Two electron systems

ll - Coupling → consider the orbital motions of two electrons and let l_1 and l_2 → their respective orbital quantum numbers, $l_1^* h/2\pi$ and $l_2^* h/2\pi$ or l_1^* and l_2^* → their respective angular momenta.

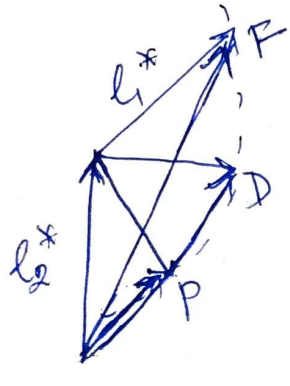
Following Russell and Saunder's coupling scheme, l_1^* and l_2^* are quantized with respect to each other in such a way that they form a resultant L^*, where $L^* = \sqrt{L(L+1)}$ and

$L = 0, 1, 2, 3, 4, 5, 6, 7$

for S, P, D, F, G, H, I, K --- terms respectively

Consider, for example, one electron in a p-orbit and the other in a d orbit. Here two vectors $l_1^* = \sqrt{2}$ and $l_2^* = \sqrt{6}$ may orient themselves in any three positions, $L^* = \sqrt{2}, \sqrt{6}$ and $\sqrt{12}$ corresponding to $L = 1, 2, 3$ or to P, D and F terms, respectively.

Space quantization of the orbital motions of two valence electrons



$l_1 = 1, \; l_2 = 2$

$L = 1, 2, 3$

With given values of l_1 and l_2 where $l_2 \geq l_1$, all integral values of L from $l_2 - l_1$ to $l_2 + l_1$ are allowed.

Where $l_2 < l_1$, the roles of two electrons are interchanged.

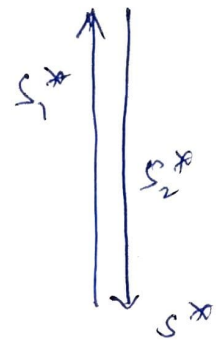
With only two valence electrons, one in a p orbital and other in a d orbital, the atom may be in a ^3P, a ^3D or a ^3F state.

Term table

s.s,	S	ps P	ds, D	fs, F
sp,	P	p.p SPD	dp, PDF	fp DFG
sd,	D	pd, PDF	d.d, SPDFG	fd, PDFGH
sf,	F	pf, DFG	d.f, PDFGH	ff, SPDFGHI

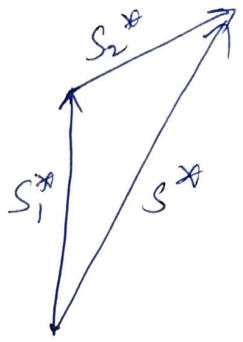
Spin - Spin, or SS - Coupling : With two electrons each having a spin angular momentum of $s^* h/2\pi$, where $s^* = \sqrt{s(s+1)}$ and $s = \frac{1}{2}$, there are two ways in which a spin resultant $S^* h/2\pi$ may be formed. Let s_1^* and s_2^* represent the respective spin vectors of the two electrons. Combining these, we find, with $s_1^* = \frac{1}{2}\sqrt{3}$ and $s_2^* = \frac{1}{2}\sqrt{3}$ two resultant: one with $S^* = 0$ and the other with $S^* = \sqrt{2}$.

These give the resultant quantum ~~number~~ values $S = 0$ and $S = 1$



$s_1 = \frac{1}{2}$, $s_2 = \frac{1}{2}$

$S = 0$



$s_1 = \frac{1}{2}$ $s_2 = \frac{1}{2}$

$S = 1$

$S^* = 0$, give rise to Singlet term

$S^* = \sqrt{2}$ Triplet term

LS -, or Russell - Saunders Coupling

Orbital motions of two electrons coupled together to give a resultant L^* and the spins of the same electrons coupled together to form S^* both L^* and S^* will in turn be coupled together to form J^* which is a vector representing $J^* h/2\pi$ the total angular momentum of the atom.

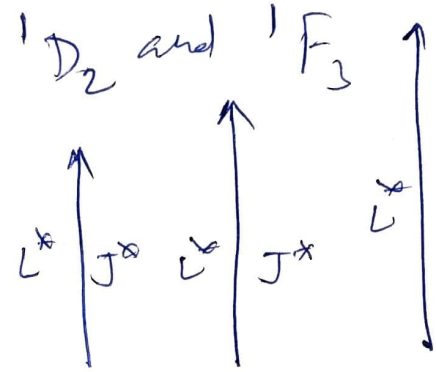
The quantum conditions imposed on this coupling $\longrightarrow$ $J^* = \sqrt{J(J+1)}$ and J takes non-negative integral values.

