

Rules for Determining the Electronic States of Molecules

There are several cases to consider for deriving molecular term symbols. Even though we are considering transition metal complexes, the following rules apply to the electronic states of molecules *in general*. The following rules are adapted from Harris and Bertolucci, *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*.

1. If all orbitals are fully occupied, the electronic state of the molecule will be the totally symmetric representation of that molecule under its point group. If, for example, we have an octahedral complex with the electronic configuration $(t_{2g})^6(e_g)^4$, the electronic term describing this state would be ${}^1A_{1g}$.

2. The only unoccupied orbital is singly occupied. The spin multiplicity for such a system must be 2, since one unpaired electron corresponds to a doublet. The symmetry of the electronic state corresponds to the symmetry of the singly occupied orbital. For example, if the singly occupied orbital has b_{2g} symmetry, then the electronic term describing this state would be ${}^2B_{2g}$.

3. There are two singly occupied orbitals that are *not* degenerate. In a situation such as this, we need to take the direct product of the irreps of the occupied orbitals. For example, the first excited state of ethylene is . . . $(b_{1u})^1(b_{2g})^1$. The direct product here is $b_{1u} \times b_{2g} = b_{3u}$. Since we can have two possible configurations of electrons in these orbitals (2 paired spins; 2 unpaired spins), we can have either singlet or triplet electronic states. The electronic terms describing these two states would be ${}^1B_{3u}$ and ${}^3B_{3u}$.

4. A degenerate orbital is lacking a single electron; it has a positive hole. This is formally equivalent to case 2. For example, a system with a $(t_{2g})^6(e_g)^3$ electronic configuration has an electronic term of 2E_g .

5. Two electrons are in a degenerate orbital. This is not a trivial case. Let's say, for example, that we have the ground state of a trigonal planar molecule with D_{3h} symmetry, which is . . . $(e')^2$. Essentially we are trying to put two electrons into four possible states; each electron could be in either of the two degenerate MOs, and could have spins of either $+\frac{1}{2}$ or $-\frac{1}{2}$. This can be represented pictorially by the following:

	$\pi_g(a)$	$\pi_g(b)$
$s = +\frac{1}{2}$		
$s = -\frac{1}{2}$		

We are trying to put 2 electrons into 4 boxes, which can be distributed as:

$$\frac{x!}{n!(x-n)!}$$

where x is the total number of places we could put an electron, and n is the number of electrons we're working with.

So, for a . . . $(e')^2$ electronic configuration, we have 6 valid ways of placing two electrons into the orbitals. We can find those 6 unique ways by doing the following.

(a) *Determine the direct product of the occupied orbitals.* For our . . . $(e')^2$ case, this would be $e' \times e' = a_1' + a_2' + e'$. We have three possible symmetries for the electronic states; how do we place electrons into those states?

(b) *The degeneracy of a term is equal to (spin multiplicity \times orbital degeneracy).* This is a useful piece of information. Once we know the degeneracy of a MO, we can use the spin multiplicity to help us. In this problem, all states with a symmetry have a degeneracy of 1, while those with e symmetry have a degeneracy of 2.

(c) *We need to find the characters of the symmetric (χ^+) and antisymmetric (χ^-) components of the direct product.* These are given by the following equations:

$$\chi^+ = \frac{1}{2} \{ [\chi(R)]^2 + \chi(R^2) \}$$

$$\chi^- = \frac{1}{2} \{ [\chi(R)]^2 - \chi(R^2) \}$$

We can apply these rules by using the D_{3h} character table, coupled with the terms we're looking for from the previous two equations.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
a_1'	1	1	1	1	1	1
a_2'	1	1	-1	1	1	-1
e'	2	-1	0	2	-1	0
a_1''	1	1	1	-1	-1	-1
a_2''	1	1	-1	-1	-1	1
e''	2	-1	0	-2	1	0
R^2	E	C_3^2	E	E	C_3^2	E
$\chi(R)^2$	2	-1	2	2	-1	2
$[\chi(R)]^2$	4	1	0	4	1	0
χ^+	3	0	1	3	0	1
χ^-	1	1	-1	1	1	-1

If we reduce the representations for χ^+ and χ^- , we find that $\chi^+ = a_1' + e'$, and $\chi^- = a_2'$. We now need to take into consideration a special relationship for electrons—the Pauli Exclusion Principle, in a slightly reformulated way. Any wavefunction, or term, for an electronic state must be written such that symmetric orbital functions (χ^+) are paired with antisymmetric (singlet) spin wavefunctions, and antisymmetric orbital functions (χ^-) are paired with symmetric (triplet) spin wavefunctions. Using this logic, the possible combinations of electronic states would be $^1A_1'$, $^1E'$, and $^3A_2'$. We can easily verify that the product of the spin multiplicity by the degeneracy for each of these terms will sum to a total of 6, the possible number of valid electronic configurations for 2 electrons in a degenerate set of orbitals.