

Chapter 10

Multielectron Atoms; the Pauli Principle and Periodic Table

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*These sections can be omitted without significant loss of continuity.

10.1 Introduction

In Chapter 8 we saw how the Schrödinger equation was used to predict the properties of the hydrogen atom. Another early triumph for the Schrödinger equation was that, unlike the Bohr model, it could be extended successfully to atoms with more than one electron. Today it appears that the Schrödinger equation can correctly account for the structure of all of the hundred or so multielectron atoms and for the way in which these atoms come together to form molecules. Thus, in principle at least, the Schrödinger equation can explain all of chemistry. It is this impressive accomplishment that we introduce in this chapter. We complete the story in Chapter 12 where we describe how atoms combine to form molecules.

Our first step is to find a way to handle quantum systems containing several particles. The simplest method — and the method we describe here — is called the independent-particle approximation. When this method was first applied to multielectron atoms, it predicted many atomic levels, some of which exist but many of which do not. This partial failure led to the discovery of a new law that applies to multielectron systems. We describe this law, called the Pauli exclusion principle, in Section 10.4. Armed with this principle, we can successfully describe the general properties of all multielectron atoms from helium through uranium and beyond, as we sketch in Sections 10.6 to 10.9.

10.2 The Independent-Particle Approximation

The Schrödinger equation for one electron moving around a nucleus can be solved exactly, as we described in Chapter 8. With two or more electrons, an exact solution is not possible, and one must resort to various approximations. The starting point for almost all calculations of multielectron atoms is called the **independent-particle approximation**, or **IPA**. This approach is called from the classical theory of the solar system, in which one starts by treating the motion of each planet independently, taking account of just the dominant force, the attraction of the sun. Once one has found the orbits of all the planets separately, one can, if desired, improve these approximate orbits by correcting for the small attraction of the planets for one another.

In treating the motion of one planet, it is a very good approximation to ignore the forces of the other planets in comparison with the force of the sun. The corresponding approximation for an atom is much less satisfactory: If, for example, we consider a neutral atom with 20 electrons (calcium), it is true that the single largest force on any one electron is the force of the nucleus, with charge $20e$; but it would be a very poor approximation to consider *only* this force and to ignore completely the repulsion of the 19 other electrons, with a combined charge of $-19e$. What we do instead is to treat the motion of each electron independently, taking account of the force of the nucleus *plus* the force of the *average static distribution of the $Z - 1$ other electrons*. We will refer to the potential energy $U(\mathbf{r})$ of each electron treated in this way as the **IPA potential energy**. The problem is now reduced to finding what the IPA potential energy $U(\mathbf{r})$ should be and then, given $U(\mathbf{r})$, to solving the Schrödinger equation to find the possible wave functions and energies of each electron in the multielectron atom.

To implement this approach quantitatively requires a whole series of successive approximations. One must first make some reasonable *guess* for the electron wave functions; from these wave functions, one can calculate the charge distribution in the atom and hence the IPA potential-energy function $U(\mathbf{r})$ of each electron. Using this potential-energy function, one can solve the Schrödinger equation for each electron and obtain an improved set of wave functions. Using these improved wave functions, an improved IPA potential-energy function $U(\mathbf{r})$ can be calculated; and so on. This iterative procedure is called the **Hartree-Fock method** and, with the aid of a large computer, can yield quite accurate atomic wave functions and energy levels.

Fortunately, we do not need to go into any details of the Hartree-Fock procedure here. Using simple known properties of the atomic charge distribution, we can get an excellent qualitative picture of the IPA potential-energy function $U(\mathbf{r})$. Using this knowledge of $U(\mathbf{r})$, we can get a good — sometimes even quantitative — understanding of the electron wave functions and hence of atomic structure.

The essential feature of the independent-particle approximation is that each electron can be considered to move independently in the average field of the $Z - 1$ other electrons plus the nucleus. In most atoms it is a good approximation to assume further that the distribution of the $Z - 1$ other electrons is spherically symmetric around the nucleus. (With this additional assumption, the IPA is often called the **central-field approximation**.) We will therefore assume that the charge distribution “seen” by any one electron is spherically symmetric, which means that the IPA potential energy $U(\mathbf{r})$ is independent of θ and ϕ , and can be written as $U(r)$. This greatly simplifies our

discussion, for as we saw in Chapter 8, when $U(r)$ is spherically symmetric, the angular part of the Schrödinger equation always has the same solutions, characterized by the familiar angular-momentum quantum numbers l and m .

The main features of $U(r)$ are easily understood if we recall two properties of spherical charge distributions, both of which follow from Gauss's law. First, if an electron is *outside* a spherical distribution of total charge Q , the electron experiences exactly the same force as if the entire charge Q were concentrated at $r = 0$, namely

$$F = k \frac{Qe}{r^2} \quad (10.1)$$

Second, if the electron is *inside* a spherical shell of charge, it experiences no force at all from the shell.

If the electron in which we are interested is close enough to the nucleus, it will be inside all the other electrons and will experience the force of the nuclear charge Ze but no force at all from the other electrons; in other words, it feels the full attractive force of the nucleus:

$$F = \frac{Zke^2}{r^2} \quad [r \text{ inside all other electrons}] \quad (10.2)$$

If we now imagine the electron moving outward from the nucleus, it will steadily move outside more and more of the other electrons; thus the force will still be given by (10.1) but with Q equal to the nuclear charge Ze reduced by the charge of those electrons inside the radius r . Eventually, when the electron is outside all of the other $Z - 1$ electrons, Q is given by Ze minus $(Z - 1)e$; that is, $Q = e$ and

$$F = \frac{ke^2}{r^2} \quad [r \text{ outside all other electrons}] \quad (10.3)$$

Therefore, an atomic electron that is outside all its fellow electrons experiences the same force as the one electron in hydrogen.

The potential energy $U(r)$ of the electron is the integral of the force. It follows from this discussion that when r is outside all the other electrons

$$U(r) = -\frac{ke^2}{r} \quad [r \text{ outside all other electrons}] \quad (10.4)$$

On the other hand, as r approaches zero,

$$U(r) \approx -\frac{Zke^2}{r} \quad [\text{as } r \rightarrow 0] \quad (10.5)$$

since, then, the electron of interest is inside all the others.* Between these two regions, $U(r)$ connects these two functions smoothly, as shown qualitatively in Fig. 10.1.

*It follows from (10.2) that $U(r)$ is $-Zke^2/r$ plus some constant. However, as $r \rightarrow 0$, this constant is negligible compared to $-Zke^2/r$, and we have ignored it in (10.5). The corresponding constant in (10.4) is exactly zero since we are defining U to be zero at $r = \infty$.

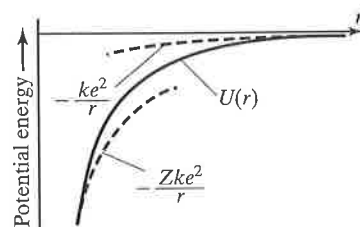


FIGURE 10.1

The IPA potential energy $U(r)$ of an atomic electron in the field of the nucleus plus the average distribution of the other $Z - 1$ electrons. As $r \rightarrow \infty$, U approaches $-ke^2/r$; as $r \rightarrow 0$, U approaches $-Zke^2/r$ as in Eq. (10.5).

We can express the behavior shown in Fig. 10.1 by writing $U(r)$ as

$$U(r) = -Z_{\text{eff}}(r) \frac{ke^2}{r} \quad (10.6)$$

Here $Z_{\text{eff}}(r)$ gives the **effective charge** “felt” by the electron and depends on r . When r is inside the other electrons, Z_{eff} approaches the full nuclear charge:

$$Z_{\text{eff}} \approx Z \quad [r \text{ inside all other electrons}] \quad (10.7)$$

As r increases and the nuclear charge is shielded, or *screened*, by more and more of the other electrons, Z_{eff} decreases steadily, until as r moves outside all other electrons, Z_{eff} approaches 1:

$$Z_{\text{eff}} \approx 1 \quad [r \text{ outside all other electrons}] \quad (10.8)$$

10.3 The IPA Energy Levels

Once the potential energy $U(r)$ is known, our next step is to find the energy levels and wave functions of each electron. The potential energy $U(r)$ is sufficiently like the hydrogen potential energy that we can get a good qualitative understanding of the solutions by analogy with what we already know about hydrogen and hydrogen-like ions.

Just as with hydrogen, $U(r)$ depends only on r , and the Schrödinger equation separates. In particular, the two angular equations are exactly the same as for hydrogen. This means that the states of definite energy have angular momentum given by the familiar orbital quantum numbers l and m , and all of the $2l + 1$ different orientations given by $m = l, l - 1, \dots, -l$ have the same energy. Since $U(r)$ does not involve the spin at all, the energy is also the same for both orientations, $m_s = \pm \frac{1}{2}$, of the spin. Thus, each level has a degeneracy of at least $2(2l + 1)$.

As was the case with hydrogen, the solutions of the radial equation are characterized by a principal quantum number n ; and a quantum state is completely specified by the four quantum numbers n, l, m , and m_s . The lowest energy level is $1s$ (that is, $n = 1, l = 0$) and is twofold degenerate because of the two possible orientations of the spin. Just as in hydrogen, the $1s$ wave function is concentrated closer to the nucleus than any other wave function. This means that in the region where the $1s$ wave function is large, $U(r)$ is close to the hydrogen-like potential energy with $Z_{\text{eff}} \approx Z$. Therefore, the $1s$ wave function approximates that of a hydrogen-like ion with nuclear charge Ze ; the $1s$ energy is close to $-Z^2 E_R$,

$$E_{1s} \approx -Z^2 E_R \quad (10.9)$$

(where E_R denotes the Rydberg energy, 13.6 eV, as usual) and the most probable radius is about a_B/Z (as described in Section 8.10).

Just as with hydrogen, the next energy level has $n = 2$. But here an important difference emerges. In hydrogen the $2s$ and $2p$ states are degenerate, whereas in multielectron atoms the $2s$ states are lower in energy. This difference is easy to understand if we look at the $2s$ and $2p$ radial distributions

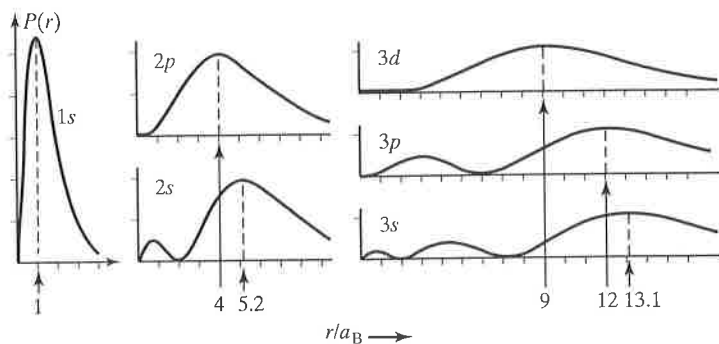


FIGURE 10.2
The radial probability distributions for the $n = 1, 2,$ and 3 states in hydrogen. The numbers shown are the most probable radii in units of a_B .

shown in Fig. 8.23, which we reproduce here as Fig. 10.2. These two distributions peak at about the same radius, four or five times further out than the $1s$ distribution. This means that the $2s$ and $2p$ wave functions are concentrated in a region where the nuclear charge Ze is screened by any electron in the $1s$ states, and the $2s$ and $2p$ electrons see an effective charge Z_{eff} which is less than Z . However, the $2s$ distribution (unlike the $2p$) has a secondary maximum much closer in. That is, a small part of the $2s$ distribution penetrates the region where Z_{eff} is close to the full nuclear value $Z_{\text{eff}} \approx Z$. Therefore, on average, a $2s$ electron is more strongly attracted to the nucleus than is a $2p$ electron. This means that the $2s$ electron is more tightly bound and has lower energy.