Specific Example $\longrightarrow$ Case of one electron in a p orbit and the other in a d orbit.

We have the following possible values to work with; $L=1$, 2 and 3 and $S=0$ and 1.

Taking first $S=0$ and $L=1, 2, 3$

S being zero, J is equal to L and $J=1, 2$ and 3. These correspond to three Singlet terms $^1P_1$, $^1D_2$ and $^1F_3$



$L=1, S=0$ $L=2, S=0$ $L=3, S=0$

$J=1$ $J=2$ $J=3$

With $S=1$ there are three possibilities for each of the three L's.

↓

Correspond to three triplets

$^3P_0$ $^3P_1$ $^3P_2$ $^3D_1$ $^3D_2$ $^3D_3$ $^3F_2$ $^3F_3$ $^3F_4$

LS-Coupling

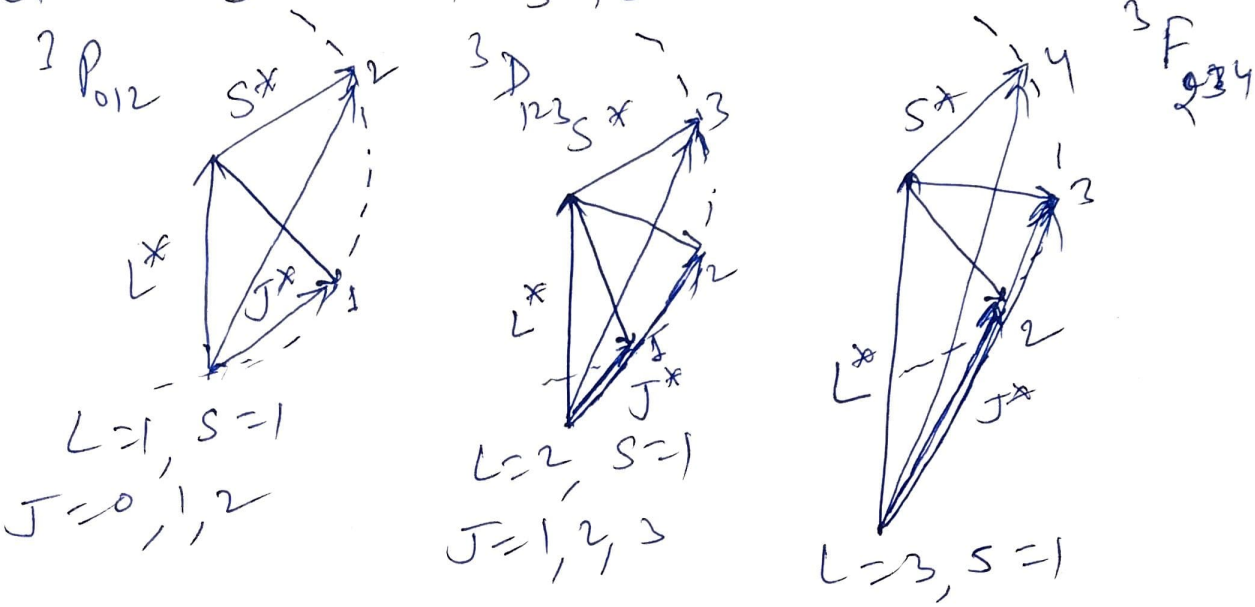
The multiplicity of the fine-structure system to which the term belongs is always $2S+1$

Singlets	Doublets	Triplets
$S=0$	$S=\frac{1}{2}$	$S=1$

The term type S, P, D etc. gives the value of L, and the subscript gives the resultant value of J. For rapid calculation of J values, with given values of L and S,

(1) When $L \geq S$, all integral values of J between L−S and L+S are allowed,

(2) where $S > L$, all integral values of J between S−L and S+L are allowed.



LS-Coupling

Terms arising from interaction of Two electrons in LS-coupling

s,s, $^1S_0$ $^3S_1$

s p, $^1P_1^o$ $^3P_{0,1,2}$

s d, $^1D_2$ $^3D_{1,2,3}$

s f, $^1F_3^o$ $^3F_{2,3,4}$

p, p $^1S_0$ $^1P_1$ $^1D_2$ $^3S_1$ $^3P_{0,1,2}$ $^3D_{1,2,3}$

Similarly for

p d,

p f,

d. d,

For the terms $l_1 + l_2$ is odd are called odd terms, all others are called even terms. Odd terms are distinguished by the small superscript "o" to the right of symbol S, P, D ——.