Atomic Term Symbols

C. David Sherrill
School of Chemistry and Biochemistry
Georgia Institute of Technology
November 2000

The following rules are helpful in determining the term symbol(s) arising from an electron configuration.

Rule 1: *Filled subshells don't matter.* Any filled subshells have a total orbital angular momentum $L = 0$ and spin angular momentum $S = 0$.

Rule 2: Each term symbol ${}^{2S+1}L$ represents a state described by one or more "L-S" eigenfunctions. An L-S eigenfunction is a function which is an eigenfunction of $\hat{L}^2, \hat{L}_z, \hat{S}^2$, and $\hat{S}_z$ simultaneously. (This means, for example, that the L-S eigenfunction has definite values of L, M_L, S, M_S). There is one L-S eigenfunction for each possible (M_L, M_S) pair, where $M_L = -L, -L+1, \cdots, L-1, L$, and $M_S = -S, -S+1, \cdots, S-1, S$. There are $(2L+1)(2S+1)$ L-S eigenfunctions for each term symbol.

Rule 3: For each Slater determinant with given values of M_L and M_S, there is *exactly one* L-S eigenfunction with $L \geq M_L$ and $S \geq M_S$ and having the same eigenvalues M_L and M_S of the operators $\hat{L}_z$ and $\hat{S}_z$, respectively.

Corollary: If an L-S state or term symbol is possible for a particular configuration, then it must be possible to construct *at least* one Slater determinant with $M_L = L$ and $M_S = S$.

Rule 4: The scalar L must be less than or equal to the sum of the magnitudes of the orbital angular momenta of the individual electrons,

$$L \leq l_1 + l_2 + l_3 + \ldots + l_n \tag{1}$$

Similarly, $S \leq n/2$, where n is the number of electrons outside closed shells.