

6. Russell - Saunders Coupling

After self-consistent field analysis performed, there is still the small perturbation W to take account of:

etc. Total $[J_x, L_x] = 0$

W : some residual term due to e-e repulsion.
It can be shown that W commutes with L^2, S^2, L_z, S_z (see e.g. Cohen-Tannoudji). The final states can thus be enumerated by their total orbital and spin angular momentum

$$\Psi_A : \text{actual state function} \quad L^2 \Psi_A = L(L+1)\hbar^2 \Psi_A \quad L_z \Psi_A = M_L \hbar \Psi_A$$

$$\Psi_A = A \sum_j c_j \Psi_{SD,j} \quad S^2 \Psi_A = S(S+1)\hbar^2 \Psi_A \quad S_z \Psi_A = M_S \hbar \Psi_A$$

Computation of the energy contributions can be done by perturbation theory, etc.

$$E = E(L, S) \quad \text{less degeneracy}$$

To determine L & S : first determine $M_L = \sum (m_{l_i})$
 $M_S = \sum (m_{s_i})$

Then note that $-L \leq M_L \leq L$ $-S \leq M_S \leq S$

Examples: $1s^2 \uparrow \downarrow$ $m_{s_1} = \pm 1/2$ $m_{s_2} = \mp 1/2$ $M_S = 0 \Rightarrow S = 0$
 $l_1 = l_2 = 0$ $m_{l_1} = m_{l_2} = 0 \Rightarrow M_L = 0 \Rightarrow L = 0$

(can also operate on proper Slater Determinant)

Notation: $\overset{\text{SINGLET}}{\uparrow} \underset{\sim}{S} \quad \text{"term symbol"}$
 $L=0$ $\text{degeneracy} = (2L+1)(2S+1) = 1$
No. of M_S values $(2S+1)$ 1 Slater determinant
"multiplicity" $\Psi_A = \Psi_{1s^2}$ discussed previously
 $S=0$ here

$1s2s \quad \begin{array}{c} \uparrow \\ \uparrow \end{array} \text{ etc.} \quad L=0 \quad m_{s_1} = \pm 1/2 \quad m_{s_2} = \pm 1/2 \quad "S"$
 $\Rightarrow M_s = 1, 0, 0, -1$

OR: $S = S_1 + S_2,$
 $S_1 + S_2 = 1, \dots |S_1 - S_2|$

$M_s = 1, 0, -1 \Rightarrow S=1$
 $M_s = 0 \Rightarrow S=0$

Term Notation: $^1S \quad ^3S$ two distinct states
 4 determinant \Rightarrow singlet triplet
 $g=4 \quad g=1 \quad g=3$

For zeroth-order SCF wave functions, must take linear combinations of Slater determinants so that Ψ_A eigenfunction of L^2, S^2 . (also cons from deg. part theory)

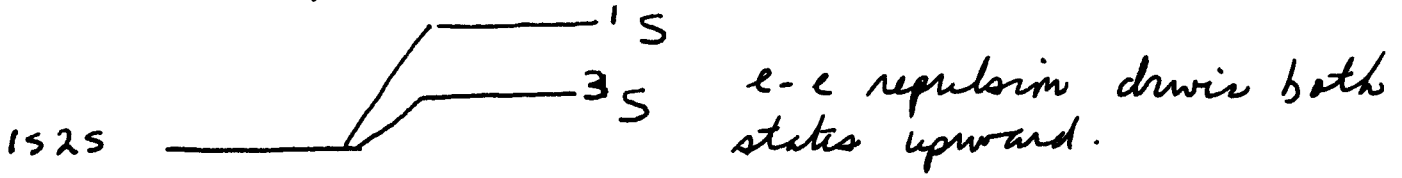
$L=0 \quad S=0 \quad ^1S \quad \Psi_A = \frac{1}{2} [\phi_{1s}(1)\phi_{2s}(2) + \phi_{1s}(2)\phi_{2s}(1)]$
 $\times [|1:+>|2:-> - |1:->|2:+>]$
 $M_s=0$

$L=0 \quad S=1 \quad ^3S \quad \Psi_A = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{1s}(2)\phi_{2s}(1)]$
 $\times \left\{ \begin{array}{l} |1:+>|2:+> \\ \frac{1}{\sqrt{2}} [|1:+>|2:-> + |1:->|2:+>] \\ |1:->|2:-> \end{array} \right\}$
 maintains degeneracy
 $\rightarrow (M_s = 1, 0, -1)$

What about relative energies of $E(^3S)$ + $E(^1S)$?

