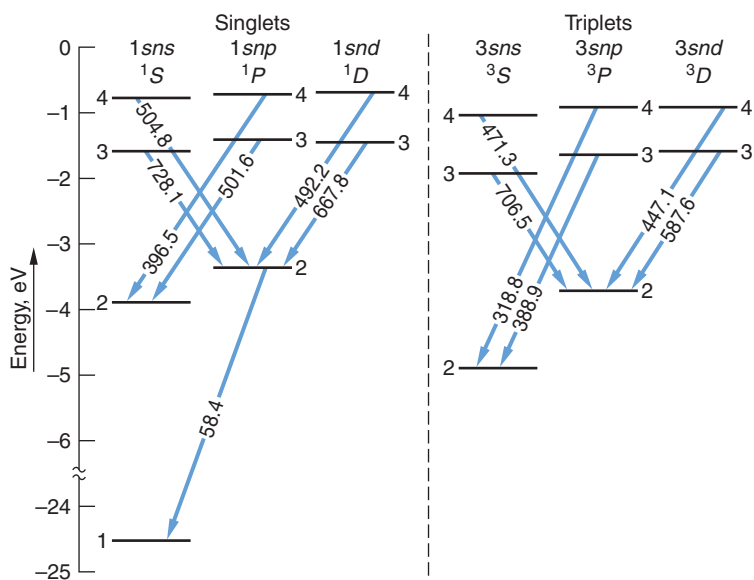


## Multielectron Atoms

The energy levels and optical spectra are much more complicated for atoms with more than one electron in the outer shell. In this section we will discuss qualitatively the energy levels for helium and the alkali earths, atoms in the second column of the periodic table. These atoms all consist of a core of electrons plus two electrons in an outer  $s$  shell. Most of the observed spectra can be understood in terms of energy levels corresponding to the raising of one of these electrons to a shell or subshell of higher energy. These are called *normal levels*. Energy levels involving excitation of both outer electrons are called *anomalous* and will be discussed only briefly here.

The model used to calculate the energy levels for these atoms consists of two identical electrons moving in a potential due to the nucleus and the core electrons. The simplest such atom is helium, but beryllium, magnesium, calcium, strontium, barium, and radium are all very similar. Let us consider magnesium ( $Z = 12$ ) as a



**FIGURE 7-24** Singlet and triplet levels for helium. The splitting of the triplet levels is too small to show on the scale of this diagram. Notice that no transitions are shown between the two sets of levels, corresponding to a selection rule  $\Delta S = 0$ .

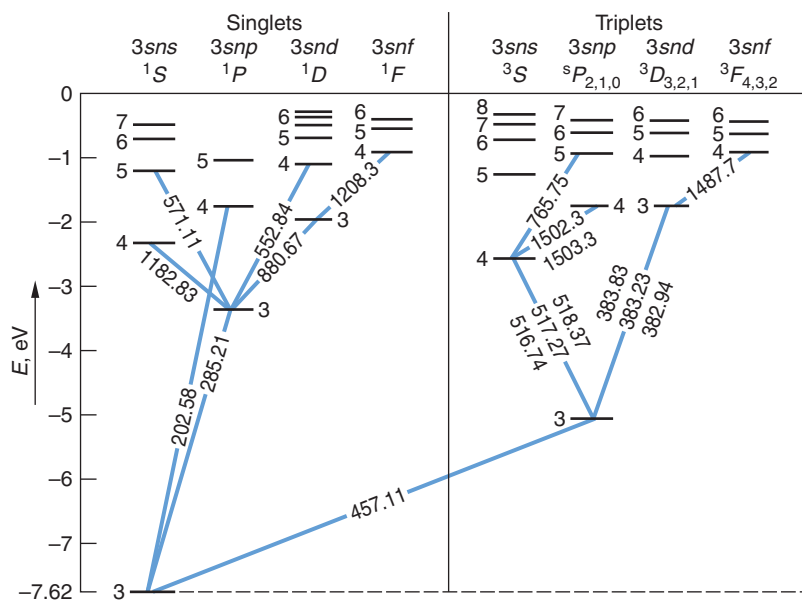
specific example. The ground-state electron configuration is  $(1s^2 2s^2 2p^6)3s^2$ . In the ground state both outer electrons have the same space quantum numbers ( $n = 3, \ell = 0, m_\ell = 0$ ), so the resultant spin must be zero. When one of the electrons is excited to a higher energy state such as  $3p$ , the spatial quantum numbers are no longer the same, so the resultant total spin need not be zero. For example, the resultant spin  $S$  for two particles with spin  $s = \frac{1}{2}$  can be either  $S = 0$  (antiparallel spins) or  $S = 1$  (parallel spins). If  $S = 0$ , the total angular momentum of the atom is due entirely to the orbital angular momentum of the excited electron, so  $j = \ell$ . The  $S = 0$  states are called *singlet* states. If  $S = 1$ , there are three possible values for the total angular momentum number  $j$  corresponding to the three possible orientations of  $\mathbf{S}$  relative to  $\mathbf{L}$ :  $j = \ell + 1$ ,  $j = \ell$ , or  $j = \ell - 1$  (except if  $\ell = 0$ , in which case  $j = \ell$  is the only possibil-

