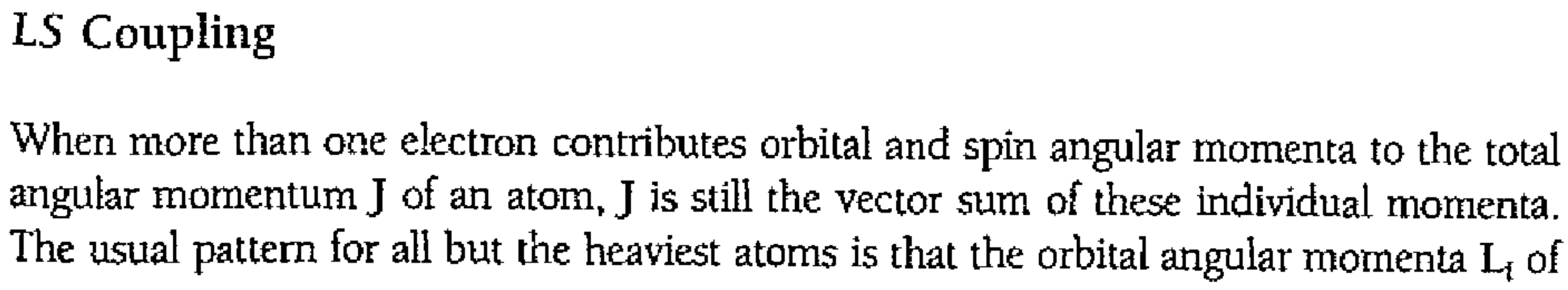
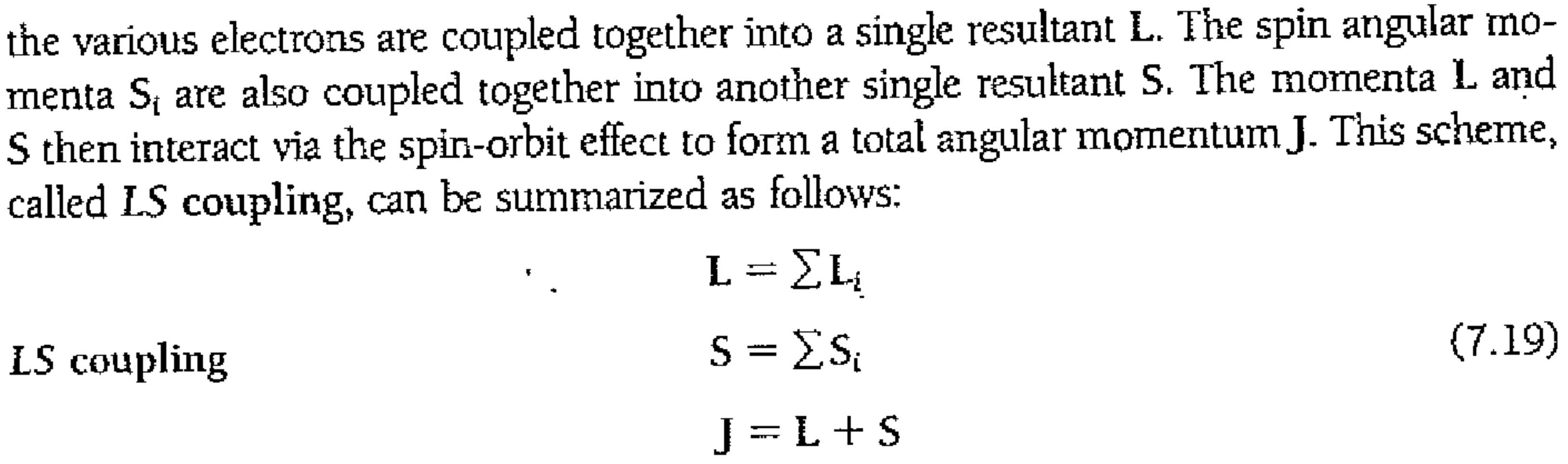
Reference: Concepts of Modern Physics: Arthur Beiser, (Chapter 7)



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 $\mathbf{L}_i$ of



the various electrons are coupled together into a single resultant **L**. The spin angular momenta $\mathbf{S}_i$ 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:

***LS* coupling**

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

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

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

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. 7.19*a*, the vectors $\mathbf{L}_1$ and $\mathbf{L}_2$ 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 $\mathbf{S}_1 + \mathbf{S}_2$ shown in Fig. 7.19*b*, corresponding to $S = 0$ and $S = 1$.

