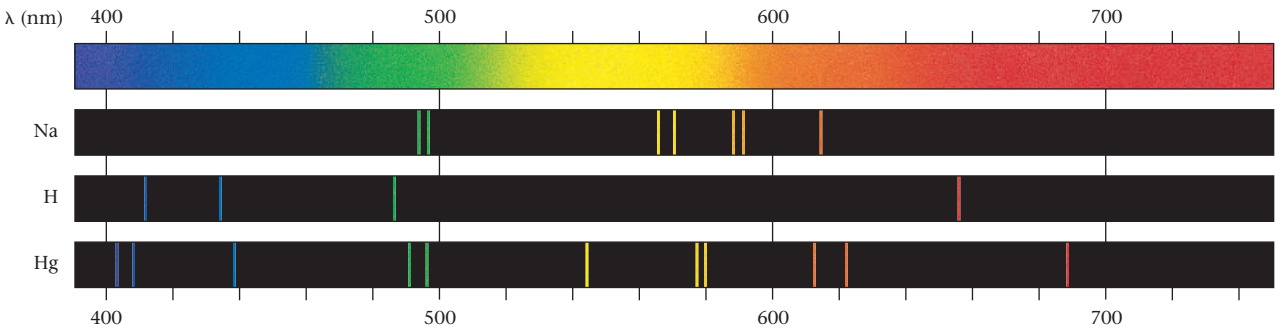


Figure 6.7 Continuous and line emission spectra. From the top down: The continuous visible spectrum; the line emission spectra for sodium (Na), hydrogen (H), and mercury (Hg).

Table 6.2 Wavelengths (nm) of Lines in the Atomic Spectrum of Hydrogen

Ultraviolet (Lyman Series)	Visible (Balmer Series)	Infrared (Paschen Series)
121.53	656.28	1875.09
102.54	486.13	1281.80
97.23	434.05	1093.80
94.95	410.18	1004.93
93.75	397.01	
93.05		

6-2 The Hydrogen Atom

The hydrogen atom, containing a single electron, has played a major role in the development of models of electronic structure. In 1913 Niels Bohr (1885–1962), a Danish physicist, offered a theoretical explanation of the atomic spectrum of hydrogen. His model was based largely on classical mechanics. In 1922 this model earned him the Nobel Prize in physics. By that time, Bohr had become director of the Institute of Theoretical Physics at Copenhagen. There, he helped develop the new discipline of quantum mechanics, used by other scientists to construct a more sophisticated model for the hydrogen atom.

Bohr, a giant of twentieth-century physics, was respected by scientists and politicians alike.

Bohr, like all the other individuals mentioned in this chapter, was not a chemist. His only real contact with chemistry came as an undergraduate at the University of Copenhagen. His chemistry teacher, Niels Bjerrum, who later became his close friend and sailing companion, recalled that Bohr set a record for broken glassware that lasted half a century.

Bohr Model

The **Bohr model** assumed that a hydrogen atom consists of a central proton about which an electron moves in a circular orbit. He related the electrostatic force of attraction of the proton for the electron to the centrifugal force due to the circular motion of the electron. In this way, Bohr was able to express the energy of the atom in terms of the radius of the electron's orbit. To this point, his analysis was purely classical, based on Coulomb's law of electrostatic attraction and Newton's laws of motion. To progress beyond this point, Bohr boldly and arbitrarily assumed, in effect, that the electron in the hydrogen atom can have only certain definite energies. Using arguments that we will not go into, Bohr obtained the following equation for the energy of the hydrogen electron:

$$E_{\mathbf{n}} = -R_H/\mathbf{n}^2 \qquad (6.3)$$

$E_{\mathbf{n}} = -2.180 \times 10^{-18}\ \text{J}/\mathbf{n}^2$

where $E_{\mathbf{n}}$ is the energy of the electron, R_H is a quantity called the *Rydberg constant* (modern value $= 2.180 \times 10^{-18}$ J), and **n** is an integer called the principal quantum number. Depending on the state of the electron, **n** can have any positive, integral value, that is,

$$\mathbf{n} = 1, 2, 3, \ldots$$

Before proceeding with the Bohr model, let us make three points:

1. In setting up his model, Bohr designated zero energy as the point at which the proton and electron are completely separated. Energy has to be absorbed to reach that point. This means that the electron, in all its allowed energy states

within the atom, must have an energy below zero; that is, it must be negative, hence the minus sign in the equation:

$$E_{\mathbf{n}} = -R_H/\mathbf{n}^2$$

2. Ordinarily the hydrogen electron is in its lowest energy state, referred to as the **ground state** or ground level, for which $\mathbf{n} = 1$. When an electron absorbs enough energy, it moves to a higher, **excited state.** In a hydrogen atom, the first excited state has $\mathbf{n} = 2$, the second $\mathbf{n} = 3$, and so on.

3. When an excited electron gives off energy as a photon of light, it drops back to a lower energy state. The electron can return to the ground state (from $\mathbf{n} = 2$ to $\mathbf{n} = 1$, for example) or to a lower excited state (from $\mathbf{n} = 3$ to $\mathbf{n} = 2$). In every case, the energy of the photon ($h\nu$) evolved is equal to the difference in energy between the two states:

$$\Delta E = h\nu = E_{\text{hi}} - E_{\text{lo}}$$

where E_{hi} and E_{lo} are the energies of the higher and lower states, respectively.

Using this expression for ΔE and the equation $E_{\mathbf{n}} = -R_H/\mathbf{n}^2$, it is possible to relate the frequency of the light emitted to the quantum numbers, $\mathbf{n}_{\text{hi}}$ and $\mathbf{n}_{\text{lo}}$, of the two states:

$$h\nu = -R_H\left[\frac{1}{(\mathbf{n}_{\text{hi}})^2} - \frac{1}{(\mathbf{n}_{\text{lo}})^2}\right]$$

$$\nu = \frac{R_H}{h}\left[\frac{1}{(\mathbf{n}_{\text{lo}})^2} - \frac{1}{(\mathbf{n}_{\text{hi}})^2}\right] \qquad (6.4)$$

The last equation written is the one Bohr derived in applying his model to the hydrogen atom. Given

$$R_H = 2.180 \times 10^{-18}\ \text{J} \qquad h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$$

you can use the equation to find the frequency or wavelength of any of the lines in the hydrogen spectrum.

EXAMPLE 6.3

Calculate the wavelength in nanometers of the line in the Balmer series that results from the transition $\mathbf{n} = 4$ to $\mathbf{n} = 2$.

ANALYSIS

Information given:	$\mathbf{n} = 2$; $\mathbf{n} = 4$
Information implied:	speed of light (2.998×10^8 m/s) Rydberg constant (2.180×10^{-18} J) Planck constant (6.626×10^{-34} J · s)
Asked for:	wavelength in nm

STRATEGY

1. Substitute into Equation 6.4 to find the frequency due to the transition.

$$\nu = \frac{R_H}{h}\left(\frac{1}{\mathbf{n}_{\text{lo}}^2} - \frac{1}{\mathbf{n}_{\text{hi}}^2}\right)$$

Use the lower value for $\mathbf{n}$ as $\mathbf{n}_{\text{lo}}$ and the higher value for $\mathbf{n}_{\text{hi}}$.

2. Use Equation 6.1 to find the wavelength in meters and then convert to nanometers.

continued

SOLUTION

1. Frequency

$$\nu = \frac{2.180 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J} \cdot \text{s}} \left(\frac{1}{(2)^2} - \frac{1}{(4)^2} \right) = 6.169 \times 10^{14}\ \text{s}^{-1}$$

2. Wavelength

$$\lambda = \frac{2.998 \times 10^{8}\ \text{m/s}}{6.169 \times 10^{14}\ \text{s}^{-1}} \times \frac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 486.0\ \text{nm}$$

END POINT

Compare this value with that listed in Table 6.2 for the second line of the Balmer series.

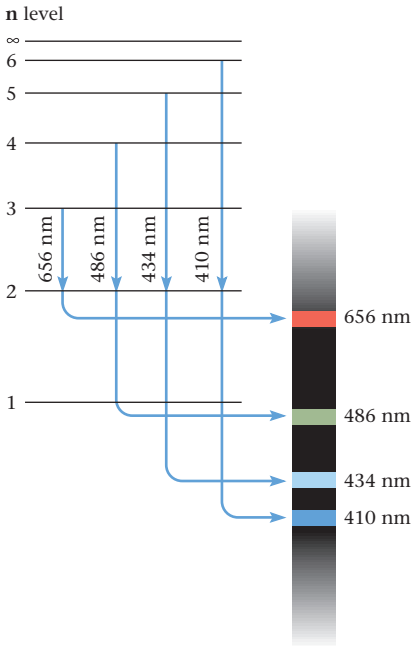


Figure 6.8 Some Balmer series lines for hydrogen. The lines in the visible region result from transitions from levels with values of **n** greater than 2 to the **n** = 2 level.

All of the lines (Figure 6.8) in the Balmer series (Table 6.2) come from transitions to the level **n** = 2 from higher levels (**n** = 3, 4, 5, . . .). Similarly, lines in the Lyman series arise when electrons fall to the **n** = 1 level from higher levels (**n** = 2, 3, 4, . . .). For the Paschen series, which lies in the infrared, the lower level is always **n** = 3.

Quantum Mechanical Model

Bohr's theory for the structure of the hydrogen atom was highly successful. Scientists of the day must have thought they were on the verge of being able to predict the allowed energy levels of all atoms. However, the extension of Bohr's ideas to atoms with two or more electrons gave, at best, only qualitative agreement with experiment. Consider, for example, what happens when Bohr's theory is applied to the helium atom. For helium, the errors in calculated energies and wavelengths are of the order of 5% instead of the 0.1% error with hydrogen. There appeared to be no way the theory could be modified to make it work well with helium or other atoms. Indeed, it soon became apparent that there was a fundamental problem with the Bohr model. The idea of an electron moving about the nucleus in a well-defined orbit at a fixed distance from the nucleus had to be abandoned.

Scientists in the 1920s, speculating on this problem, became convinced that an entirely new approach was required to treat electrons in atoms and molecules. In 1924 a young French scientist, Louis de Broglie (1892–1987), in his doctoral dissertation at the Sorbonne, made a revolutionary suggestion. He reasoned that if light could show the behavior of particles (photons) as well as waves, then perhaps an electron, which Bohr had treated as a particle, could behave like a wave. In a few years, de Broglie's postulate was confirmed experimentally. This led to the development of a whole new discipline, first called wave mechanics, more commonly known today as *quantum mechanics*.

The quantum mechanical atom differs from the Bohr model in several ways. In particular, according to quantum mechanics—

- ***the kinetic energy of an electron is inversely related to the volume of the region to which it is confined.*** This phenomenon has no analog in classical mechanics, but it helps to explain the stability of the hydrogen atom. Consider what happens when an electron moves closer and closer to the nucleus. The electrostatic energy decreases; that is, it becomes more negative. If this were the only factor, the electron should radiate energy and "fall" into the nucleus. However, the kinetic energy is increasing at the same time, because the electron is moving within a smaller and smaller volume. The two effects oppose each other; at some point a balance is reached and the atom is stable.
- ***it is impossible to specify the precise position of an electron in an atom at a given instant.*** Neither can we describe in detail the path that an electron takes about the nucleus. (After all, if we can't say where the electron is, we certainly don't know how it got there.) The best we can do is to estimate the *probability* of finding the electron within a particular region.

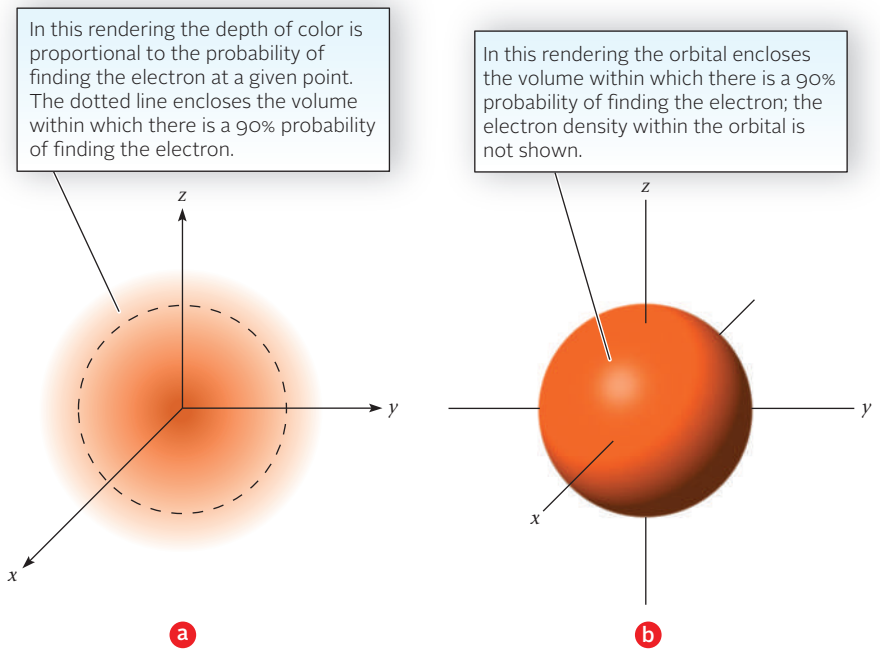


Figure 6.9 Two different ways of showing the electron distribution in the ground state of the hydrogen atom.