ity). Because of the spin-orbit effect, these three states have slightly different energies; that is, there is fine-structure splitting. The states with  $S = 1$  are therefore called *triplet* states. Thus, there are *two* sets of energy levels and *two* sets of spectral lines. A few of the lowest energy levels and allowed transitions in each set for helium are shown in Figure 7-24.

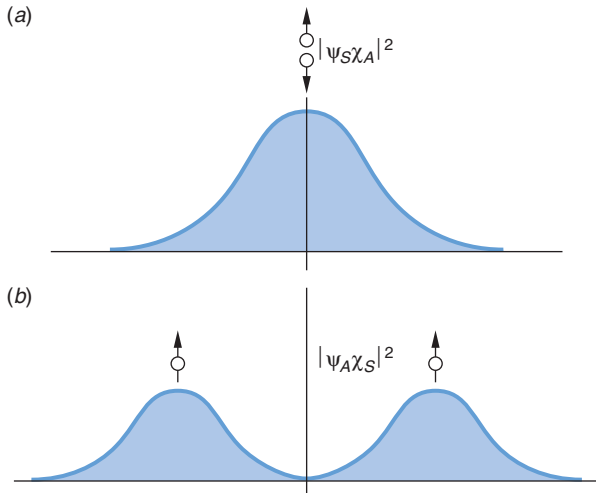
Figure 7-25 is an energy-level diagram for magnesium with observed transitions indicated. On the scale of this diagram, as in Figure 7-24, the fine-structure splitting of the triplet states is not evident. Note that all but one of the transitions shown for magnesium follow the selection rule  $\Delta S = 0$ ; that is, the triplet and singlet states don't mix. The one transition indicated (from the triplet state  $3s3p$  to the ground state) that does not obey this selection rule is called an *intercombination line*. Note that in the absence of intercombination lines, there exist certain excited states from which the atom cannot readily decay. The  $2^1S_0$  and  $2^3S_1$  states of helium in Figure 7-24 are two examples. Such states are called *metastable* states. Their existence is critical to the operation of lasers, as we will discuss further in Chapter 9. We will return to the matter of intercombination lines in a moment after first considering the energy difference between the singlet and triplet states.

If you examine Figure 7-25 closely, you will see that the singlet energy levels are higher than the triplet energy levels with the same electron configuration. For example, consider the states that have one electron in the  $3p$  state. If it were not for the electrostatic interaction of the two electrons, the singlet state  $^1P_1$  ( $j = 1$  since  $S = 0$  and  $\ell = 1$ ) and the triplet states  $^3P_j$  (with  $J = 2, 1,$  or  $0$  for  $\ell = 1$  and  $S = 1$ ) would have the same energy, except for the small fine-structure splitting. Evidently the electrostatic interaction energy of the two electrons is considerably greater in the singlet states than in the triplet states.

