FIGURE 1.27 The radial distribution function tells us the probability density for finding an electron at a given radius regardless of the direction. The graph shows the radial distribution function for the 1s-, 2s-, and 3s-orbitals in hydrogen. Note how the most probable radius (corresponding to the greatest maximum) increases as n increases.

SELF-TEST 1.10A Calculate the same ratio but for the more distant point at $r = 2a_0$, twice as far from the nucleus.

[Answer: 0.018]

SELF-TEST 1.10B Calculate the same ratio but for a point at $3a_0$ from the nucleus.

The **radial distribution function**, P, is closely related to the wavefunction ψ = RY and is given by

$$P(r) = r^2 R(r)^2 \tag{20a}$$

For s-orbitals, this expression turns out to be the same as

$$P(r) = 4\pi r^2 \psi(r)^2 \tag{20b*}$$

and this expression is the form that you will normally see used; however, it applies only to s-orbitals, whereas Eq. 20a applies to any kind of orbital. The radial distribution function has a very special significance: it tells us *the probability that the electron will be found at a particular radius regardless of the direction*. Specifically, the probability that the electron will be found anywhere in a thin shell of radius r and thickness δr is given by P(r)δr (Fig. 1.27). Be careful to distinguish the radial distribution function from the wavefunction and its square, the probability density:

The wavefunction itself tells us, through $\psi(r)^2 \delta V$, the probability of finding the electron in the small volume δV at a particular location (specified by r, θ, and φ).

The radial distribution function tells us, through P(r)δr, the probability of finding the electron in the range of radii δr, at a particular radius, regardless of the values of θ and φ.

The radial distribution function for the population of the Earth, for instance, is zero up to about 6400 km from the center of the Earth, rises sharply, and then falls back to almost zero (to take into account the small number of people who are on mountains or flying in airplanes).

Note that for *all* orbitals, not just s-orbitals, P is zero at the nucleus, simply because the shell in which we are looking for the electron has shrunk to zero size. (The probability density for an s-orbital is nonzero at the nucleus, but here we are multiplying it by a volume that becomes zero at the nucleus.) As r increases, the value of $4\pi r^2$ increases (the shell is getting bigger), but, for a 1s-orbital, the square of the wavefunction, $\psi(r)^2$, falls toward zero; as a result, the product of $4\pi r^2$ and $\psi(r)^2$ starts off at zero, goes through a maximum, and then declines to zero. The value of P is a maximum at a_0, the Bohr radius. Therefore, the Bohr radius corresponds to the radius at which an electron in a 1s-orbital is most likely to be found.

Instead of drawing the s-orbital as a cloud, chemists usually draw its **boundary surface**, a surface that encloses the densest regions of the cloud. However, although the boundary surface is easier to draw, it does not give the best picture of an atom; an atom has fuzzy edges and is not as smooth as the boundary surface might suggest. An electron is likely to be found only inside the boundary surface of the orbital. An s-orbital has a spherical boundary surface (Fig. 1.28), because the electron cloud is spherical. s-Orbitals with higher energies have spherical boundary surfaces of greater diameter. They also have a more complicated radial variation with nodes at locations that can be found by examining the wavefunctions (Fig. 1.29).

A subshell with l = 1 consists of three p-orbitals. A p-orbital has two lobes of opposite sign (Fig. 1.30). The two lobes are separated by a planar region called a **nodal plane**, which cuts through the nucleus and on which ψ = 0. A p-electron will never be found on this plane, and so a p-electron is never found at the nucleus. This difference from s-orbitals will prove to be of major importance for understanding the structure of the periodic table and stems from the fact that an

What is the three-dimensional appearance of an s-orbital?

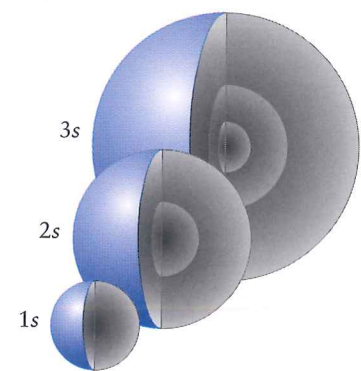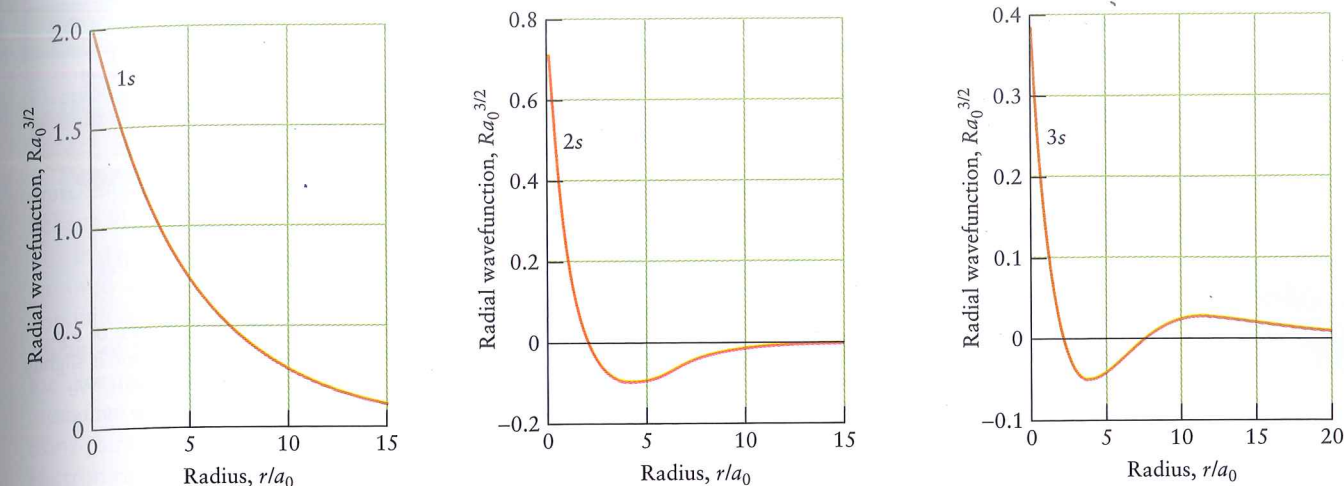

FIGURE 1.28 The three s-orbitals of lowest energy. The simplest way of drawing an atomic orbital is as a boundary surface, a surface within which there is a high probability (typically 90%) of finding the electron. We shall use blue to denote s-orbitals, but that color is only an aid to their identification. The shading within the boundary surfaces is an approximate indication of the electron density at each point.

