

Figure 7.14 Spin-orbit coupling splits the $2p$ state in the hydrogen atom into two substates ΔE apart. The result is a doublet (two closely spaced lines) instead of a single spectral line for the $2p \rightarrow 1s$ transition.

The orbiting electron “sees” itself circled f times per second by the proton of charge $+e$ that is the nucleus, for a resulting magnetic field of

$$B = \frac{\mu_0 f e}{2r}$$

The frequency of revolution and orbital radius for $n = 2$ are, from Eqs. (4.4) and (4.14),

$$f = \frac{v}{2\pi r} = 8.4 \times 10^{14} \text{ s}^{-1}$$

$$r = n^2 a_0 = 4a_0 = 2.1 \times 10^{-10} \text{ m}$$

Hence the magnetic field experienced by the electron is

$$B = \frac{(4\pi \times 10^{-7} \text{ T} \cdot \text{m/A})(8.4 \times 10^{14} \text{ s}^{-1})(1.6 \times 10^{-19} \text{ C})}{(2)(2.1 \times 10^{-10} \text{ m})} = 0.40 \text{ T}$$

which is a fairly strong field. Since the value of the Bohr magneton is $\mu_B = e\hbar/2m = 9.27 \times 10^{-24} \text{ J/T}$, the magnetic energy of the electron is

$$U_m = \mu_B B = 3.7 \times 10^{-24} \text{ J} = 2.3 \times 10^{-5} \text{ eV}.$$

The energy difference between the upper and lower substates is twice this, $4.6 \times 10^{-5} \text{ eV}$, which is not far from what is observed (Fig. 7.14).

7.8 TOTAL ANGULAR MOMENTUM

Both magnitude and direction are quantized

Each electron in an atom has a certain orbital angular momentum L and a certain spin angular momentum S , both of which contribute to the total angular momentum J of the atom. Let us first consider an atom whose total angular momentum is provided by a single electron. Atoms of the elements in group 1 of the periodic

table—hydrogen, lithium, sodium, and so on—are of this kind. They have single electrons outside closed inner shells (except for hydrogen, which has no inner electrons) and the exclusion principle ensures that the total angular momentum and magnetic moment of a closed shell are zero. Also in this category are the ions He^+ , Be^+ , Mg^+ , B^{2+} , Al^{2+} , and so on.

In these atoms and ions, the outer electron's total angular momentum J is the vector sum of L and S :

$$\begin{array}{ll} \text{Total atomic} & J = L + S \\ \text{angular momentum} & \end{array} \quad (7.16)$$

Like all angular momenta, J is quantized in both magnitude and direction. The magnitude of J is given by

$$J = \sqrt{j(j+1)}\hbar \quad j = l + s = l \pm \frac{1}{2} \quad (7.17)$$

If $l = 0$, j has the single value $j = \frac{1}{2}$. The component J_z of J in the z direction is given by

$$J_z = m_j \hbar \quad m_j = -j, -j+1, \dots, j-1, j \quad (7.18)$$

Because of the simultaneous quantization of J , L , and S they can have only certain specific relative orientations. This is a general conclusion; in the case of a one-electron atom, there are only two relative orientations possible. One relative orientation corresponds to $j = l + s$, so that $J > L$, and the other to $j = l - s$, so that $J < L$. Figure 7.15 shows the two ways in which L and S can combine to form J when $l = 1$. Evidently the orbital and spin angular-momentum vectors can never be exactly parallel or antiparallel to each other or to the total angular-momentum vector.

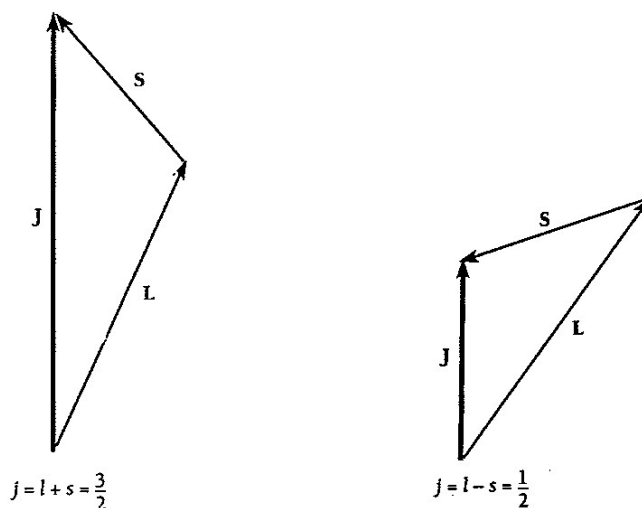


Figure 7.15 The two ways in which L and S can be added to form J when $l = 1$, $s = \frac{1}{2}$.