The cause of this energy difference is a rather subtle quantum-mechanical effect that has to do with the symmetry requirements on the total wave function for two identical particles. In Section 4-7 we wrote the wave function for two particles in one dimension, with one in state  $n$  and the other in state  $m$ , as



**FIGURE 7-25** Energy-level diagram for the two-electron atom magnesium. On this scale the fine-structure separation of the triplet levels is not evident. Note that the energy of each singlet level is greater than that of the corresponding triplet levels. This is because the average separation of the outer electrons is greater in the triplet states than in the singlet states, as indicated in Figure 7-26.



**FIGURE 7-26** Probability density versus separation for two electrons. (a) In the singlet state, the space part  $\psi_S$  of the wave function is symmetric and the spin part  $\chi_A$  is antisymmetric. The probability density is large at  $x = 0$ . (b) In the triplet state, the space part is antisymmetric and the spin part is symmetric. The probability density is zero at  $x = 0$ . Because the average separation in the triplet state is greater, the energy of the system is lower in this state.

$$\psi(x_1, x_2) = C[\psi_n(x_1)\psi_m(x_2) \pm \psi_n(x_2)\psi_m(x_1)] \quad \text{7-66}$$

where the plus sign gives a function that is symmetric on exchange of the particles and the minus sign one that is antisymmetric. We stated earlier the exclusion-principle requirement that electrons have antisymmetric wave functions, so we must now include spin in the wave function. The total wave function for two particles can be written as a product of an ordinary space part  $\psi(x)$  given by Equation 7-66 and a part that describes the spin  $\chi$ . The total wave function including spin is then equal to  $\psi\chi$ . The spin part  $\chi$  of the wave function turns out to be symmetric for the  $S = 1$  triplet state and antisymmetric for the  $S = 0$  singlet state. *The space part  $\psi$  of the wave function must therefore be antisymmetric in the triplet state and symmetric in the singlet state so that the total wave function is antisymmetric.* We note from Equation 7-66 that if  $x_1 = x_2$ , the antisymmetric space wave function is identically zero. This is an example of a general result illustrated in Figure 7-26 that, *in an antisymmetric space state, the particles tend to be farther apart than in a symmetric space state.* Since the interaction energy due to the electrostatic repulsion is positive and varies inversely as the separation distance, the energy is greater when the electrons are close

together in the space-symmetric singlet state  $S = 0$  than it is when the electrons are relatively far apart in the space-antisymmetric triplet state. The energy difference is of the order of 1 eV, which is much greater than for the fine-structure splitting.<sup>16</sup>

The symmetry of the wave functions also explains the selection rule  $\Delta S = 0$  that forbids transitions between the singlet and triplet states. As described in the More section *Transitions Between Energy States* on the home page for Chapter 6, an oscillating charge distribution is the origin of a transition between two states  $\psi_m$  and  $\psi_n$ . In the case of electric dipole radiation, the time-varying dipole moment of a single electron was given by

$$q\langle x \rangle = 2qab \cos \omega_{nm}t \int \psi_n x \psi_m dx + \text{stationary terms}$$

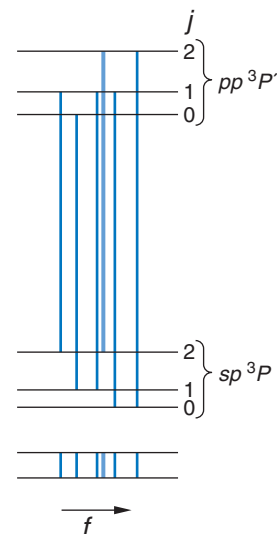
For two-electron states the matrix element  $\int \psi_n x \psi_m dx$  becomes  $\int \psi_n(x_1 + x_2) \psi_m dx$ . As we concluded above, the space part of the total wave function is antisymmetric for the triplet states and symmetric for the singlet states. Thus, for a triplet-to-singlet transition,  $\psi_m$  is an antisymmetric function  $\psi_a$  and  $\psi_n$  is a symmetric function  $\psi_s$  and the time-varying part of the equation becomes

$$q\langle x \rangle = 2qab \cos \omega_{nm}t \int \psi_s(x_1 + x_2) \psi_a dx \quad \text{7-67}$$

