

## 7.17: How to recognize LS-coupling

$LS$ -coupling is in practice a good approximation in light atoms, but there are appreciable departures from  $LS$ -coupling in the heavier atoms. Generally the several lines in a multiplet in  $LS$ -coupling are fairly close together in wavelength for  $LS$ -coupling, but, as departures from  $LS$ -coupling become more pronounced, the lines in a multiplet may become more widely separated and may appear in quite different parts of the spectrum.

In  $LS$ -coupling, multiplets always connect terms with the same value of  $S$ . Thus, while  $^3D - ^3P$  would be "allowed" for  $LS$ -coupling,  $^3D - ^1P$  would not.  $\Delta S = 0$  is a necessary condition for  $LS$ -coupling, but is not a sufficient condition. Thus while a multiplet with  $\Delta S \neq 0$  certainly indicates departure from  $LS$ -coupling,  $\Delta S = 0$  by no means guarantees that you have  $LS$ -coupling. In spectroscopy, the term "forbidden" generally refers to transitions that are forbidden to electric dipole radiation. Transitions that are forbidden merely to  $LS$ -coupling are usually referred to as "semi-forbidden", or as "intersystem" or "intercombination" transitions. We shall have more on selection rules in section 7.24.

The energies, or term values, of the levels (each defined by  $LSJ$ ) within a term are given, for  $LS$ -coupling, by a simple formula:

$$T = \frac{1}{2}a[J(J+1) - L(L+1) - S(S+1)]. \quad (7.17.1)$$

Here  $a$  is the spin-orbit coupling coefficient, whose value depends on the electron configuration. What is the separation in term values between two adjacent levels, say between level  $J$  and  $J-1$ ? Evidently (if you apply equation 7.17.1) it is just  $aJ$ . Hence Landé's Interval Rule, which is a good test for  $LS$ -coupling: *The separation between two adjacent levels within a term is proportional to the larger of the two  $J$ -values involved.* For example, in the  $KL3s(^2S)3p^3P^o$  term of  $Mg_{\text{I}}$  (the first excited term above the ground term), the separation between the  $J=2$  and  $J=1$  levels is  $4.07 \text{ mm}^{-1}$ , while the separation between  $J=1$  and  $J=0$  is  $2.01 \text{ mm}^{-1}$ . Landé's rule is approximately satisfied, showing that the term conforms closely, but not exactly, to  $LS$ -coupling. It is true that for doublet terms (and all the terms in  $Na_{\text{I}}$  and  $K_{\text{I}}$  for example, are doublets) this is not of much help, since there is only one interval. There are, however, other indications. For example, the value of the spin-orbit coupling coefficient can be calculated from  $LS$ -theory, though I do not do that here. Further, the relative intensities of the several lines within a multiplet (or indeed of multiplets within a polyad) can be predicted from  $LS$ -theory and compared with what is actually observed. We discuss intensities in a later chapter.

The spin-orbit coupling coefficient  $a$  can be positive or negative. If it is positive, the level within a term with the largest  $J$  lies highest; such a term is called a *normal term*, though terms with negative  $a$  are in fact just as common as "normal" terms. If  $a$  is negative, the level with largest  $J$  lies lowest, and the term is called an *inverted term*. Within a shell (such as the  $L$ -shell) all the  $s$  electrons may be referred to as a subshell, and all the  $p$  electrons are another *subshell*. The subshell of  $s$  electrons can hold at most two electrons; the subshell of  $p$  electrons can hold at most six electrons. If the outermost subshell (i.e. the electrons responsible for the optical spectrum) is less than half full,  $a$  is positive and the terms are normal. If it is more than half full,  $a$  is negative and the terms are inverted. If the subshell is exactly half full,  $a$  is small, the term is compact and may be either normal or inverted. For example in  $Al_{\text{I}}$ , the term  $3p^2\ ^4P$  (which has three levels - write down their  $J$ -values) is normal. There are only two  $p$  electrons out of six allowed in that subshell, so the subshell is less than half full. The term  $2s2p^4\ ^4P$  of  $O_{\text{II}}$  has four  $p$  electrons, so the subshell is more than half full, and the term is inverted. The term  $2s^22p^3\ ^2P^o$  of the same atom has a subshell that is exactly half full. The term happens to be normal, but the two levels are separated by only  $0.15 \text{ mm}^{-1}$ , which is relatively quite tiny.

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