

Chemistry 4507 - Physical Chemistry I

Lecture Handout – Term Symbols

How to find Term Symbols for Atoms:

$$^{2S+1}L_J$$

1. Determine the ground state valence subshell configuration.
2. If there is only one electron in the subshell, or if there is only one electron missing from the subshell, the value of L for the subshell is l , and the value for $S = 1/2$. Continue with step 6 below.
3. For all other configurations, write out all possible combinations of the l , m_l , and m_s for these configurations.
4. For each possible combination, add up the m_l for the electrons. The absolute values of these sums correspond to the values of L . Group the combinations that would correspond to the possible M_L values for a given L .
5. For each of the possible combinations of L and M_L , add up all the values m_s . The absolute value of each sum corresponds to the value of S .
6. Once the L 's and S 's are found, each combination (i.e. ^{2S+1}L) will have associated with it a number of J 's: $J = L+S, L+S-1, \dots, |L-S|$
7. Use Hund's rules to decide which of the possible states is the lowest in energy.
8. For excited states, use the same technique on the highest partially filled subshells, AND be aware that Hund's rules do not always give the lowest energy

Hund's Rules:

1. For a given configuration, the term with the largest S has the lowest energy (maximizing exchange stabilization)
2. For a given spin multiplicity, the term with the largest L has the lowest energy (minimizing spatial overlap)
3. To find the lowest energy of the spin-orbit coupling (J), check the occupation of the subshell:
 - a. Less than half full subshell - minimize J
 - b. More than half full subshell - maximize J