In 1926 Erwin Schrödinger (1887–1961), an Austrian physicist, made a major contribution to quantum mechanics. He wrote down a rather complex differential equation to express the wave properties of an electron in an atom. This equation can be solved, at least in principle, to find the **amplitude** (height) Ψ of the electron wave at various points in space. The quantity ψ (psi) is known as the *wave function*. Although we will not use the Schrödinger wave equation in any calculations, you should realize that much of our discussion of electronic structure is based on solutions to that equation for the electron in the hydrogen atom.

In case you're curious, the equation is $\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m(E - V)}{h^2}\Psi = 0$ (and that's just in one dimension).

For the hydrogen electron, the square of the wave function, ψ^2, is directly proportional to the probability of finding the electron at a particular point. If ψ^2 at point A is twice as large as at point B, then we are twice as likely to find the electron at A as at B. Putting it another way, over time the electron will turn up at A twice as often as at B.

Figure 6.9a, an *electron cloud* diagram, shows how ψ^2 for the hydrogen electron in its ground state ($\mathbf{n} = 1$) varies moving out from the nucleus. The depth of the color is supposed to be directly proportional to ψ^2 and hence to the probability of finding the electron at a point. As you can see, the color fades moving out from the nucleus in any direction; the value of ψ^2 drops accordingly.

Seems strange, but an electron is more likely to be found at the nucleus than at any other point.

Another, more common way of showing the electron distribution in the ground state of the hydrogen atom is to draw the **orbital** (Figure 6.9b) within which there is a 90% chance of finding the electron. Notice that the orbital is spherical, which means that the probability is independent of direction; the electron is equally likely to be found north, south, east, or west of the nucleus.

6-3 Quantum Numbers

The Schrödinger equation can be solved approximately for atoms with two or more electrons. There are many solutions for the wave function, ψ, each associated with a set of numbers called **quantum numbers.** Three such numbers are given the symbols **n**, ℓ, and $\mathbf{m}_\ell$. A wave function corresponding to a particular set

of three quantum numbers (e.g., $\mathbf{n} = 2$, $\ell = 1$, $\mathbf{m}_\ell = 0$) is associated with an electron occupying an atomic orbital. From the expression for ψ, we can deduce the relative energy of that orbital, its shape, and its orientation in space.

For reasons we will discuss later, a fourth quantum number is required to completely describe a specific electron in a multielectron atom. The fourth quantum number is given the symbol $\mathbf{m}_s$. Each electron in an atom has a set of four quantum numbers: **n**, ℓ, $\mathbf{m}_\ell$, and $\mathbf{m}_s$. We will now discuss the quantum numbers of electrons as they are used in atoms beyond hydrogen.

First Quantum Number, n; Principal Energy Levels

The first quantum number, given the symbol **n**, is of primary importance in determining the energy of an electron. For the hydrogen atom, the energy depends upon only **n** (recall Equation 6.3). In other atoms, the energy of each electron depends mainly, but not completely, upon the value of **n**. As **n** increases, the energy of the electron increases and, on the average, it is found farther out from the nucleus. The quantum number **n** can take on only integral values, starting with 1:

$$\mathbf{n} = 1, 2, 3, 4, \ldots \tag{6.5}$$

An electron for which $\mathbf{n} = 1$ is said to be in the first **principal energy level.** If $\mathbf{n} = 2$, we are dealing with the second principal level, and so on.

Second Quantum Number, ℓ; Sublevels (s, p, d, f)

Each principal energy level includes one or more **sublevels.** The sublevels are denoted by the second quantum number, ℓ. As we will see later, the general shape of the electron cloud associated with an electron is determined by ℓ. Larger values of ℓ produce more complex shapes. The quantum numbers **n** and ℓ are related; ℓ can take on any integral value starting with 0 and going up to a maximum of $(\mathbf{n} - 1)$.ℹ That is,

$$\ell = 0, 1, 2, \ldots, (\mathbf{n} - 1) \tag{6.6}$$

ℹ This relation between **n** and ℓ comes from the Schrödinger equation.

If $\mathbf{n} = 1$, there is only one possible value of ℓ—namely 0. This means that, in the first principal level, there is only one sublevel, for which $\ell = 0$. If $\mathbf{n} = 2$, two values of ℓ are possible, 0 and 1. In other words, there are two sublevels ($\ell = 0$ and $\ell = 1$) within the second principal energy level. In the same way,

if $\mathbf{n} = 3$:	$\ell = 0$, 1, or 2	(three sublevels)
if $\mathbf{n} = 4$:	$\ell = 0$, 1, 2, or 3	(four sublevels)

In general, ***in the* n*th principal level, there are* n *different sublevels.***

Another method is commonly used to designate sublevels. Instead of giving the quantum number ℓ, the letters s, p, d, or f* indicate the sublevels $\ell = 0$, 1, 2, or 3, respectively. That is,

quantum number, ℓ	0	1	2	3
type of sublevel	s	p	d	f

Usually, in designating a sublevel, a number is included (Table 6.3) to indicate the principal level as well. Thus reference is made to a 1s sublevel ($\mathbf{n} = 1$, $\ell = 0$), a 2s sublevel ($\mathbf{n} = 2$, $\ell = 0$), a 2p sublevel ($\mathbf{n} = 2$, $\ell = 1$), and so on.

For atoms containing more than one electron, the energy is dependent on ℓ as well as **n.** Within a given principal level (same value of **n**), sublevels increase in energy in the order

$$\mathbf{n}s < \mathbf{n}p < \mathbf{n}d < \mathbf{n}f$$

*These letters come from the adjectives used by spectroscopists to describe spectral lines: *s*harp, *p*rincipal, *d*iffuse, and *f*undamental.

Table 6.3 Sublevel Designations for the First Four Principal Levels

n	1	2		3			4			
ℓ	0	0	1	0	1	2	0	1	2	3
Sublevel	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f

Thus a 2p sublevel has a slightly higher energy than a 2s sublevel. By the same token, when $\mathbf{n} = 3$, the 3s sublevel has the lowest energy, the 3p is intermediate, and the 3d has the highest energy.

Which would have the higher energy, 4p or 3s?

Third Quantum Number, m_ℓ; Orbitals

Each sublevel contains one or more orbitals, which differ from one another in the value assigned to the third quantum number, $\mathbf{m}_\ell$. This quantum number determines the direction in space of the electron cloud surrounding the nucleus. The value of $\mathbf{m}_\ell$ is related to that of ℓ. For a given value of ℓ, $\mathbf{m}_\ell$ can have any integral value, including 0, between ℓ and $-\ell$, that is

$$\mathbf{m}_\ell = \ell, \ldots, +1, 0, -1, \ldots, -\ell \qquad (6.7)$$

To illustrate how this rule works, consider an s sublevel ($\ell = 0$). Here $\mathbf{m}_\ell$ can have only one value, 0. This means that an s sublevel contains only one orbital, referred to as an s orbital. For a p orbital ($\ell = 1$) $\mathbf{m}_\ell = 1, 0$, or -1. Within a given p sublevel there are three different orbitals described by the quantum numbers $\mathbf{m}_\ell = 1,\ 0$, and -1. All three of these orbitals have the same energy.

An electron occupies an orbital within a sublevel of a principal energy level.

For the d and f sublevels

d sublevel:	$\ell = 2$	$\mathbf{m}_\ell = 2, 1, 0, -1, -2$	5 orbitals
f sublevel:	$\ell = 3$	$\mathbf{m}_\ell = 3, 2, 1, 0, -1, -2, -3$	7 orbitals

Here again all the orbitals in a given d or f sublevel have the same energy.

Fourth Quantum Number, m_s; Electron Spin

The fourth quantum number, $\mathbf{m}_s$, is associated with **electron spin.** An electron has magnetic properties that correspond to those of a charged particle spinning on its axis. Either of two spins is possible, clockwise or counterclockwise (Figure 6.10).

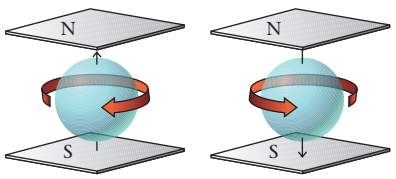


Figure 6.10 Electron spin. The spins can be represented as clockwise and counterclockwise, with the different values of $\mathbf{m}_s$ of $+\frac{1}{2}$ and $-\frac{1}{2}$.

The quantum number $\mathbf{m}_s$ was introduced to make theory consistent with experiment. In that sense, it differs from the first three quantum numbers, which came from the solution to the Schrödinger wave equation for the hydrogen atom. This quantum number is not related to **n,** ℓ, or $\mathbf{m}_\ell$. It can have either of two possible values:

$$\mathbf{m}_s = +\tfrac{1}{2} \quad \text{or} \quad -\tfrac{1}{2} \qquad (6.8)$$

Electrons that have the same value of $\mathbf{m}_s$ (i.e., both $+\frac{1}{2}$ or both $-\frac{1}{2}$) are said to have *parallel* spins. Electrons that have different $\mathbf{m}_s$ values (i.e., one $+\frac{1}{2}$ and the other $-\frac{1}{2}$) are said to have *opposed* spins.

Pauli Exclusion Principle

The four quantum numbers that characterize an electron in an atom have now been considered. There is an important rule, called the **Pauli exclusion principle,** that relates to these numbers. It requires that ***no two electrons in an atom can have the same set of four quantum numbers.*** This principle was first stated in 1925 by Wolfgang Pauli (1900–1958), a colleague of Bohr, again to make theory consistent with the properties of atoms.

Our model for electronic structure is a pragmatic blend of theory and experiment.

Table 6.4 Permissible Values of the Quantum Numbers Through n = 4

n	ℓ	m_ℓ	m_s
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (2p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (3p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (3d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$
	1 (4p)	−1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ
	2 (4d)	−2, −1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ
	3 (4f)	−3, −2, −1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ

The Pauli exclusion principle has an implication that is not obvious at first glance. It requires that only two electrons can fit into an orbital, since there are only two possible values of m_s. Moreover, if two electrons occupy the same orbital, they must have opposed spins. Otherwise they would have the same set of four quantum numbers.

The rules for assigning quantum numbers are summarized in Table 6.4 and applied in Examples 6.4 and 6.5.

EXAMPLE 6.4

Consider the following sets of quantum numbers (n, ℓ, m_ℓ, m_s). Which ones could not occur? For the valid sets, identify the orbital involved.

(a) $3, 1, 0, +\frac{1}{2}$ (b) $1, 1, 0, -\frac{1}{2}$ (c) $2, 0, 0, +\frac{1}{2}$
(d) $4, 3, 2, +\frac{1}{2}$ (e) $2, 1, 0, 0$

STRATEGY

1. Use the selection rules to identify quantum numbers that are not valid.
2. Recall the letter and number designations for ℓ.

$\ell = 0 = s$; $\ell = 1 = p$; $\ell = 2 = d$; $\ell = 3 = f$

SOLUTION

(a) $3, 1, 0, +\frac{1}{2}$	valid; $n = 3$, $\ell = 1 = p$; 3p
(b) $1, 1, 0, -\frac{1}{2}$	not valid; $n = 1$, $\ell = 1$, ℓ cannot equal n
(c) $2, 0, 0, +\frac{1}{2}$	valid; $n = 2$, $\ell = 0 = s$; 2s
(d) $4, 3, 2, +\frac{1}{2}$	valid; $n = 4$, $\ell = 3 = f$; 4f
(e) $2, 1, 0, 0$	not valid; m_s can only be $+\frac{1}{2}$ or $-\frac{1}{2}$.

EXAMPLE 6.5

(a) What is the capacity for electrons of an s sublevel? A p sublevel? A d sublevel? An f sublevel?

(b) What is the total capacity for electrons of the fourth principal level?

ANALYSIS

Information given:	sublevels
Information implied:	capacity of an orbital ($2e^-$) number of orbitals in a sublevel
Asked for:	(a) number of electrons in each sublevel (b) number of electrons in $\mathbf{n} = 4$

STRATEGY

1. Recall the number designations that correspond to the letter designation of sublevels.
2. Use the rule that tells you how many orbitals there are to a particular sublevel.

SOLUTION

(a) s sublevel	ℓ = s = 0; $\mathbf{m}_\ell = 0$; 1 orbital × $2e^-$/orbital = $2e^-$
p sublevel	ℓ = p = 1; $\mathbf{m}_\ell = -1, 0, +1$; 3 orbitals × $2e^-$/orbital = $6e^-$
d sublevel	ℓ = d = 2; $\mathbf{m}_\ell = -2, -1, 0, +1, +2$; 5 orbitals × $2e^-$/orbital = $10e^-$
f sublevel	ℓ = f = 3; $\mathbf{m}_\ell = -3, -2, -1, 0, +1, +2, +3$; 7 orbitals × $2e^-$/orbital = $14e^-$
(b) Number of e^- in $\mathbf{n} = 4$	$\mathbf{n} = 4$; $\ell = 0, 1, 2, 3$ From (a): ($\ell = 0 = 2e^-$) + ($\ell = 1 = 6e^-$) + ($\ell = 2 = 10e^-$) + ($\ell = 3 = 14e^-$) = $32e^-$

Using the approach in Example 6.5, you can readily obtain the electron capacities of any principal level or sublevel. In Table 6.5, these capacities are listed through $\mathbf{n} = 4$. Notice that

- a principal level of quantum number $\mathbf{n}$ has a capacity of $2\mathbf{n}^2$. For example, the total capacity of the fourth principal energy level is $2(4)^2 = 32e^-$.
- a sublevel of quantum number (ℓ) has a capacity of $2(2\ell + 1)$. For example, a 3d sublevel ($\ell = 2$) has a capacity of $2(2 \times 2 + 1) = 10e^-$.