Qualitative View: Consider two electrons in same partition!
 $i=2 \quad (r_1 \theta \phi_1 = r_2 \theta_2 \phi_2)$. Then $\Psi_A(^1S) \neq 0$ but $\Psi_A(^3S) = 0$.
 It is therefore likely that the triplet state, in which the electronic motions are better "correlated", is the lower in energy.

Actual perturbation calculation:

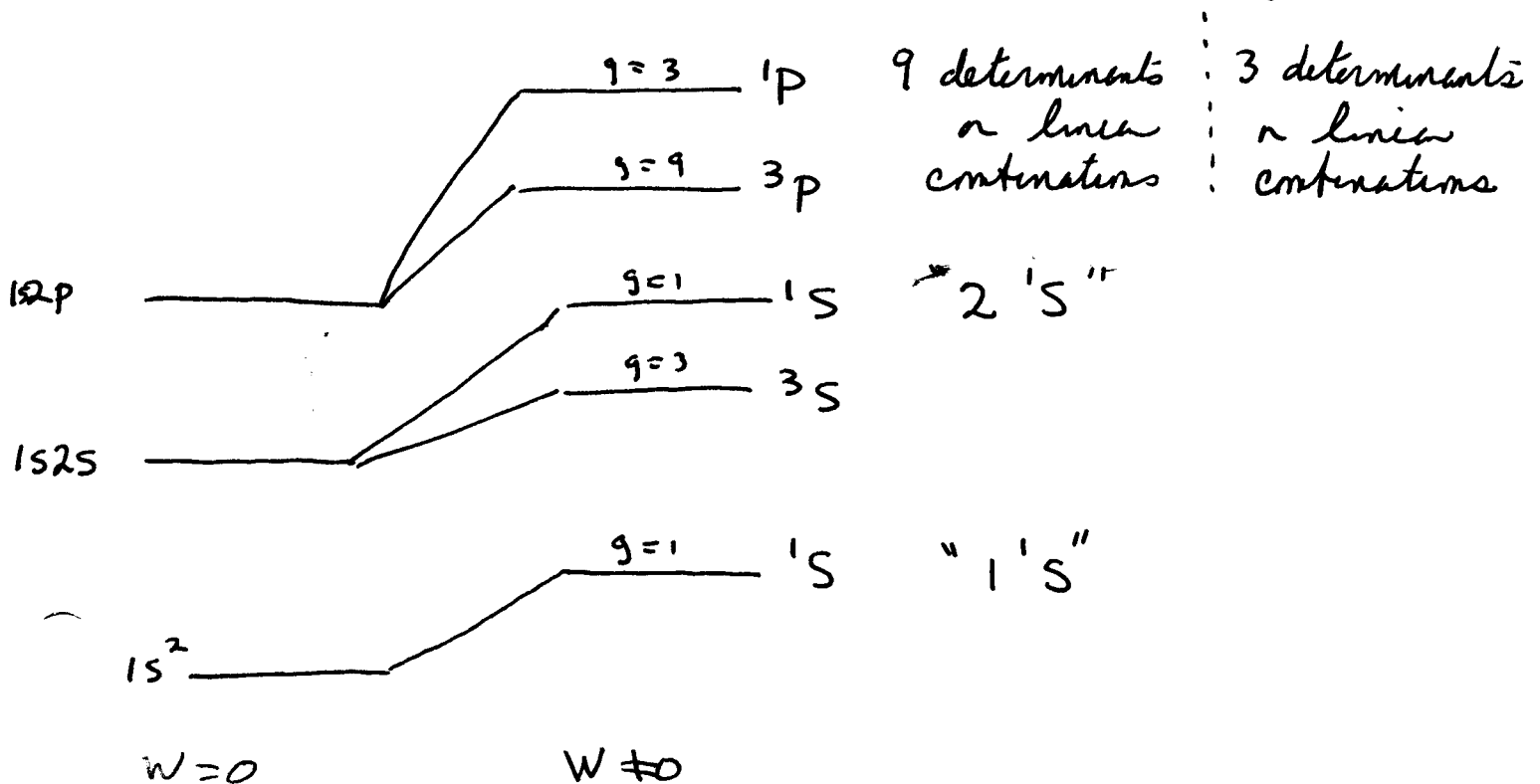


Hund has formulated some general qualitative rules on the relative ordering of terms:

(1) For a given configuration (e.g. 1s2s) the greater the multiplicity $(2S+1)$ the lower the energy
 $3S < 1S$.

(2) If several terms have the same multiplicity (e.g. 3S 3P) the higher the L , the lower the energy.
 $3P < 3S < 1P < 1S$

1s2p $S=1, 0$ as in 1s2s
 $l_1=0, l_2=1 \Rightarrow L=1$ $3P < 1P$
 $(M_L = 1, 0, -1)$ $g=9$ $g=3$



Now let's consider a highly excited configuration:

$2p^2$ Standard approach: $S=1, 0 \quad l_1=l_2=1$

$$m_{l_1} = 1, 0, -1$$

$$m_{l_2} = 1, 0, -1$$

\therefore We would conclude that

$$M_L = 2, 1, 0, 1, 0, -1, 0, -1, -2$$

$$\Rightarrow L = 2 \quad (M_L = 2, 1, 0, -1, -2)$$

$$L = 1 \quad (M_L = 1, 0, -1)$$

$$L = 0 \quad (M_L = 0)$$