We note that if the vector sums are not 0, $\mathbf{L}_1$ and $\mathbf{L}_2$ can never be exactly parallel to **L**, nor can $\mathbf{S}_1$ and $\mathbf{S}_2$ 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.

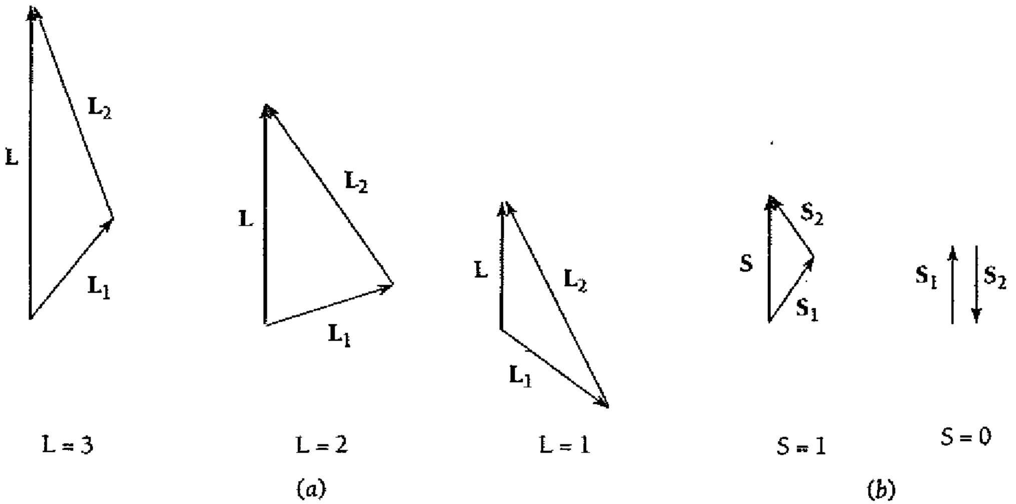


Figure 7.19 When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which $\mathbf{L}_1$ and $\mathbf{L}_2$ can combine to form **L** and two ways in which $\mathbf{S}_1$ and $\mathbf{S}_2$ can combine to form **S**.

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:

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

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 $2\mathsf{S} + 1$ in the usual situation where $\mathsf{L} > \mathsf{S}$, since J ranges from $\mathsf{L} + \mathsf{S}$ to $\mathsf{L} - \mathsf{S}$. Thus when $\mathsf{S} = 0$, the multiplicity is 1 (a **singlet** state) and $\mathsf{J} = \mathsf{L}$; when $\mathsf{S} = \frac{1}{2}$, the multiplicity is 2 (a **doublet** state) and $\mathsf{J} = \mathsf{L} \pm \frac{1}{2}$; when $\mathsf{S} = 1$, the multiplicity is 3 (a **triplet** state) and $\mathsf{J} = \mathsf{L} + 1$, L, or $\mathsf{L} - 1$; and so on. (In a configuration in which $\mathsf{S} > \mathsf{L}$, the multiplicity is given by $2\mathsf{L} + 1$.) 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 $\mathsf{S} = \frac{1}{2}$, $\mathsf{L} = 1$, and $\mathsf{J} = \frac{3}{2}$. 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 $\mathsf{L} = 0$.

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

$$3^2S_{1/2}\text{: } n = 3, l = 0, j = \tfrac{1}{2}, m_j = \pm\tfrac{1}{2}$$
$$3^2P_{1/2}\text{: } n = 3, l = 1, j = \tfrac{3}{2}, m_j = \pm\tfrac{1}{2}, \pm\tfrac{3}{2}$$
$$n = 3, l = 1, j = \tfrac{1}{2}, m_j = \pm\tfrac{1}{2}$$

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.