3. Interaction Energy (Triplet Separations) in L-S and j-j Couplings

As a result of spin-orbit interaction the atomic terms consist of multiplet components of slightly different energy, each corresponding to a different value of J. The interaction, and hence the multiplet splitting, increases rapidly with atomic number Z, and is specially large in excited states of heavier atoms.

We have already seen in chapter 5 that for a single-electron atom the interaction energy *i.e.* the shift of each fine-structure level from the hypothetical centre is given by

$$-\Delta T_{ls} = \frac{R_\infty \ \alpha^2 Z^4}{2n^3 l(l+\frac{1}{2})\ (l+1)} [j(j+1) - l(l+1) - s(s+1)] \text{ cm}^{-1}$$

$$= a \frac{j^{*2} - l^{*2} - s^{*2}}{2},$$

where $a = \frac{R_\infty \alpha^2 Z^4}{n^3 l(l+\frac{1}{2})\ (l+1)}$ cm^{-1}, $j^* = \sqrt{j(j+1)}$, $l^* = \sqrt{l(l+1)}$ and $s^* = \sqrt{s(s+1)}$. Using cosine law†, the last expression may be written as

$$-\Delta T_{ls} = a l^* s^* \cos (l^* s^*). \qquad \ldots\text{(i)}$$

In the case of two optical electrons there are four angular momenta l_1^*, l_2^*, s_1^* and s_2^* with six possible interactions :

(1) s_1^* with s_2^*, (2) l_1^* with l_2^*, (3) l_1^* with s_1^*,
(4) l_2^* with s_2^*, (5) l_1^* with s_2^*, (6) l_2^* with s_1^*.

† $j^{*2} = l^{*2} + s^{*2} + 2l^* s^* \cos (l^* s^*)$.

In L-S coupling, the interactions (1) and (2) predominate over (3) and (4), while (5) and (6) are negligibly small.

Applying eq. (i), the energies corresponding to the interactions (1), (2), (3), (4) are

$$\left.\begin{aligned}\Delta T_1 &= a_1\, s_1^*\, s_2^* \cos(s_1^*\, s_2^*)\\ \Delta T_2 &= a_2\, l_1^*\, l_2^* \cos(l_1^*\, l_2^*)\\ \Delta T_3 &= a_3\, l_1^*\, s_1^* \cos(l_1^*\, s_1^*)\\ \Delta T_4 &= a_4\, l_2^*\, s_2^* \cos(l_2^*\, s_2^*)\end{aligned}\right\} \qquad \text{...(ii)}$$

Again, in L-S coupling, s_1^* and s_2^* precess rapidly with *fixed* angles around their resultant S^*, which remains invariant in magnitude. Therefore, we have by cosine law

$$S^{*2} = s_1^{*2} + s_2^{*2} + 2s_1^*\, s_2^* \cos(s_1^*\, s_2^*).$$

This gives

$$\Delta T_1 = \tfrac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}). \qquad \text{...(iii)}$$

Similarly, l_1^* and l_2^* precess rapidly with *fixed* angles around their resultant L^*, so that

$$\Delta T_2 = \tfrac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2}). \qquad \text{...(iv)}$$

Now L^* and S^* precess around their resultant J^* in the same way as l^* and s^* of a single electron precess around their resultant j^*. The interaction energy corresponding to this precession is due to couplings between l_1^* and s_1^* and between l_2^* and s_2^*, that is, ΔT_3 and ΔT_4. Here the average values of the cosines must be evaluated since the angles between the vectors are continually changing. The average values are given by

$$\overline{\cos(l_1^*\, s_1^*)} = \cos(l_1^*\, L^*) \cos(L^*\, S^*) \cos(S^*\, s_1^*)$$

and $$\overline{\cos(l_2^*\, s_2^*)} = \cos(l_2^*\, L^*) \cos(L^*\, S^*) \cos(S^*\, s_2^*).$$

Using these *average* values of the cosines in eq. (ii), we get

$$\Delta T_3 + \Delta T_4 = [a_3\, l_1^*\, s_1^* \cos(l_1^*\, L^*) \cos(S^*\, s_1^*) + a_4\, l_2^*\, s_2^* \cos(l_2^*\, L) \cos(S^*\, s_2^*)] \cos(L^*\, S^*).$$

Applying cosine law for the various terms, we get

$$\Delta T_3 + \Delta T_4 = \left[a_3\, l_1^*\, s_1^* \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2\, l_1^*\, L^*} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2\, S^*\, s_1^*} + a_4\, l_2^*\, s_2^* \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2\, l_2^*\, L^*} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2\, S^*\, s_2^*}\right] \frac{J^{*2} - L^{*2} - S^{*2}}{2\, L^*\, S^*}$$

$$= \left[a_3 \frac{l_1^{*2} + L^{*2} - l_2^{*2}}{2\, L^{*2}} \frac{S^{*2} + s_1^{*2} - s_2^{*2}}{2\, S^{*2}} + a_4 \frac{l_2^{*2} + L^{*2} - l_1^{*2}}{2\, L^{*2}} \frac{S^{*2} + s_2^{*2} - s_1^{*2}}{2\, S^{*2}}\right] \frac{J^{*2} - L^{*2} - S^{*2}}{2}.$$

This may be written as

$$\Delta T_3 + \Delta T_4 = \tfrac{1}{2} (a_3 \alpha_3 + a_4 \alpha_4) (J^{*2} - L^{*2} - S^{*2}), \quad \text{...(v)}$$

where
$$\alpha_3 = \frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2 L^{*2}} \; \frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2 S^{*2}} \quad \text{...(vi)}$$

and
$$\alpha_4 = \frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2 L^{*2}} \; \frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2 S^{*2}} . \quad \text{...(vii)}$$

For any given triplet l_1^*, l_2^*, s_1^*, s_2^*, L^*, S^* etc. are fixed in magnitude so that a_3, a_4, α_3, α_4 are constants. Writing

$$a_3 \alpha_3 + a_4 \alpha_4 = A, \quad \text{...(viii)}$$

eq. (v) becomes

$$\Delta T_3 + \Delta T_4 = \frac{1}{2} A (J^{*2} - L^{*2} - S^{*2}). \quad \text{(ix)}$$

We may now write any fine-structure term by the formula

$$T = T_0 - \Delta T_1 - \Delta T_2 - \Delta T_3 - \Delta T_4 , \quad \text{..(x)}$$

where T_0 is a hypothetical term value for the centre of gravity of the entire electron configuration.