Table 6.5 Capacities of Electronic Levels and Sublevels in Atoms

Level n	Total Number of Electrons in Principal Level n: $2n^2$	Maximum Number of Electrons in Sublevels: $2(2\ell + 1)$			
		$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$
		s	p	d	f
1	2	2	____	____	____
2	8	2	6	____	____
3	18	2	6	10	____
4	32	2	6	10	14

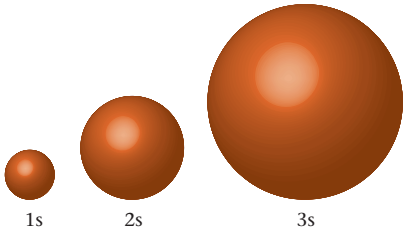
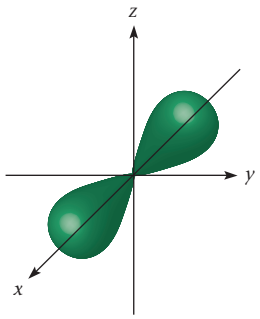
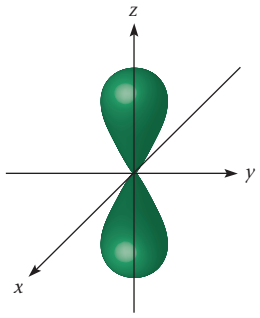


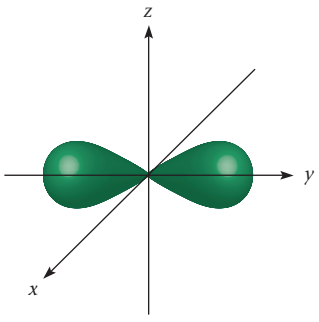
Figure 6.11 s orbitals. The relative sizes of the 90% contours (see Figure 6.9b) are shown for the 1s, 2s, and 3s orbitals.



p_x orbital

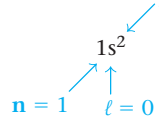


p_z orbital



p_y orbital

Figure 6.12 p orbitals. The electron density of the three p orbitals is directed along the *x*-, *y*-, or *z*-axis. The three p orbitals are located at 90° angles to each other.



6-4 Atomic Orbitals; Shapes and Sizes

You will recall (Section 6-2, page 133) that an orbital occupied by an electron in an atom can be represented physically by showing the region of space in which there is a 90% probability of finding the electron. Orbitals are commonly designated by citing the corresponding sublevels. Thus we refer to 1s, 2s, 2p, 3s, 3p, 3d, . . . orbitals.

All s sublevels are spherical; they differ from one another only in size. As **n** increases, the radius of the orbital becomes larger (Figure 6.11). This means that an electron in a 2s orbital is more likely to be found far out from the nucleus than is a 1s electron.

The shapes and orientations of p orbitals are shown in Figure 6.12. Notice that

- a p orbital consists of two lobes along an axis (*x*, *y*, or *z*). Among other things, this means that, in a p orbital, there is zero probability of finding an electron at the origin, that is, at the nucleus of the atom.
- the three p orbitals in a given sublevel are oriented at right angles to one another along the *x*-, *y*-, and *z*-axis. For that reason, the three orbitals are often designated as p_x, p_y, and p_z.

Although it is not shown in Figure 6.12, p orbitals, like s orbitals, increase in size as the principal quantum number **n** increases. Also not shown are the shapes and sizes of d and f orbitals. We will say more about the nature of d orbitals in Chapter 19.

6-5 Electron Configurations in Atoms

Given the rules referred to in Section 6-3, it is possible to assign quantum numbers to each electron in an atom. Beyond that, electrons can be assigned to specific principal levels, sublevels, and orbitals. There are several ways to do this. Perhaps the simplest way to describe the arrangement of electrons in an atom is to give its **electron configuration,** which shows the number of electrons, indicated by a superscript, in each sublevel. For example, a species with the electron configuration

$$1s^2 2s^2 2p^5$$

has two electrons in the 1s sublevel, two electrons in the 2s sublevel, and five electrons in the 2p sublevel.

In this section, you will learn how to predict the electron configurations of atoms of elements. There are a couple of different ways of doing this, which we consider in turn. It should be emphasized that, throughout this discussion, we *refer to isolated gaseous atoms in the ground state.* (In *excited* states, one or more electrons are promoted to a higher energy level.)

Electron Configuration from Sublevel Energies

Electron configurations are readily obtained if the order of filling sublevels is known. Electrons enter the available sublevels in order of increasing sublevel energy. Ordinarily, a sublevel is filled to capacity before the next one starts to fill. The relative energies of different sublevels can be obtained from experiment. Figure 6.13 is a plot of these energies for atoms through the **n** = 4 principal level.

From Figure 6.13 it is possible to predict the electron configurations of atoms of elements with atomic numbers 1 through 36. Because an s sublevel can hold only two electrons, the 1s is filled at helium ($1s^2$). With lithium ($Z = 3$), the third

electron has to enter a new sublevel: This is the 2s, the lowest sublevel of the second principal energy level. Lithium has one electron in this sublevel ($1s^2 2s^1$). With beryllium ($Z = 4$), the 2s sublevel is filled ($1s^2 2s^2$). The next six elements fill the 2p sublevel. Their electron configurations are

$_5$B	$1s^2 2s^2 2p^1$	$_8$O	$1s^2 2s^2 2p^4$
$_6$C	$1s^2 2s^2 2p^2$	$_9$F	$1s^2 2s^2 2p^5$
$_7$N	$1s^2 2s^2 2p^3$	$_{10}$Ne	$1s^2 2s^2 2p^6$

Beyond neon, electrons enter the third principal level. The 3s sublevel is filled at magnesium:

$$_{12}\text{Mg} \qquad 1s^2 2s^2 2p^6 3s^2$$

Six more electrons are required to fill the 3p sublevel with argon:

$$_{18}\text{Ar} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6$$

After argon, an "overlap" of principal energy levels occurs. The next electron enters the *lowest* sublevel of the fourth principal level (4s) instead of the *highest* sublevel of the third principal level (3d). Potassium ($Z = 19$) has one electron in the 4s sublevel; calcium ($Z = 20$) fills it with two electrons:

$$_{20}\text{Ca} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

Now the 3d sublevel starts to fill with scandium ($Z = 21$). Recall that a d sublevel has a capacity of ten electrons. Hence the 3d sublevel becomes filled at zinc ($Z = 30$):

$$_{30}\text{Zn} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$$

The next sublevel, 4p, is filled at krypton ($Z = 36$):

$$_{36}\text{Kr} \qquad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$$

Say one s two not one s squared.

These are ground-state configurations; $1s^2 2s^1 2p^2$ would be an excited state for boron.

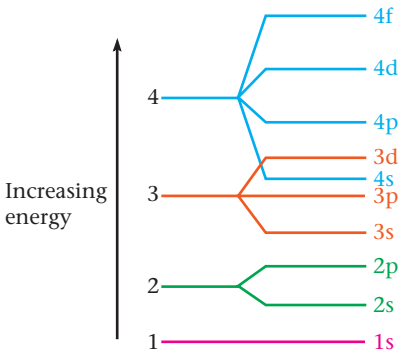


Figure 6.13 Electron energy sublevels in the order of increasing energy. The order shown is the order of sublevel filling as atomic number increases, starting at the bottom with 1s.

The order of filling, through $Z = 36$, is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p.

EXAMPLE 6.6

Find the electron configurations of the sulfur and iron atoms.

ANALYSIS

Information given:	identity of the atoms
Information implied:	atomic number of the atoms Figure 6.13; energy diagram
Asked for:	electron configurations for (a) S and (b) Fe

STRATEGY

1. Find the atomic numbers of S and Fe in the periodic table.

   S: atomic number = 16; Fe: atomic number = 26

2. Use Figure 6.13 and fill the appropriate sublevels.

   Remember 4s fills before 3d.

SOLUTION

S	$1s^2 2s^2 2p^6 3s^2 3p^4$
Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

END POINT

Use the periodic table to check your answer. See Figure 6.14 (page 141) and the accompanying discussion.

Often, to save space, electron configurations are shortened; the **abbreviated electron configuration** starts with the preceding noble gas. For the elements sulfur and nickel,

	Electron Configuration	Abbreviated Electron Configuration
$_{16}S$	$1s^2 2s^2 2p^6 3s^2 3p^4$	[Ne] $3s^2 3p^4$
$_{28}Ni$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$	[Ar] $4s^2 3d^8$

The symbol [Ne] indicates that the first 10 electrons in the sulfur atom have the neon configuration $1s^2 2s^2 2p^6$; similarly, [Ar] represents the first 18 electrons in the nickel atom.

Filling of Sublevels and the Periodic Table

In principle, a diagram such as Figure 6.13 can be extended to include all sublevels occupied by electrons in any element. As a matter of fact, that is a relatively simple thing to do; such a diagram is in effect incorporated into the periodic table introduced in Chapter 2.

To understand how position in the periodic table relates to the filling of sublevels, consider the metals in the first two groups. Atoms of the Group 1 elements all have one s electron in the outermost principal energy level (Table 6.6). In each Group 2 atom, there are two s electrons in the outermost level. A similar relationship applies to the elements in any group:

The periodic table works because an element's chemical properties depend on the number of outer electrons.

> ***The atoms of elements in a group of the periodic table have the same distribution of electrons in the outermost principal energy level.***

This means that the order in which electron sublevels are filled is determined by position in the periodic table. Figure 6.14 shows how this works. Notice the following points:

1. ***The elements in Groups 1 and 2 are filling an s sublevel.*** Thus Li and Be in the second period fill the 2s sublevel. Na and Mg in the third period fill the 3s sublevel, and so on.

2. ***The elements in Groups 13 through 18 (six elements in each period) fill p sublevels,*** which have a capacity of six electrons. In the second period, the 2p sublevel starts to fill with B ($Z = 5$) and is completed with Ne ($Z = 10$). In the third period, the elements Al ($Z = 13$) through Ar ($Z = 18$) fill the 3p sublevel.

Table 6.6 Abbreviated Electron Configurations of Group 1 and 2 Elements

Group 1		Group 2	
$_3Li$	[He] $\mathbf{2s^1}$	$_4Be$	[He] $\mathbf{2s^2}$
$_{11}Na$	[Ne] $\mathbf{3s^1}$	$_{12}Mg$	[Ne] $\mathbf{3s^2}$
$_{19}K$	[Ar] $\mathbf{4s^1}$	$_{20}Ca$	[Ar] $\mathbf{4s^2}$
$_{37}Rb$	[Kr] $\mathbf{5s^1}$	$_{38}Sr$	[Kr] $\mathbf{5s^2}$
$_{55}Cs$	[Xe] $\mathbf{6s^1}$	$_{56}Ba$	[Xe] $\mathbf{6s^2}$

