Types of MOs

Skills to Develop

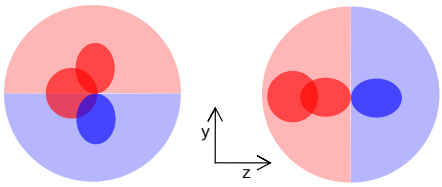
- Label the parts of an MO diagram

Bonding, Anti-bonding, and Non-bonding MOs

In the previous section, we introduced bonding and anti-bonding MOs. Bonding MOs have more electron density between the nuclei, and lower energy than the atomic orbitals they were made from. Putting electrons in bonding orbitals tends to make a bond between the nuclei, because when the electrons spend time between the nuclei, both nuclei are attracted to the negative charge between them.

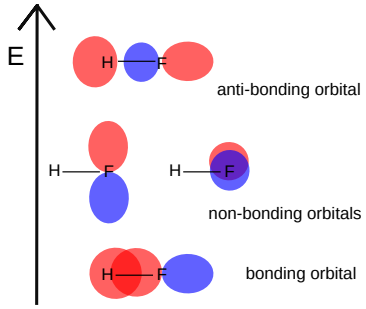
Anti-bonding orbitals have less electron density between the nuclei, because they have a node there. They have higher energy than the AOs they were made of. Putting electrons in anti-bonding orbitals tends to break bonds, because with the electrons on the outside, the nuclei repel each other and all the electrons repel each other.

There is a third type of MO: non-bonding MOs. In order to make a bond, orbitals have to have **net overlap**, which means that if you multiply them together and take the integral over the whole molecule, the integral isn't 0. Consider the HF molecule. The H 1s orbital can make a bond with the F 2s or F $2p_z$ orbital. However, there is no net overlap between the H 1s and the F $2p_x$ and $2p_y$. This is shown in the figure. When we multiply Ψ_{1s}times Ψ_{2p}, the top half is + * + = +. The bottom half is + * — = —. Except for the sign, the top half and bottom half are symmetrical, so when we add up the values of $\Psi_{1s}\Psi_{2p}$ everywhere, the top half and bottom half cancel out, and $\int \Psi_{1s}\Psi_{2p}\, dV = 0$. (Note that multiplying the wavefunctions is different from adding them, which would give us the wave interference patterns we saw in hybrids and MOs.) For this reason, the F $2p_x$ and $2p_y$ orbitals in HF are called **non-bonding orbitals**. In contrast, the $2p_z$ orbital does have net overlap with 1s, because $|\Psi_{1s}\Psi_{2p}|$ on the red side in the figure is bigger than $|\Psi_{1s}\Psi_{2p}|$ on the blue side.



Overlap between an s and p orbital, such as in HF. The s orbital is shown as a small red circle. The p orbital is shown in red and blue, representing the sign (+/—) of the wavefunction. The large circle in light red and light blue shows that the p orbital has a small amplitude over a large area. Left: the 1s and $2p_y$ orbitals have no net overlap. Right: the 1s and $2p_z$ orbitals do have net overlap.

The figure below shows a summary illustration of bonding, non-bonding, and anti-bonding orbitals in HF.

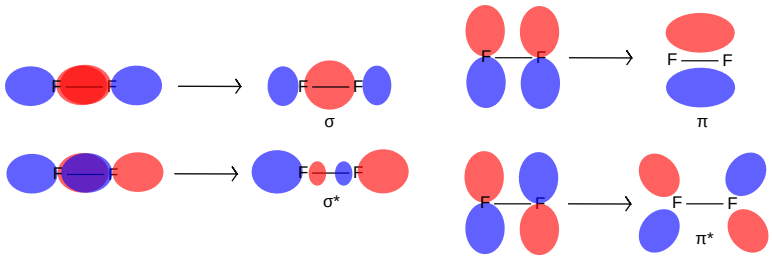


Types of MOs in HF. The sign (+/—) of the wavefunction is shown using red and blue. The MOs are ordered from bottom to top by increasing energy. Electrons in bonding MOs form bonds, electrons in anti-bonding orbitals break bonds, and electrons in non-bonding orbitals don't have any effect on bonding.

σ and π MOs

The bonding and anti-bonding MOs shown above are both σ-type MOs. Recall from the section on multiple bonds that we can classify bonds as σ or π bonds. σ-bonds are symmetrical around the bond (if you rotate them around the bond, they don't change). π-bonds change sign when you rotate them 180° around the bond.

If we think about making MOs for F_2, we can imagine making a bonding and anti-bonding combination of the $2p_z$ orbitals, which point toward each other. This will make a σ-bonding MO and an σ-anti-bonding MO. We can also make σ-type combinations of the 2s orbitals. When we combine the $2p_x$ and $2p_y$ orbitals, these are perpendicular to each other, so they will make π-type bonding and anti-bonding combinations. These are shown below. Note that for both σ combinations and π combinations electron density increases between the nuclei in bonding MOs and decreases between nuclei in anti-bonding MOs.



Formation of σ and π bonding and anti-bonding MOs in F_2. The sign (+/—) of the wavefunction is shown using red and blue. Left: σ MOs. Right: π MOs. Top: bonding MOs. Bottom: anti-bonding MOs.

Naming MOs

The easiest way to name and label MOs is using σ and π. Anti-bonding character is shown using a *, such as π* which means a π-type anti-bonding orbital. Each MO in the figure above is labeled in this way. There are other more complicated ways to name MOs, but you won't learn them unless you take Inorganic Chemistry.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)