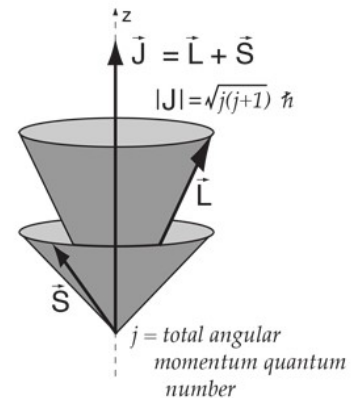# L-S coupling

L-S coupling or Russell-Saunders coupling predicts results in good agreement with the observed spectral details for many light atoms. In such cases of multi-electron atoms the spin-orbit coupling is weak. In this coupling scheme it is presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum **L**. Similarly, the individual spin angular momenta should couple to produce a resultant spin angular momentum **S**. Then **L** and **S** combine to form the total angular momentum.

This scheme of coupling may be visualized in terms of a vector model of angular momentum.

$$J = L + S$$

Orbit-Orbit Interaction

Consider orbital motion of two electrons, ℓ_1 and ℓ_2 are their quantum numbers, $\ell_1^*h/2\pi$ and ℓ_2^* are their angular momenta. ℓ_1^* and ℓ_2^* are quantized with respect to each other in such a way that they form resultant

$$L^* \text{ where } L^* = [L(L+1)]^{1/2} \text{ and}$$

$$L = 0, 1, 2, 3, 4, 5, 6, 7, \dots \text{for S, P, D, F, G, H, I, J,...}$$

Consider an electron in the p orbit and other in the d orbit. Here two vectors $\ell_1^* = \sqrt{2}$ and $\ell_2^* = \sqrt{6}$ may orient themselves in any one of three positions $L^* = \sqrt{2}, \sqrt{6}$ and $\sqrt{12}$ corresponding to L=1, 2, 3 or P, D, F terms. All integral values of L from $\ell_2 - \ell_1$ to $\ell_2 + \ell_1$ are allowed.

Spin Spin Interaction

With two electrons each having a spin angular momentum of $s^*h/2\pi$ where $s^* = [s(s+1)]^{1/2}$ and s=1/2. There are two ways in which a spin resultant $S^*h/2\pi$ may be formed.

s_1 and s_2 are spin quantum number of two electrons. This implies $s_1^* = (1/2)\sqrt{3}$ and $s_2^* = (1/2)\sqrt{3}$. The two resultant quantum numbers are S=0 and S=1. S=0 gives rise to singlet and S=1 to triplet.

Table 1 recapitulates the situation for an excited helium atom in the 1s 2p configuration. To derive the term symbols for the different spin-orbit states, we first need to calculate the total orbital angular momentum and total spin from those of the individual electrons, respectively. Then **L** and **S** are combined to find the total angular momentum of this group of electrons, J. The possible combinations for L, S and J are given as following:

$$L = |\ell_1 - \ell_2| \dots\dots \ell_1 + \ell_2 \text{ (in integer steps)}$$

$$S = |s_1 - s_2| \dots\dots s_1 + s_2 \text{ (in integer steps)}$$

$$J = |L - S| \dots\dots L + S \text{ (in integer steps)}$$

TABLE 1

LS coupling				
sub-shell	orbital	spin	total	term
1s	$\text{'s'} \rightarrow l_1 = 0$	$s_1 = \frac{1}{2}$		
2p	$\text{'p'} \rightarrow l_2 = 1$	$s_2 = \frac{1}{2}$		
combi	$L = |l_1 - l_2|$ $= l_1 + l_2$ $= 1$	$S = |s_1 - s_2|$ $= 0$	$J = |L - S|$ $= L + S = 1$	$^1P_1$
		$S = s_1 + s_2$ $= 1$	$J = |L - S| = 0$	$^3P_0$
			$J = |L - S| + 1 = 1$	$^3P_1$
			$J = L + S = 2$	$^3P_2$

The term symbols are then composed by writing the total orbital angular momentum, L, in spectroscopic notation (S,P,D,F,... - capitalised, since this refers to the total orbital angular momentum of a group of electrons) with the total angular momentum **J**, as a subscript. Finally, the spin multiplicity, 2S+1, is calculated from the total spin and attached to the term symbol as a leading superscript. The term symbols for all four terms in the 1s 2p configuration are shown in green in the table 1. In this case, there is a singlet state ($^1P_1$) and a triplet of states ($^3P0_3$, $^3P_1$, $^3P_2$). The spin multiplicity indicates how many states there are in each group.

