

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  $\mathcal{Y}_A$  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  $l$   $M = \text{no. electrons in that shell}$

EXAMPLES:

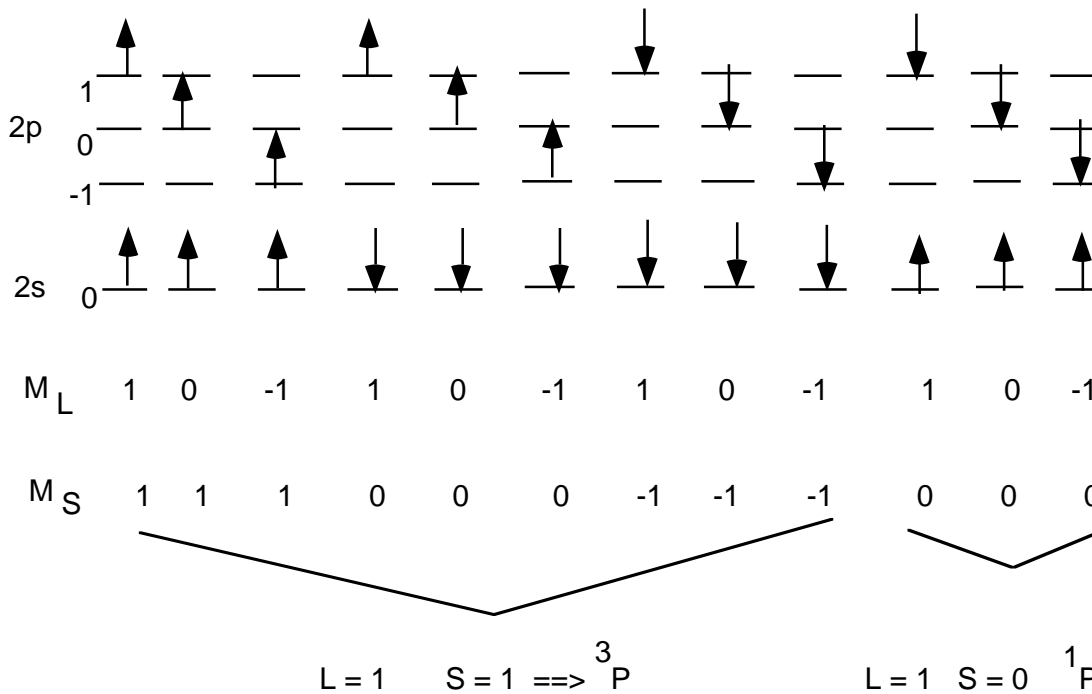
$$2p^2 \quad N = 2 \times 3 = 6 \quad (l=1) \quad M = 2 \quad W = 6! / (2! 4!) = 15$$

$$2p3p \quad M = 1 \text{ for each shell} \quad W = W_1 \times W_2 = 6! / (1! 5!) \times 6! / (1! 5!) = 36$$

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

EXAMPLE

$$1s^2 2s^1 2p^1 \quad - \text{ only consider } 2s2p \quad W = 6 \times 2 = 12$$



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.