FIGURE 1.29 The radial wavefunctions of the first three s-orbitals of a hydrogen atom. Note that the number of radial nodes increases (as n − 1), as does the average distance of the electron from the nucleus (compare with Fig. 1.27). Because the probability density is given by ψ², all s-orbitals correspond to a nonzero probability density at the nucleus.

electron in a p-orbital has nonzero orbital angular momentum that flings it away from the nucleus. There are three p-orbitals in each subshell, corresponding to the quantum numbers $m_l = +1, 0, -1$. However, chemists commonly refer to the orbitals according to the axes along which the lobes lie; hence, we refer to p_x, p_y, and p_z orbitals (Fig. 1.31).

A subshell with l = 2 consists of five d-orbitals. Each d-orbital has four lobes, except for the orbital designated d_{z^2}, which has a more complicated shape (Fig. 1.32). A subshell with l = 3 consists of seven f-orbitals with even more complicated shapes (Fig. 1.33).

The total number of orbitals in a shell with principal quantum number n is n^2. To confirm this rule, we need to recall that l has integer values from 0 to n − 1 and that the number of orbitals in a subshell for a given value of l is 2l + 1. For instance, for n = 4, there are four subshells with l = 0, 1, 2, 3, consisting of one s-orbital, three p-orbitals, five d-orbitals, and seven f-orbitals, respectively. There are therefore 1 + 3 + 4 + 5 + 7 = 16, or 4^2, orbitals in the shell with n = 4 (Fig. 1.34).

The location of an electron in an atom is described by a wavefunction known as an atomic orbital; atomic orbitals are designated by the quantum numbers n, l, and m_l and fall into shells and subshells as summarized in Fig. 1.25.
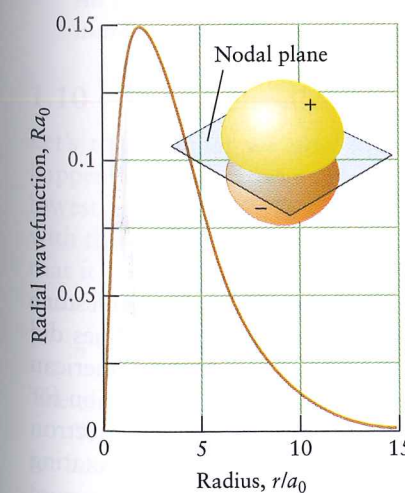
There is no *direct* relation between the values of m_l and the x, y, z designation of the orbitals: the orbitals labeled with the axes are combinations of the orbitals labeled with the quantum number m_l.

How do the three p-orbitals differ?

FIGURE 1.30 The boundary surface and the radial variation of a 2p-orbital along the (vertical) z-axis. All p-orbitals have boundary surfaces with similar shapes, including one nodal plane. Note that the orbital has opposite signs (as depicted by the depth of color) on each side of the nodal plane.
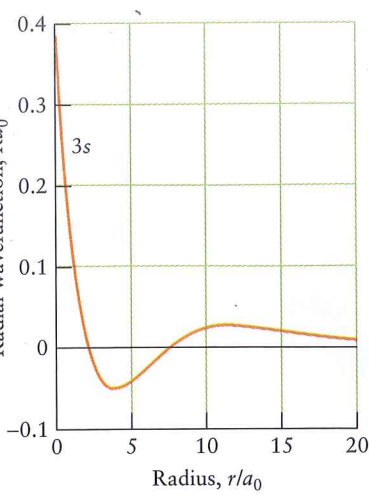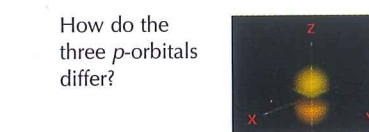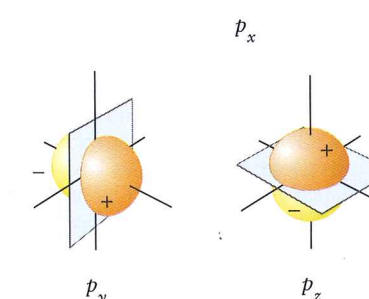
FIGURE 1.31 There are three p-orbitals of a given energy, and they lie along three perpendicular axes. We shall use yellow to indicate p-orbitals: dark yellow for the positive lobe and light yellow for the negative lobe.
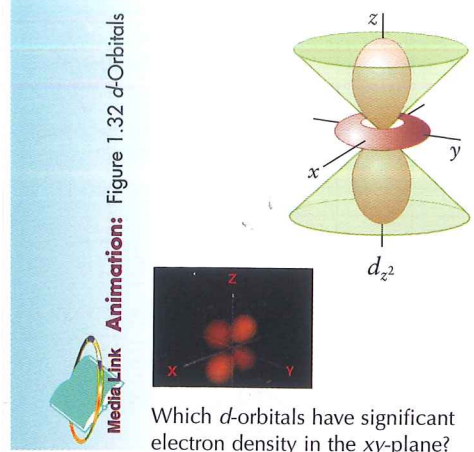
Media Link **Animation:** Figure 1.32 d-Orbitals

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

Which d-orbitals have significant electron density in the xy-plane?

FIGURE 1.32 The boundary surface of a d-orbital is more complicated than that of an s- or a p-orbital. There are, in fact, five d-orbitals of a given energy; four of them have four lobes, one is slightly different. In each case, an electron that occupies a d-orbital will not be found at the nucleus. We shall use orange to indicate d-orbitals: dark orange for the positive lobes, and light orange for the negative lobes.
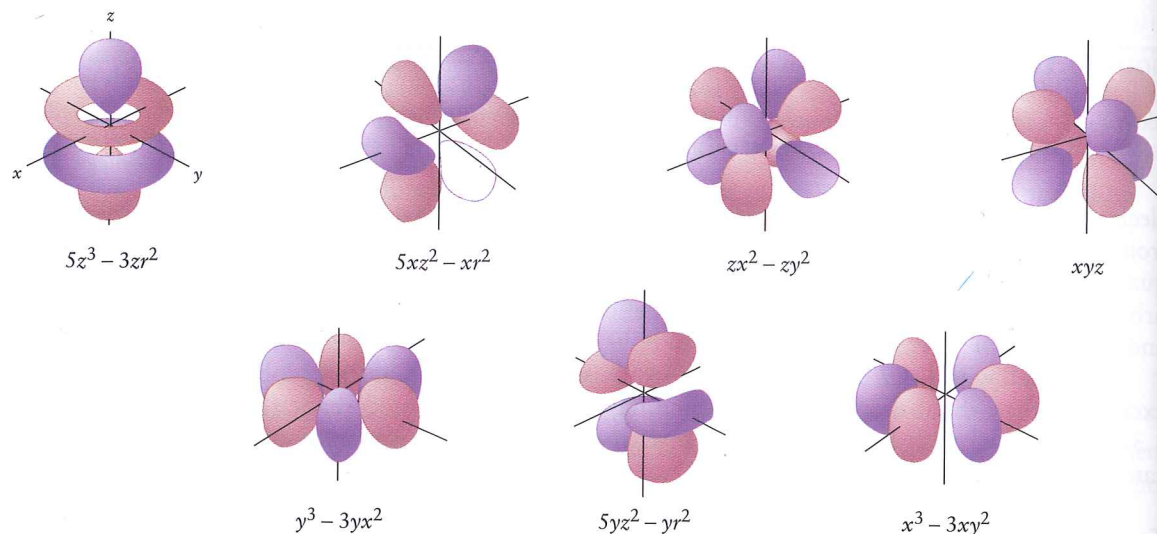

