

Bonding and molecular orbitals

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Description: Students learn how to compute and visualize molecular orbitals using *IQmol* and review the key concepts of the MO-LCAO picture of bonding and symmetry of electronic wave functions.

Suggested level: Beginning graduate.

Learning objectives: Learn how to compute and visualize molecular orbitals and how to assign their characters (bonding, lone pairs, antibonding); review symmetry concepts.

I. BONDING AND MO-LCAO THEORY

Molecular orbitals are linear combinations of atomic orbitals (hence, MO-LCAO); they describe one-electron states in polyatomic systems. At the Hartree-Fock level, a single determinant composed of N spin-orbitals represents an N -electron wave function. MOs are delocalized leading to electron sharing between the atoms and, consequently, chemical bonding. Orbitals featuring an increased electron density between two atoms (say, X and Y) are said to be of a bonding character (with respect to XY), whereas orbitals that have a node (and, therefore, depleted density) are called anti-bonding. The bond order is defined as follows:

$$\frac{1}{2}(n_b - n_{ab}) \quad (1)$$

where n_b and n_{ab} denote the number of electrons on bonding and anti-bonding orbitals, respectively.

The character of the orbitals is defined by looking at where the largest density is. Molecular orbitals are delocalized and to derive a simple bonding picture you may need to consider a block of two (or more) orbitals. For example, the two canonical Hartree-Fock MOs in water that have bonding character with respect to OH can be described as linear combinations of two localized σ_{OH} orbitals, thus, 4 electrons on these two orbitals give rise to the two OH single bonds (see Fig. 1).

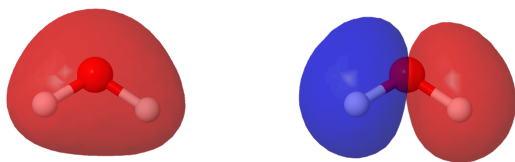


FIG. 1: Two molecular orbitals of water that have bonding σ_{OH} character, $2a_1$ and $1b_1$. Their combined contribution leads to 2 single OH bonds: $(2a_1)^2(1b_1)^2 \rightarrow (\sigma_{OH1})^2(\sigma_{OH2})^2$

σ orbitals are oriented along the bonds, whereas π -orbitals are oriented perpendicular to the molecular plane.

In a symmetric molecule, orbitals belong to different irreducible representations (irreps) of the total symmetry group; the irreps differ by how orbitals are transformed by different symmetry operations. For example, the left orbital in Fig. 1 is fully symmetric (a_1) and does

not change sign upon any symmetry operation, whereas the right one, b_1 , changes sign upon application of the C_2 and σ_v operations. The symmetry of the many-electron wave function can be determined by considering how the total many electron wave function changes under different symmetry operations. See <http://iopshell.usc.edu/resources/howto/symmetry>.

A. Preparation and symmetry review

The equilibrium structure of formaldehyde is of C_{2v} symmetry. Write down C_{2v} character table. What are unique symmetry elements? Draw the molecular structure and show these symmetry elements. Answer the following:

- Functions belonging to which irreps would change sign when acted on by the C_2 symmetry element?
- Describe, in words, what happens with a function that belongs to the A_2 irrep upon different symmetry operations?

B. Determining the bonding picture and electronic configuration of formaldehyde

Use the ω B97X-D/6-31G* optimized structure of formaldehyde from the “*Introduction to IQmol: Exploring potential energy surfaces*” lab (refer to the *IQmol* tutorial how to build and optimize structures).

At this geometry, perform a single-point Hartree-Fock calculation using the 6-31G* basis set. Visualize the MOs and prepare a summary of all *occupied* orbitals. For each molecular orbital, write down its symmetry, energy, and assign its character, i.e., bonding/anti-bonding (with respect to XY atoms), lone pair (on X); σ or π , etc. Answer the following:

1. How many occupied spin-orbitals does formaldehyde have? How many doubly occupied molecular orbitals are there?
2. Write down the electronic configuration of this Hartree-Fock wave function using the symmetry labels of the MOs.
3. What irrep does the total wave function belong to? Explain your answer.
4. Based on your assignment of the orbital characters, write down the electronic configuration in terms of bonding/antibonding/lone pair orbitals and draw a Lewis structure that this configuration represents.