

## 9.9: Group Theoretical Approach to Molecular Orbitals

One of the more powerfully predictive things we can do with Group Theory is predict the symmetries of molecular orbitals. Molecular orbital symmetries can have huge ramification on chemical bonding and chemical reactions.

The first thing we would like to be able to do is to predict the symmetries of the molecular orbitals that arise from the linear combinations of atomic orbitals. This is not too difficult. In fact, the process has many aspects in common with determining molecular vibration symmetries. The process can be summarized as follows:

1. Separate the molecule into groups of equivalent atoms.
2. For each set of equivalent atoms, determine the reducible representation that describe the atomic orbitals to be used in the construction of molecular orbitals. This is determined by assuming that the point group is centered on an atom containing the orbitals. Call this  $\Gamma_{ao}$ .
3. Determine  $\Gamma_{unmoved}$  for the set of equivalent atoms.
4. Multiply  $\Gamma_{ao} \otimes \Gamma_{unmoved}$  to determine  $\Gamma_{reducible}$  for each set of equivalent atoms.
5. Add all of the  $\Gamma_{reducible}$  that you have determined for each individual set of equivalent atoms. Call the result  $\Gamma_{MO}$ .
6.  $\Gamma_{MO}$  can then be resolved into components. These components give the symmetries of the molecular orbitals that result from the linear combinations of the atomic orbitals you have selected.

### ✓ Example 9.9.1

The Molecular Orbitals for a Water Molecule.

#### Solution

For this example, we shall consider the 1s orbitals on the H atoms, and the 2s and 2p orbitals on O. As it turns out, s orbitals are always totally symmetric in any point group, since they possess spherical symmetry. The p orbitals will transform as the x, y and z axes. So the following set of tables is used to generate  $\Gamma_{MO}$  for water.

First, determine  $\Gamma_H$  describing the H atoms.

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{H(1s)}$	1	1	1	1
$\Gamma_{unm}$	2	0	0	2
$\Gamma_H$	2	0	0	2

Next, determine  $\Gamma_O$  describing the four orbitals on the O atom.

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{O(2s)}$	1	1	1	1
$\Gamma_{O(2p)}$	3	-1	1	1
$\Gamma_{red}$	4	0	2	2
$\Gamma_{unm}$	1	1	1	1
$\Gamma_O$	4	0	2	2

Next, determine  $\Gamma_{MO}$  as the sum of  $\Gamma_H + \Gamma_O$

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_H$	2	0	0	2
$\Gamma_O$	4	0	2	2
$\Gamma_{MO}$	6	0	2	4

Now, decompose  $\Gamma_{MO}$  under  $C_{2v}$  symmetry!

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{MO}$	6	0	2	4
$-3 A_1$	3	3	3	3
	3	-3	-1	1
$-B_1$	1	-1	1	-1
	2	-2	-2	2
$-2 B_2$	2	-2	-2	2
	0	0	0	0

So

$$\Gamma_{MO} = 3A_1 + B_1 + 2B_2$$

The molecular orbitals of water are shown below.

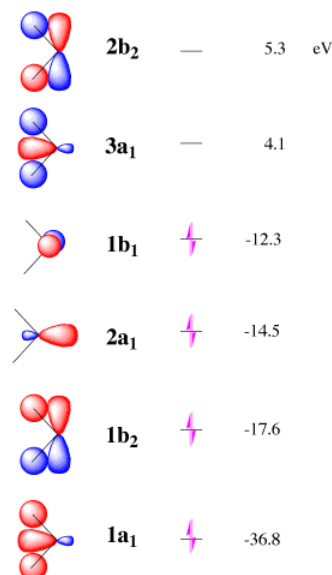


Figure 9.9.1: The above orbitals are generated based on a PM3 (semiempirical) orbital calculation of water. The numbering does not match the actual orbitals, but the symmetries are correct.

The  $1a_1$  orbital was not generated in this example because it is essentially the  $1s$  orbital on oxygen, which was not included in the basis set of functions we originally used. Also missing from our set are the  $2b_2$  and  $3b_2$  orbitals, which require the addition of  $3p_x$  and  $3d_{xz}$  orbitals on oxygen, which were not included. These orbitals are “virtual orbitals” as they are unoccupied.