$5z^3 - 3zr^2$ $5xz^2 - xr^2$ $zx^2 - zy^2$ xyz

$y^3 - 3yx^2$ $5yz^2 - yr^2$ $x^3 - 3xy^2$

FIGURE 1.33 The seven f-orbitals of a shell (with n = 3) have a very complex appearance. Their detailed form will not be used again in this text. However, their existence is important for understanding the periodic table, the presence of the lanthanides and actinides, and the properties of the later d-block elements. A darker color denotes a positive lobe, a lighter color a negative lobe.

4f	+3	+2	+1	0	−1	−2	−3
4d		+2	+1	0	−1	−2	
4p			+1	0	−1		
4s				0			16

FIGURE 1.34 There are 16 orbitals in the shell with n = 4, each of which can hold two electrons (see Section 1.12), for a total of 32 electrons.

1.9 Electron Spin

Schrödinger's calculation of the energies of the hydrogen orbitals was a milestone in the development of modern atomic theory. Yet the observed spectral lines did not have exactly the frequencies he predicted. In 1925, two Dutch-American physicists, Samuel Goudsmit and George Uhlenbeck, proposed an explanation for the tiny deviations that had been observed. They suggested that an electron behaves in some respects like a spinning sphere, something like a planet rotating on its axis. This property is called **spin.**

Electron spin was first detected experimentally by two German scientists, Otto Stern and Walter Gerlach, in 1920. They made use of the fact that a moving electric charge generates a magnetic field, and so a spinning electron should behave like a tiny bar magnet.

In their experiment (see illustration), Stern and Gerlach removed all the air from a container and set up a highly nonuniform magnetic field across it. They then shot a narrow stream of silver atoms through the container toward a detector. For reasons that are explained in Section 1.12, a silver atom has one unpaired electron, with its remaining 46 electrons paired. The atom therefore behaves like a single unpaired electron riding on a heavy platform, the rest of the atom.
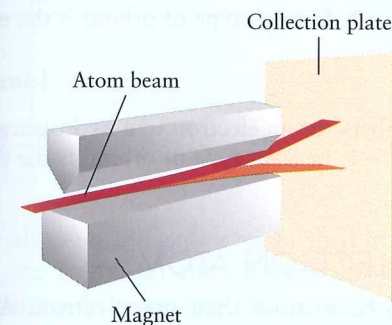
A schematic representation of the apparatus used by Stern and Gerlach. In the experiment, a stream of atoms splits into two as it passes between the poles of a magnet. The atoms in one stream have an odd ↑ electron, and those in the other an odd ↓ electron.

If a spinning electron behaved like a spinning ball, the axis of spin could point in any direction. The electron would behave like a bar magnet that could have any orientation relative to the applied magnetic field. In that case, a broad band of silver atoms should appear at the detector, because the field would push the silver atoms by different amounts according to the orientation of the spin. Indeed, that is exactly what Stern and Gerlach observed when they first carried out the experiment.

However, the first results were misleading. The experiment is difficult because the atoms collide with one another in the beam. An atom moving in one direction might easily be knocked by its neighbors into a different direction. When Stern and Gerlach repeated their experiment, they used a much less dense beam of atoms, thereby reducing the number of collisions between the atoms. They now saw only two narrow bands. One band consisted of atoms flying through the magnetic field with one orientation of their spin; the other band consisted of the atoms with opposite spin. The two narrow bands confirmed not only that an electron has spin but also that it can have only two orientations.

Electron spin is the basis of the experimental technique called *electron paramagnetic resonance* (EPR), which is used to study the structures and motions of molecules and ions that have unpaired electrons. This technique is based on detecting the energy needed to flip an electron between its two spin orientations. Like Stern and Gerlach's experiment, it works only with ions or molecules that have an unpaired electron.

According to quantum mechanics, an electron has two spin states, represented by the arrows ↑ and ↓ or the Greek letters α and β. We can think of an electron as being able to spin counterclockwise at a certain rate (the ↑ state) or clockwise at exactly the same rate (the ↓ state). These two spin states are distinguished by a fourth quantum number, the **spin magnetic quantum number,** m_s. This quantum number can have only two values: $+\frac{1}{2}$ indicates an ↑ electron and $-\frac{1}{2}$ indicates a ↓ electron (Fig. 1.35). Box 1.1 describes an experiment that confirmed these properties of electron spin.

An electron has the property of spin; the spin is described by the quantum number m_s, which may have one of two values.

1.10 The Electronic Structure of Hydrogen

Let's review what we now know about the hydrogen atom by imagining what happens to its electron as the atom acquires energy. Initially, the electron is in the lowest energy level, the ground state of the atom, with n = 1. The only orbital with this energy is the 1s-orbital; we say that the electron **occupies** a 1s-orbital or that it is a "1s-electron." The electron in the ground state of a hydrogen atom is described by the following values of the four quantum numbers:

$$n = 1 \quad l = 0 \quad m_l = 0 \quad m_s = +\tfrac{1}{2} \text{ or } -\tfrac{1}{2}$$

The electron can have either spin state.

When the atom acquires enough energy (by absorbing a photon of radiation, for instance) for its electron to reach the shell with n = 2, it can occupy any of the four orbitals in that shell. There are one 2s- and three 2p-orbitals in this shell; in

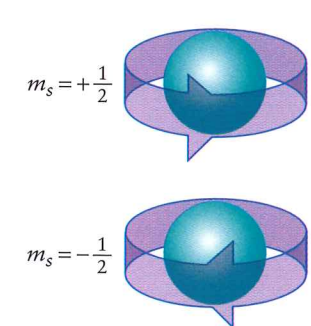

$m_s = +\frac{1}{2}$

$m_s = -\frac{1}{2}$

FIGURE 1.35 The two spin states of an electron can be represented as clockwise or counterclockwise rotation around an axis passing through the electron. The two states are identified by the quantum number m_s and depicted by the arrows shown on the right.

hydrogen, they all have the same energy. When an electron is described by one of these wavefunctions, we say that it "occupies" a 2s-orbital or one of the 2p-orbitals or that it is a 2s- or 2p-electron. The average distance of an electron from the nucleus when it occupies any of the orbitals in the shell with $n = 2$ is greater than when $n = 1$, and so we can think of the atom as swelling up as it is excited energetically. When the atom acquires even more energy, the electron moves into the shell with $n = 3$; the atom is now even larger. In this shell, the electron can occupy any of nine orbitals (one 3s-, three 3p-, and five 3d-orbitals). More energy moves the electron still farther from the nucleus to the $n = 4$ shell, where sixteen orbitals are available (one 4s-, three 4p-, five 4d-, and seven 4f-orbitals).