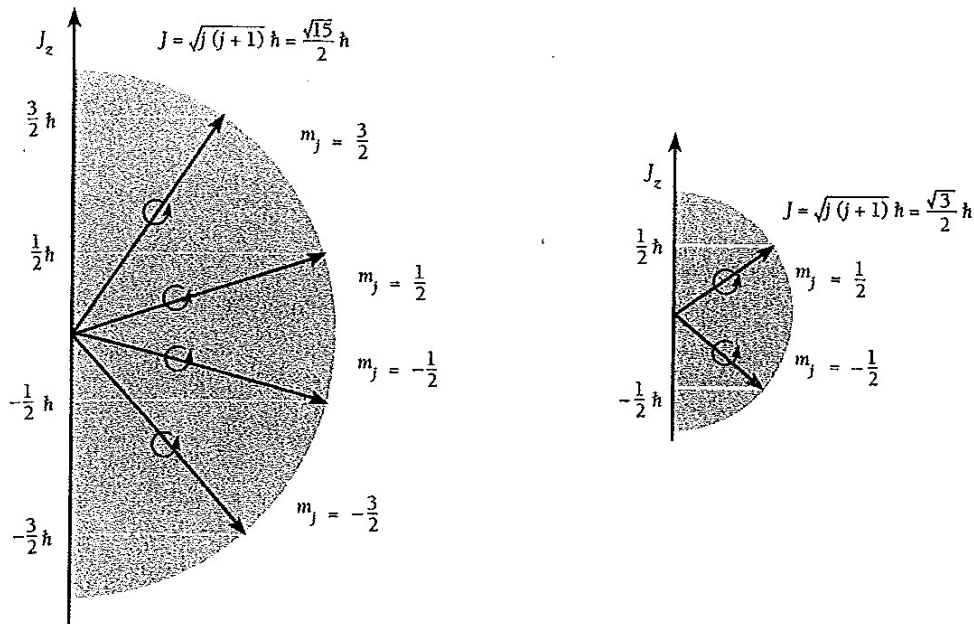


Figure 7.16 Space quantization of total angular momentum when the orbital angular momentum is $l = 1$.

Example 7.4

What are the possible orientations of J for the $j = \frac{3}{2}$ and $j = \frac{1}{2}$ states that correspond to $l = 1$?

Solution

For the $j = \frac{3}{2}$ state, Eq. (7.18) gives $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$. For the $j = \frac{1}{2}$ state, $m_j = -\frac{1}{2}, \frac{1}{2}$. Figure 7.16 shows the orientations of J relative to the z axis for these values of j .

The angular momenta L and S interact magnetically, as we saw in Sec. 7.7. If there is no external magnetic field, the total angular momentum J is conserved in magnitude and direction, and the effect of the internal torques is the precession of L and S around the direction of their resultant J (Fig. 7.17). However, if there is an external magnetic field B present, then J precesses about the direction of B while L and S continue precessing about J , as in Fig. 7.18. The precession of J about B is what gives rise to the anomalous Zeeman effect, since different orientations of J involve slightly different energies in the presence of B .

LS Coupling

When more than one electron contributes orbital and spin angular momenta to the total angular momentum J of an atom, J is still the vector sum of these individual momenta. The usual pattern for all but the heaviest atoms is that the orbital angular momenta L_i of

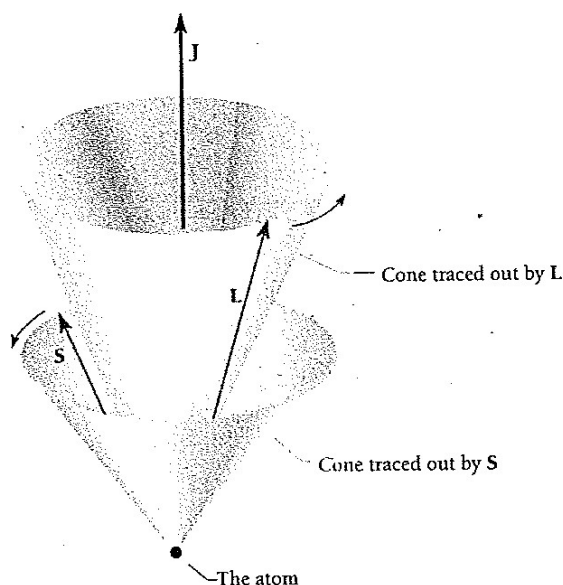


Figure 7.17 The orbital and spin angular-momentum vectors L and S precess about J .