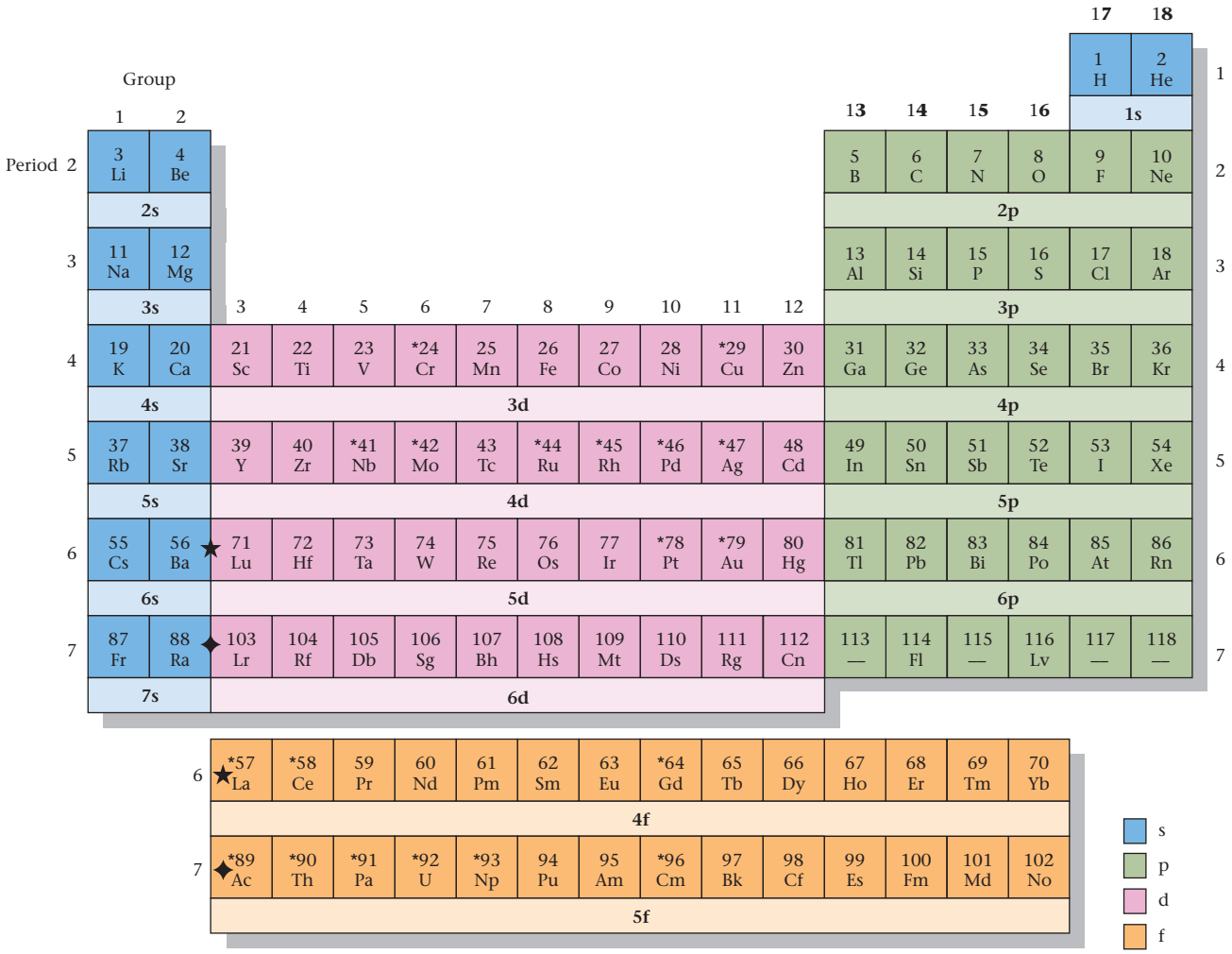


Figure 6.14 The periodic table and electron configurations. The periodic table can be used to deduce the electron configurations of atoms. The color code in the figure shows the energy sublevels being filled across each period. Elements marked with asterisks have electron configurations slightly different from those predicted by the table.

3. ***The transition metals, in the center of the periodic table, fill d sublevels.*** Remember that a d sublevel can hold ten electrons. In the fourth period, the ten elements Sc ($Z = 21$) through Zn ($Z = 30$) fill the 3d sublevel. In the fifth period, the 4d sublevel is filled by the elements Y ($Z = 39$) through Cd ($Z = 48$). The ten transition metals in the sixth period fill the 5d sublevel. Elements 103 to 112 in the seventh period are believed to be filling the 6d sublevel.

4. ***The two sets of 14 elements listed separately at the bottom of the table are filling f sublevels with a principal quantum number two less than the period number.*** That is,

- 14 elements in the sixth period ($Z = 57$ to 70) are filling the 4f sublevel. These elements are sometimes called rare earths or, more commonly, **lanthanides,** after the name of the first element in the series, lanthanum (La). Modern separation techniques, notably chromatography, have greatly increased the availability of compounds of these elements. A brilliant red phosphor used in color TV receivers contains a small amount of europium oxide, Eu_2O_3. This is added to yttrium oxide, Y_2O_3, or gadolinium oxide, Gd_2O_3. Cerium(IV) oxide is used to coat interior surfaces of "self-cleaning" ovens, where it prevents the buildup of tar deposits.

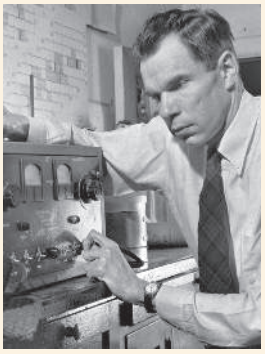
Mendeleev developed the periodic table before the discovery of protons and electrons. Amazing!

CHEMISTRY THE **HUMAN** SIDE

One name, more than any other, is associated with the actinide elements: Glenn Seaborg (1912–1999). Between 1940 and 1957, Seaborg and his team at the University of California, Berkeley, prepared nine of these elements (at. no. 94–102) for the first time. Moreover, in 1945 Seaborg made the revolutionary suggestion that the actinides, like the lanthanides, were filling an f sublevel. For these accomplishments, he received the 1951 Nobel Prize in Chemistry.

Glenn Seaborg was born in a small town in middle America, Ishpeming, Michigan. After obtaining a bachelor's degree in chemistry from UCLA, he spent the rest of his scientific career at Berkeley, first as a Ph.D. student and then as a faculty member. During World War II, he worked on the Manhattan Project. Along with other scientists, Seaborg recommended that the devastating power of the atomic bomb be demonstrated by dropping it on a barren island before United Nations observers. Later he headed the U.S. Atomic Energy Commission under Presidents Kennedy, Johnson, and Nixon.

Sometimes referred to as the "gentle giant" (he was 6 ft 4 in. tall), Seaborg had a charming, self-deprecating sense of humor. He recalled that friends advised him *not* to publish his theory about the position of the actinides in the periodic table, lest it ruin his scientific reputation. Seaborg went on to say that, "I had a great advantage. I didn't have any scientific reputation, so I went ahead and published it." Late in his life there was considerable controversy as to whether a transuranium element should be named for him; that honor had always been bestowed posthumously. Seaborg commented wryly that, "They don't want to do it because I'm still alive and they can prove it." Element 106 was named seaborgium (Sg) in 1997; he considered this his greatest honor, even above the Nobel Prize.



Lawrence Berkeley National Laboratory

Glenn Theodore Seaborg
(1912–1999)

- 14 elements in the seventh period (Z = 89 to 102) are filling the 5f sublevel. The first element in this series is actinium (Ac); collectively, these elements are referred to as **actinides.** All these elements are radioactive; only thorium and uranium occur in nature. The other actinides have been synthesized in the laboratory by nuclear reactions. Their stability decreases rapidly with increasing atomic number. The longest lived isotope of nobelium ($_{102}$No) has a half-life of about 3 minutes; that is, in 3 minutes half of the sample decomposes. Nobelium and the preceding element, mendelevium ($_{101}$Md), were identified in samples containing one to three atoms of No or Md.

Electron Configuration from the Periodic Table

Figure 6.14 (or any periodic table) can be used to deduce the electron configuration of any element. It is particularly useful for heavier elements such as iodine (Example 6.7).

To obtain electron configurations from the periodic table, consider what sublevels are filled going across each period.

EXAMPLE 6.7

For the iodine atom, write its electron configuration and its abbreviated electron configuration.

ANALYSIS

Information given:	Identity of the atom (I)
Information implied:	atomic number of I periodic table or Figure 6.14
Asked for:	electron configuration abbreviated electron cofiguration

continued

STRATEGY

For its electron configuration, use Figure 6.14 or any periodic table. Go across each period in succession, noting the sublevels occupied until you get to I. For its abbreviated electron configuration, start with the preceding noble gas, krypton (Kr).

SOLUTION

Period 1	$1s^2$
Period 2	$2s^2 2p^6$
Period 3	$3s^2 3p^6$
Period 4	$4s^2 3d^{10} 4p^6$
Period 5	$5s^2 4d^{10} 5p^5$
Electron Configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$
$[_{36}Kr]$	Kr accounts for periods 1–4
Abbreviated electron configuration	$[_{36}Kr]$ + period 5 = $[Kr]5s^2 4d^{10} 5p^5$

END POINT

Check your answer by adding all the electrons (superscripts) in your electron configuration. Your answer must equal the atomic number, which is the number of electrons in the atom.

As you can see from Figure 6.14, the electron configurations of several elements (marked*) differ slightly from those predicted. In every case, the difference involves a shift of one or, at the most, two electrons from one sublevel to another of very similar energy. For example, in the first transition series, two elements, chromium and copper, have an extra electron in the 3d as compared with the 4s orbital.

	Predicted	Observed
$_{24}Cr$	[Ar] $4s^2 3d^4$	[Ar] $4s^1 3d^5$
$_{29}Cu$	[Ar] $4s^2 3d^9$	[Ar] $4s^1 3d^{10}$

These anomalies reflect the fact that the 3d and 4s orbitals have very similar energies. Beyond that, it has been suggested that there is a slight increase in stability with a half-filled (Cr) or completely filled (Cu) 3d sublevel.

6-6 Orbital Diagrams of Atoms

For many purposes, electron configurations are sufficient to describe the arrangements of electrons in atoms. Sometimes, however, it is useful to go a step further and show how electrons are distributed among orbitals. In such cases, **orbital diagrams** are used. Each orbital is represented by parentheses ( ), and electrons are shown by arrows written ↑ or ↓, depending on spin.

To show how orbital diagrams are obtained from electron configurations, consider the boron atom ($Z = 5$). Its electron configuration is $1s^2 2s^2 2p^1$. The pair of electrons in the 1s orbital must have opposed spins ($+\frac{1}{2}$, $-\frac{1}{2}$, or ↑↓). The same is true of the two electrons in the 2s orbital. There are three orbitals in the 2p sublevel. The single 2p electron in boron could be in any one of these orbitals.

Its spin could be either "up" or "down." The orbital diagram is ordinarily written

	1s	2s	2p
$_5$B	(↑↓)	(↑↓)	(↑) ( ) ( )

with the first electron in an orbital arbitrarily designated by an up arrow, ↑.

With the next element, carbon, a complication arises. In which orbital should the sixth electron go? It could go in the same orbital as the other 2p electron, in which case it would have to have the opposite spin, ↓. It could go into one of the other two orbitals, either with a parallel spin, ↑, or an opposed spin, ↓. Experiment shows that there is an energy difference among these arrangements. The most stable is the one in which the two electrons are in different orbitals with parallel spins. The orbital diagram of the carbon atom is

	1s	2s	2p
$_6$C	(↑↓)	(↑↓)	(↑) (↑) ( )

Similar situations arise frequently. There is a general principle that applies in all such cases; **Hund's rule** (Friedrich Hund, 1896–1997) predicts that, ordinarily,

> ***when several orbitals of equal energy are available, as in a given sublevel, electrons enter singly with parallel spins.***

Hund was still lecturing, colorfully and coherently, in his nineties.

Only after all the orbitals are half-filled do electrons pair up in orbitals.

Following this principle, the orbital diagrams for the elements boron through neon are shown in Figure 6.15. Notice that

- ***in all filled orbitals, the two electrons have opposed spins.*** Such electrons are often referred to as being *paired*. There are four paired electrons in the B, C, and N atoms, six in the oxygen atom, eight in the fluorine atom, and ten in the neon atom.
- ***in accordance with Hund's rule, within a given sublevel there are as many half-filled orbitals as possible.*** Electrons in such orbitals are said to be *unpaired*. There is one unpaired electron in atoms of B and F, two unpaired electrons in C and O atoms, and three unpaired electrons in the N atom. When there are two or more unpaired electrons, as in C, N, and O, those electrons have parallel spins.

Hund's rule, like the Pauli exclusion principle, is based on experiment. It is possible to determine the number of unpaired electrons in an atom. With solids, this is done by studying their behavior in a magnetic field. If there are unpaired electrons present, the solid will be attracted into the field. Such a substance is said to be **paramagnetic**. If the atoms in the solid contain only paired electrons, it is slightly repelled by the field. Substances of this type are called **diamagnetic**. With gaseous atoms, the atomic spectrum can also be used to establish the presence and number of unpaired electrons.

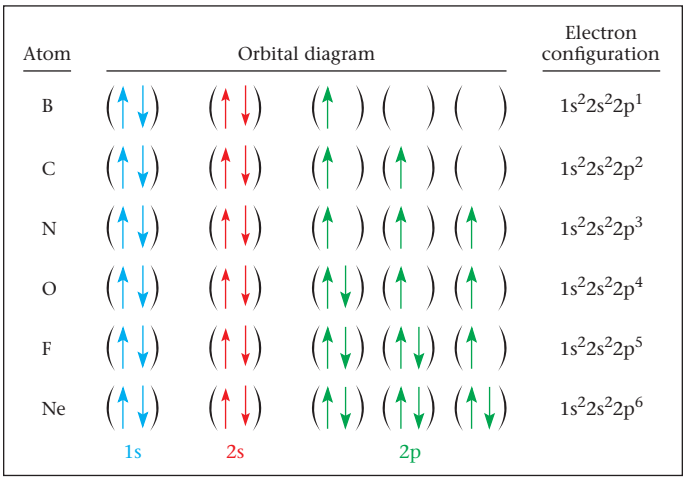


Figure 6.15 Orbital diagrams for atoms with five to ten electrons. Orbitals of equal energy are all occupied by unpaired electrons before pairing begins.

EXAMPLE 6.8

Construct orbital diagrams for atoms of sulfur and iron.

ANALYSIS

Information given:	identity of the atoms (S and Fe)
Information implied:	periodic table number designations for ℓ number of orbitals in each sublevel
Asked for:	orbital diagram for S and Fe

STRATEGY

1. Write the electron configurations for S and Fe.

   See Example 6.6 where the electron configuration for these atoms is obtained.
2. Recall the number of orbitals per sublevel and the number of electrons allowed in each orbital.