In principle, any other electron configuration can be treated in exactly the same way, although the number of different terms can become quite large. Table 2 shows a simple example of a configuration

with two valence electrons, 2p 3p. The total orbital angular momentum and the total spin are calculated from those of the individual electrons. In this case, three possible values for L rather than just one is obtained. Spin-wise, the situation is the same for any two-electron configuration since the spin of a single electron is always s=1/2. We then have to look at all possible permutations of the total orbital angular momenta and the total spin, as shown in the table 2. For each permutation, we calculate the total angular momentum, **J**, and work out the term symbol as before. There are three separate singlets, two proper triplets consisting of three states each, and one additional triplet state, $^3S_1$.

TABLE 2

sub-shell	orbital		spin		
2p	'p' $\rightarrow l_1 = 1$		$s_1 = \frac{1}{2}$		
3p	'p' $\rightarrow l_2 = 1$		$s_2 = \frac{1}{2}$		
combi	$L = \|l_1 - l_2\| = 0$ $L = \|l_1 - l_2\| + 1 = 1$ $L = l_1 + l_2 = 2$		$S = \|s_1 - s_2\| = 0$ $S = s_1 + s_2 = 1$		
$\overset{L\rightarrow}{S\downarrow}$	0→'S'	1→'P'		2→'D'	
0	$J = \|L - S\|$ $= L + S$ $= 0 \rightarrow {}^1S_0$	$J = \|L - S\|$ $= L + S$ $= 1 \rightarrow {}^1P_1$		$J = \|L - S\|$ $= L + S$ $= 2 \rightarrow {}^1D_2$	
1	$J = \|L - S\|$ $= L + S$ $= 1 \rightarrow {}^3S_1$	$J = \|L - S\|$ $= 0 \rightarrow {}^3P_0$ $J = \|L - S\| + 1$ $= 1 \rightarrow {}^3P_1$ $J = L + S$ $= 2 \rightarrow {}^3P_2$		$J = \|L - S\|$ $= 1 \rightarrow {}^3D_1$ $J = \|L - S\| + 1$ $= 2 \rightarrow {}^3D_2$ $J = L + S$ $= 3 \rightarrow {}^3D_3$	

j-j Coupling

For heavier atoms, another coupling scheme called j-j coupling provides better agreement with experiment.

In j-j coupling, the orbital angular momentum ℓ, and spin s, of each electron are first coupled to form a total angular momentum j for that electron. These single-electron total

$\vec{J} = \vec{L} + \vec{S}$

$j = 3/2$
$m_j = 3/2, 1/2, -1/2, -3/2$

$j = 1/2$
$m_j = 1/2, -1/2$
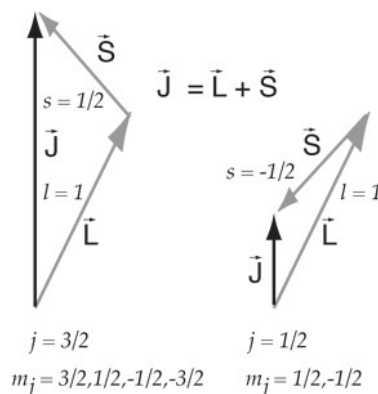
$$J_1 = L_1 + S_1$$
$$J_2 = L_2 + S_2$$
$$J = \sum_i J_i$$