> *The state of an electron in a hydrogen atom is defined by the four quantum numbers n, l, m_l, and m_s; as the value of n increases, the size of the atom increases.*

SELF-TEST 1.11A The three quantum numbers for an electron in a hydrogen atom in a certain state are $n = 4$, $l = 2$, and $m_l = -1$. In what type of orbital is the electron located?

[Answer: 4d]

SELF-TEST 1.11B The three quantum numbers for an electron in a hydrogen atom in a certain state are $n = 3$, $l = 1$, and $m_l = -1$. In what type of orbital is the electron located?

THE STRUCTURES OF MANY-ELECTRON ATOMS

All neutral atoms other than hydrogen have more than one electron. A neutral atom of an element with atomic number $Z > 1$ has Z electrons. Such an atom is a **many-electron atom,** an atom with more than one electron. In the next three sections, we build on what we have learned about the hydrogen atom to see how the presence of more than one electron affects the energies of atomic orbitals. The resulting electronic structures are the key to the periodic properties of the elements and the abilities of atoms to form chemical bonds.

Many-electron atoms are also called polyelectron atoms.

1.11   Orbital Energies

The electrons in a many-electron atom occupy orbitals like those of hydrogen. However, the energies of these orbitals are not the same as those for a hydrogen atom. The nucleus of a many-electron atom is more highly charged than the hydrogen nucleus, and the greater charge attracts electrons more strongly and hence lowers their energy. However, the electrons also repel one another; this repulsion opposes the nuclear attraction and raises the energies of the orbitals. In a helium atom, for instance, with two electrons, the charge of the nucleus is $+2e$ and the total potential energy is given by three terms:

Along with code breakers and weather forecasters, chemists are now among the heaviest users of computers, which they use to calculate the detailed electronic structures of atoms and molecules.

$$V = -\underbrace{\frac{2e^2}{4\pi\varepsilon_0 r_1}}_{\text{attraction}} - \underbrace{\frac{2e^2}{4\pi\varepsilon_0 r_2}}_{\text{attraction}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\text{repulsion}} \qquad (21)$$

where r_1 is the distance of electron 1 from the nucleus, r_2 is the distance of electron 2 from the nucleus, and r_{12} is the distance between the two electrons. The two terms with negative signs (indicating that the energy falls as r_1 or r_2 decreases) represent the attractions between the nucleus and the two electrons. The term with a positive sign (indicating an increase in energy as r_{12} decreases) represents the repulsion between the two electrons. The Schrödinger equation based on this potential energy is impossibly difficult to solve exactly, but highly accurate numerical solutions can be obtained by using computers.

The number of electrons in an atom affects the properties of the atom. The hydrogen atom, with one electron, has no electron–electron repulsions; we have
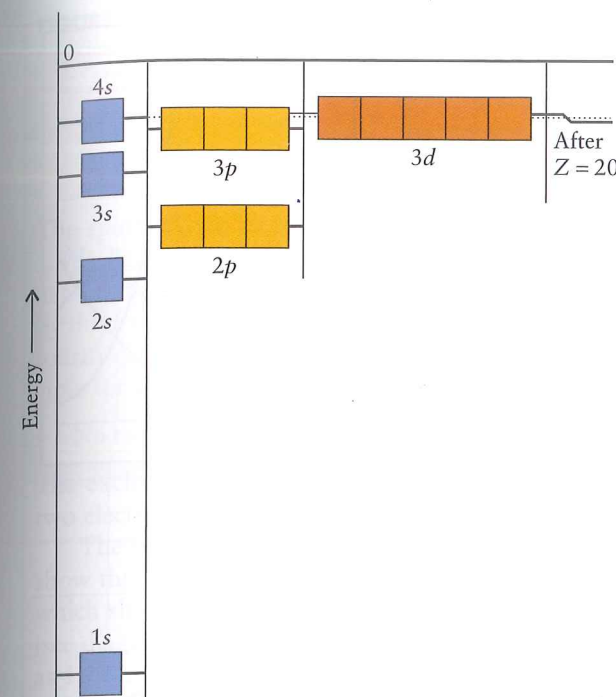
FIGURE 1.36 The relative energies of the shells, subshells, and orbitals in a many-electron atom. Each of the boxes can hold at most two electrons. Note the change in the order of energies of the 3d- and 4s-orbitals after $Z = 20$.

seen that all the orbitals of a given shell in the hydrogen atom are degenerate. For instance, the 2s-orbital and all three 2p-orbitals have the same energy. In many-electron atoms, however, the results of spectroscopic experiments and calculations show that electron–electron repulsions cause the energy of a 2p-orbital to be higher than that of a 2s-orbital. Similarly, in the $n = 3$ shell, the three 3p-orbitals lie higher than the 3s-orbital, and the five 3d-orbitals lie higher still (Fig. 1.36). How can we explain these energy differences?

As well as being attracted by the nucleus, each electron in a many-electron atom is repelled by the other electrons present. As a result, it is less tightly bound to the nucleus than it would be if those other electrons were absent. We say that each electron is **shielded** from the full attraction of the nucleus by the other electrons in the atom. The shielding effectively reduces the pull of the nucleus on an electron. The **effective nuclear charge,** $Z_{eff}e$, experienced by the electron is always less than the actual nuclear charge, Ze, because the electron–electron repulsions work against the pull of the nucleus. A *very* approximate form of the energy of an electron in a many-electron atom is a version of Eq. 16b in which the true atomic number is replaced by the effective atomic number:

$$E_n = -\frac{Z_{eff}^2 h\mathcal{R}}{n^2} \qquad (22)$$

Note that the other electrons do not "block" the influence of the nucleus; they simply provide additional repulsive coulombic interactions that partly counteract the pull of the nucleus. For example, the pull of the nucleus on an electron in the helium atom is less than its charge of $+2$ would exert but greater than the net charge of $+1$ that we would expect if each electron balanced one positive charge exactly.