   $\mathbf{m}_\ell = 2\ell + 1$; $2e^-$ per orbital
3. Apply Hund's rule.

   Electrons enter singly in parallel spins when several orbitals of equal energy are available.

SOLUTION

For S:

1. Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^4$
2. Number of orbitals:
   s = 0; 2(0) + 1 = 1 orbital for s sublevels
   p = 1; 2(1) + 1 = 3 orbitals for p sublevels
3. Orbital diagram:

1s	2s	2p	3s	3p
(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑)(↑)

For Fe:

1. Electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
2. Number of orbitals:
   s = 0; 2(0) + 1 = 1 orbital for s sublevels
   p = 1; 2(1) + 1 = 3 orbitals for p sublevels
   d = 2; 2(2) + 1 = 5 orbitals for p sublevels
3. Orbital diagram:

1s	2s	2p	3s	3p	4s	3d
(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑)(↑)(↑)(↑)

END POINT

You can't write an orbital diagram without knowing: (a) the number designations for ℓ, (b) the number of orbitals in each sublevel, (c) the electron configuration, and (d) Hund's rule.

6-7 Electron Arrangements in Monatomic Ions

The discussion so far in this chapter has focused on electron configurations and orbital diagrams of neutral atoms. It is also possible to assign electronic structures to monatomic ions, formed from atoms by gaining or losing electrons. In general, when a monatomic ion is formed from an atom, *electrons are added to or removed from sublevels in the highest principal energy level.*

Important ideas are worth repeating.

Ions with Noble-Gas Structures

As pointed out in Chapter 2, elements close to a noble gas in the periodic table form ions that have the same number of electrons as the noble-gas atom. This means that these ions have noble-gas electron configurations. Thus the three elements preceding neon (N, O, and F) and the three elements following neon (Na, Mg, and Al) all form ions with the neon configuration, $1s^2 2s^2 2p^6$. The three nonmetal atoms achieve this structure by gaining electrons to form anions:

$$_7\text{N}\ (1s^2 2s^2 2p^3) + 3e^- \longrightarrow {}_7\text{N}^{3-}\ (1s^2 2s^2 2p^6)$$
$$_8\text{O}\ (1s^2 2s^2 2p^4) + 2e^- \longrightarrow {}_8\text{O}^{2-}\ (1s^2 2s^2 2p^6)$$
$$_9\text{F}\ (1s^2 2s^2 2p^5) + e^- \longrightarrow {}_9\text{F}^-\ (1s^2 2s^2 2p^6)$$

The three metal atoms acquire the neon structure by losing electrons to form cations:

$$_{11}\text{Na}\ (1s^2 2s^2 2p^6 3s^1) \longrightarrow {}_{11}\text{Na}^+\ (1s^2 2s^2 2p^6) + e^-$$
$$_{12}\text{Mg}\ (1s^2 2s^2 2p^6 3s^2) \longrightarrow {}_{12}\text{Mg}^{2+}\ (1s^2 2s^2 2p^6) + 2e^-$$
$$_{13}\text{Al}\ (1s^2 2s^2 2p^6 3s^2 3p^1) \longrightarrow {}_{13}\text{Al}^{3+}\ (1s^2 2s^2 2p^6) + 3e^-$$

The species N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} are said to be *isoelectronic;* that is, they have the same electron configuration.

There are a great many monatomic ions that have noble-gas configurations; Figure 6.16 shows 24 ions of this type. Note, once again, that ions in a given main group have the same charge (+1 for Group 1, +2 for Group 2, −2 for Group 16, −1 for Group 17). This explains, in part, the chemical similarity among elements in the same main group. In particular, ionic compounds formed by such elements have similar chemical formulas. For example,

- halides of the alkali metals have the general formula MX, where M = Li, Na, K, . . . and X = F, Cl, Br, ...
- halides of the alkaline earth metals have the general formula MX_2, where M = Mg, Ca, Sr, . . . and X = F, Cl, Br, ...
- oxides of the alkaline earth metals have the general formula MO, where M = Mg, Ca, Sr, ...

Transition Metal Cations

The transition metals to the right of the scandium subgroup do not form ions with noble-gas configurations. To do so, they would have to lose four or more electrons. The energy requirement is too high for that to happen. However, as pointed out in Chapter 2, these metals do form cations with charges of +1, +2, or +3. Applying the principle that, in forming cations, electrons are removed from the sublevel of highest **n**, you can predict correctly that ***when transition metal atoms***

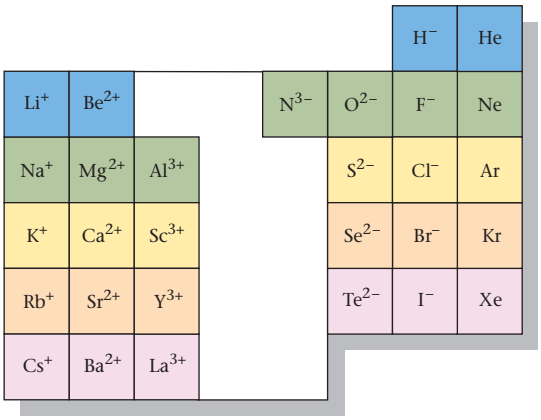


Figure 6.16 Cations, anions, and atoms with ground state noble-gas electron configurations. Atoms and ions shown in the same color are *isoelectronic;* that is, they have the same electron configurations.

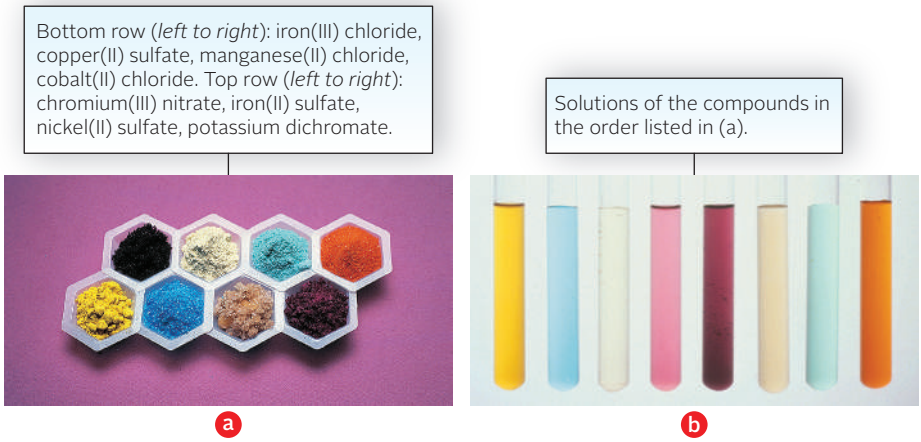


Figure 6.17 Transition metal ions. Transition metal ions impart color to many of their compounds and solutions.

form positive ions, the outer s electrons are lost first. Consider, for example, the formation of the Mn^{2+} ion from the Mn atom:

$$_{25}Mn \quad [Ar]\ 4s^2 3d^5 \qquad _{25}Mn^{2+} \quad [Ar] 3d^5$$

Notice that it is the 4s electrons that are lost rather than the 3d electrons. This is known to be the case because the Mn^{2+} ion has been shown to have five unpaired electrons (the five 3d electrons). If two 3d electrons had been lost, the Mn^{2+} ion would have had only three unpaired electrons.

The s electrons are "first in" with the atoms and "first out" with the cations.

All the transition metals (Figure 6.17) form cations by a similar process, that is, loss of outer s electrons. Only after those electrons are lost are electrons removed from the inner d sublevel. Consider, for example, what happens with iron, which, you will recall, forms two different cations. First the 4s electrons are lost to give the Fe^{2+} ion:

$$_{26}Fe(Ar\ 4s^2 3d^6) \longrightarrow {}_{26}Fe^{2+}(Ar\ 3d^6) + 2e^-$$

Then an electron is removed from the 3d level to form the Fe^{3+} ion:

$$_{26}Fe^{2+}(Ar\ 3d^6) \longrightarrow {}_{26}Fe^{3+}(Ar\ 3d^5) + e^-$$

In the Fe^{2+} and Fe^{3+} ions, as in all transition metal ions, there are no outer s electrons.

You will recall that for fourth period *atoms*, the 4s sublevel fills before the 3d. In the corresponding *ions*, the electrons come out of the 4s sublevel before the 3d. This is sometimes referred to as the "first in, first out" rule.

Seniority rules don't apply to electrons.

EXAMPLE 6.9

Give the electron configuration of Fe^{2+} and Br^-.

ANALYSIS

Information given:	Identity of the ions and their charge: (Fe^{2+}, Br^-)
Information implied:	atomic number of the atoms; electron configuration of the atoms
Asked for:	electron configuration of the ions

STRATEGY

1. Write the electron configuration of each atom.
2. Add electrons (for anions) or subtract electrons (for cations) from sublevels of the highest **n**. If there is more than one sublevel in the highest **n**, add or subtract electrons in the highest ℓ of that **n**.

continued

SOLUTION	
Fe electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cation with +2 charge	subtract 2 electrons
Highest **n**	4 with only one sublevel
Fe^{2+} electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^{2-2} 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
Br electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
Anion with −1 charge	add 1 electron
Highest **n**	4 with 2 sublevels (s and p)
Highest ℓ in **n**	p
Br^- electron configuration	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^{5+1} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
END POINT	
The electron configuration for Br^- is the same as that for the noble gas closest to it, krypton.	

6-8 Periodic Trends in the Properties of Atoms

One of the most fundamental principles of chemistry is the periodic law, which states that

> ***The chemical and physical properties of elements are a* periodic function *of atomic number.***

This is, of course, the principle behind the structure of the periodic table. Elements within a given vertical group resemble one another chemically because chemical properties repeat themselves at regular intervals of 2, 8, 18, or 32 elements.

In this section we will consider how the periodic table can be used to correlate properties on an atomic scale. In particular, we will see how atomic radius, ionic radius, ionization energy, and electronegativity vary horizontally and vertically in the periodic table.

Atomic Radius

Strictly speaking, the "size" of an atom is a rather nebulous concept. The electron cloud surrounding the nucleus does not have a sharp boundary. However, a quantity called the **atomic radius** can be defined and measured, assuming a spherical atom. Ordinarily, the atomic radius is taken to be one half the distance of closest approach between atoms in an elemental substance (Figure 6.18).

The atomic radii of the main-group elements are shown at the top of Figure 6.19. Notice that, in general, atomic radii

- decrease across a period from left to right in the periodic table.
- increase down a group in the periodic table.

It is possible to explain these trends in terms of the electron configurations of the corresponding atoms. Consider first the increase in radius observed as we move down the table, let us say among the alkali metals (Group 1). All these elements have a single s electron outside a filled level or filled p sublevel. Electrons in these inner levels are much closer to the nucleus than the outer s electron and hence effectively shield it from the positive charge of the nucleus. To a first approximation, each inner electron cancels the charge of one proton in the nucleus, so the outer s electron is attracted by a net positive charge of +1. In this sense, it has the properties of an electron in the hydrogen atom. Because the average distance of the electron from the hydrogen nucleus increases with the principal

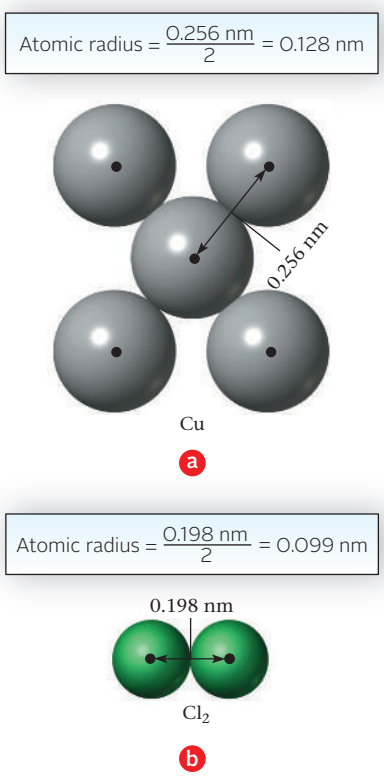


Figure 6.18 Atomic radii. The radii are determined by assuming that atoms in closest contact in an element touch one another. The atomic radius is taken to be one half of the closest internuclear distance.