With the $n = 3$ states, there is a similar separation of energies. In Fig. 10.2 it can be seen that both the $3s$ and $3p$ distributions have secondary peaks near $r = 0$, with one of the $3s$ peaks much closer in. Therefore, the $3s$ state penetrates closest to the nucleus and has the lowest energy, the $3p$ is next, and finally the $3d$. This trend is repeated in all higher levels: For each value of n , states with smaller l penetrate closer to the nucleus and are lower in energy. This systematic lowering of the energy for states with lower l is shown schematically in Fig. 10.3.

In many atoms the lowering in energy of the “penetrating orbits” becomes so important that the order of certain levels can be reversed, as compared to hydrogen. This is illustrated in Fig. 10.3, which shows the $4s$ level slightly below the $3d$. We will see that such reversals of the order of energy levels have an important effect on the chemical properties of many elements.

For a hydrogen-like ion, we saw that all states with a given n tend to cluster in a spatial shell, with radius roughly equal to the Bohr value $r \approx n^2 a_B / Z$.

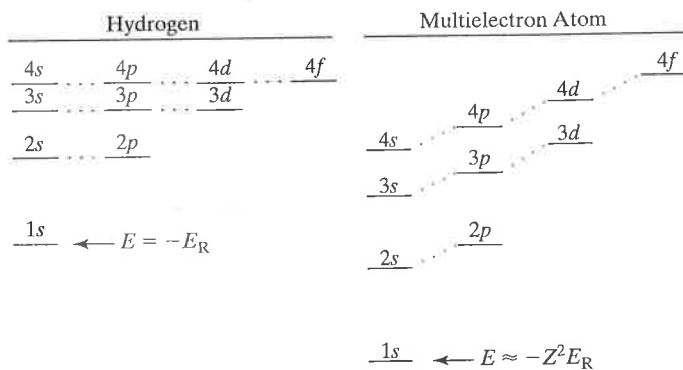


FIGURE 10.3
Schematic energy-level diagrams for a hydrogen atom and for one of the electrons in a multielectron atom. In hydrogen, all states with the same n are degenerate. In multielectron atoms states with lower l are more tightly bound because they penetrate closer to the nucleus. In many atoms this effect results in the $4s$ level being lower than the $3d$, as shown here.

This same clustering into spatial shells occurs in multielectron atoms and is, in fact, more pronounced. The $n = 1$ states are closest to the nucleus and feel nearly the full nuclear charge Ze ; therefore, their most probable radius is close to the Bohr value, a_B/Z , for the $n = 1$ state of a hydrogen-like ion with charge Ze . The states with successively higher n are concentrated at progressively larger radii where they feel an effective charge $Z_{\text{eff}}e$ that is progressively smaller. The most probable radius for these states is roughly

$$r_{\text{mp}} \approx \frac{n^2 a_B}{Z_{\text{eff}}} \quad (10.10)$$

Since Z_{eff} gets smaller as n gets larger, the proportionate separation of the spatial shells is even greater in a multielectron atom than it is in hydrogen. Notice that this clustering into spatial shells is according to n , exactly as it is in hydrogen. This contrasts with the energy levels, whose order deviates, as we have seen, from the simple hydrogen ordering.

Occasionally, the IPA energy levels can be calculated easily and with surprising accuracy, as the following example illustrates.

Wolfgang Pauli
(1900–1958, Austrian)



At the age of 21, Pauli published a review of relativity that is still regarded as a masterpiece. He made many fundamental contributions to quantum physics, including the exclusion principle (1925) for which he won the 1945 Nobel Prize in physics, the neutrino hypothesis (Chapter 17), and work in relativistic quantum field theory. His powerful personality was legendary. He generously credited others with ideas that he originated and detailed in letters to colleagues, but did not publish. Yet he often displayed a biting wit and mercilessly denounced any evidence of sloppy thinking among his peers. Of a paper submitted by a colleague, he said, "This isn't right. This isn't even wrong."

Example 10.1

As we will see in Section 10.6, the ground state of lithium ($Z = 3$) has two electrons in the $1s$ level and one in the $2s$. Estimate the energy of the third electron when it is raised to the $3d$ level.

When the outer electron has been raised to the $3d$ level, its wave function is concentrated far outside two inner, $1s$, electrons. Thus, to a very good approximation, we can say that it is moving outside an effective charge of $+e$ (that is, $Z_{\text{eff}} = 1$), and its energy should be just the hydrogenic energy $E_3 = -E_R/Z^2 = -1.512 \text{ eV}$. This means that the energy to remove the outer electron (in this level) should be 1.512 eV , a prediction that agrees outstandingly well with the observed value of 1.513 eV .

10.4 The Pauli Exclusion Principle

Knowing the possible states of each electron in a multielectron atom, we are now ready to discuss the possible states of the whole atom. Let us consider first the atomic ground states. For these, our problem is to decide how the electrons are to be distributed among their possible states so that the atom as a whole has the minimum possible energy.

One might expect that the ground state of any atom would be found by placing all of its Z electrons into the lowest, $1s$, state; but this is not what is observed to happen. The explanation for what does happen was discovered by the Austrian physicist Wolfgang Pauli, who proposed a new law, now called the **Pauli exclusion principle**. This principle states that:*

*The Pauli principle applies to many other particles besides the electron. For example, it applies to protons and to neutrons and has important consequences for the energy levels of nuclei, as we will see in Chapter 16. In this chapter, however, we are concerned only with electrons.

PAULI EXCLUSION PRINCIPLE

No two electrons in a quantum system
can occupy the same quantum state. (10.11)

Pauli was led to this law by a study of the states of many atoms, and to this day, the best evidence for the Pauli principle is its success in explaining the diverse properties of all the atoms. There is, however, evidence from many other fields as well. For example, the electrons in a conductor are found to obey the exclusion principle, and many of the observed properties of conductors (conductivity, specific heat, magnetic susceptibility, etc.) depend in a crucial way on the validity of the principle.

To illustrate the exclusion principle and some of the evidence for it, let us consider two simple atoms, helium and lithium. First, let us imagine putting together a helium atom ($Z = 2$) from a helium nucleus and two electrons. If we add one electron to the nucleus, its lowest possible state is the $1s$ state ($n = 1, l = m = 0$), with its spin either up or down ($m_s = \pm \frac{1}{2}$). If we next add the second electron, it too can go into the $1s$ state. But according to the exclusion principle, the two electrons cannot occupy exactly the same quantum state. Since they have the same values of n, l , and m , they must have different values of m_s ; that is, if both electrons are in the $1s$ state, their spins must be antiparallel. This situation is sketched in Fig. 10.4, where part (a) shows two electrons in the $1s$ state with spins parallel, a situation that is never observed; on the other hand, Fig. 10.4(b) shows two electrons in the $1s$ state with spins antiparallel, the situation that is observed. The two possibilities shown in Fig. 10.4 would be easily distinguishable, since the first would have a nonzero magnetic moment, while the second has $\mu = 0$. That the helium ground state is always found to have $\mu = 0$ is clear evidence for the exclusion principle.

The situation with the excited states of helium is different. For example, there is an excited state with one electron in the $1s$ level and the other in the $2s$ level. In this case the two electrons are certainly in different quantum states, whatever their spin orientations (parallel or antiparallel), as shown in Fig. 10.5. Thus, the Pauli principle does not forbid either of these arrangements, and both are observed, the first with $\mu \neq 0$ and the second with $\mu = 0$.

As a second example, let us imagine putting together a lithium atom ($Z = 3$) from a lithium nucleus and three electrons. When we add the first two electrons, they can both go into the $1s$ level, provided that their spins are antiparallel. But since there are only two possible orientations of the spin, there is now no way in which the third electron can go into the $1s$ level [Fig. 10.6(a)]. The Pauli principle requires that the third electron go into some higher level, the lowest of which is the $2s$. Therefore, the ground state of lithium has to be as shown in Fig. 10.6(b), with the third electron in the $2s$ level and its spin either up or down.

In general, the Pauli principle implies that any s level ($1s, 2s$, etc.) can accommodate two electrons but no more. Levels with higher angular momentum can accommodate more electrons because their degeneracy is larger. For example, any level with $l = 1$ contains six distinct quantum states ($6 = 2 \times 3$ since there are two orientations of \mathbf{S} and three orientations of \mathbf{L}); therefore, any p level ($l = 1$) can accommodate six electrons, but no more. Similarly, any d level, with $l = 2$, has ten distinct states (2×5) and can accommodate ten electrons, but no more.

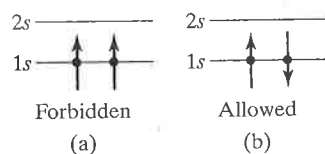


FIGURE 10.4

The ground state of helium has both electrons in the $1s$ level. As required by the Pauli principle, their spins have to be in opposite directions.

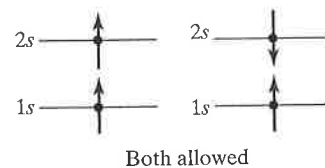


FIGURE 10.5

The lowest excited state of helium has one electron in the $1s$ and one in the $2s$ level. The Pauli principle places no restrictions on the spin orientations in this case.

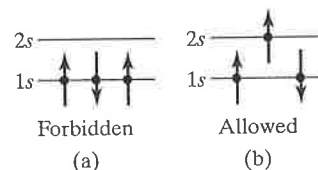


FIGURE 10.6

- (a) It is impossible to put three electrons in the $1s$ level without violating the Pauli principle.
(b) Therefore, the ground state of lithium has two electrons in the $1s$ level and one in the $2s$ level. The third electron's spin can point either way.

10.5 Fermions and Bosons; the Origin of the Pauli Principle*

*In this section we describe how the Pauli principle follows from certain symmetry properties of the multiparticle wave function. The ideas described here are of great theoretical importance but will not be used again until Chapter 13, and this section could be omitted on a first reading.