$${}^3D < {}^3P < {}^3S < {}^1D < {}^1P < {}^1S$$

OK for $2p^3p$

but we'd be wrong since the P.E.P. limits the number of possibilities as in $1s^2$.

Diagrammatic Method $2p^2$

m_l	1	$\uparrow\downarrow$	\uparrow	\uparrow	-	-	\uparrow	\uparrow	-	\downarrow	\downarrow	-	\downarrow	\downarrow	-	$\uparrow\downarrow$	
0	-	-	\downarrow	-	\uparrow	-	\uparrow	-	\uparrow	\uparrow	-	\downarrow	\downarrow	-	\downarrow	$\uparrow\downarrow$	
-1	-	-	-	\downarrow	\downarrow	$\uparrow\downarrow$	-	\uparrow	\uparrow	-	\uparrow	\uparrow	-	\downarrow	\downarrow	-	
M_L	2	1	0	-1	-2		1	0	-1	1	0	-1	1	0	-1	0	
M_S	0	0	0	0	0		1	1	1	0	0	0	-1	-1	-1	0	
	$L=2 \quad S=0$						$L=1 \quad S=1$						$L=0 \quad S=0$				
	${}^1D (g=5)$						${}^3P (9)$						${}^1S (1)$				



In this method, there is some arbitrariness in assigning specific $M_L M_S$ diagrams to specific terms. In reality, differing linear combinations of Slater determinants are used to obtain proper L, S eigenvalues.

More Than Two Electrons

I ignore inner electrons in "closed shells" since they contribute only $l=0 \quad S=0$ anyway. ($1s^2 p^6 d^{10}$)

(Sub)Shell \equiv Set of m_l values for given n, l .