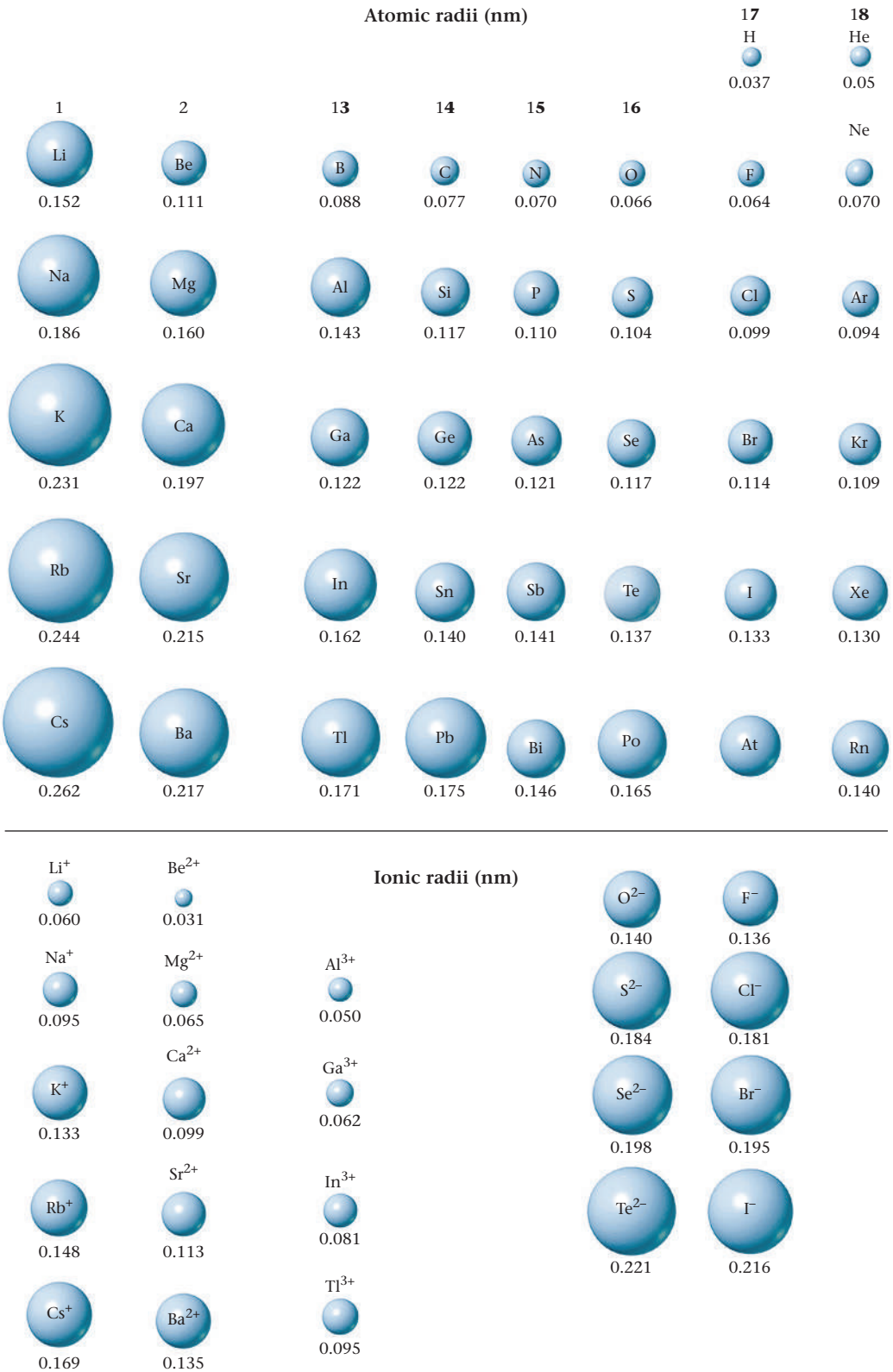


Figure 6.19 Atomic and ionic radii of the main-group elements. Negative ions are always larger than atoms of the same element, whereas positive ions are always smaller than atoms of the same element.

quantum number, **n**, the radius increases moving from Li (2s electron) to Na (3s electron) and so on down the group.

The decrease in atomic radius moving across the periodic table can be explained in a similar manner. Consider, for example, the third period, where electrons are being added to the third principal energy level. The added electrons should be relatively poor shields for each other because they are all at about the same distance from the nucleus. Only the ten **core electrons** in inner, filled levels (**n** = 1, **n** = 2) are expected to shield the outer electrons from the nucleus. This means that the charge felt by an outer electron, called the **effective nuclear charge**, should increase steadily with atomic number as we move across the period. As effective nuclear charge increases, the outermost electrons are pulled in more tightly, and atomic radius decreases.

Ionic Radius

The radii of cations and anions derived from atoms of the main-group elements are shown at the bottom of Figure 6.19. The trends referred to previously for atomic radii are clearly visible with ionic radius as well. Notice, for example, that **ionic radius** increases moving down a group in the periodic table. Moreover, the radii of both cations (left) and anions (right) decrease from left to right across a period.

Comparing the radii of cations and anions with those of the atoms from which they are derived

- ***positive ions are smaller than the metal atoms from which they are formed*** (Figure 6.20). The Na^+ ion has a radius, 0.095 nm, only a little more than half that of the Na atom, 0.186 nm.
- ***negative ions are larger than the nonmetal atoms from which they are formed*** (Figure 6.20). The radius of the Cl^- ion, 0.181 nm, is nearly twice that of the Cl atom, 0.099 nm.

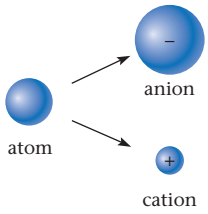


Figure 6.20 Relative size of the parent atom and its ions.

As a result of these effects, anions in general are larger than cations. Compare, for example, the Cl^- ion (radius = 0.181 nm) with the Na^+ ion (radius = 0.095 nm). This means that in sodium chloride, and indeed in the vast majority of all ionic compounds, most of the space in the crystal lattice is taken up by anions.

The differences in radii between atoms and ions can be explained quite simply. A cation is smaller than the corresponding metal atom because the excess of protons in the ion draws the outer electrons in closer to the nucleus. In contrast, an extra electron in an anion adds to the repulsion between outer electrons, making a negative ion larger than the corresponding nonmetal atom.

EXAMPLE 6.10

Using only the periodic table, arrange each of the following sets of atoms and ions in order of increasing size.

(a) Mg, Al, Ca (b) S, Cl, S^{2-} (c) Fe, Fe^{2+}, Fe^{3+}

STRATEGY

Recall the following:

- The definition of a period and a group in the periodic table.
- The radius decreases across a period and increases going down a group.
- An atom is larger than its cation but smaller than its anion.

SOLUTION

(a) Mg, Al, Ca

Mg and Al belong to the same period: Al < Mg.
Mg and Ca belong to the same group: Mg < Ca.
Thus Al < Mg < Ca.

continued

(b) S, Cl, S^{2-}	S and Cl belong to the same period: Cl < S. An atom is smaller than its anion: S < S^{2-}. Thus Cl < S < S^{2-}.
(c) Fe, Fe^{2+}, Fe^{3+}	A cation is smaller than its atom: Fe^{2+} < Fe, Fe^{3+} < Fe Increasing the charge of cations of the same atom decreases size: Fe^{3+} < Fe^{2+}. Thus Fe^{3+} < Fe^{2+} < Fe (Figure 6.21).

Ionization Energy

Ionization energy is a measure of how difficult it is to remove an electron from a gaseous atom. Energy must always be *absorbed* to bring about ionization, so ionization energies are always *positive* quantities.

The (first) ionization energy is the energy change for the removal of the outermost electron from a gaseous atom to form a +1 ion:

$$M(g) \longrightarrow M^+(g) + e^- \qquad \Delta E_1 = \text{first ionization energy}$$

The more difficult it is to remove electrons, the larger the ionization energy.

Ionization energies of the main-group elements are listed in Figure 6.22. Notice that ionization energy

- increases across the periodic table from left to right.
- decreases moving down the periodic table.

Figures 6.19 and 6.22 show an inverse correlation between ionization energy and atomic radius. The smaller the atom, the more tightly its electrons are held to the positively charged nucleus and the more difficult they are to remove. Conversely, in a large atom such as that of a Group 1 metal, the electron is relatively far from the nucleus, so less energy has to be supplied to remove it from the atom.

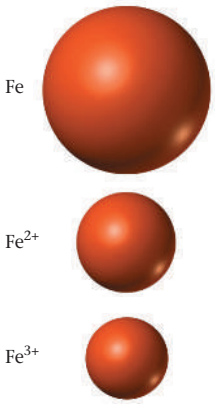


Figure 6.21 Relative sizes of the iron atom and its ions.

1	2					17	18
						H 1312	He 2372
Li 520	Be 900	13 B 801	14 C 1086	15 N 1402	16 O 1314	F 1681	Ne 2081
Na 496	Mg 738	Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520
K 419	Ca 590	Ga 579	Ge 762	As 944	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	In 558	Sn 709	Sb 832	Te 869	I 1009	Xe 1170
Cs 376	Ba 503	Tl 589	Pb 716	Bi 703	Po 812	At	Rn 1037

Ionization energy decreases

Ionization energy increases

Figure 6.22 First ionization energies of the main-group elements, in kilojoules per mole. In general, ionization energy decreases moving down the periodic table groups and increases across the periods, although there are several exceptions.

EXAMPLE 6.11

Consider the three elements C, N, and Si. Using only the periodic table, predict which of the three elements has

(a) the largest atomic radius; the smallest atomic radius.

(b) the largest ionization energy; the smallest ionization energy.

continued

STRATEGY

1. Because these three elements form a block (N next to C and Si below C), in the periodic table, it is convenient to compare both silicon and nitrogen to carbon.
2. Recall the trends for atomic radius and ionization energy.

SOLUTION

(a) atomic radius	C > N; C < Si
	Si is the largest atom, N is the smallest.
(b) ionization energy	C < N; C > Si
	Si has the smallest first ionization energy.
	N has the largest first ionization energy.

END POINT

Check your answers against Figures 6.19 and 6.22.

If you look carefully at Figure 6.22, you will note a few exceptions to the general trends referred to above and illustrated in Example 6.11. For example, the ionization energy of B (801 kJ/mol) is *less* than that of Be (900 kJ/mol). This happens because the electron removed from the boron atom comes from the 2p as opposed to the 2s sublevel for beryllium. Because 2p is higher in energy than 2s, it is not too surprising that less energy is required to remove an electron from that sublevel.

Electronegativity

The ionization energy of an atom is a measure of its tendency to lose electrons; the larger the ionization energy, the more difficult it is to remove an electron. There are several different ways of comparing the tendencies of different atoms to gain electrons. The most useful of these for our purposes is the **electronegativity**, which measures the ability of an atom to attract to itself the electron pair forming a covalent bond.

Electronegativity is a positive quantity.

The greater the electronegativity of an atom, the greater its attraction for electrons. Table 6.7 shows a scale of electronegativities first proposed by Linus Pauling (1901–1994). Each element is assigned a number, ranging from 4.0 for the most electronegative element, fluorine, to 0.8 for cesium, the least electronegative. Among the main-group elements, electronegativity increases moving from left to right in the periodic table. Ordinarily, it decreases, moving down a group. You will find Table 6.7 very helpful when we discuss covalent bonding in Chapter 7.

Table 6.7 Electronegativity Values

H 2.2							—*
Li 1.0	Be 1.6	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	—*
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2	—*
K 0.8	Ca 1.0	Sc 1.4	Ge 2.0	As 2.2	Se 2.5	Br 3.0	Kr 3.3
Rb 0.8	Sr 0.9	Y 1.2	Sn 1.9	Sb 2.0	Te 2.1	I 2.7	Xe 3.0
Cs 0.8	Ba 0.9						

*The noble gases He, Ne, and Ar are not listed because they form no stable compounds.

Why Do Lobsters Turn Red When Cooked?

Harry A. Frank, *University of Connecticut*

Many biological organisms exhibit visible coloration. This occurs when specific molecules become bound in proteins or membranes of an organism and absorb light in the visible region of the electromagnetic spectrum. As described in this chapter, absorption occurs when an atom or molecule is excited by light from the ground electronic state to a higher excited state. Wavelengths of light not absorbed are either scattered or reflected. This may result in coloration or patterns that either blend with the environment or stand out from it. Why animal species select specific molecules for coloration has much to do with the pressures of survival in the wild. However, not all animals are able to synthesize what they need for this purpose. In many cases, dietary intake plays a role.

Animals ingest plant material in the course of their normal dietary intake, and the plant pigments then find their way into the outer covering of the organism, where they may be exhibited as coloration. Many complex biochemical and metabolic pathways are involved after ingestion in modifying and transporting the molecules that ultimately become pigments.

An excellent case in point is the coloration of the American lobster, *Homarus americanus*. The pigment associated with the typical greenish-brown outer layer of the lobster shell is the carotenoid, astaxanthin (Figure A), an oxygenated derivative of β-carotene, also known as the molecule that imparts the orange color to carrots.

Both astaxanthin and β-carotene belong to a class of pigments known as carotenoids. Carotenoids are not synthesized by any member of the animal kingdom, but are taken in through the diet. The lobster diet consists primarily of fish, mollusks, and other crustaceans. Therefore, the color of a live lobster can vary due to differences in available food sources and environmental conditions. This is why some lobsters may be orange, speckled, or even bright blue. Indeed, blue coloration is frequently observed in the joints of a live lobster's appendages (Figure B). When cooked, the color of the lobster turns red. How does this happen?

After being ingested, astaxanthin molecules are assembled in a large protein called crustacyanin and then bound in the calcified outer layer of the lobster shell. When an astaxanthin molecule is bound in the crustacyanin protein, its structure becomes twisted and pairs up with another astaxanthin. This combination of twisting and pairing of astaxanthin molecules produces a pigment-protein complex that absorbs the long wavelengths of visible light (Figure C) and hence appears blue. Free astaxanthin dissolved in organic solvents, such as methanol, absorbs the shorter wavelengths of blue-green light (Figure C) and therefore appears the complement of this color, which is red.