An s-electron of any shell can be found very close to the nucleus (remember that ψ^2 for an s-orbital is nonzero at the nucleus), and so we say that it can **penetrate** through the inner shells. A p-electron penetrates much less because its orbital angular momentum prevents it from approaching close to the nucleus (Fig. 1.37). We have seen that its wavefunction has a node passing through the nucleus, and so there is zero probability density for finding a p-electron at the nucleus. Because a p-electron penetrates less than an s-electron through the inner shells of the atom, it is more effectively shielded from the nucleus and hence experiences a smaller

FIGURE 1.37 The radial distribution functions for s-, p-, and d-orbitals in the first three shells of a hydrogen atom. Note that the probability maxima for orbitals of the same shell are close to each other; however, note that an electron in an ns-orbital has a higher probability of being found close to the nucleus than does an electron in an np-orbital or an nd-orbital.
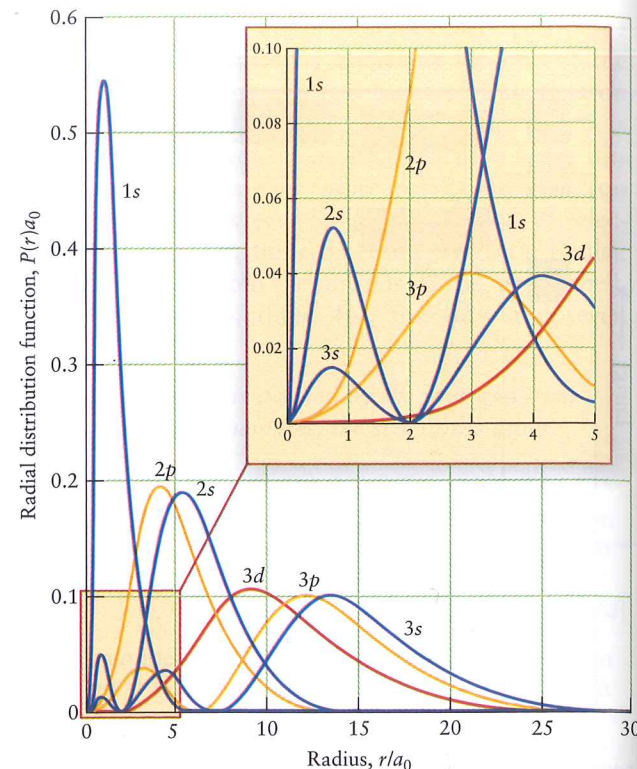
effective nuclear charge than an s-electron does. In other words, an s-electron is bound more tightly than a p-electron and has a slightly lower (more negative) energy. A d-electron is bound less tightly than a p-electron of the same shell because its orbital angular momentum is higher and it is therefore even less able to approach the nucleus closely. That is, d-electrons are higher in energy than p-electrons of the same shell, which are in turn higher in energy than s-electrons of that shell.

The effects of penetration and shielding can be large. A $4s$-electron generally has a much lower energy than that of a $4p$- or $4d$-electron; it may even have lower energy than that of a $3d$-electron of the same atom (see Fig. 1.36). The precise ordering of orbitals depends on the number of electrons in the atom, as we shall see in the next section.

In a many-electron atom, because of the effects of penetration and shielding, the order of energies of orbitals in a given shell is typically $s < p < d < f$.

1.12   The Building-Up Principle

The electronic structure of an atom determines its chemical properties, and so we need to be able to describe that structure. To do so, we write the **electron configuration** of the atom—a list of all its occupied orbitals, with the numbers of electrons that each one contains. In the ground state of a many-electron atom, the electrons occupy atomic orbitals in such a way that the total energy of the atom is a minimum. At first sight, we might expect an atom to have its lowest energy when all its electrons are in the lowest energy orbital (the $1s$-orbital), but except for hydrogen and helium, which have no more than two electrons, that can never happen. In 1925, the Austrian scientist Wolfgang Pauli discovered a general and very fundamental rule about electrons and orbitals that is now known as the **Pauli exclusion principle:**

- No more than two electrons may occupy any given orbital. When two electrons do occupy one orbital, their spins must be paired.

FIGURE 1.38 (a) Two electrons are said to be paired if they have opposite spins (one clockwise, the other counterclockwise). (b) Two electrons are classified as having parallel spins if their spins are in the same direction; in this case, both ↑.
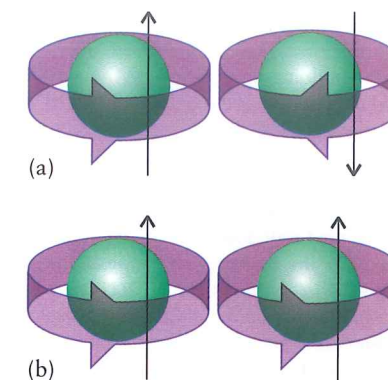
The spins of two electrons are said to be **paired** if one is ↑ and the other ↓ (Fig. 1.38). Paired spins are denoted ↑↓, and electrons with paired spins have spin magnetic quantum numbers of opposite sign. Because an atomic orbital is designated by three quantum numbers (n, l, and m_l) and the two spin states are specified by a fourth quantum number, m_s, another way of expressing the Pauli exclusion principle for atoms is

- No two electrons in an atom can have the same set of four quantum numbers.

The exclusion principle implies that each atomic orbital can hold no more than two electrons.

The hydrogen atom in its ground state has one electron in the $1s$-orbital. To show this structure, we place a single arrow in the $1s$-orbital in a "box diagram," which shows each orbital as a box that can be occupied by at most two electrons (see diagram **1**, which is a fragment of Fig. 1.36). We then report its configuration as $1s^1$ ("one s one"). In the ground state of a helium (He) atom ($Z = 2$), both electrons are in a $1s$-orbital, which is reported as $1s^2$ ("one s two"). As we see in (**2**), the two electrons are paired. At this point, the $1s$-orbital and the shell with $n = 1$ are fully occupied. We say that the helium atom has a **closed shell**, a shell containing the maximum number of electrons allowed by the exclusion principle.

Lithium ($Z = 3$) has three electrons. Two electrons occupy the $1s$-orbital and complete the $n = 1$ shell. The third electron must occupy the next available orbital up the ladder of energy levels, the $2s$-orbital (see Fig. 1.36). The ground state of a lithium (Li) atom is therefore $1s^2 2s^1$ (**3**). We can think of this atom as consisting of a core made up of the inner heliumlike closed shell, the $1s^2$ core, which we denote [He], surrounded by an outer shell containing a higher-energy electron. Therefore, the electron configuration of lithium is $[He]2s^1$. Electrons in the outermost shell are called **valence electrons.** In general, only valence electrons can be lost in chemical reactions, because core electrons (those in lower-energy orbitals) are too tightly bound. Thus, lithium loses only one electron when it forms compounds; it forms Li^+ ions, rather than Li^{2+} or Li^{3+} ions.

The element with $Z = 4$ is beryllium (Be), with four electrons. The first three electrons form the configuration $1s^2 2s^1$, like lithium. The fourth electron pairs with the $2s$-electron, giving the configuration $1s^2 2s^2$, or more simply $[He]2s^2$ (**4**). A beryllium atom therefore has a heliumlike core surrounded by a valence shell of two paired electrons. Like lithium—and for the same reason—a Be atom can lose only its valence electrons in chemical reactions. Thus, it loses both $2s$-electrons to form a Be^{2+} ion.