angular momenta are then combined into a total angular momentum J, for the group of electrons. This is in contrast to LS coupling, where the total orbital angular momentum L, and total spin S, of the system are calculated first and then combined to the total angular momentum, J, of the whole system.
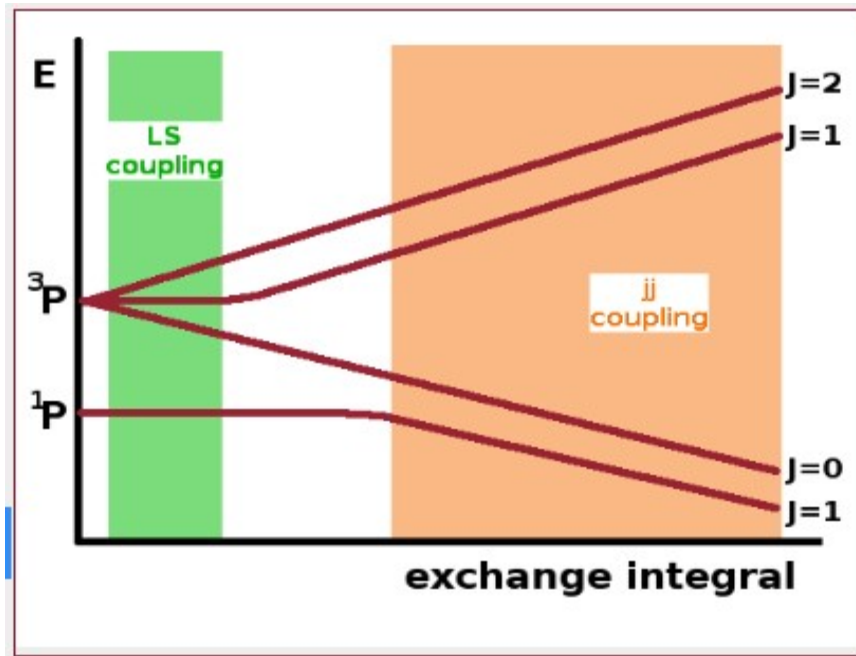

TABLE 3

$j_1 \rightarrow$ $j_2 \downarrow$	$\frac{1}{2}$
$\frac{1}{2}$	$J = \lvert j_1 - j_2 \rvert \cdots j_1 + j_2 = 0 \text{ or } 1$
$\frac{3}{2}$	$J = \lvert j_1 - j_2 \rvert \cdots j_1 + j_2 = 1 \text{ or } 2$

In general, the results from both coupling schemes are different. For example, for the 1s 2p configuration, jj coupling results in two doublets rather than a singlet and a triplet: For the 1s electron $j_1 = \lvert \ell_1 - s_1 \rvert = \lvert \ell_1 + s_1 \rvert = 1/2$ and for the 2p electron $j_2 = \lvert \ell_2 - s_2 \rvert \dots \ell_2 + s_2 = 1/2$ or $3/2$. These combine as shown in the table 3, resulting in two doublets.

Consider pd electrons

$s_1 = 1/2$ $\qquad\qquad \ell_1 = 1$ $\qquad\qquad\qquad\qquad\qquad\qquad s_2 = 1/2$ $\qquad\qquad \ell_2 = 2$

$\qquad J_1 = 1/2$ or $3/2$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad j_2 = 3/2$ or $5/2$

Combining these four values in all possible ways

$\qquad\qquad\qquad\qquad\qquad J_1 = 1/2, j_2 = 3/2 \qquad\qquad J = 1$ and2

$\qquad\qquad\qquad\qquad\qquad J_1 = 3/2, j_2 = 3/2 \qquad\qquad J = 0, 1, 2$

$$j_1=1/2, j_2=5/2 \qquad J=2, 3$$

$$j_1=3/2, j_2=5/2 \qquad J=1, 2, 3, 4$$

Energy states in terms of jj coupling for pd electrons will be

$(1/2, 3/2)_1 \ (1/2, 3/2)_2$

$(3/2, 3/2)_0 \ (3/2, 3/2)_1 \ (3/2, 3/2)_2 \ (3/2, 3/2)_3$

$(1/2, 5/2)_2 \ (1/2, 5/2)_3$

$(3/2, 5/2)_1 \ (3/2, 5/2)_2 \ (3/2, 5/2)_3 \ (3/2, 5/2)_4$