Before exploring further the consequences of the Pauli principle, we take a moment to describe in this section where the principle comes from. One can take the view that the Pauli principle is an observed property of electrons (and some other particles, including protons and neutrons) — a property for which there is overwhelming experimental evidence. If you would like to take this view, then you can safely skip this section for now. Nevertheless, the Pauli principle actually follows from a more fundamental idea — the complete indistinguishability of identical particles in quantum mechanics. This result is interesting in its own right and has a remarkable consequence. All the particles of nature fall into just two categories: First there are the so-called *fermions*, which *do* obey the Pauli principle, and second there are the *bosons*, which do not. We will describe some of the striking differences between these two kinds of particles in Chapter 13.

We say that two particles are **identical** if they have all the same intrinsic properties — same mass, same charge, and same spin. Thus any two electrons are identical, but an electron and a proton are certainly not. In classical mechanics, even identical particles are **distinguishable** in the sense that we could, in principle at least, keep track of which is which: Consider, for example, the two electrons in a helium atom. In the classical view each electron follows a definite orbit around the nucleus. Armed with a powerful enough microscope, we could label as number 1 the electron that is on the right at noon today; and then by following their orbits carefully, we could still say tomorrow which is electron 1 and which electron 2. In quantum mechanics this experiment is doomed to failure. We might imagine, in principle at least, measuring the two electrons' positions at noon today and labeling as number 1 the one on the right. But within some fraction of a second their two wave functions will overlap, and when we measure their positions again there is absolutely no way of saying which electron is which. We say that in quantum mechanics two identical particles are **indistinguishable** — we simply cannot say which is which.

Perhaps surprisingly, the indistinguishability of identical particles in quantum mechanics has profound consequences. To describe these, we have to discuss the wave functions for two or more particles. For two spinless particles in one dimension this would have the form $\psi(x_1, x_2)$ where

$$|\psi(x_1, x_2)|^2 dx_1 dx_2 = \begin{cases} \text{probability of finding one particle between} \\ x_1 \text{ and } x_1 + dx_1, \text{ and the other between} \\ x_2 \text{ and } x_2 + dx_2 \end{cases} \quad (10.12)$$

If the same particles have spin, the wave function would have to have another variable to identify the spin states of the particles. For instance, we might write $\psi = \psi(x_1, m_1, x_2, m_2)$, where

$$|\psi(x_1, m_1, x_2, m_2)|^2 dx_1 dx_2 = \begin{cases} \text{probability of finding one particle} \\ \text{between } x_1 \text{ and } x_1 + dx_1 \text{ with} \\ S_z = m_1\hbar \text{ and the other between} \\ x_2 \text{ and } x_2 + dx_2 \text{ with } S_z = m_2\hbar \end{cases} \quad (10.13)$$

In three dimensions the variables x_1 and x_2 would be replaced by position vectors \mathbf{r}_1 and \mathbf{r}_2 . To cover all these cases, we will simply write the two-particle wave function as $\psi = \psi(1, 2)$, where the "1" and "2" are shorthand for whatever variables are needed to identify each particle. For instance, in the case of Eq. (10.13), "1" stands for (x_1, m_1) . In most of the discussion that follows, you might want to focus on the simplest case of Eq. (10.12), for which "1" is just short for x_1 and "2" for x_2 .

Suppose first that our two particles are not identical; for example, $\psi(1, 2)$ could be a state of a high-energy electron and a low-energy proton. In this case the wave function $\psi(2, 1)$, in which the roles of the two particles are reversed, would represent a high-energy proton and a low-energy electron — an entirely distinct situation. But suppose instead that $\psi(1, 2)$ were the wave function for two *identical* particles, two electrons for instance. The indistinguishability of identical particles requires that the states represented by $\psi(1, 2)$ and $\psi(2, 1)$ (with the roles of 1 and 2 reversed) must be physically indistinguishable. It makes no difference which is particle 1 and which is particle 2. In particular, the probability densities associated with $\psi(1, 2)$ and $\psi(2, 1)$ must be the same:

$$|\psi(2, 1)|^2 = |\psi(1, 2)|^2 \quad (10.14)$$

It turns out that there are only two ways in which this indistinguishability requirement can be met. For a given kind of particle (electron or proton, for instance), *either*

$$\psi(2, 1) = +\psi(1, 2) \quad (10.15)$$

for all two-particle states, *or*

$$\psi(2, 1) = -\psi(1, 2) \quad (10.16)$$

for all two-particle states.* Wave functions that satisfy (10.15) are said to be **symmetric** under particle exchange; particles whose multiparticle wave functions are symmetric in this way include photons and pions and are called **bosons**, after the Indian physicist Satyendranath Bose. Wave functions that satisfy (10.16) are said to be **antisymmetric** under particle exchange; particles whose multiparticle wave functions are antisymmetric include electrons, protons, and neutrons and are called **fermions**, after the Italian-American physicist Enrico Fermi.

It is found experimentally that all bosons have integer spin, $s = 0, 1, 2, \dots$, whereas all fermions have half-odd-integer spin, $^\dagger s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$. This connection often lets one decide quickly whether a given particle is a fermion or boson. For example, electrons, protons, and neutrons all have spin half, so have to be fermions; photons have spin 1, so have to be bosons. We will describe several of the dramatic differences between bosons and fermions in Chapter 13. Here we will just describe how the requirement (10.16) implies that fermions obey the Pauli exclusion principle.

*The proof that (10.15) and (10.16) are the only two possibilities is actually quite simple, though it requires a little more knowledge of quantum mechanics than we have yet developed. It is one of the fundamental postulates of quantum mechanics that if two wave functions represent the same physical state, one must be a constant multiple of the other. Therefore, in our case $\psi(2, 1) = k\psi(1, 2)$. Interchanging the particles again, we find that $\psi(1, 2) = k\psi(2, 1) = k^2\psi(1, 2)$, which implies that $k^2 = 1$ or $k = \pm 1$.

[†]In relativistic quantum field theory, one can in fact *prove* this connection.

Satyendranath Bose

(1894–1974, Indian)



Bose was born and educated in Calcutta, India. In a paper written in 1924 he derived the Planck formula for blackbody radiation by treating the photons as what we would now call bosons. This paper drew the attention of Einstein and secured an invitation for Bose to visit Europe, where he met Einstein, de Broglie, Born, and others. Einstein extended Bose's ideas, and the rules that govern bosons are now called Bose–Einstein statistics. We will see some of the dramatic consequences of these ideas in Chapter 13.

Consider a two-particle wave function that happens to be a simple product

$$\psi(1, 2) = \phi(1)\chi(2) \quad (10.17)$$

First, suppose the two particles concerned are nonidentical, an electron and a proton, for instance. Then the wave function (10.17) represents a state in which the electron occupies the state ϕ and the proton occupies the state χ . The function $\psi(2, 1) = \phi(2)\chi(1)$ represents the completely distinct state with the proton in state ϕ and the electron in state χ . Suppose, however, the two particles are identical fermions (two electrons, for example). In this case, their wave function must satisfy the antisymmetry requirement (10.16), which (10.17) does not (unless one of the functions ϕ or χ is identically zero). The only way to reconcile (10.17) with (10.16) is to use the antisymmetric combination

$$\psi(1, 2) = \phi(1)\chi(2) - \chi(1)\phi(2) \quad (10.18)$$

[Notice that this automatically satisfies $\psi(2, 1) = -\psi(1, 2)$. Note also that as it stands, this wave function is generally not normalized; this requirement is easily taken care of, but need not concern us here.] A wave function of the form (10.18) represents two identical fermions, one of which is in state ϕ and one in state χ (though we can't say which is which). Notice that this actually makes good sense: We can view (10.18) as an equal mixture of two states, one with particle 1 in state ϕ and particle 2 in state χ and the other with the two particles reversed. Given the indistinguishability of the two particles, this is a very natural compromise.

The “antisymmetrized” wave function (10.18) is the only way to construct a state of two identical fermions with one in the state ϕ and one in the state χ . But if $\phi = \chi$, then (10.18) is identically zero. Therefore, there is no way to construct a state in which two identical fermions occupy the same one-particle state, and this is the Pauli principle.

If our two identical particles were bosons, then the same argument shows that the wave function with one particle in the state ϕ and one in the state χ must be the “symmetrized” combination

$$\psi(1, 2) = \phi(1)\chi(2) + \chi(1)\phi(2) \quad (10.19)$$

which gives no trouble if $\phi = \chi$. Thus, two identical bosons *can* occupy the same one-particle state, and bosons do not have to satisfy the Pauli principle. In fact, as we will see in Chapter 13, while two identical fermions cannot occupy the same state, there is a sense in which identical bosons actually *prefer* to occupy the same state.

10.6 Ground States of the First Few Elements

Let us return to the consequences of the Pauli principle for multielectron atoms. To determine the ground state of an atom, we have only to assign its Z electrons to the lowest individual energy levels consistent with the Pauli principle (that no two electrons occupy the same quantum state). In this section we use this procedure to find the ground states of the lightest few atoms, starting with hydrogen ($Z = 1$) and going as far as sodium ($Z = 11$).

The ground state of hydrogen has its one electron in the $1s$ level, with its spin pointing either way. The energy is $E = -E_R = -13.6$ eV, which means

that the energy needed to remove the electron — the **ionization energy** — is 13.6 eV.

Moving on to helium, we already saw that the ground state has both electrons in the $1s$ level, with their spins antiparallel. Because of the greater nuclear charge ($Z = 2$), the $1s$ level of helium is much lower in energy than that of hydrogen. If we write the energy of either electron as $-Z_{\text{eff}}^2 E_R$, then Z_{eff} will not be equal to the full nuclear charge, 2, since each electron is screened by the other. Nevertheless, Z_{eff} should be appreciably more than 1 — perhaps around 1.5. Thus, we would expect that helium should be significantly more tightly bound than hydrogen. This prediction is well borne out by experiment. The first ionization energy of helium (the energy to remove one electron) is found to be 24.6 eV, nearly twice that of hydrogen; since the ionization energy is proportional to Z_{eff}^2 , this implies that Z_{eff} is close to $\sqrt{2} \approx 1.4$.

Another measure of an atom's stability is its first excitation energy, the energy to lift it to its first excited state: In both H and He this involves lifting one electron from the $1s$ to the $2s$ level. In helium this should require a larger energy by a factor of roughly Z_{eff}^2 , the same ratio as for the ionization energies. This, too, is confirmed by experiment: The first excitation energy of He is 19.8 eV, compared to 10.2 eV in H.

The ionization and excitation energies of an atom are important indicators of the atom's stability. On both of these counts, helium is about twice as stable as hydrogen. In fact, helium has the largest ionization and excitation energies of *any* atom. Since high stability tends to imply low chemical activity, we might guess that helium should be chemically inactive; and this proves to be the case. Helium is one of the six **noble**, or **inert**, **gases**, which show almost no chemical activity at all, form no really stable compounds, and can bind together into liquid or solid form only at relatively low temperatures.