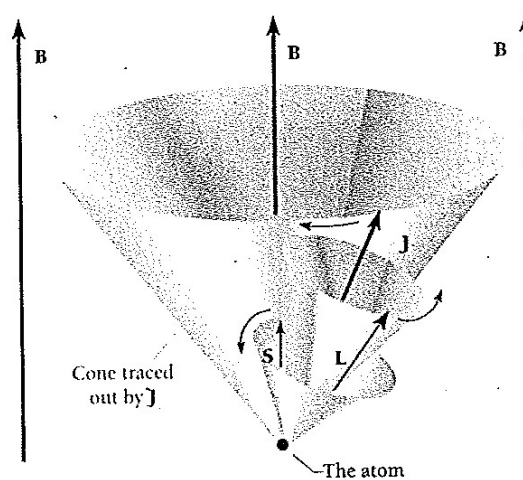


Figure 7.18 In the presence of an external magnetic field B , the total angular-momentum vector J precesses about B .

the various electrons are coupled together into a single resultant L . The spin angular momenta S_i are also coupled together into another single resultant S . The momenta L and S then interact via the spin-orbit effect to form a total angular momentum J . This scheme, called *LS coupling*, can be summarized as follows:

$$\begin{aligned}
 L &= \sum L_i \\
 S &= \sum S_i \\
 J &= L + S
 \end{aligned}
 \tag{7.19}$$

The angular momentum magnitudes L , S , J and their z components L_z , S_z , and J_z are all quantized in the usual ways, with the respective quantum numbers L , S , J , M_L , M_S , and M_J . Hence

$$\begin{aligned}
 L &= \sqrt{L(L+1)}\hbar \\
 L_z &= M_L\hbar \\
 S &= \sqrt{S(S+1)}\hbar \\
 S_z &= M_S\hbar \\
 J &= \sqrt{J(J+1)}\hbar \\
 J_z &= M_J\hbar
 \end{aligned}
 \tag{7.20}$$

Both L and M_L are always integers or 0, while the other quantum numbers are half-integral if an odd number of electrons is involved and integral or 0 if an even number of electrons is involved. When $L > S$, J can have $2S + 1$ values; when $L < S$, J can have $2L + 1$ values.

Example 7.5

Find the possible values of the total angular-momentum quantum number J under LS coupling of two atomic electrons whose orbital quantum numbers are $l_1 = 1$ and $l_2 = 2$.

Solution

As in Fig. 7.19a, the vectors L_1 and L_2 can be combined in three ways into a single vector L that is quantized according to Eq. (7.20). These correspond to $L = 1, 2$, and 3 since all values of L are possible from $|l_1 - l_2|$ ($= 1$ here) to $l_1 + l_2$. The spin quantum number s is always $\frac{1}{2}$, which gives the two possibilities for $S_1 + S_2$ shown in Fig. 7.19b, corresponding to $S = 0$ and $S = 1$.

We note that if the vector sums are not 0, L_1 and L_2 can never be exactly parallel to L , nor can S_1 and S_2 be parallel to S . Because J can have any value between $|L - S|$ and $L + S$, the five possible values here are $J = 0, 1, 2, 3$, and 4 .

Atomic nuclei also have intrinsic angular momenta and magnetic moments, and these contribute to the total atomic angular momenta and magnetic moments. Such contributions are small because nuclear magnetic moments are $\sim 10^{-3}$ the magnitude of electronic moments. They lead to the **hyperfine structure** of spectral lines with typical spacings between components of $\sim 10^{-3}$ nm as compared with typical fine-structure spacings a hundred times greater.