Boron ($Z = 5$) has five electrons. Two enter the $1s$-orbital and complete the $n = 1$ shell. Two enter the $2s$-orbital. The fifth electron occupies an orbital of the next available subshell, which Fig. 1.36 shows is a $2p$-orbital. This arrangement of electrons is reported as the configuration $1s^2 2s^2 2p^1$ or $[He]2s^2 2p^1$ (**5**).

We need to make another decision at carbon ($Z = 6$): does the sixth electron join the one already in the $2p$-orbital or does it enter a different $2p$-orbital? (Remember, there are three p-orbitals in the subshell, all of the same energy.) To answer this question, we note that electrons are farther from each other and repel each other less when they occupy different p-orbitals than when they occupy the same orbital. So the sixth electron goes into an empty $2p$-orbital, and the ground state of carbon is $1s^2 2s^2 2p_x^1 2p_y^1$ (**6**). We write out the individual orbitals like this only when we need to emphasize that electrons occupy different orbitals within a subshell. In most cases, we can write the shorter form, such as $[He]2s^2 2p^2$. Note that in the orbital diagram we have drawn the two $2p$-electrons with **parallel spins**

(a)

(b)

$1s$

1   H $1s^1$

$1s$

2   He $1s^2$

$2s$

$1s$

3   Li $1s^2 2s^1$, $[He]2s^1$
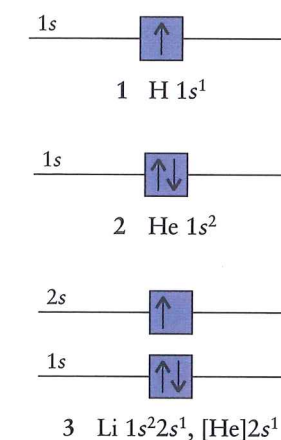
The outermost electrons are used in the formation of chemical bonds (Chapter 2), and the theory of bond formation is called *valence theory*; hence the name of these electrons.
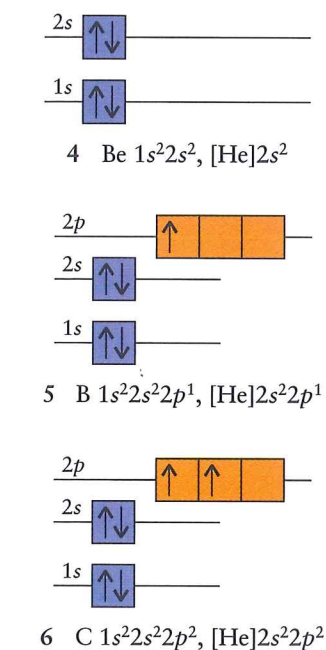
$2s$

$1s$

4   Be $1s^2 2s^2$, $[He]2s^2$

$2p$

$2s$

$1s$

5   B $1s^2 2s^2 2p^1$, $[He]2s^2 2p^1$

$2p$

$2s$

$1s$

6   C $1s^2 2s^2 2p^2$, $[He]2s^2 2p^2$

FIGURE 1.39 The order in which atomic orbitals are occupied according to the building-up principle. When we add an electron, we move one place to the right until all the electrons (Z electrons for an element of atomic number Z) have been accommodated. At the end of a row, move to the beginning of the next row down. The names of the blocks of the periodic table indicate the last subshell being occupied according to the building-up principle. The numbers of electrons that each type of orbital can accommodate are shown by the numbers across the bottom of the table. The colors of the blocks match the colors that we are using for the corresponding orbitals.
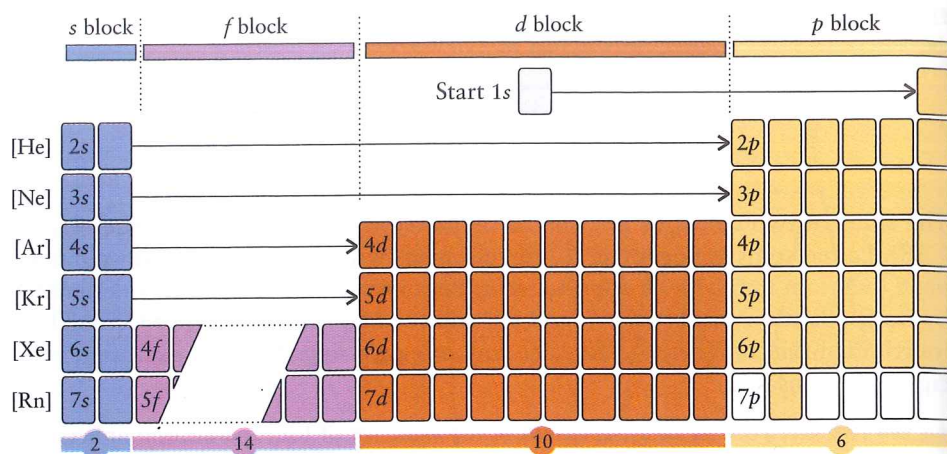
($\uparrow\uparrow$), indicating that they have the same spin magnetic quantum numbers. For reasons based in quantum mechanics, which result in two electrons with parallel spins tending to avoid each other, this arrangement has slightly lower energy than that of a paired arrangement. However, it is allowed only when the electrons occupy different orbitals.

The procedure that we have been using is called the **building-up principle.** It can be summarized by two rules. To predict the ground-state configuration of an element with atomic number Z:

1   Add Z electrons, one after the other, to the orbitals in the order shown in Fig. 1.39 but with no more than two electrons in any one orbital.

2   If more than one orbital in a subshell is available, add electrons with parallel spins to different orbitals of that subshell rather than pairing two electrons in one of the orbitals.

The first rule takes into account the Pauli exclusion principle. The second rule is called **Hund's rule,** for the German spectroscopist Friedrich Hund, who first proposed it. This procedure gives the configuration of the atom that corresponds to the lowest total energy, allowing for the attraction of the electrons to the nucleus and their repulsion by one another. An atom with electrons in energy states higher than predicted by the building-up principle is said to be in an **excited state.** For example, the electron configuration $[He]2s^12p^3$ represents an excited state of a carbon atom. An excited state is unstable and emits a photon as the electron returns to an orbital that restores the atom to a lower energy.

In general, we can think of an atom of any element as having a noble-gas core surrounded by a number of electrons in the **valence shell,** the outermost occupied shell. The valence shell is the occupied shell with the largest value of n.