As an example, let us consider a *ps* configuration. We have

$l_1 = 1, l_2 = 0$; $\quad \therefore \quad L = 1$ (P term)

$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}$; $\quad \therefore \quad S = 0, 1.$

For $S = 0$ (singlet state)

$$J = |L - S|, |L - S| + 1, \ldots\ldots (L + S)$$
$$= 1$$

and for $S = 1$ (triplet state)

$$J = 0, 1, 2.$$

The configuration gives a singlet term ${}^1P_1$ and a triplet term ${}^3P_{0,1,2}$. The shift of each term from the centre of gravity is $\Delta T_1 + \Delta T_2$. Now,

$$\Delta T_1 + \Delta T_2 = \tfrac{1}{2} a_1 (S^{*2} - s_1^{*2} - s_2^{*2}) + \tfrac{1}{2} a_2 (L^{*2} - l_1^{*2} - l_2^{*2}).$$

Putting $S = 0$, $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$, $L = 1$, $l_1 = 1$, $l_2 = 0$, we get

$$\Delta T_1 + \Delta T_2 = -\frac{3a_1}{4} .$$

Thus the singlet term is shifted *up* the hypothetical centre by $3a_1/4$, as shown in Fig. 7.

Again, putting $S = 1$, $s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$, $L = 1$, $l_1 = 1$, $l_2 = 0$, we get

$$\Delta T_1 + \Delta T_2 = \frac{a_1}{4} .$$

The triplet term is shifted *down* the hypothetical centre by $a_1/4$, as shown in Fig. 7. This has been so chosen because singlet levels lie above the corresponding triplet levels of the same electron configuration.

Now, the shift of each fine-structure level from the hypothetical centre of the *triplet* term is $\Delta T_3 + \Delta T_4$. Now,

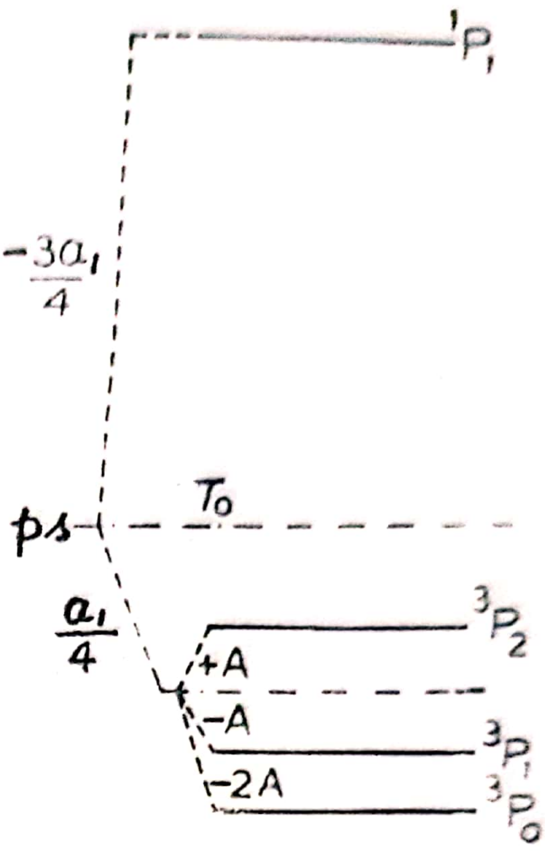
$$\Delta T_3 + \Delta T_4 = \tfrac{1}{2} A\, (J^{*2} - L^{*2} - S^{*2}).$$

Putting $L=1$, $S=1$ and $J=0, 1, 2$; we get

$$\Delta T_3 + \Delta T_4 = -2A, \ -A, \ A.$$

Taking it a regular triplet, the levels $^3P_0$ and $^3P_1$ are *lowered* by $2A$ and A from the centre while the level $^3P_2$ is *raised* up by A (Fig. 7).

The total ^3P separation, that is, the $^3P_0 - {^3P_2}$ interval is $3A$. By eq. (vi), (vii) and (viii), we have



(Fig. 7)

$$A = a_3\,\alpha_3 + a_4\,\alpha_4$$

$$= a_3\,\frac{l_1^{*2} - l_2^{*2} + L^{*2}}{2\,L^{*2}}\;\frac{s_1^{*2} - s_2^{*2} + S^{*2}}{2\,S^{*2}}$$

$$+ a_4\,\frac{l_2^{*2} - l_1^{*2} + L^{*2}}{2\,L^{*2}}\;\frac{s_2^{*2} - s_1^{*2} + S^{*2}}{2\,S^{*2}}.$$

Putting $l_1=1$, $l_2=0$, $L=1$, $s_1=\frac{1}{2}$, $s_2=\frac{1}{2}$, $S=1$, we get

$$A = \frac{a_3}{2}.$$

Thus in *ps* configuration the total ^3P separation is $3a_3/2$.