Term Symbols

In Sec. 6.5 we saw that individual orbital angular-momentum states are customarily described by a lowercase letter, with s corresponding to $l = 0$, p to $l = 1$, d to $l = 2$, and so on. A similar scheme using capital letters is used to designate the entire electronic state of an atom according to its total orbital angular-momentum quantum number L as follows:

$$\begin{array}{cccccccc} L = 0 & 1 & 2 & 3 & 4 & 5 & 6 \dots \\ S & P & D & F & G & H & I \dots \end{array}$$

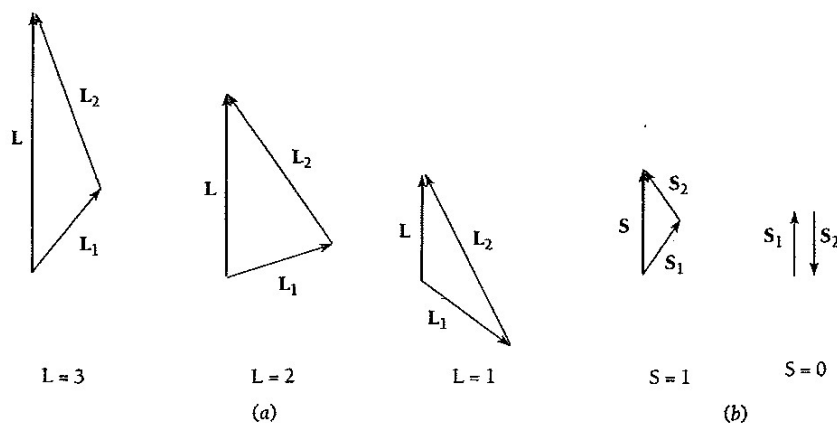


Figure 7.19 When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which L_1 and L_2 can combine to form L and two ways in which S_1 and S_2 can combine to form S .

A superscript number before the letter (2P , for instance) is used to indicate the **multiplicity** of the state, which is the number of different possible orientations of L and S and hence the number of different possible values of J . The multiplicity is equal to $2S + 1$ in the usual situation where $L > S$, since J ranges from $L + S$ to $L - S$. Thus when $S = 0$, the multiplicity is 1 (a **singlet** state) and $J = L$; when $S = \frac{1}{2}$, the multiplicity is 2 (a **doublet** state) and $J = L \pm \frac{1}{2}$; when $S = 1$, the multiplicity is 3 (a **triplet** state) and $J = L + 1, L$, or $L - 1$; and so on. (In a configuration in which $S > L$, the multiplicity is given by $2L + 1$.) The total angular-momentum quantum number J is used as a subscript after the letter, so that a $^2P_{3/2}$ state (read as "doublet P three-halves") refers to an electronic configuration in which $S = \frac{1}{2}$, $L = 1$, and $J = \frac{3}{2}$. For historical reasons, these designations are called **term symbols**.

In the event that the angular momentum of the atom arises from a single outer electron, the principal quantum number n of this electron is used as a prefix. Thus the ground state of the sodium atom is described by $3^2S_{1/2}$, since its electronic configuration has an electron with $n = 3$, $l = 0$, and $s = \frac{1}{2}$ (and hence $j = \frac{1}{2}$) outside closed $n = 1$ and $n = 2$ shells. For consistency it is conventional to denote the above state by $3^2S_{1/2}$ with the superscript 2 indicating a doublet, even though there is only a single possibility for J since $L = 0$.

Example 7.6

The term symbol of the ground state of sodium is $3^2S_{1/2}$ and that of its first excited state is $3^2P_{1/2}$. List the possible quantum numbers n , l , j , and m_j of the outer electron in each case.

Solution

$$\begin{aligned} 3^2S_{1/2}: n = 3, l = 0, j = \frac{1}{2}, m_j = \pm \frac{1}{2} \\ 3^2P_{1/2}: n = 3, l = 1, j = \frac{1}{2}, m_j = \pm \frac{1}{2}, \pm \frac{3}{2} \\ n = 3, l = 1, j = \frac{3}{2}, m_j = \pm \frac{1}{2} \end{aligned}$$

Example 7.7

Why is it impossible for a $2^2P_{5/2}$ state to exist?

Solution

A P state has $L = 1$ and $J = L \pm \frac{1}{2}$, so $J = \frac{5}{2}$ is impossible.

7.9 X-RAY SPECTRA

They arise from transitions to inner shells

In Chap. 2 we learned that the x-ray spectra of targets bombarded by fast electrons show narrow spikes at wavelengths characteristic of the target material. These are besides a continuous distribution of wavelengths down to a minimum wavelength inversely proportional to the electron energy (see Fig. 2.17). The continuous x-ray spectrum is the result of the inverse photoelectric effect, with electron kinetic energy being transformed into photon energy $h\nu$. The line spectrum, on the other hand, comes from electronic transitions within atoms that have been disturbed by the incident electrons.