The electronic configuration of  $H_2O$  is given by

$$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$$

The overall symmetry of the electronic state is given by the product of the symmetries, counting each one twice since each orbital contains two electrons. In fact, all closed shell molecules (all subshells filled) will have an electronic symmetry that is totally symmetric. In this case, the electronic state is  $^1A_1$ .

If the lowest unoccupied molecular orbital is of  $B_2$  symmetry, then the first excited state of the molecule will be

$$(1b_1)^1(4a_1)^1$$

The total electronic symmetry is given by  $B_1 \otimes A_1 = B_1$ . The electronic configuration would give rise to both singlet and triplet states.

To test whether or not the transition to this state is allowed, the transition moment integral must not vanish.

$$\int \psi' \vec{\mu} \psi'' d\tau = \int B_1 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

This integral clearly will not vanish by symmetry for the component along the x-axis. Hence, the transition to this excited state of water will be a perpendicular transition.

### ✓ Example 9.9.2

Formaldehyde

#### Solution

To generate the molecular orbitals in formaldehyde, consider the 1s orbitals on H, the 2s and 2p orbitals on C and O.

First, determine  $\Gamma_H$  describing the H atoms.

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{H(1s)}$	1	1	1	1
$\Gamma_{unm}$	2	0	0	2
$\Gamma_H$	2	0	0	2

Next, determine  $\Gamma_C$  and  $\Gamma_O$  describing the four orbitals on the C atom and the O atom.

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{C(2s)}$	1	1	1	1
$\Gamma_{C(2p)}$	3	-1	1	1
$\Gamma_{red}$	4	0	2	2
$\Gamma_{unm}$	1	1	1	1
$\Gamma_C$	4	0	2	2

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{O(2s)}$	1	1	1	1
$\Gamma_{O(2p)}$	3	-1	1	1
$\Gamma_{red}$	4	0	2	2
$\Gamma_{unm}$	1	1	1	1
$\Gamma_O$	4	0	2	2

The total reducible representation to be reduced is given by  $\Gamma_H + \Gamma_C + \Gamma_O$ .

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_H$	2	0	0	2
$\Gamma_C$	4	0	2	2
$\Gamma_O$	4	0	2	2

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{MO}$	10	0	4	6

Decomposition of this reducible representation shows

$$\Gamma_{MO} = 5A_1 + 2B_1 + 3B_2$$

The electronic configuration for formaldehyde is given by

$$(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(5a_1)^2(1b_1)^2(2b_2)^2$$

The  $(1a_1)$  and  $(2a_1)$  orbitals did not come from the above analysis as they are essentially the  $s$  orbitals on O and C that were not included in the basis set. The lowest energy unoccupied orbital is  $(2b_1)$ , so the first excited electronic state will have an electronic configuration given by

$$(5a_1)^2(1b_1)^2(2b_2)^1(2b_1)^1$$

This yields both triplet and singlet spin functions and an orbital function with symmetry given by  $b_2 \otimes b_1 = a_2$ . And as it turns out, the first electronic transition in formaldehyde is **orbitally forbidden** since no choice of a component of the dipole moment operator can be used to create a totally symmetric integrand for the electric dipole transition moment integral.

$$\int A_2 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

In order to see this transition in formaldehyde, there must be some involvement from vibrational motion that changes the symmetry of the overall wavefunction. Recall that

$$\Psi_{tot} = \psi_{elec} \psi_{vib}$$

if the Born-Oppenheimer approximation holds. The symmetries for the vibrational wavefunctions (which can be derived using the method previously discussed) are given by

$$\Gamma_{vib} = 3A_1 + B_1 + 2B_2$$

So excitation of a  $B_1$  or  $B_2$  vibrational mode (yielding an overall symmetry for the total wavefunction of either  $B_2$  or  $B_1$  respectively) will cause the transition to “turn on”. This type of **vibronically allowed transition** is not uncommon (similar behavior is observed in benzene) and is characterized by a missing 0-0 band in the electronic spectrum of the molecule.

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