Another important difference between the hydrogen and helium atoms concerns their sizes. We have seen that the wave functions of a hydrogen-like ion are scaled inward by a factor of $1/Z$, compared to the corresponding wave functions of hydrogen. Therefore, the radius of the $1s$ wave function of helium should be about $1/Z_{\text{eff}}$ times that of hydrogen, and the He atom should therefore be roughly two-thirds the size of the H atom. This prediction also is correct. The precise value of the atomic radius depends on how one chooses to define it, but representative values are 0.08 nm for H and 0.05 nm for He.

The differences in energy and radius between hydrogen and helium reflect the larger nuclear charge ($Z = 2$) of helium. When we consider the lithium atom ($Z = 3$), we encounter a new kind of difference, due to the Pauli exclusion principle. Let us consider first an electron in the $1s$ level of Li. Because of the greater nuclear charge, this $1s$ electron is more tightly bound and concentrated at a smaller radius than a corresponding electron in either He or H. However, the Pauli principle allows only two of lithium's three electrons to occupy the $1s$ level; the third electron must occupy the $2s$ level and is much less tightly bound. In fact, we can easily estimate the binding energy of this outermost electron. Because it is outside the two other electrons, it sees an effective charge of order $Z_{\text{eff}} = 1$, about the same as for the one electron in hydrogen. Therefore, since it is in the $n = 2$ level, it should have about the same ionization energy as an $n = 2$ electron in hydrogen, 3.4 eV. This estimate agrees reasonably with lithium's observed ionization energy of 5.4 eV. (That the actual value, 5.4 eV, is a bit larger than our estimate of 3.4 eV shows that the outer electron is not perfectly shielded by the inner two and sees an effective charge somewhat greater than $Z_{\text{eff}} = 1$.) This ionization energy is the fifth smallest of any stable atom and means that the lithium atom can easily lose its

outermost electron. This is the main reason why lithium is so chemically active, as we describe in Section 12.2.

Because the outer electron of lithium is in the $n = 2$ level, the Li atom should have a much larger radius than either He or H. This prediction is confirmed by the data in Table 10.1, which shows the ionization energies and radii of the first four atoms, ${}^1\text{H}$, ${}^2\text{He}$, ${}^3\text{Li}$, and ${}^4\text{Be}$. (When convenient, we indicate the atomic number, Z , by a *subscript* on the left of the atomic symbol — not to be confused with the mass number, A , which is sometimes shown as a *superscript* on the left.)

TABLE 10.1

Ionization energies and radii of the first four atoms. Atomic numbers Z are shown as subscripts on the left of chemical symbols. The energy levels are not to scale, since corresponding levels get deeper as Z increases.

	${}^1\text{H}$	${}^2\text{He}$	${}^3\text{Li}$	${}^4\text{Be}$
Ionization energy (eV):	13.6	24.6	5.4	9.3
Radius (nm):	0.08	0.05	0.20	0.14
Occupancy of energy levels:	$2s$ ——— $1s$ \uparrow	$2s$ ——— $1s$ $\uparrow\downarrow$	$2s$ \uparrow $1s$ $\uparrow\downarrow$	$2s$ $\uparrow\downarrow$ $1s$ $\uparrow\downarrow$

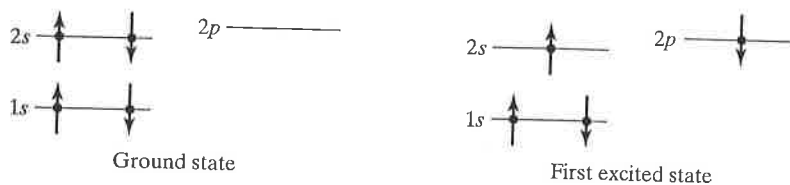
In beryllium ($Z = 4$) the fourth electron can join the third electron in the $2s$ level, provided that their spins are antiparallel. Because of the larger nuclear charge, this level is more tightly bound and its radius smaller than in ${}^3\text{Li}$. Therefore, the ${}^4\text{Be}$ atom should have a larger ionization energy and a smaller radius, as the data in Table 10.1 confirm.

To some small extent, the ${}^4\text{Be}$ atom with its filled $2s$ level is similar to the ${}^2\text{He}$ atom with its filled $1s$ level. But the differences are more important than the similarities. In particular, the ${}^2\text{He}$ atom is not only hard to ionize, it is also hard to excite, 19.8 eV being needed to lift one of the electrons from the $1s$ to the $2s$ level. Excitation of the ${}^4\text{Be}$ atom requires only that one of the $2s$ electrons be lifted to the nearby $2p$ level, just 2.7 eV higher (see Fig. 10.7). This means that one of the electrons in Be can easily move to the higher level. As we will see in Chapter 12 (see especially Problem 12.30), this allows Be to bond to other atoms. For this reason, Be, unlike He, is chemically active and forms a number of compounds.

After beryllium (${}^4\text{Be}$) comes boron (${}^5\text{B}$). The first four electrons of ${}^5\text{B}$ go into the $1s$ and $2s$ levels, just as with ${}^4\text{Be}$. But as required by the Pauli principle, the last electron of ${}^5\text{B}$ must occupy the $2p$ level. Therefore, in moving from ${}^4\text{Be}$ to ${}^5\text{B}$, we see two competing effects: The increase in Z causes any given

FIGURE 10.7

Excitation of beryllium ($Z = 4$) requires only 2.7 eV to lift one of the $2s$ electrons to the nearby $2p$ level. In the excited state the spins of the $2s$ and $2p$ electrons can point either way.



level to be somewhat more tightly bound, but the final electron has to occupy a level that is slightly higher and hence somewhat less tightly bound. As far as ionization energy is concerned, the second effect wins. The ionization energy of ${}_5\text{B}$ is 8.3 eV, just a little less than the 9.3 eV of ${}_4\text{Be}$. On the other hand, the radius of ${}_5\text{B}$ is less than that of ${}_4\text{Be}$ and continues the trend of shrinking radii with increasing Z . In neither case is the difference large.

The six elements after ${}_4\text{Be}$ are

Element:	boron	carbon	nitrogen	oxygen	fluorine	neon
Symbol:	${}_5\text{B}$	${}_6\text{C}$	${}_7\text{N}$	${}_8\text{O}$	${}_9\text{F}$	${}_{10}\text{Ne}$

In all of these atoms the first four electrons fill the $1s$ and $2s$ levels. Since the $2p$ level can hold six electrons, the remaining electrons all go into the $2p$ level. Thus, as we move from ${}_5\text{B}$ to ${}_{10}\text{Ne}$, the additional electron of each succeeding atom goes into the same level, and the main differences should be due to the increasing nuclear charge Z ; in particular, the ionization energy should increase and the radius should decrease. These trends show up clearly in Fig. 10.8, in which the ionization energies and atomic radii are plotted as functions of Z for all the first 11 atoms. With one small exception, the two graphs change steadily in the expected directions (ionization energy increasing, radius decreasing) as Z increases from 5 to 10. The one exception is the small drop in ionization energy as one moves from ${}_7\text{N}$ to ${}_8\text{O}$; we will return to this anomaly later.

When we reach ${}_{10}\text{Ne}$, the $2p$ level has its full allotment of six electrons. Therefore, when we move on to sodium, ${}_{11}\text{Na}$, the last electron must go into the next, and much higher, level — the $3s$ level. This reverses all of the trends set by the last eight atoms: The ionization energy drops abruptly, and the radius increases abruptly, as is shown clearly in Fig. 10.8.

Both of the graphs in Fig. 10.8 suggest a parallel between ${}_3\text{Li}$ and ${}_{11}\text{Na}$. Both atoms have unusually low ionization energies and unusually large radii. The low ionization energies mean that both atoms can easily lose one electron. This allows lithium and sodium to combine with other atoms to form many different chemical compounds and is the reason why both atoms are chemically so active, as we describe in Chapter 12.

The similarity between ${}_3\text{Li}$ and ${}_{11}\text{Na}$ is an example of the *periodic* behavior of the elements. As we consider elements with successively higher Z , chemical similarities recur at certain regular, or periodic, intervals. Another example of this periodicity is the pair of elements ${}_2\text{He}$ and ${}_{10}\text{Ne}$. Both are very stable (large ionization and excitation energies) and very small in size. In Chapter 8 we mentioned that the word “shell” is often used for a group of

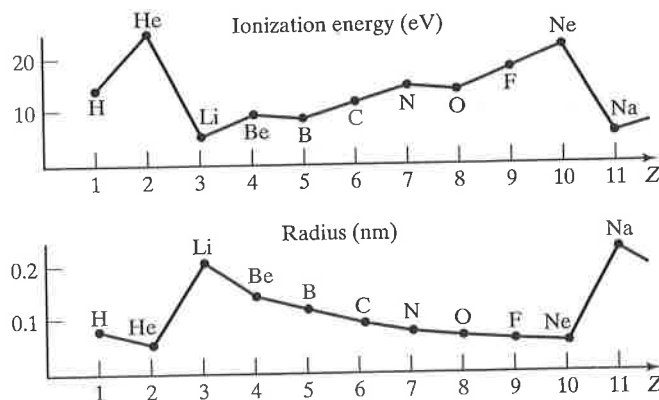


FIGURE 10.8
The ionization energies and atomic radii of the first 11 elements.

energy levels that are close to one another and well separated from any others. From the first graph in Fig. 10.8, it is clear that the $1s$ level should be considered as one shell by itself, and $2s$ and $2p$ together as another. For this reason, helium and neon are called closed-shell atoms. We will see that there are six closed-shell atoms in all and that they are the six noble gases. In the same way, lithium and sodium can be described as being **closed-shell-plus-one** and are the first of six such elements, called the **alkali metals**.

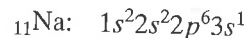
Just before the stable $_{10}\text{Ne}$ is fluorine, $_{9}\text{F}$. The ionization energy of fluorine is 17.4 eV, which is the third largest ionization energy of any atom. One might, therefore, imagine that fluorine would be chemically inactive, but such is definitely not the case. Fluorine is one of the most active of all the elements. The reason for this activity is that the fluorine atom is **closed-shell-minus-one** since its $2p$ level is one short of the full complement of six electrons. Because of the large nuclear charge, the $2p$ level is very well bound (as the large ionization energy testifies). In fact, the $2p$ level of F is so well bound that it can bind an extra, sixth electron. That is, the negative ion, F^- , is stable, with the extra electron just filling the $2p$ level. The tendency of an atom to bind an extra electron is measured by its **electron affinity**. This is defined as the energy released when the atom captures an extra electron and forms a negative ion (or, equivalently, the energy needed to remove one electron from the negative ion). The electron affinity of fluorine is 3.4 eV, the third largest for any element. As we discuss in Chapter 12, it is because of its ability to bind an extra electron that fluorine is so active.

10.7 The Remaining Elements

In Section 10.6 we examined the ground states of the first 11 elements. In this section we sketch a similar analysis of some of the remaining 90 or so elements. This will emphasize what was already becoming apparent. Because of the Pauli principle, the properties of atoms do not vary smoothly and uniformly as functions of Z . Rather, as we examine atoms with successively more electrons, their properties vary more or less smoothly as long as each extra electron can be accommodated in the same shell; but each time a shell is filled and a new shell comes into play, there is an abrupt change in the properties, reversing the previous smooth trends. As we saw in Section 10.6, this leads to the periodic occurrence of atoms with similar physical and chemical properties.