C ground configuration $\underbrace{1s^2 2s^2}_{l=0 \ S=0} 2p^2 \rightarrow 2p^2$

$n \ 2p^6$ $\begin{matrix} \uparrow\downarrow \\ \uparrow\downarrow \\ \uparrow\downarrow \end{matrix}$ $M_L = M_S = 0 \Rightarrow L=0 \ S=0$

Number of Diagonals $n = \frac{N!}{(N-M)! M!}$ per shell

$N: 2(2l+1)$ no. of places an electron can be put in a given shell
 $l=1 \quad 2l+1 = 3 \quad 2 \times 3 = 6 \text{ places}$

$M: \text{no electrons}$

$$2p^2 \quad n = \frac{6!}{2! 4!} = 15$$

$$2p^2 3p^2 \quad n = \frac{6!}{2! 4!} \frac{6!}{2! 4!} = 15 \times 15$$

$$2p 3p \quad n = \frac{6!}{1! 5!} \frac{6!}{1! 5!} = 36$$

For last example, diagrammatic method not necessary since electrons not equivalent (already differ in n).

$l_1=1 \ l_2=1 \quad L=2, 1, 0$ (vectorial addition)
 $S=1, 0$

$3D < 3P < 3S < 1D < 1P < 1S$

Dipole Selection Rules

Ψ_A'' lower state $\langle \Psi_A' | \mu | \Psi_A'' \rangle \neq 0$
 Ψ_A' upper state

$\Rightarrow \Delta L = \pm 1 \quad \Delta S = 0$ one $\Delta l_i = \pm 1$
(also $\Delta L = 0$ but not 0-0) $\Delta l_{j \neq i} = 0$

Examples

configuration changes	$1s 2s \leftarrow 1s^2$	X	$\Delta l_1 = \Delta l_2 = 0$
	$1s 2p \leftarrow 1s^2$	✓	$\Delta l_1 = 0 \quad \Delta l_2 = 1$
	$2p^2 \leftarrow 1s^2$	X	$\Delta l_1 = \Delta l_2 = 1$

term changes

$1P \leftarrow 1S$	✓	$\Delta L = 1 \quad \Delta S = 0$
$3P \leftarrow 1S$	X	$\Delta S = 1$
$3S \leftarrow 3P$	✓	$\Delta L = -1 \quad \Delta S = 0$

ENUMERATING THE STATES OF COMPLEX ATOMS

1. Build atomic configurations from the single-electron energy level scheme using the ordering $1s < 2s < 2p < 3s < 3p < 4s < 3d \dots$ and the Pauli Exclusion Principle.

Example: Li (3 electrons) Lowest Configuration $1s^2 2s^1$ 1st Excited Configuration $1s^2 2p^1$

2. Configurations may contain degeneracy. Enumerate the possible values of L and S in a given configuration. Sets of L, S values correspond to states of different energy with symbols known as term symbols.

3. The possible values of L and S within a given configuration can be deduced in the following manner:

a) ignore closed shell electrons (e.g. $1s^2$ or $1s^2 2s^2$ or $1s^2 2s^2 2p^6$) since they contribute only $L = S = 0$

b) find the number of diagrams or ψ_A involving the open-shell electrons:

$$W = \text{no. of diagrams} = N! / (M! [N-M]!)$$

$N = 2(2l+1)$ for an unfilled shell of angular momentum l $M = n$ electrons in that shell

EXAMPLES:

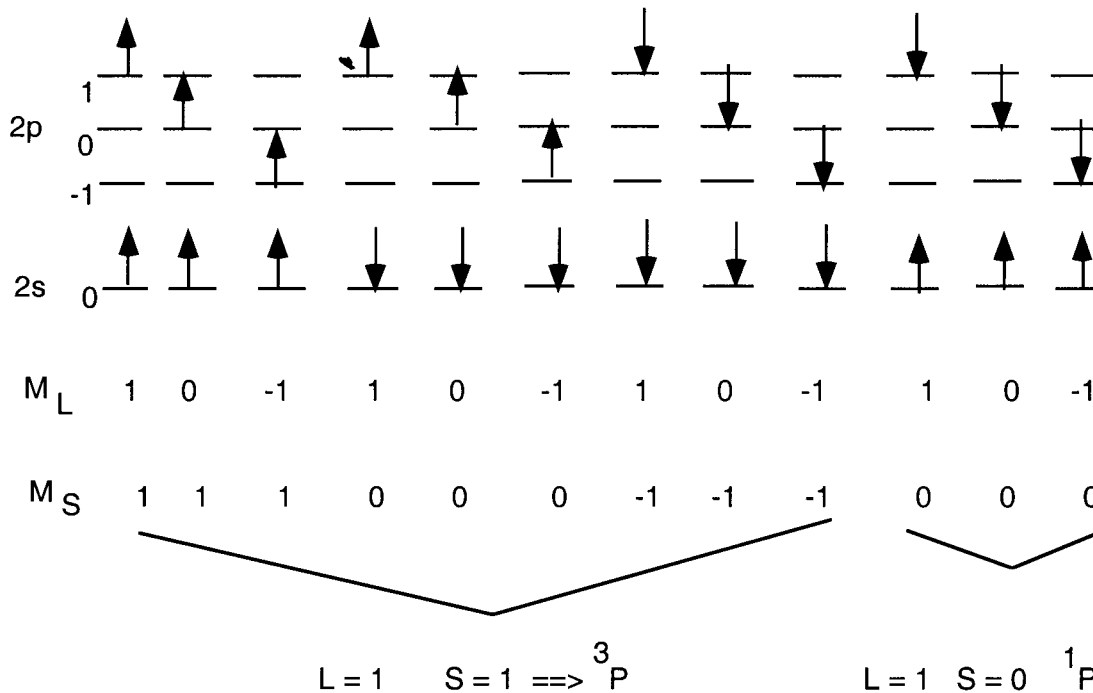
$$2p^2 \quad N = 2 \times 3 = 6 \quad (l=1) \quad M = 2 \quad W = 6! / (2! 4!) = 15$$

$$2p^3 \quad M = 1 \text{ for each shell} \quad W = W_1 \times W_2 = 6! / (1! 5!) \times 6! / (1! 5!) = 36$$

c) group the diagrams according to M_L and M_S and deduce the possible L and S values.

EXAMPLE

$$1s^2 2s^1 2p^1 \quad - \text{ only consider } 2s 2p \quad W = 6 \times 2 = 12$$



For complex cases, try to enumerate the highest L term first followed by the term of highest multiplicity. The other terms are then easier to deduce.

(d) If the Pauli Exclusion Principle need not be invoked, a simpler method is to add the l and s of open shell electrons.

EXAMPLE: $2s2p \quad l_1 = 0 \quad l_2 = 1 \implies L = 1 \quad (L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|)$
 $s_1 = 1/2 \quad s_2 = 1/2 \implies S = 1, 0$

$L = 1 \quad S = 1 \implies {}^3P$ while $L = 1 \quad S = 0 \implies {}^1P$

4. If L and S are both non-zero, spin-orbit coupling occurs. The total angular momentum quantum number $J = L+S, L+S-1, \dots, |L-S|$ and

$$E_J = A/2 [J(J+1) - L(L+1) - S(S+1)]$$

EXAMPLE: ${}^3P \quad L = 1 \quad S = 1 \quad J = 2, 1, 0 \quad A > 0 \quad {}^3P_0 < {}^3P_1 < {}^3P_2$ (ascending energy)
 $A < 0 \quad {}^3P_2 < {}^3P_1 < {}^3P_0$

5. States can be ordered by **Hund's Rules** (based on actual calculations). Hund's Rules state that for a given configuration, the energy ordering of the individual states is given by 3 rules (rule 1 being most important):

1. The higher the spin multiplicity, the lower the energy (e.g. ${}^3P < {}^1P$)
2. The higher the L, the lower the energy (e.g. ${}^1D < {}^1S$)
3. For open shells less than half-full, the lower the J the lower the energy ($A > 0$), while for open shells more than half-full, the higher the J the lower the energy ($A < 0$). For exactly half-full shells (e.g. p^3, d^5), ignore rule 3.