

Spin and Intensity Rules

The inclusion of spin does not change things very much. It is true that the initial states and the final states can each be in an “up” or “down” spin state, but since the interaction in atomic transitions is spin independent, only “up” → “up” and “down” → “down” transitions are allowed. Hence the transition rates will not only be independent of m_l (as we saw in Chapter 17) but also of m_s , and hence, m_j . With the inclusion of spin-orbit coupling, there will be small (on the scale of the $2p - 1s$ energy difference) level splittings. For example, the $n = 1$ and $n = 2$ level structure is changed, as shown in Fig. 17-A1. The spectral line corresponding to the transition $2p \rightarrow 1s$ is split into two lines, $2^2P_{3/2} \rightarrow 1^2S_{1/2}$ and $2^2P_{1/2} \rightarrow 1^2S_{1/2}$. For the split states, the radial integral and the phase space are almost unchanged, and hence *the ratio of the intensity of the two lines can be determined from the angular parts of the integral alone—that is, purely from angular momentum considerations.*

The following table lists the wave functions for the states in question.

J	m_j	Odd Parity $l = 1$	Even Parity $l = 0$
3/2	3/2	$Y_{11}\chi_+$	—
3/2	1/2	$\sqrt{2/3} Y_{10}\chi_+ + \sqrt{1/3} Y_{11}\chi_-$	—
3/2	-1/2	$\sqrt{1/3} Y_{1,-1}\chi_+ + \sqrt{2/3} Y_{10}\chi_-$	—
3/2	-3/2	$Y_{1,-1}\chi_-$	—
1/2	1/2	$\sqrt{1/3} Y_{10}\chi_+ - \sqrt{2/3} Y_{11}\chi_-$	$Y_{00}\chi_+$
1/2	-1/2	$\sqrt{2/3} Y_{1,-1}\chi_+ - \sqrt{1/3} Y_{10}\chi_-$	$Y_{00}\chi_-$

In the squares of the matrix elements, the radial parts are common to all of them. Thus, in considering the rates for $P_{3/2} \rightarrow S_{1/2}$ we must add the squares of the transition matrix elements for $m_j = 3/2 \rightarrow m_j = 1/2$, $m_j = 3/2 \rightarrow m_j = -1/2$, . . . , $m_j = -3/2 \rightarrow m_j = -1/2$, while the rate for the $P_{1/2} \rightarrow S_{1/2}$ involves the sum of the squares of the matrix elements for $m_j = 1/2 \rightarrow m_j = 1/2$, . . . , $m_j = -1/2 \rightarrow m_j = -1/2$. This can be done directly by techniques that are quite sophisticated and beyond the scope of this book. One can, however, work out these quantities in detail, using the fact that the spin wave functions are orthonormal.

$$\begin{array}{ll}
 \frac{P_{3/2} \rightarrow S_{1/2}}{m_j = 3/2 \rightarrow m_j = 1/2} & |\langle Y_{11} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = C \\
 3/2 \rightarrow -1/2 & 0 \quad \text{since } \chi_+^* \chi_- = 0 \\
 1/2 \rightarrow 1/2 & |\langle \sqrt{2/3} Y_{10} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = 0 \quad (\Delta m = 0) \\
 1/2 \rightarrow -1/2 & |\langle \sqrt{1/3} Y_{11} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = C/3 \\
 -1/2 \rightarrow 1/2 & |\langle \sqrt{1/3} Y_{1,-1} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = C/3 \\
 -1/2 \rightarrow -1/2 & |\langle \sqrt{2/3} Y_{10} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = 0 \quad (\Delta m = 0) \\
 -3/2 \rightarrow 1/2 & 0 \\
 -3/2 \rightarrow -1/2 & |\langle Y_{1,-1} | \mathbf{r} \cdot \boldsymbol{\epsilon} | Y_{00} \rangle|^2 = C
 \end{array} \tag{17A-1}$$

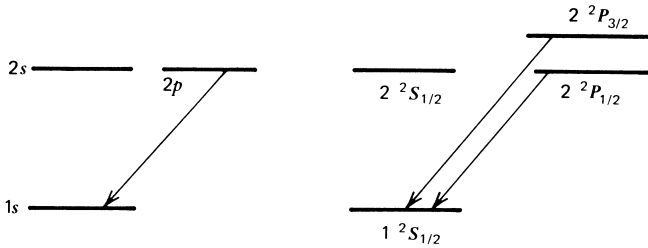


Figure 17A-1 The splitting of the $2p - 1s$ spectral line by spin-orbit coupling.

If we sum the terms we get

$$\sum R = \frac{8C}{3} \quad (17A-2)$$

Similarly,

$$\begin{array}{ll} \frac{P_{1/2} \rightarrow S_{1/2}}{m_j = 1/2 \rightarrow m_j = 1/2} & |\langle \sqrt{1/3} Y_{10} | \boldsymbol{\epsilon} \cdot \mathbf{r} | Y_{00} \rangle|^2 = 0 \\ 1/2 \rightarrow -1/2 & |\langle -\sqrt{2/3} Y_{11} | \boldsymbol{\epsilon} \cdot \mathbf{r} | Y_{00} \rangle|^2 = 2C/3 \\ -1/2 \rightarrow 1/2 & |\langle \sqrt{2/3} Y_{1,-1} | \boldsymbol{\epsilon} \cdot \mathbf{r} | Y_{00} \rangle|^2 = 2C/3 \\ -1/2 \rightarrow -1/2 & |\langle -\sqrt{1/3} Y_{10} | \boldsymbol{\epsilon} \cdot \mathbf{r} | Y_{00} \rangle|^2 = 0 \end{array} \quad (17A-3)$$

Again,

$$\sum R = \frac{4C}{3} \quad (17A-4)$$

Thus the ratio of the intensities is

$$\frac{R(P_{3/2} \rightarrow S_{1/2})}{R(P_{1/2} \rightarrow S_{1/2})} = \frac{8C/3}{4C/3} = 2 \quad (17A-5)$$

The reason for *summing* over all the initial states is that when the atom is excited, all the p -levels are equally occupied, since their energy difference is so tiny compared to the $2p - 1s$ energy difference. We also sum over all the final states if we perform an experiment that does not discriminate between them, as is the case for a spectroscopic measurement. In our calculation of the $2p \rightarrow 1s$ transition rate, we *averaged* over the initial m -states. There we were concerned with the problem of asking: "If we have N atoms in the $2p$ states, how many will decay per second?" The averaging came about because of the fact that under most circumstances, when N atoms are excited, about $N/3$ go into each one of the $m = 1, 0, -1$ states. Here, the fact that there are more levels in the $P_{3/2}$ state than there are in the $P_{1/2}$ state is relevant. There will be altogether six levels, (four with $j = 3/2$ and two with $j = 1/2$), and there will be on the average $N/6$ atoms in each of the states. The fact that there are more atoms in the $j = 3/2$ subset of levels just means that more atoms decay, and that therefore the intensity will be larger.