To find the ground state of an atom, we must assign the Z electrons to the lowest levels consistent with the Pauli principle. For $_{1}\text{H}$ and $_{2}\text{He}$ the electrons go into the $1s$ level. For $_{3}\text{Li}$ through $_{10}\text{Ne}$, the $1s$ level is full, and the outer, or **valence**, electrons go into the $2s$ and then $2p$ levels. Similarly, when we move on to the elements 11 through 18 (sodium through argon), the $1s$, $2s$, and $2p$ levels are all full, and the valence electrons go into the $3s$ and then $3p$ levels.

Perhaps the most descriptive way to show the assignment of electrons to energy levels is with energy-level diagrams like those in Fig. 10.7. Unfortunately, these diagrams become increasingly cumbersome as we discuss atoms with more electrons. A more compact way to show the same information is to give the **electron configuration**, which is just a list of the occupied levels, each with a superscript to indicate the number of electrons in it. For example, the electron configuration of the sodium ground state is



With this notation, the ground states of the first 18 elements are as shown in Table 10.2.

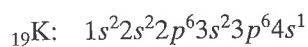
TABLE 10.2

Electron configurations of the ground states of the first 18 elements.

First Shell	Second Shell	Third Shell
${}_1\text{H} : 1s^1$	${}_3\text{Li} : 1s^2 2s^1$	${}_{11}\text{Na} : 1s^2 2s^2 2p^6 3s^1$
${}_2\text{He} : 1s^2$	${}_4\text{Be} : 1s^2 2s^2$	${}_{12}\text{Mg} : 1s^2 2s^2 2p^6 3s^2$
	${}_5\text{B} : 1s^2 2s^2 2p^1$	${}_{13}\text{Al} : 1s^2 2s^2 2p^6 3s^2 3p^1$
	${}_6\text{C} : 1s^2 2s^2 2p^2$	${}_{14}\text{Si} : 1s^2 2s^2 2p^6 3s^2 3p^2$
	${}_7\text{N} : 1s^2 2s^2 2p^3$	${}_{15}\text{P} : 1s^2 2s^2 2p^6 3s^2 3p^3$
	${}_8\text{O} : 1s^2 2s^2 2p^4$	${}_{16}\text{S} : 1s^2 2s^2 2p^6 3s^2 3p^4$
	${}_9\text{F} : 1s^2 2s^2 2p^5$	${}_{17}\text{Cl} : 1s^2 2s^2 2p^6 3s^2 3p^5$
	${}_{10}\text{Ne} : 1s^2 2s^2 2p^6$	${}_{18}\text{Ar} : 1s^2 2s^2 2p^6 3s^2 3p^6$

The properties of elements 11 to 18 closely parallel those of elements 3 to 10. As we have already noted, ${}_{11}\text{Na}$ and ${}_3\text{Li}$ are both easily ionized and are chemically very active. As one moves from $Z = 11$ to $Z = 18$ and the $3s$ and $3p$ levels fill, the ionization energies increase (with two small exceptions) and the atomic radii decrease, just as occurred between $Z = 3$ and $Z = 10$. At $Z = 18$ the $3p$ level is completely full and ${}_{18}\text{Ar}$, like ${}_{10}\text{Ne}$, is very stable and chemically inert. Just before ${}_{18}\text{Ar}$ is chlorine (${}_{17}\text{Cl}$), which, like ${}_9\text{F}$, is able to accept an extra electron into the one vacancy in its outer p level and is therefore chemically active.

When we move beyond ${}_{18}\text{Ar}$ to ${}_{19}\text{K}$ (potassium), the story becomes more complicated. One might expect that the next level occupied would be the $3d$ level. In fact, however, the tendency for levels with low angular momentum (the “penetrating orbits”) to have lower energy causes the $4s$ level to be slightly lower than the $3d$, as discussed in Section 10.3. Therefore, the configuration of the ground state of ${}_{19}\text{K}$ is



The order in which the energy levels fill is shown in Fig. 10.9. In this picture we have also shown the grouping of the energy levels into **shells** containing levels that are close to one another but well separated from other levels. (Note that in this context an individual level within a shell is sometimes called a **subshell**.) We see, for example, that the $3s$ and $3p$ levels are close together, but that the gap from $3p$ to $4s$ is large. Thus $3s$ and $3p$ form a shell by themselves, just like $2s$ and $2p$. Therefore, ${}_{18}\text{Ar}$ is a closed-shell atom, like ${}_{10}\text{Ne}$ and ${}_2\text{He}$, and is the third of the noble gases. The next element, potassium (${}_{19}\text{K}$), is a *closed-shell-plus-one* atom, with low ionization energy, and is one of the alkali metals, similar to its two predecessors, ${}_{11}\text{Na}$ and ${}_3\text{Li}$.

It can be seen in Fig. 10.9 that, as it happens, the lowest level in each shell is always an s level and the highest is a p level (except in the first shell, which has only the $1s$ level). Thus all the closed-shell-plus-one atoms have a single s electron outside a closed-shell core; all closed-shell-minus-one atoms (often called **halogens**) have one vacancy, or *hole*, in the p level of an otherwise filled shell.

FIGURE 10.9

Schematic diagram showing the order in which levels are occupied as one considers atoms with successively higher Z . This is not the energy-level diagram for any one atom; it just gives the order in which levels are occupied as Z increases. The shaded rectangles indicate the groupings of nearby levels into energy shells. The figure to the right of each level or shell gives the number of electrons that can be accommodated; the figures on the far right are the atomic numbers Z of the closed-shell atoms. Note that some levels are too close to be ordered unambiguously; for example, $5d$ is partially occupied before $4f$, but $4f$ is completely filled before $5d$. The exact sequence of occupancy can be found from the electron configurations shown inside the back cover.

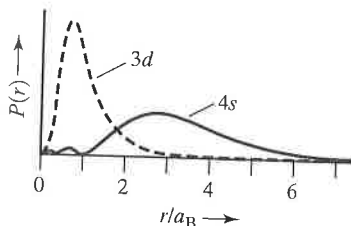
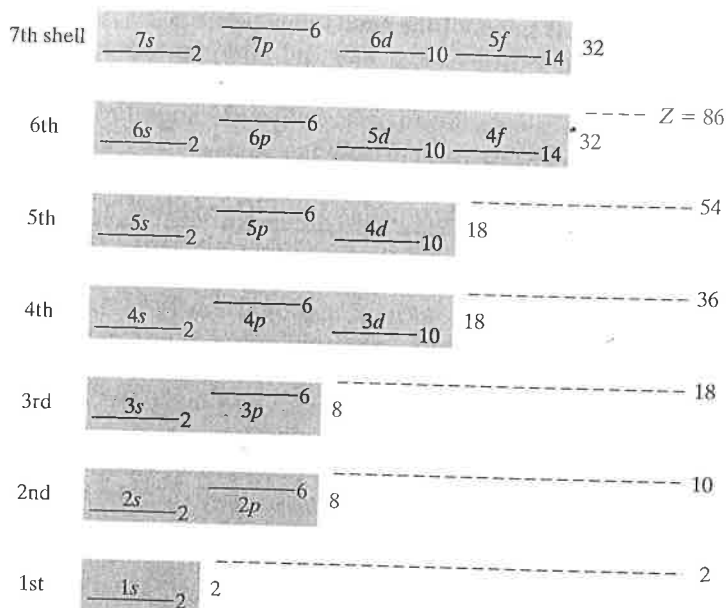


FIGURE 10.10

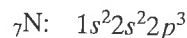
Typical radial probability distributions for a $3d$ and $4s$ electron in the transition elements $_{21}\text{Sc}$ through $_{30}\text{Zn}$. Note how the $4s$ distribution peaks more than four times farther out than the $3d$. For this reason, it is the $4s$ electrons that determine the chemical properties of the transition metals.

After $_{19}\text{K}$ comes calcium ($_{20}\text{Ca}$), whose $4s$ level is full. Then with scandium ($_{21}\text{Sc}$), the $3d$ level begins to fill. Since any d level can hold 10 electrons, the filling of the $3d$ level takes us from $_{21}\text{Sc}$ through $_{30}\text{Zn}$ (zinc). These 10 elements are called **transition metals** and are alike in several ways. This is because the $3d$ wave functions peak at a much smaller radius than the $4s$ functions (Fig. 10.10). Thus, although it is the $3d$ level that is filling in this sequence of elements, it is the $4s$ electrons that are farthest out. Since it is the outer electrons that can interact with other atoms, all of the transition metals from $_{21}\text{Sc}$ to $_{30}\text{Zn}$ have similar chemical properties.

Once the $3d$ level is full at $_{30}\text{Zn}$, the $4p$ level starts to fill, and the sequence of six elements from $_{31}\text{Ga}$ (gallium) to $_{36}\text{Kr}$ (krypton) is analogous to the sequences from $_{13}\text{Al}$ to $_{18}\text{Ar}$ and from $_{5}\text{B}$ to $_{10}\text{Ne}$, in which the $3p$ and $2p$ levels were filling. In particular, $_{36}\text{Kr}$ is a closed-shell atom and is the fourth of the noble gases.

Beyond $_{36}\text{Kr}$, the fifth, sixth, and, finally, seventh shells are occupied, but since there are no really important new features, we need not go into details. The periodic recurrence of similar atomic properties can be clearly seen in plots of a variety of properties as functions of Z . In Fig. 10.11 we show ionization energies, atomic radii, and electron affinities for $Z = 1$ through 86. (The first two graphs are extensions of those shown in Fig. 10.8.) Notice how the ionization energies have pronounced maxima at the closed-shell noble gases and minima at the closed-shell-plus-one alkali metals. The ionization energies have smaller maxima at several other points, and most of these are easily explained. For example, the small peak at $_{4}\text{Be}$ is because the $2s$ level (or subshell) is filled; that at $_{30}\text{Zn}$ is because the $3d$ level is filled.