Because the lobster accumulates a combination of protein-bound (blue) and free (red) astaxanthin in its shell, the live animal appears greenish-brown, which apparently serves it well as a disguise against predators on the ocean floor. The color change upon cooking occurs because high temperatures denature the crustacyanin protein and release the bound astaxanthin. No longer constrained by the protein, but still intact, astaxanthin imparts the same red color to the shell that it exhibits as a free molecule in organic solvent. Our world is colored by an abundance of these carotenoid pigments in mammals, fish, reptiles, birds, and other living creatures.

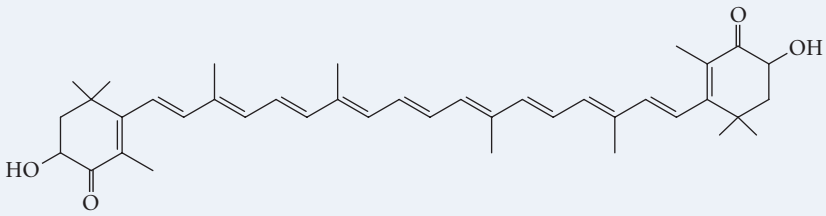


Figure A The molecular structure of astaxanthin. β-Carotene is the same molecule where the =O and —OH groups are replaced with hydrogens.

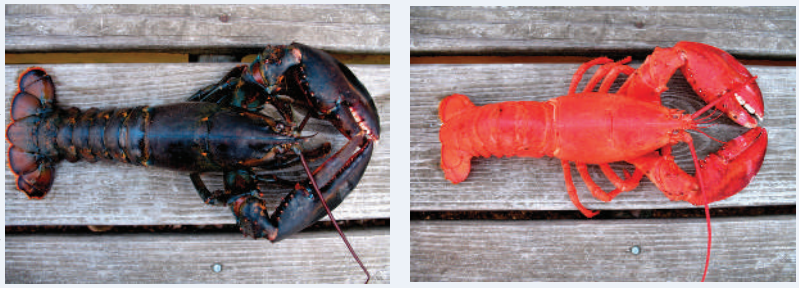


Figure B *Homarus americanus* before and after cooking.

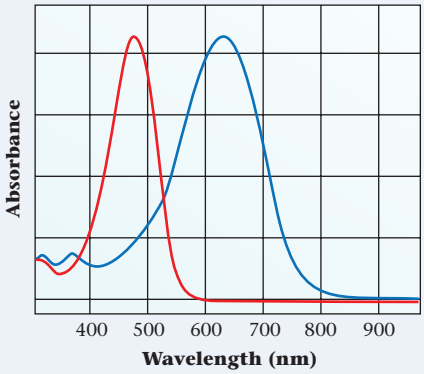


Figure C Absorption spectra of astaxanthin (red line) in methanol and astaxanthin bound in crustacyanin protein (blue line).

Key Concepts

1. Relate wavelength, frequency, and energy. **(Examples 6.1, 6.2; Problems 1–8, 61–63)**
2. Use the Bohr model to identify lines in the hydrogen spectrum. **(Example 6.3; Problems 9–16)**
3. Identify quantum numbers of electrons in atoms. **(Example 6.4; Problems 17–22, 27, 28)**
4. Derive the electron capacities of energy levels. **(Example 6.5; Problems 23–26)**
5. Write electron configurations, full or abbreviated, for atoms or ions. **(Examples 6.6, 6.7, 6.9; Problems 29–38, 49, 50)**
6. Draw orbital diagrams for atoms and ions. **(Example 6.8; Problems 39–52)**
7. Identify periodic trends in radii, ionization energy, and electronegativity. **(Examples 6.10, 6.11; Problems 53–60)**

Key Equations

Frequency-wavelength $\lambda\nu = c = 2.998 \times 10^8$ m/s

Energy-frequency $E = h\nu = hc/\lambda$;
$h = 6.626 \times 10^{-34}$ J · s

Bohr model $E_{\mathbf{n}} = -R_H/\mathbf{n}^2$;
$R_H = 2.180 \times 10^{-18}$ J

$$\nu = \frac{R_H}{h}\left[\frac{1}{(\mathbf{n}_{lo})^2} - \frac{1}{(\mathbf{n}_{hi})^2}\right]$$

Quantum numbers $\mathbf{n} = 1, 2, 3, 4, \ldots$

$\ell = 0, 1, 2, \ldots, (\mathbf{n} - 1)$

$\mathbf{m}_\ell = \ell, \ldots, +1, 0, -1, \ldots, -\ell$

$\mathbf{m}_s = +\frac{1}{2}, -\frac{1}{2}$

Key Terms

actinides
atomic radius
atomic spectrum
electron configuration
—abbreviated electron configuration
electron spin
electronegativity
excited state
frequency
ground state
Hund's rule
ionic radius
ionization energy
lanthanides
orbital
orbital diagrams
Pauli exclusion principle
photons
principal energy level
quantum numbers
sublevels
wavelength

Summary Problem

Consider the element vanadium ($Z = 23$).

(a) There is a line in the vanadium spectrum at 318.5 nm.

(1) In what region of the spectrum (ultraviolet, visible, or infrared) is this line found?

(2) What is the frequency of the line?

(3) What is the energy difference between the two levels responsible for this line in kilojoules per mole?

(4) The ionization energy of vanadium from the ground state is 650.2 kJ/mol. Assume that the transition in (3) is from the ground state to an excited state. If that is the case, calculate the ionization energy from the excited state.

(b) Give the electron configuration of the V atom; the V^{3+} ion.

(c) Give the orbital diagram (beyond argon) for V and V^{3+}.

(d) How many unpaired electrons are in the V atom? In the V^{3+} ion?

(e) How many electrons in V have $\ell = 1$ quantum number?

(f) How many electrons in V^{3+} have $\ell = 2$ quantum number?

(g) Rank V, V^{2+}, and V^{3+} in order of increasing size.

Answers

(a) **(1) ultraviolet; (2) 9.413×10^{14} s^{-1}; (3) 375.6 kJ/mol; (4) 274.6 kJ/mol**

(b) **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$**

(c)

	4s	3d
V:	(↑↓)	(↑) (↑) (↑) ( ) ( )
V^{3+}:	( )	(↑) (↑) ( ) ( ) ( )

(d) **3; 2**

(e) **12**

(f) **2**

(g) **$V^{3+} < V^{2+} < V$**

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

6-1 Light, Photon Energies, and Atomic Spectra

1. A photon of violet light has a wavelength of 423 nm. Calculate
(**a**) the frequency.
(**b**) the energy in joules per photon.
(**c**) the energy in kilojoules per mole.

2. Most retinal tears and detachments are treated by photocoagulation with a laser. A commonly used laser is one with a wavelength of 514 nm. Calculate
(**a**) the frequency.
(**b**) the energy in joules/photon.
(**c**) the energy in kJ/mol.

3. A line in the spectrum of neon has a wavelength of 837.8 nm.
(**a**) In what spectral range does the absorption occur?
(**b**) Calculate the frequency of this absorption.
(**c**) What is the energy in kilojoules per mole?

4. Ozone absorbs energy with a frequency of $1.29 \times 10^{15}\ s^{-1}$.
(**a**) What is the wavelength (in nm) of the absorption?
(**b**) In what spectral range does the absorption occur?
(**c**) What is the energy absorbed by one photon?

5. The ionization energy of rubidium is 403 kJ/mol. Do x-rays with a wavelength of 85 nm have sufficient energy to ionize rubidium?

6. Energy from radiation can cause chemical bonds to break. To break the nitrogen-nitrogen bond in N_2 gas, 941 kJ/mol is required.
(**a**) Calculate the wavelength of the radiation that could break the bond.
(**b**) In what spectral range does this radiation occur?

7. Lasers are now used for the total or partial removal of skin tattoos. A laser with a wavelenth of 755 nm is used to remove tattoos in green or blue inks.
(**a**) How much energy (in kJ/mol) is given off by the laser?
(**b**) Compare the energy obtained in (a) with that given off by an x-ray ($\lambda = 1 \times 10^{-9}$ m).

8. Your instructor may use a laser pointer while giving a lecture. The pointer uses a red-orange diode with a wavelength of 635 nm. If 0.255 mol of photons are emitted by the pointer, how much energy (in kJ) does the pointer give off?

6-2 The Hydrogen Atom

9. Consider the transition from the energy levels $\mathbf{n} = 5$ to $\mathbf{n} = 3$.
(**a**) What is the frequency of light associated with this transition?
(**b**) In what spectral region does the transition occur?
(**c**) Is energy absorbed?

10. Consider the transition from the energy levels $\mathbf{n} = 2$ to $\mathbf{n} = 5$.
(**a**) What is the wavelength associated with this transition?
(**b**) In what spectral region does the transition occur?
(**c**) Is energy absorbed?

11. According to the Bohr model, the radius of a circular orbit is given by the equation

$$r(\text{in nm}) = 0.0529\ \mathbf{n}^2$$

Draw successive orbits for the hydrogen electron at $\mathbf{n} = 1, 2, 3$, and 4. Indicate by arrows transitions between orbits that lead to lines in the
(**a**) Lyman series ($\mathbf{n}_{lo} = 1$).
(**b**) Balmer series ($\mathbf{n}_{lo} = 2$).

12. Calculate E_n for $\mathbf{n} = 1, 2, 3$, and 4 ($R_H = 2.180 \times 10^{-18}$ J). Make a one-dimensional graph showing energy, at different values of **n,** increasing vertically. On this graph, indicate by vertical arrows transitions in the
(**a**) Lyman series ($\mathbf{n}_{lo} = 1$).
(**b**) Balmer series ($\mathbf{n}_{lo} = 2$).

13. For the Pfund series, $\mathbf{n}_{lo} = 5$.
(**a**) Calculate the wavelength in nanometers of a transition from $\mathbf{n} = 7$ to $\mathbf{n} = 5$.
(**b**) In what region of the spectrum are these lines formed?

14. In the Brackett series, $\mathbf{n}_{lo} = 4$.
(**a**) Calculate the wavelength in nanometers of a transition from $\mathbf{n} = 6$ to $\mathbf{n} = 4$.
(**b**) In what spectral region are these lines formed?

15. A line in the Lyman series ($\mathbf{n}_{lo} = 1$) occurs at 97.23 nm. Calculate $\mathbf{n}_{hi}$ for the transition associated with this line.

16. In the Pfund series, $\mathbf{n}_{lo} = 5$. Calculate the longest wavelength (in nanometers) possible for a transition in this series.

6-3 Quantum Numbers

17. What are the possible values for $\mathbf{m}_\ell$ for
(**a**) the d sublevel?
(**b**) the s sublevel?
(**c**) all sublevels where $\mathbf{n} = 2$?

18. What are the possible values for $\mathbf{m}_\ell$ for
(**a**) the d sublevel?
(**b**) the s sublevel?
(**c**) all sublevels where $\mathbf{n} = 5$?

19. For the following pairs of orbitals, indicate which is lower in energy in a many-electron atom.
(**a**) 3d or 4s
(**b**) 4f or 3d
(**c**) 2s or 2p
(**d**) 4f or 4d

20. For the following pairs of orbitals, indicate which is higher in energy in a many-electron atom.
(**a**) 3s or 2p
(**b**) 4s or 4d
(**c**) 4f or 6s
(**d**) 1s or 2s

21. What type of electron orbital (i.e., s, p, d, or f) is designated by an electron with quantum numbers
(a) $n = 1, \ell = 0, m_\ell = 0$?
(b) $n = 3, \ell = 2, m_\ell = -1$?
(c) $n = 4, \ell = 3, m_\ell = 3$?

22. What type of electron orbital (i.e., s, p, d, or f) is designated by
(a) $n = 3, \ell = 1, m_\ell = 1$?
(b) $n = 5, \ell = 0, m_\ell = 0$?
(c) $n = 6, \ell = 4, m_\ell = -4$?

23. What is the total electron capacity for
(a) $n = 3$?
(b) a 5s orbital?
(c) an f subshell?
(d) a 7p orbital?

24. Give the number of orbitals in
(a) $n = 3$.
(b) a 4p sublevel.
(c) an f sublevel.
(d) a d sublevel.

25. How many electrons in an atom can have each of the following quantum number designations?
(a) $n = 2, \ell = 1, m_\ell = 0$
(b) $n = 2, \ell = 1, m_\ell = -1$
(c) $n = 3, \ell = 1, m_\ell = 0, m_s = +\frac{1}{2}$

26. How many electrons in an atom can have the following quantum designation?
(a) 1s
(b) 4d, $m_\ell = 0$
(c) $n = 5, \ell = 2$

27. Given the following sets of quantum numbers, indicate those that could not occur and explain your answer.
(a) $1, 2, 0, +\frac{1}{2}$
(b) $2, 1, 2, +\frac{1}{2}$
(c) $3, 0, 0, -\frac{1}{2}$
(d) $3, 2, 1, +\frac{1}{2}$
(e) $4, 2, -2, 0$

28. Given the following sets of electron quantum numbers, indicate those that could not occur, and explain your answer.
(a) $1, 0, 0, -\frac{1}{2}$
(b) $1, 1, 0, +\frac{1}{2}$
(c) $3, 2, -2, +\frac{1}{2}$
(d) $2, 1, 2, +\frac{1}{2}$
(e) $4, 0, 2, +\frac{1}{2}$

29. Write the ground state electron configuration for
(a) C (b) Cl (c) Co (d) Cs (e) Cd

30. Write the ground state electron configuration for
(a) S (b) Sc (c) Si (d) Sr (e) Sb

31. Write an abbreviated ground state electron configuration for
(a) N (b) Nb (c) Na (d) Ni (e) Nd

32. Write the abbreviated ground state electron configuration for
(a) Mg (b) Os (c) Ge (d) V (e) At

33. Give the symbol of the element of lowest atomic number whose ground state has
(a) a completed f subshell.
(b) twenty p electrons.
(c) two 4d electrons.
(d) five 5p electrons.