Now (read carefully: this is subtle!) if the two electrons are interchanged, the value of  $q\langle x \rangle$  cannot change since the electrons are identical; however, in such an interchange  $\psi_a$  will change sign, but  $\psi_s$  will not (see Section 6-7) and neither will  $(x_1 + x_2)$ . Since the value of the integral cannot change due to the interchange of the two electrons, its value can only be zero. Thus, transitions between the singlet and triplet states are forbidden, or  $\Delta S = 0$ . (This result can be generalized to other sets of states and other types, i.e., multipole orders, of radiation.)

The question then arises as to why the intercombination lines or transitions, such as the 457.1 nm line of magnesium noted above and in Figure 7-25, exist at all. The answer lies in our assumption that the total wave function, which *must* be antisymmetric to the interchange of identical particles, can be written as a product  $\psi\chi$  of a space function and a spin function, which individually are either symmetric or antisymmetric. When the spin-orbit coupling becomes appreciable, the separation of the space and spin coordinates implied by the product function is no longer strictly possible and there is no longer a separated function  $\psi$  whose matrix element can become zero. The spin-orbit coupling is relatively weak for low- $Z$  elements; hence the prohibition of intercombinations,  $\Delta S = 0$ , holds almost absolutely for them, for example, He in Figure 7-24, but holds less rigorously with increasing  $Z$ , as for Mg in Figure 7-25.

Up to now we have been discussing the normal levels of multielectron atoms in which only one of the electrons outside of the completed shells changes its quantum level. It is also possible for two or even more of the outer electrons to be simultaneously raised to excited states. We will close this section with a brief discussion of these so-called anomalous levels. Again using magnesium as the discussion example, we see that the first excited normal state is the  $3^3P$  level (see Figure 7-25), for which the outer electron configuration is  $3s3p$ . We would expect, and it is experimentally verified, that the lowest-lying anomalous level is that with both outer electrons raised to the  $3p$  state, that is, with a  $3p^2$  configuration. The excitation energy of the atom should then be approximately twice that of the normal  $3^3P$  level, 2.4 eV in Figure 7-25, or about 5 eV. This, too, is experimentally observed. The normal and anomalous  $3^3P$  levels, including the spin-orbit energy, are shown in Figure 7-27, along with a diagram of the observed spectral lines emitted in transitions between them. The six transitions (called an anomalous triplet) that occur between  $3P' \rightarrow 3P$  levels in Figure 7-27 all violate the  $\Delta\ell = \pm 1$  selection rule, Equation 7-28. That rule arose out of the solution of Schrödinger's equation for a *single* electron. For transitions involving excited states of two or more electrons,  $\Delta\ell$  for the atom may be zero, provided that the electron making the transition still satisfies  $\Delta\ell = \pm 1$ . Anomalous terms have been found for most atoms, although relatively few occur for low  $Z$  elements since most would lie above the ionization energy. However, such levels are very numerous for heavier elements and account in part for the greater complexity of their spectra compared with that of the lighter elements.



**FIGURE 7-27** The normal and anomalous  $3^3P$  states for magnesium. The upper states, labeled  $3P'$ , are the anomalous states and lie approximately twice as far above the ground state (not shown) as do the normal  $3P$  states. Notice that transitions between the levels, illustrated by the observed spectrum at the bottom, violate the  $\Delta\ell = \pm 1$  selection rule.