The small peak in the ionization energy at $_{7}\text{N}$ is a little harder to explain and is due to a subtle but important change when we move from $_{7}\text{N}$ to $_{8}\text{O}$. The configuration of nitrogen is



with three electrons in the $2p$ level. The six distinct quantum states of the $2p$ level arise from the three possible wave functions (the orbitals $2p_x$, $2p_y$, and

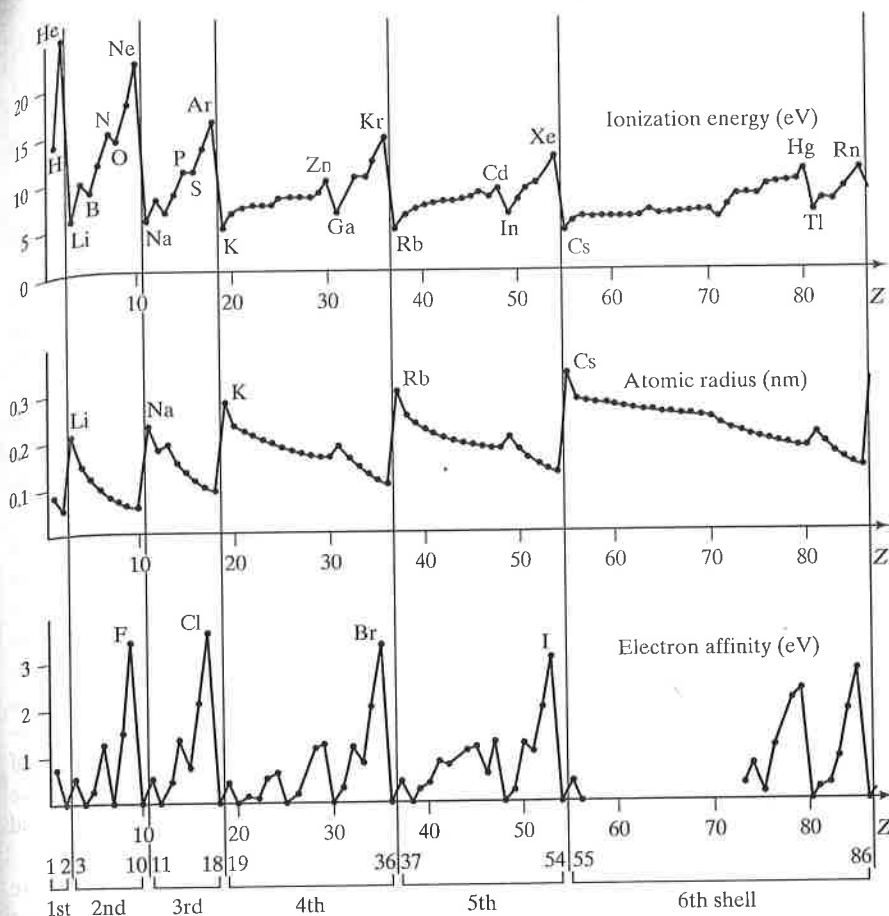


FIGURE 10.11

Ionization energy, atomic radius, and electron affinity as functions of atomic number Z . The vertical lines separate complete shells. The electron affinities for elements 57 through 72 have not been measured.

$2p_z$, shown in Fig. 8.21*) each with two possible spin orientations. Therefore, the three outer electrons in nitrogen can occupy three distinct orbitals. This arrangement keeps the electrons well separated, reducing their electrostatic repulsion, and makes the nitrogen atom relatively stable, with a comparatively large ionization energy. In oxygen the fourth $2p$ electron must occupy the same orbital as one of the others (with opposite spin, of course). Because the distributions of these two electrons overlap strongly, their electrostatic repulsion is relatively large, and the ionization energy of oxygen is a little less. It is for this reason that the plot of ionization energy in Fig. 10.11 has the small drop after ${}^7\text{N}$. For the same reason, there is a small drop in ionization energy after ${}^{15}\text{P}$ also visible in Fig. 10.11.

The graph of atomic radius against Z shows the expected trends, with R falling to a minimum at each of the noble gases and jumping abruptly to a maximum at each closed-shell-plus-one atom. The downward slope from ${}_{21}\text{Sc}$ to ${}_{30}\text{Zn}$ is very gentle because the last electrons of these transition elements go into the $3d$ level, which is concentrated at a smaller radius than the occupied $4s$ level. Thus the atomic radius is determined by the $4s$ electrons and changes little from $Z = 21$ to 30 (from 0.21 to 0.15 nm). The even gentler slope from $Z = 57$ to 71 is a similar effect: With these *inner transition* elements, the level

*One can arrive at the same conclusion using the wave functions with $m = 1, 0, -1$, but the argument is a little more complicated.

being filled is the $4f$ level, which has *much* smaller radius than the occupied $6s$ level; thus the atomic radius is almost completely determined by the $6s$ radius and changes very little (from 0.27 to 0.22 nm).

The third graph in Fig. 10.11 shows the electron affinity. As expected, this shows sharp maxima at the closed-shell-minus-one atoms (the halogens, ${}^9\text{F}$, ${}^{17}\text{Cl}$, etc.) and drops abruptly to zero at the closed shells (${}^2\text{He}$, ${}^{10}\text{Ne}$, etc.). It is also zero at those atoms with closed subshells, such as ${}^4\text{Be}(1s^2 2s^2)$ and ${}^{12}\text{Mg}(1s^2 2s^2 2p^6 3s^2)$. Some atoms with *half-filled* subshells also have zero electron affinity. For example, an eighth electron in ${}^7\text{N}$ would have to occupy the same orbital, $2p_x$, $2p_y$, or $2p_z$, as one of the other $2p$ electrons, and the resulting Coulomb repulsion would raise its energy so high that it would not be bound.

To conclude this section, we mention one more atomic property that can be predicted from our knowledge of the electron states — the angular momentum of the whole atom. For many atoms, calculation of the total angular momentum is difficult and well beyond our present discussion. However, there are several cases that are quite straightforward. This is because the total angular momentum of all the electrons in any filled level is zero. To understand this useful result, we have only to note that in a filled level there are equal numbers of electrons with spin up and spin down; therefore, the total spin $\sum \mathbf{S}$ is certainly zero. Further, for each electron with a given value of L_z , there is another with exactly the opposite value (since all the values $m = l, l-1, \dots, -l$ are occupied); therefore, the total orbital angular momentum $\sum \mathbf{L}$ is also zero. It follows that the total angular momentum of any closed-shell or closed-subshell atom must be zero. For example, the total angular momenta of ${}^2\text{He}$ and ${}^{10}\text{Ne}$, and of ${}^4\text{Be}$ and ${}^{30}\text{Zn}$, should be and are zero.

The total angular momenta of the closed-shell-plus-one alkali atoms are also easy to predict. These atoms all contain various filled levels, with zero total angular momenta, plus a single electron in an s level ($l = 0$). Therefore, the total angular momentum of any alkali atom (${}^3\text{Li}$, ${}^{11}\text{Na}$, etc.) is equal to the spin angular momentum ($s = \frac{1}{2}$) of its one valence electron.

One can also predict the angular momentum of the closed-shell-minus-one atoms. These all consist of filled levels, with zero total angular momentum, plus a p level containing five of its six possible electrons. We know that the *addition of one more p electron* (with $l = 1$) would produce a filled level, with total $l = 0$. The addition of one vector to another can give zero only if the two vectors have the same magnitude. It follows that the total orbital angular momentum of the original five electrons must also have total $l = 1$. A similar argument shows that the total spin of the five electrons must be $s = \frac{1}{2}$. Therefore, the closed-shell-minus-one atoms must have total $l = 1$ and $s = \frac{1}{2}$, and this is what is observed. The resulting *total* angular momentum depends on the relative orientation of \mathbf{L} and \mathbf{S} ; this, also, can be predicted, but would take us too far afield at present.

10.8 The Periodic Table

The periodic recurrence of atoms with similar properties had been noticed long before the discovery of quantum mechanics and the understanding of atomic structure. In 1869, a German chemist, Lothar Meyer, had plotted several different properties of the elements as functions of their atomic masses. In particular, he had noticed that his plot of atomic volume (which was very

similar to the plot of atomic radius in Fig. 10.11) was divided by five sharp peaks into six distinct sections, or periods, corresponding (as we now know) to the successive filling of the first six shells.

In the same year, 1869, the Russian chemist Dmitri Mendeleev had proposed his **periodic table**, an ingenious array in which the elements are arranged so as to highlight their periodic properties. In most modern periodic tables, the elements are arranged in order of increasing atomic number, placed from left to right in rows, with a new row starting each time a shell is closed. Within each row, the elements are placed so that atoms with similar properties are contained in the same vertical column of the table.

One popular arrangement of the entire table is shown in Fig. 10.12. The horizontal rows, or **periods**, contain different numbers of elements, corresponding to the different capacities of the various shells. The first period contains just two elements, H and He; the next two periods contain eight elements each; and the next two contain 18 each. The sixth period contains 32 elements, from $Z = 55$ to 86, but to save space, the part of this period from $Z = 57$ to 71 is usually detached and arranged in a separate row below. For the same reason, the corresponding elements (from $Z = 89$ to 103) in the seventh period are placed in a second additional row.

The vertical columns, or **groups**, contain elements with corresponding arrangements of their valence electrons. The leftmost group, often called group I, contains the closed-shell-plus-one atoms, each with a single s electron outside a closed core. The next column, group II, has the closed-shell-plus-two atoms, each with two s electrons outside a closed core. On the right side of the table are the six columns, groups III to VIII, whose atoms have a filled or partially

Dmitri Mendeleev (1834–1907, Russian)



Several chemists had recognized that when arranged by atomic mass, the elements show periodic behavior, but the Russian chemist Mendeleev was unique in his recognition that certain elements were clearly missing from this scheme. When three of the missing elements were discovered with exactly the properties he had predicted, his periodic table gained international acceptance.

	Group I		Group II		Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group VIII																
Period 1	1	H																	2	He																
2	3	Li	4	Be																																
3	11	Na	12	Mg																																
4	19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
5	37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
6	55	Cs	56	Ba	57–71	*	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn
7	87	Fr	88	Ra	89–103	†	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt																		

Inner transition elements																														
*Lanthanides	57	La	58	Ce	59	Pr	60	Nd	61	Pm	62	Sm	63	Eu	64	Gd	65	Tb	66	Dy	67	Ho	68	Er	69	Tm	70	Yb	71	Lu
†Actinides	89	Ac	90	Th	91	Pa	92	U	93	Np	94	Pu	95	Am	96	Cm	97	Bk	98	Cf	99	Es	100	Fm	101	Md	102	No	103	Lr

FIGURE 10.12

The periodic table of elements, showing atomic numbers and chemical symbols. Each horizontal row is called a period and each vertical column, a group. Our labeling of the groups is one of several schemes in common use. To save space, the inner transition elements have been detached from the main table at the positions indicated by the asterisk and dagger. Elements shown in color are "artificial" in the sense that they do not occur in appreciable amounts on earth.

toward the beginning and not at the end of each period. In other words, metals should be on the left of the periodic table, exactly as is observed to be the case.

The periodic table is a convenient way to tabulate many different atomic properties. A large table (turned on its side to fit the page better) can be found inside the back cover and includes the atomic number, atomic mass, name, symbol, and electron configuration of every element. With a little use, you will quickly learn to locate elements in the table. If you have any difficulty, you can first find the atomic number, Z , in one of the alphabetical lists of elements in Appendix C and then locate the element itself in the periodic table.

10.9 Excited States of Atoms*

*This section could be omitted without significant loss of continuity.