The underlying organization of the periodic table described in Section B now begins to unfold. All the atoms of the main-group elements in a given period have a valence shell with the same principal quantum number, which is equal to the period number. For example, the valence shell of elements in Period 2 (from lithium to neon) is the shell with n = 2. Thus all the atoms in a given period have the same type of core. For example, the atoms of Period 2 elements all have a heliumlike $1s^2$ core, and those of Period 3 elements have a neonlike $1s^22s^22p^6$ core, denoted [Ne]. All the atoms of a given *group* (in the main groups, particularly) have analogous valence electron configurations that differ only in the value of n. For instance, all the members of Group 1 have the valence configuration ns^1; and all the members of Group 14/IV have the valence configuration ns^2np^2.

With these points in mind, let's continue building up the electron configurations across Period 2. Nitrogen has Z = 7 and one more electron than carbon, giving $[He]2s^22p^3$. Each p-electron occupies a different orbital, and the three have parallel spins (7). Oxygen has Z = 8 and one more electron than nitrogen; there-

fore, its configuration is $[He]2s^22p^4$ (8) and two of its 2p-electrons are paired. Similarly, fluorine, with Z = 9 and one more electron than oxygen, has the configuration $[He]2s^22p^5$ (9), with only one unpaired electron. Neon, with Z = 10, has one more electron than fluorine. This electron completes the 2p-subshell, giving $[He]2s^22p^6$ (**10**). According to Figs. 1.36 and 1.39, the next electron enters the 3s-orbital, the lowest-energy orbital of the next shell. The configuration of sodium is therefore $[He]2s^22p^63s^1$, or more briefly, $[Ne]3s^1$, where [Ne] denotes the neon-like core.

SELF-TEST 1.12A Predict the ground-state configuration of a magnesium atom.
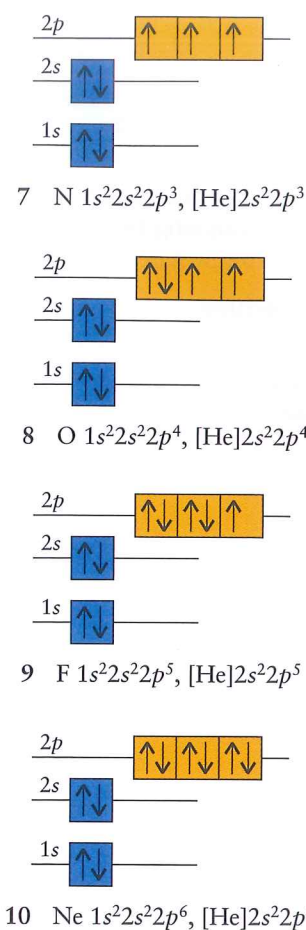
[*Answer:* $1s^22s^22p^63s^2$, or $[Ne]3s^2$]

SELF-TEST 1.12B Predict the ground-state configuration of an aluminum atom.

The s- and p-orbitals of the shell with n = 3 are full by the time we get to argon, $[Ne]3s^23p^6$, which is a colorless, odorless, unreactive gas resembling neon. Argon completes the third period. From Fig. 1.36, we see that the energy of the 4s-orbital is slightly lower than that of the 3d-orbitals. As a result, instead of electrons entering the 3d-orbitals, the fourth period now begins by filling the 4s-orbitals (see Fig. 1.39). Hence, the next two electron configurations are $[Ar]4s^1$ for potassium and $[Ar]4s^2$ for calcium, where [Ar] denotes the argonlike core, $1s^22s^22p^63s^23p^6$. At this point, however, the 3d-orbitals begin to be occupied, and there is a change in the rhythm of the periodic table.

According to the pattern of increasing energy of the orbitals (see Fig. 1.36), the next 10 electrons (for scandium, with Z = 21, through zinc, with Z = 30) enter the 3d-orbitals. The ground-state electron configuration of scandium, for example, is $[Ar]3d^14s^2$, and that of its neighbor titanium is $[Ar]3d^24s^2$. Note that, beginning at scandium, we write the 4s-electrons after the 3d-electrons: once they contain electrons, the 3d-orbitals lie lower in energy than the 4s-orbital (recall Fig. 1.36; the same relation holds true for nd- and (n + 1)s-orbitals in subsequent periods). Successive electrons are added to the d-orbitals as Z increases. However, there are two exceptions: the half-complete subshell configuration d^5 and the complete subshell configuration d^{10} turn out to have a lower energy than simple theory suggests. As a result, a lower total energy may be achieved if an electron enters a 3d-orbital instead of the expected 4s-orbital, if that arrangement completes a half-subshell or a full subshell. For example, the experimental electron configuration of chromium is $[Ar]3d^54s^1$ instead of $[Ar]3d^44s^2$, and that of copper is $[Ar]3d^{10}4s^1$ instead of $[Ar]3d^94s^2$. Other exceptions to the building-up principle can be found in the complete listing of electron configurations in Appendix 2C and in the periodic table inside the front cover.

As we can anticipate from the structure of the periodic table (see Fig. 1.39), electrons occupy 4p-orbitals once the 3d-orbitals are full. The configuration of germanium, $[Ar]3d^{10}4s^24p^2$, for example, is obtained by adding two electrons to the 4p-orbitals outside the completed 3d-subshell. The fourth period of the table contains 18 elements, because the 4s- and 4p-orbitals together can accommodate a total of 8 electrons and the 3d-orbitals can accommodate 10. Period 4 is the first long period of the periodic table.

Next in line for occupation at the beginning of Period 5 is the 5s-orbital, followed by the 4d-orbitals. As in Period 4, the energy of the 4d-orbitals falls below that of the 5s-orbital after 2 electrons have been accommodated in the 5s-orbital. A similar effect is seen in Period 6, but now another set of inner orbitals, the 4f-orbitals, begins to be occupied. Cerium, for example, has the configuration $[Xe]4f^15d^16s^2$. Electrons then continue to occupy the seven 4f-orbitals, which are complete after 14 electrons have been added, at ytterbium, $[Xe]4f^{14}6s^2$. Next, the 5d-orbitals are occupied. The 6p-orbitals are occupied only after the 6s-, 4f-, and 5d-orbitals are filled at mercury; thallium, for example, has the configuration $[Xe]4f^{14}5d^{10}6s^26p^1$. Toolbox 1.1 outlines a procedure for writing the electron configuration of a heavy element.

7   N $1s^22s^22p^3$, $[He]2s^22p^3$

8   O $1s^22s^22p^4$, $[He]2s^22p^4$

9   F $1s^22s^22p^5$, $[He]2s^22p^5$

10   Ne $1s^22s^22p^6$, $[He]2s^22p^6$

TOOLBOX 1.1 HOW TO PREDICT THE GROUND-STATE ELECTRON CONFIGURATION OF AN ATOM

Conceptual Basis

Electrons occupy orbitals in such a way as to minimize the total energy of an atom by maximizing attractions and minimizing repulsions in accord with the Pauli exclusion principle and Hund's rule.