34. Give the symbol of the element of lowest atomic number that has
(a) an f subshell with 7 electrons.
(b) twelve d electrons.
(c) three 3p electrons.
(d) a completed p subshell.

35. What fraction of the total number of electrons is in p sublevels for the following atoms?
(a) Al (b) Au (c) Ag

36. What fraction of the total number of electrons is in p sublevels in
(a) Mg (b) Mn (c) Mo

37. Which of the following electron configurations (a–f) are for atoms in the ground state? In the excited state? Which are impossible?
(a) $1s^2 2s^2 3s^2$
(b) $1s^2 2p^3$
(c) $1s^2 2s^3 2p^5$
(d) $1s^2 2s^2 2p^7$
(e) $1s^2 2s^2 2p^6 3s^1$
(f) $1s^2 2s^2 2p^6 3s^2 3d^1$

38. Which of the following electron configurations (a–e) are for atoms in the ground state? In the excited state? Which are impossible?
(a) $1s^2 2s^2 1d^1$
(b) $1s^2 2s^2 2p^6 3s^2 3p^4$
(c) $1s^2 2s^1 2p^7 3s^2$
(d) $1s^2 2s^2 3s^1 3p^4$
(e) $1s^2 2s^2 3s^2 3p^6 4s^2$

6-6 Orbital Diagrams of Atoms

39. Write the orbital diagram for
(a) Li (b) P (c) F (d) Fe

40. Write the orbital diagram for an atom of
(a) Na (b) O (c) Co (d) Cl

41. Give the symbol of the atom with the following orbital diagram.

	1s	2s	2p	3s	3p
(a)	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	( )( )( )
(b)	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑)(↑)(↑)
(c)	(↑↓)	(↑↓)	(↑↓)(↑)(↑)	( )	( )( )( )

42. What is the symbol of the atom with the following orbital diagram?

	1s	2s	2p	3s	3p
(a)	(↑↓)	(↑)	( )( )( )	( )	( )( )( )
(b)	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑↓)	(↑↓)(↑↓)(↑)
(c)	(↑↓)	(↑↓)	(↑↓)(↑↓)(↑↓)	(↑)	( )( )( )

43. Write the symbol of
(a) all the elements in which all the 4d orbitals are half-full.
(b) all the nonmetals in period 2 that have 2 or more unpaired electrons.
(c) all the elements in group 2 in which the 4p sublevel is full.
(d) all the metalloids that have unpaired 5p electrons.

44. Write the symbols of
(a) all the elements in period 5 that have at least two half-filled 5p orbitals.
(b) all the elements in Group 1 that have full 3p orbitals.
(c) all the metalloids that have paired 3p electrons.
(d) all the nonmetals that have full 3d orbitals and 3 half-filled 3p orbitals.

45. How many unpaired electrons are there in an atom of
(a) phosphorus?
(b) potassium?
(c) plutonium (Pu)?

46. How many unpaired electrons are there in the following atoms?
(a) aluminum
(b) argon
(c) arsenic

47. In what main group(s) of the periodic table do elements have the following number of half-filled p-orbitals in the outermost principal energy level?
(a) 0 (b) 1 (c) 2 (d) 3

48. Give the symbol of the main-group metals in period 4 with the following number of unpaired electrons per atom. (Transition metals are not included.)
(a) 0 (b) 1 (c) 2 (d) 3

6-7 Electron Arrangements in Monatomic Atoms

49. Write the ground state electron configuration for
(a) Mg, Mg^{2+}
(b) N, N^{3-}
(c) Ti, Ti^{4+}
(d) Sn^{2+}, Sn^{4+}

50. Write the ground state electron configuration for the following atoms and ions.
(a) F, F^-
(b) Sc, Sc^{3+}
(c) Mn^{2+}, Mn^{5+}
(d) O^-, O^{2-}

51. How many unpaired electrons are there in the following ions?
(a) V^{3+} (b) Sn^{4+} (c) I^- (d) W^{4+}

52. How many unpaired electrons are there in the following ions?
(a) Al^{3+} (b) Cl^- (c) Sr^{2+} (d) Zr^{4+}

6-8 Periodic Trends in the Properties of Atoms

53. Arrange the elements Na, Si, and S in the order of
(a) decreasing atomic radius.
(b) increasing first ionization energy.
(c) decreasing electronegativity.

54. Arrange the elements Mg, S, and Cl in order of
(a) increasing atomic radius.
(b) increasing first ionization energy.
(c) decreasing electronegativity.

55. Which of the four atoms Rb, Sr, Sb, or Cs
(a) has the smallest atomic radius?
(b) has the lowest ionization energy?
(c) is the least electronegative?

56. Which of the four atoms Na, P, Cl, or K
(a) has the largest atomic radius?
(b) has the highest ionization energy?
(c) is the most electronegative?

57. Select the larger member of each pair.
(a) Ca and Ca^{2+}
(b) Sr and Sr^{2+}
(c) F and F^-
(d) Cu^+ and Cu^{2+}

58. Select the smaller member of each pair.
(a) P and P^{3-}
(b) V^{2+} and V^{4+}
(c) K and K^+
(d) Co and Co^{3+}

59. Arrange the following species in order of decreasing radius.
(a) C, Mg, Ca, Si
(b) Sr, Cl, Br, I

60. Arrange the following species in order of increasing radius.
(a) Rb, K, Cs, Kr
(b) Ar, Cs, Si, Al

Unclassified

61. A lightbulb radiates 8.5% of the energy supplied to it as visible light. If the wavelength of the visible light is assumed to be 565 nm, how many photons per second are emitted by a 75-W lightbulb? (1 W = 1 J/s)

62. The speed of a computer chip is measured by its frequency. Advanced Micro Devices (ADM) has developed a microprocessor, "The Piledriver," that operates at 8.429 GHz ($1\ GHz = 1 \times 10^9\ Hz$).
(a) What is the wavelength (in nm) of the frequency?
(b) In what spectral range does it belong?
(c) What is the energy (in kJ/mol) associated with this frequency?

63. A carbon dioxide laser produces radiation of wavelength 10.6 micrometers (1 micrometer = 10^{-6} meter). If the laser produces about one joule of energy per pulse, how many photons are produced per pulse?

64. Name and give the symbol of the element that has the characteristic given below.
(a) Its electron configuration in the excited state can be $1s^2 2s^2 2p^6 3s^1\ 3p^3$.
(b) It is the least electronegative element in period 3.
(c) Its +3 ion has the configuration $[_{36}Kr]$.
(d) It is the halogen with the largest atomic radius.
(e) It has the largest ionization energy in Group 16.

Conceptual Questions

65. Compare the energies and frequencies of two photons, one with a short wavelength and the other with a long wavelength.

66. Consider the following transitions
1. **n** = 3 to **n** = 1
2. **n** = 2 to **n** = 3
3. **n** = 4 to **n** = 3
4. **n** = 3 to **n** = 5

(a) For which of the transitions is energy absorbed?
(b) For which of the transitions is energy emitted?

(c) Which transitions involve the ground state?
(d) Which transition absorbs the most energy?
(e) Which transition emits the most energy?

67. Write the symbol of each element described below.
(a) largest atomic radius in Group 1
(b) smallest atomic radius in period 3
(c) largest first ionization energy in Group 2
(d) most electronegative in Group 16
(e) element(s) in period 2 with no unpaired p electron
(f) abbreviated electron configuration is [Ar] $4s^2 3d^3$
(g) A +2 ion with abbreviated electron configuration [Ar] $3d^5$
(h) A transition metal in period 4 forming a +2 ion with no unpaired electrons

68. Answer the following questions.
(a) What characteristic of an atomic orbital does the quantum number $\mathbf{m}_s$ describe?
(b) Does a photon with a frequency of 35.8 Hz have more or less energy than one with a frequency of 125 Hz?
(c) How many orbitals can be associated with the following set of quantum numbers: $\mathbf{n} = 3$, $\ell = 2$?
(d) Is a sample of $ZnCl_2$ containing the Zn^{2+} ion diamagnetic?

69. Explain in your own words what is meant by
(a) the Pauli exclusion principle.
(b) Hund's rule.
(c) a line in an atomic spectrum.
(d) the principal quantum number.

70. Explain the difference between
(a) the Bohr model of the atom and the quantum mechanical model.
(b) wavelength and frequency.
(c) the geometries of the three different p orbitals.

71. Indicate whether each of the following statements is true or false. If false, correct the statement.
(a) An electron transition from $\mathbf{n} = 3$ to $\mathbf{n} = 1$ gives off energy.
(b) Light emitted by an $\mathbf{n} = 4$ to $\mathbf{n} = 2$ transition will have a longer wavelength than that from an $\mathbf{n} = 5$ to $\mathbf{n} = 2$ transition.
(c) A sublevel of $\ell = 3$ has a capacity of ten electrons.
(d) An atom of Group 13 has three unpaired electrons.

72. Criticize or comment on the following statements:
(a) The energy of a photon is inversely proportional to its wavelength.
(b) The energy of the hydrogen electron is inversely proportional to the quantum number ℓ.
(c) Electrons start to enter the fifth principal level as soon as the fourth is full.

73. No currently known elements contain electrons in g ($\ell = 4$) orbitals in the ground state. If an element is discovered that has electrons in the g orbital, what is the lowest value for $\mathbf{n}$ in which these g orbitals could exist? What are the possible values of $\mathbf{m}_\ell$? How many electrons could a set of g orbitals hold?

74. Indicate whether each of the following is true or false.
(a) Effective nuclear charge stays about the same when one goes down a group.
(b) Group 17 elements have seven electrons in their outer level.
(c) Energy is given off when an electron is removed from an atom.

75. Explain why
(a) negative ions are larger than their corresponding atoms.
(b) scandium, a transition metal, forms an ion with a noble-gas structure.
(c) electronegativity decreases down a group in the periodic table.

Challenge Problems

76. The energy of any one-electron species in its $\mathbf{n}$th state ($\mathbf{n}$ = principal quantum number) is given by $E = -BZ^2/\mathbf{n}^2$, where Z is the charge on the nucleus and B is 2.180×10^{-18} J. Find the ionization energy of the Li^{2+} ion in its first excited state in kilojoules per mole.

77. In 1885, Johann Balmer, a mathematician, derived the following relation for the wavelength of lines in the visible spectrum of hydrogen

$$\lambda = \frac{364.5\ \mathbf{n}^2}{(\mathbf{n}^2 - 4)}$$

where λ is in nanometers and $\mathbf{n}$ is an integer that can be 3, 4, 5, . . . Show that this relation follows from the Bohr equation and the equation using the Rydberg constant. Note that in the Balmer series, the electron is returning to the $\mathbf{n} = 2$ level.

78. Suppose the rules for assigning quantum numbers were as follows

$$\mathbf{n} = 1, 2, 3, \ldots$$
$$\ell = 0, 1, 2, \ldots, \mathbf{n}$$
$$\mathbf{m}_\ell = 0, 1, 2, \ldots, \ell + 1$$
$$\mathbf{m}_s = +\tfrac{1}{2} \text{ or } -\tfrac{1}{2}$$

Prepare a table similar to Table 6.3 based on these rules for $\mathbf{n} = 1$ and $\mathbf{n} = 2$. Give the electron configuration for an atom with eight electrons.

79. Suppose that the spin quantum number could have the values $\frac{1}{2}$, 0, and $-\frac{1}{2}$. Assuming that the rules governing the values of the other quantum numbers and the order of filling sublevels were unchanged,
(a) what would be the electron capacity of an s sublevel? a p sublevel? a d sublevel?
(b) how many electrons could fit in the $\mathbf{n} = 3$ level?
(c) what would be the electron configuration of the element with atomic number 8? 17?

80. In the photoelectric effect, electrons are ejected from a metal surface when light strikes it. A certain minimum energy, E_{min}, is required to eject an electron. Any energy absorbed beyond that minimum gives kinetic energy to the electron. It is found that when light at a wavelength of 540 nm falls on a cesium surface, an electron is ejected with a kinetic energy of 2.60×10^{-20} J. When the wavelength is 400 nm, the kinetic energy is 1.54×10^{-19} J.
(a) Calculate E_{min} for cesium in joules.
(b) Calculate the longest wavelength, in nanometers, that will eject electrons from cesium.