So far in this chapter, we have discussed only the ground states of multielectron atoms. In this section we give a brief introduction to the excited states. Recall that in the atomic ground state the Z electrons occupy the lowest possible levels consistent with the Pauli principle. To obtain the excited states, we must simply raise one or more of the electrons to higher levels, as illustrated in Fig. 10.15. This picture shows the energy levels of any one electron in the sodium atom ($Z = 11$). The 11 dots show the 11 electrons as they are distributed in the atom's ground state. We obtain the excited states by moving electrons to higher levels; in the picture we have indicated five possibilities — for example, the arrow labeled 1 represents an excitation in which the outer valence electron is raised from the $3s$ to the $3p$ level.

Even for an atom as simple as sodium, there is an enormous number of different excited states, corresponding to the many possible arrangements of the Z electrons among the numerous different levels. Fortunately, not all of them are equally important: States in which several electrons have been raised to higher levels are usually less important than those involving a single electron. For example, when an atom absorbs light, the most probable excitations involve moving just a single electron from its ground-state position (as with any one of the arrows in Fig. 10.15). Here we will confine attention to these one-electron excitations.

It is clear in Fig. 10.15 that the excitations that require the least energy are those that involve moving a valence electron to a higher level (arrows 1 or 2,

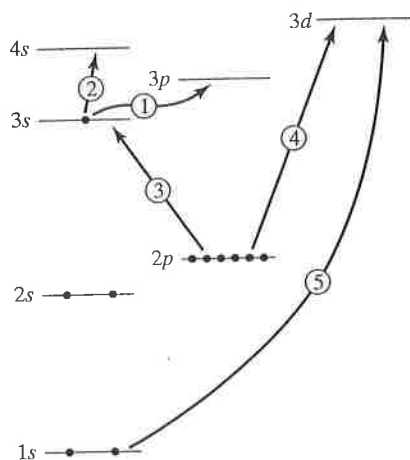


FIGURE 10.15

The energy levels for any one electron in sodium. In the ground state of the atom, the 11 electrons are distributed as shown by the dots. The five arrows indicate five ways in which electrons could be excited to higher levels. (Although the ordering of the levels shown here is correct, they are not drawn to scale; in particular, the $n = 1$ and $n = 2$ levels are much deeper than shown.)

for example). Since the energy required to excite a valence electron is almost always a few eV, which is the energy of a visible (or nearly visible) photon, these excitations are often called **optical excitations**. Because these are the lowest excitations, a photon (or other projectile) with just enough energy to produce optical excitations cannot produce any other kinds of excitation. Thus it is a simplifying feature of the optical excitations that they often occur in a context where no other kinds of excitation are possible.

If we increase the energy of the photons (or other projectiles) colliding with an atom, they may be able to excite some of the inner electrons (arrows 3, 4, and 5 in Fig. 10.15). It is clear from Fig. 10.15 that the highest-energy excitations are those that involve the innermost, $1s$, electrons. The most striking thing about these is the very large energies involved. We saw in (10.9) that the energy of the $1s$ level is

$$E_{1s} \approx -Z^2 E_R$$

For sodium ($Z = 11$) this is more than 1 keV, and for a heavy atom such as uranium ($Z = 92$) it is more than 100 keV. Because of the Pauli principle, it is impossible to excite a $1s$ electron to any level that is already full. (Thus, in Fig. 10.15 one cannot excite a $1s$ electron to either of the $n = 2$ levels.) Therefore a $1s$ electron can be excited only by lifting it all the way to the valence level or higher. Since the binding energy of these upper levels is only a few eV, the energy required to excite one of the innermost electrons (in all but the very lightest atoms) is several keV or more, the energy of X-ray photons. For this reason, excitations of the inner electrons are called **X-ray excitations**.

Once a vacancy has been created in an inner shell, any one of the higher electrons can drop down into the vacancy, emitting an X-ray photon as it does so. This is the origin of the X-rays studied by Henry Moseley and described in Section 5.9. The discussion there was based on the Bohr model but depended only on the formula $E_n \approx -Z^2 E_R/n^2$ for the inner energy levels.* Therefore, the results of Section 5.9 carry straight over to a modern quantum treatment and need not be repeated here.

Optical Excitations in Alkali Atoms

To conclude this section, we take a slightly closer look at those excitations involving only the valence electrons — the so-called optical excitations. To simplify the discussion further, we consider only atoms with a single valence electron. These are the closed-shell-plus-one atoms, Li, Na, K, Rb, Cs, Fr, which appear in group I of the periodic table and are called the alkali atoms (or alkali metals, since they all form metals).

In each of the alkali atoms the single valence electron is concentrated outside a core consisting of the nucleus (with charge Ze) and $Z - 1$ electrons, all arranged in spherically symmetric closed shells. The total charge of this core is $+e$, the same as that of the single proton in hydrogen. If the valence electron were entirely outside this core, it would have exactly the same allowed energies as the electron in hydrogen. In reality, the wave function of the valence electron penetrates the core, where the positive charge of the nucleus is less

*Notice that in the discussion of Section 5.9, we took for granted that an electron in one of the levels $n = 2, 3, \dots$ could only drop to the $n = 1$ level after one of the $n = 1$ electrons had been ejected. Thus, we were implicitly assuming the Pauli principle in that discussion.

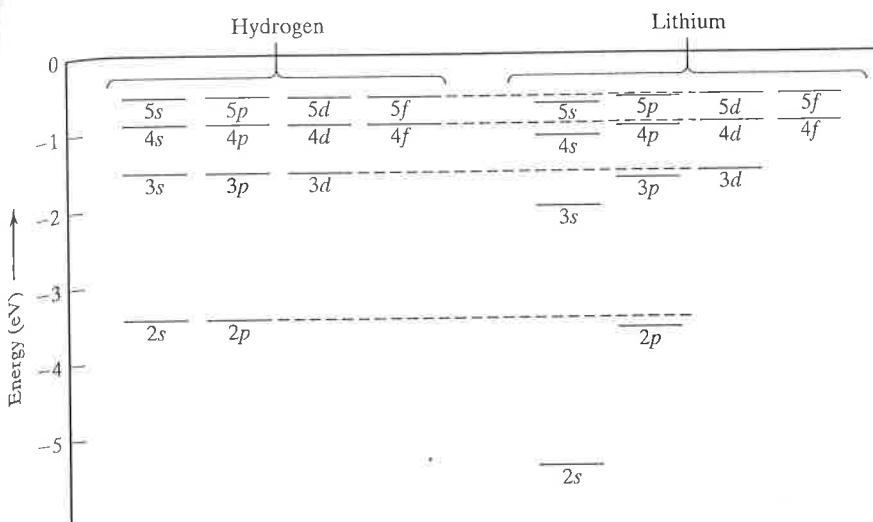


FIGURE 10.16

The energy levels of the H atom compared with the levels of the valence electron in the lithium atom.

shielded and attracts the electron more strongly. Thus all the levels of the valence electron of an alkali atom lie a little lower than the corresponding levels in hydrogen. Since the $l = 0$ states penetrate closest to the nucleus, they are affected the most. For the states of higher l , the wave functions penetrate the core very little and the energies are very close to the corresponding energies in hydrogen (as was illustrated in Example 10.1).

The close relationship between the optical levels of an alkali atom and the levels of hydrogen is illustrated in Fig. 10.16, which shows the levels of the valence electron in lithium ($Z = 3$). In the ground state the valence electron occupies the $2s$ level, which is appreciably lower (by nearly 2 eV) than the $n = 2$ level in hydrogen, as we would expect. The higher s levels shown are all visibly lower than the corresponding levels of hydrogen, although the difference is smaller for the states of higher n , since these are concentrated at larger radii and penetrate the core less. The difference between corresponding p states is much smaller, and for the d and f states the difference cannot be seen on the scale of Fig. 10.16.

The optical levels of the other alkali atoms have the same general behavior as those of lithium, although the lowest level of the valence electron is one shell higher in each successive atom, Na, K, and so on. Thus the lowest level of the valence electron in sodium ($Z = 11$) is the $3s$ level. The next level in Na is the $3p$ level, about 2.1 eV above the ground state. As we see in the following example, the $3p \rightarrow 3s$ transition in Na produces the yellow light characteristic of the sodium-vapor lamps used to light many streets.

Example 10.2

(a) The first excited state of the sodium atom is the $3p$ level, 2.10 eV above the $3s$ level. What is the wavelength of the light emitted in the $3p \rightarrow 3s$ transition? (b) Because of the spin-orbit interaction (Section 9.7) the $3p$ level is actually two levels, 2.1×10^{-3} eV apart (whereas the $3s$ is still just a single level). What is the difference $\Delta\lambda$ between the two wavelengths produced by $3p \rightarrow 3s$ transitions in Na?

(a) The wavelength of a photon with energy $E_\gamma = 2.10 \text{ eV}$ is

$$\begin{aligned}\lambda &= \frac{hc}{E_\gamma} \\ &= \frac{1240 \text{ eV} \cdot \text{nm}}{2.10 \text{ eV}} = 590 \text{ nm}\end{aligned}\quad (10.20)$$

Light with this wavelength is yellow, which is why sodium lamps produce their characteristic yellow glow.

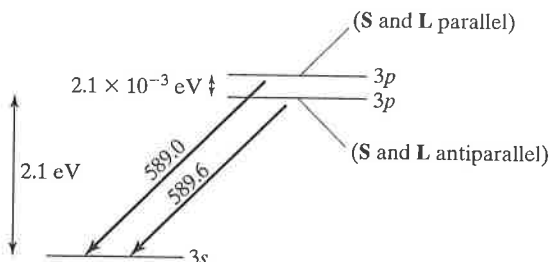
(b) Differentiating (10.20) with respect to E_γ , we find that

$$\begin{aligned}\Delta\lambda &\approx \frac{d\lambda}{dE_\gamma} \Delta E_\gamma = -\frac{hc}{E_\gamma^2} \Delta E_\gamma = -\lambda \frac{\Delta E_\gamma}{E_\gamma} \\ &= -(590 \text{ nm}) \times \frac{2.1 \times 10^{-3}}{2.1} \approx -0.6 \text{ nm}\end{aligned}$$

The actual wavelengths of the two transitions are indicated in Fig. 10.17. It is because of this small “fine structure” splitting that the yellow line of sodium is actually a doublet of two lines, making the sodium spectrum very easy to identify.

FIGURE 10.17

The spin-orbit interaction splits the $3p$ level in Na into two levels, with the states in which **S** and **L** are parallel having slightly higher energy. The wavelengths of the two transitions are shown in nanometers.