Procedure

We use the following rules of the building-up principle to assign a ground-state configuration to an element with atomic number Z:

1 Add Z electrons, one after the other, to the orbitals in the order shown in Figs. 1.36 and 1.39 but with no more than two electrons in any one orbital (the Pauli exclusion principle).

2 If more than one orbital in a subshell is available, add electrons to different orbitals of the subshell before doubly occupying any of them (Hund's rule).

3 Write the letters identifying the orbitals in order of increasing energy, with a superscript that gives the number of electrons in that orbital. The configuration of a filled shell is represented by the symbol of the noble gas having that configuration, as in [He] for $1s^2$.

4 When drawing a box diagram, show the electrons in different orbitals of the same subshell with parallel spins; electrons sharing an orbital have paired spins.

This procedure gives the ground-state electron configuration of an atom. Any other arrangement corresponds to an excited state of the atom. Note that we can use the structure of the periodic table to predict the electron configurations of most elements once we realize which orbitals are being filled in each block of the periodic table (see Fig. 1.39).

A useful shortcut for atoms of elements with large numbers of electrons is to write the electron configuration from the group number, which gives the number of valence electrons in the ground state of the atom, and the period number, which gives the value of the principal quantum number of the valence shell. The core consists of the preceding noble-gas configuration together with any completed d- and f-subshells.

Example 1.9 shows how these rules (specifically the shortcut) are applied.

EXAMPLE 1.9 Sample exercise: Predicting the ground-state electron configuration of a heavy atom

Predict the ground-state electron configuration of (a) a vanadium atom and (b) a lead atom.

SOLUTION (a) Vanadium is in Period 4, and so it has an argon core. The $4s$-orbitals fill next, and then the last three electrons fill two separate $3d$-orbitals. The electron configuration is $[Ar]3d^34s^2$. (b) Lead belongs to Group 14/IV and Period 6. It therefore has four electrons in its valence shell, two in a $6s$-orbital and two in different $6p$-orbitals. The atom has complete $5d$- and $4f$-subshells, and the preceding noble gas is xenon. The electron configuration of lead is therefore $[Xe]4f^{14}5d^{10}6s^26p^2$.

SELF-TEST 1.13A Write the ground-state configuration of a bismuth atom.

[*Answer:* $[Xe]4f^{14}5d^{10}6s^26p^3$]

SELF-TEST 1.13B Write the ground-state configuration of an arsenic atom.

We account for the ground-state electron configuration of an atom by using the building-up principle in conjunction with Fig. 1.36, the Pauli exclusion principle, and Hund's rule.

1.13 Electronic Structure and the Periodic Table

The periodic table (Section B) was formulated long before the structures of atoms were known, by noting trends in experimental data (Box 1.2). However, to understand the organization of the periodic table, we need to consider the electron configurations of the elements. The table is divided into s, p, d, and f blocks, named for the last subshell that is occupied according to the building-up principle (as shown in Fig. 1.36). Two elements are exceptions. Strictly, helium belongs in the s block, but it is shown in the p block. It is a gas with properties matching those of the noble gases in Group 18/VIII, rather than the reactive metals in Group 2. Its place in Group 18/VIII

BOX 1.2 THE DEVELOPMENT OF THE PERIODIC TABLE

The periodic table is one of the most notable achievements in chemistry because it helps to organize what would otherwise be a bewildering array of properties of the elements. However, the fact that its structure corresponds to the electronic structure of atoms was unknown to its discoverers. The periodic table was developed solely from a consideration of physical and chemical properties of the elements.

Dmitri Ivanovich Mendeleev (1834–1907).

In 1860, the Congress of Karlsruhe brought together many prominent chemists in an attempt to resolve issues such as the existence of atoms and the correct atomic masses. One of the new ideas presented was *Avogadro's principle*—that the numbers of molecules in samples of different gases of equal volume, pressure, and temperature are the same (see section 4.6). This principle allowed the relative atomic masses of the gases to be determined. Two scientists attending the congress were the German Lothar Meyer and the Russian Dmitri Mendeleev, both of whom left with copies of Avogadro's paper. In 1869, Meyer and Mendeleev discovered independently that the elements fell

into families with similar properties when they were arranged in order of increasing atomic mass. Mendeleev called this observation the *periodic law.*

Mendeleev's chemical insight led him to leave gaps for elements that would be needed to complete the pattern but were unknown at the time. When they were discovered later, he turned out (in most cases) to be strikingly correct. For example, his pattern required an element that he named "eka-silicon" below silicon and between gallium and arsenic. He predicted that the element would have a relative atomic mass of 72 (taking the mass of hydrogen as 1) and properties similar to those of silicon. This prediction spurred the German chemist Clemens Winkler in 1886 to search for eka-silicon, which he eventually discovered and named germanium. It has a relative atomic mass of 72.59 and properties similar to those of silicon, as shown in the accompanying table.

One problem with Mendeleev's table was that some elements seemed to be out of place. For example, when argon was isolated, it did not seem to have the correct mass for its location. Its relative atomic mass of 40 is the same as that of calcium, but argon is an inert gas and calcium a reactive metal. Such anomalies led scientists to question the use of relative atomic mass as the basis for organizing the elements. When Henry Moseley examined x-ray spectra of the elements in the early twentieth century, he realized that he could infer the atomic number itself. It was soon discovered that elements fall into the uniformly repeating pattern of the periodic table if they are organized according to atomic number, rather than atomic mass.

Related Exercise: 1.100

Mendeleev's Predictions for Eka-Silicon (Germanium)

Property	Eka-silicon, E	Germanium, Ge
molar mass	72 g·mol^{-1}	72.59 g·mol^{-1}
density	5.5 g·cm^{-3}	5.32 g·cm^{-3}
melting point	high	937°C
appearance	dark gray	gray-white
oxide	EO_2; white solid; amphoteric; density 4.7 g·cm^{-3}	GeO_2; white solid; amphoteric; density 4.23 g·cm^{-3}
chloride	ECl_4; boils below 100°C; density 1.9 g·cm^{-3}	$GeCl_4$; boils at 84°C; density 1.84 g·cm^{-3}

is justified because it has a filled valence shell, like all the other Group 18/VIII elements. Hydrogen occupies a unique position in the periodic table. It has one s-electron, and so it belongs in Group 1; but it is also one electron short of a noble-gas configuration, and so it can act like a member of Group 17/VII. Because hydrogen has such a unique character, we do not ascribe it to any group; however, you will often see it placed in Group 1 or Group 17/VII, and sometimes in both.

The s and p blocks form the main groups of the periodic table. The similar electron configurations for the elements in the same main group are the reason for the similar properties of these elements. The group number tells us how many valence-shell electrons are present. In the s block, the group number (1 or 2) is the