CHECKLIST FOR CHAPTER 10

CONCEPT	DETAILS
Independent-particle approx. (IPA)	Each electron moves in the field of the nucleus and the average distribution of the other $Z - 1$ electrons (Sec. 10.2)
IPA potential energy	$U(r) = -Z_{\text{eff}}(r)ke^2/r$ (10.6), where $Z_{\text{eff}}(r) \rightarrow Z$, as $r \rightarrow 0$ and $Z_{\text{eff}}(r) \rightarrow 1$, as $r \rightarrow \infty$
IPA energy levels	See Fig. 10.3
Pauli exclusion principle	No two electrons can occupy the same quantum state (Sec. 10.4)
Bosons and fermions*	Bosons — symmetric multiparticle wave functions (10.15) — do not obey the Pauli principle Fermions — antisymmetric multiparticle wave functions (10.16) — obey the Pauli principle
Electron configuration	List of occupied energy levels, with numbers of electrons shown as superscripts (Sec. 10.7)

Periodic behavior

Shells

Periodic table

Excited states of atoms*

Ionization energy, atomic radius, electron affinity (Fig. 10.11)

Spatial shell = group of levels with similar radii

Energy shell = group of levels with similar energies

Closed-shell atom = noble gas (He, Ne, ...)

Closed-shell-plus-one = alkali metal (Li, Na, ...)

Closed-shell-minus-one = halogen (F, Cl, ...)

Table of the elements highlighting periodic properties (Fig. 10.12)

Optical excitations — valence electrons,

X-ray excitations — inner electrons (Sec. 10.9)

PROBLEMS FOR CHAPTER 10

SECTION 10.2 (The Independent-Particle Approximation)

- 10.1 •• Find the electric field \mathcal{E} at $r = a_B$ in the $1s$ state of a hydrogen atom. Compare with the breakdown field of dry air, about 3×10^6 V/m. [Hint: Use Gauss's law; treat the atomic electron as a static charge distribution with charge density $\rho(r) = -e|\psi(r)|^2$; and use the result of Problem 8.43.]
- 10.2 ••• The IPA potential-energy function $U(\mathbf{r})$ is the potential energy "felt" by an atomic electron in the average field of the other $Z - 1$ electrons plus the nucleus. If one knew the average charge distribution $\rho(\mathbf{r})$ of the $Z - 1$ other electrons, it would be a fairly simple matter to find $U(\mathbf{r})$. The calculation of an accurate distribution $\rho(\mathbf{r})$ is very hard, but it is easy to make a fairly realistic guess. For example, one might guess that $\rho(\mathbf{r})$ is spherically symmetric and given by

$$\rho(r) = \rho_0 e^{-r/R}$$

where R is some sort of mean atomic radius. (a) Given that $\rho(r)$ is the average charge distribution of $Z - 1$ electrons, find ρ_0 in terms of Z , e , and R . (b) Use Gauss's law to find the electric field \mathcal{E} at a point r due to the nucleus and the charge distribution ρ . (c) Verify that as $r \rightarrow 0$ and $r \rightarrow \infty$, \mathcal{E} behaves as required by (10.2) and (10.3). [Hint: The integrals needed in parts (a) and (b) are in Appendix B.]

SECTION 10.3 (The IPA Energy Levels)

- 10.3 • (a) Estimate the energy of the innermost electron of lead. (b) What is its most probable radius? (Appendix C has a list of atomic numbers.)
- 10.4 • Answer the same questions as in Problem 10.3, but for silver.
- 10.5 •• The ground state of sodium ($Z = 11$) has two electrons in the $1s$ level, two in the $2s$, six in the $2p$, and one in the $3s$. Consider an excited state in which the outermost electron has been raised to a $3d$ state (but all of the inner electrons are unchanged). Because

the $3d$ wave function is not very penetrating, you can treat the outer electron as if it were completely outside all the other electrons. (a) In this approximation what is the potential-energy function $U(r)$ felt by the outer electron? (b) In the same approximation, what should be the energy of an electron in a $3d$ state? Compare your answer with the observed value of -1.52 eV. Why is the observed value lower than your estimate?

- 10.6 •• The ground state of lithium ($Z = 3$) has two electrons in the $1s$ level and one in the $2s$. Consider an excited state in which the outermost electron has been raised to the $3p$ level. Since the $3p$ wave functions are not very penetrating, you can estimate the energy of this electron by assuming it is completely outside both the other electrons. (a) In this approximation what is the potential-energy function felt by the outermost electron? (b) In the same approximation write the formula for the energy of the outer electron if its principal quantum number is n . (c) Estimate the energy of the $3p$ electron in this way and compare with the observed value of -1.556 eV. (d) Repeat for the case that the outer electron is in the $3d$ level, whose observed energy is -1.513 eV. (e) Explain why the agreement is better for the $3d$ level than for the $3p$. Why is the observed energy for $3p$ lower than that for $3d$?

SECTION 10.4 (The Pauli Exclusion Principle)

- 10.7 • (a) How many electrons can be accommodated in an electron energy level with $l = 2$? (b) How many if $l = 3$? (c) Give a formula (in terms of l) for the number of electrons that can be accommodated in a level with arbitrary l .
- 10.8 • (a) Imagine an electron (spin $s = \frac{1}{2}$) confined in a one-dimensional rigid box. What are the degeneracies of its energy levels? (b) Make a sketch of the lowest few levels, showing their occupancy for the lowest state of six electrons confined in the same box. (Ignore the Coulomb repulsion among the electrons.)

- 10.25 •• (a) Use the information in Fig. 10.9 to find the ground-state configurations of the following atoms: $_{30}\text{Zn}$, $_{80}\text{Hg}$, $_{37}\text{Rb}$, $_{55}\text{Cs}$. (b) What is the total angular momentum of each of these atoms?
- 10.26 •• (a) Use the information in Fig. 10.9 to find the ground-state configurations of the following atoms: $_{30}\text{Zn}$, $_{31}\text{Ga}$, $_{39}\text{Y}$, $_{48}\text{Cd}$, $_{53}\text{I}$, $_{54}\text{Xe}$, $_{55}\text{Cs}$. (b) What is the total spin angular momentum for each of these atoms? (c) What are their total orbital angular momenta?
- 10.27 •• Give the ground-state configurations that the atoms of $_{8}\text{O}$, $_{10}\text{Ne}$, and $_{21}\text{Sc}$ would have if the electron had spin $s = \frac{3}{2}$. (See Problem 10.20.)
- 10.28 •• The degeneracies of the levels in hydrogen are 2, 8, 18, 32, ... The numbers of electrons in successive shells of multielectron atoms are 2, 8, 8, 18, 18, 32, ... Given the groupings of levels into shells shown in Fig. 10.9, explain the similarities and differences between these two sets of numbers.

SECTION 10.8 (The Periodic Table)

- 10.29 • Use the periodic table inside the back cover to write down the full electron configurations of $_{3}\text{Li}$, $_{10}\text{Ne}$, $_{12}\text{Mg}$, $_{19}\text{K}$, $_{28}\text{Ni}$, and $_{48}\text{Cd}$. [Hint: That periodic table gives the configuration of the outer-shell electrons only; to find the full configuration, you must add the configuration of the preceding closed-shell element. For example, for $_{12}\text{Mg}$, add the configuration of $_{10}\text{Ne}$.]
- 10.30 • Use the periodic table inside the back cover to find the full configurations of the following atoms: iron, silver, iodine, polonium. (See the hint for Problem 10.29, and use the alphabetical list in Appendix C if necessary.)
- 10.31 • Use the periodic table inside the back cover to find the names, atomic numbers, and full electron configurations of the following atoms: Ga, Xe, W, At, Md, Sg. (See the hint for Problem 10.30.)
- 10.32 • (a) Find the ground-state configurations of nickel and copper from the periodic table inside the back cover. (b) Draw energy-level diagrams, similar to those in Fig. 10.7, to illustrate these two ground states. (Note: In Fig. 10.9 we showed the $4s$ level below $3d$ since it fills first. Nevertheless, $4s$ and $3d$ are very close together; as Z increases, the $3d$ level becomes almost exactly degenerate with $4s$, and $4s$ can lose one electron to $3d$ — as happens in copper.)
- 10.33 •• Because of the way that atomic properties vary smoothly along the rows and columns of the periodic table, one can often predict the properties of an element from the known properties of its neighbors. (This is how Mendeleev predicted the existence and several properties of the elements now called scandium, gallium, and germanium.) (a) The ionization energies of $_{20}\text{Ca}$ and $_{38}\text{Sr}$ are 6.11 eV and 5.70 eV. If one guessed that ionization energies should change

linearly as one moves through a group, what would one predict for the ionization energy of $_{56}\text{Ba}$? (The observed value is 5.21 eV.) (b) Use the same argument to predict the electron affinity of $_{35}\text{Br}$, given that $_{17}\text{Cl}$ has electron affinity 3.61 eV and $_{53}\text{I}$ has 3.06 eV. (The observed value is 3.36 eV.) (c) Predict the radius of the $_{9}\text{F}$ atom, given that $_{7}\text{N}$ and $_{8}\text{O}$ have radii of 0.075 and 0.065 nm. (The actual value for $_{9}\text{F}$ is 0.057 nm.)

- 10.34 •• (a) The electron affinities of $_{26}\text{Fe}$ and $_{27}\text{Co}$ are 0.163 and 0.661 eV. Using arguments similar to those outlined in Problem 10.33, predict the electron affinity of $_{28}\text{Ni}$. (The observed value is 1.156 eV.) (b) In the same way, predict the boiling point of $_{32}\text{Ge}$, given that the boiling point of $_{14}\text{Si}$ is 3540 K and that of $_{50}\text{Sn}$ is 2876 K. (The observed value is 3107 K.) (c) Similarly, predict the melting point of $_{86}\text{Rn}$, given that those of $_{36}\text{Kr}$ and $_{54}\text{Xe}$ are 116 K and 161 K. (The observed value is 202 K.)
- 10.35 •• The simple estimation of atomic properties as described in Problems 10.33 and 10.34 does not always work very well. Here is a well-known example where it is fairly unsuccessful: The electron affinities of $_{17}\text{Cl}$ and $_{35}\text{Br}$ are 3.62 and 3.36 eV. Assuming that electron affinity varies linearly within the groups of the periodic table, what would you predict for the electron affinity of $_{9}\text{F}$? The observed value is 3.40 eV.

SECTION 10.9 (Excited States of Atoms*)

- 10.36 • The ground-state configuration of the lithium atom is $1s^2 2s^1$. Give the configurations of the lowest five excited levels. (See Fig. 10.16, and ignore fine structure.)
- 10.37 • Give the configurations of the lowest four levels of a sodium atom. (See Fig. 10.15, and ignore fine structure.)
- 10.38 • The spectrum of atomic lithium has a red line at $\lambda = 671$ nm, arising from the transition $2p \rightarrow 2s$. On close inspection, this line is seen to be a doublet of lines separated by 0.0152 nm. What is the fine-structure splitting of the $2p$ energy level in lithium?
- 10.39 • Give the configurations of the lowest six levels of the He atom.



COMPUTER PROBLEM

- 10.40 ••• (Section 10.2) If you have not already done it, do Problem 10.2. What is the potential energy $U(r)$ of an electron in this electric field? Use any graphing software to make a plot that shows $U(r)$ as well as the expected forms (10.4) and (10.5) for the case that $Z = 4$. Does your plot confirm the behavior sketched in Fig. 10.1?