Chem 201 Day 5: Molecular Orbital Model for Valence Electrons

Take-home Lessons

Chem 101 should have taught you basic ideas about assigning atom hybridization (and its connection with bond angles), and the use of hybrid orbitals to form sigma (σ) and pi (π) molecular orbitals from Chem 101. Sorrell reviews this material so read the book carefully and try the problems in the book.

The <u>extra</u> material that I would like to give you is the information that appears in an **orbital mixing diagram** like the following:



The diagram shows two atomic (or hybrid) orbitals (AO) that can be combined to make <u>two</u> molecular orbitals (MO). In other words, when we talk about electrons in the atoms, we use the atomic orbital picture, and when we talk about electrons in the molecule, we use the molecular orbital picture. The key is to know how we get from one picture to the other.

Rule #1 – the energy ordering is always BMO < both AO's < ABMO

This has one important consequence: when the AOs are half-filled, the BMO will be filled and the ABMO will be empty (see diagram). This makes the molecule's energy much lower than the energy of the separated atoms. Bonding orbitals stabilize electrons.

Rule #2 – the ABMO is more destabilized than the BMO is stabilized

There is an inherent asymmetry in the energies of the MOs. When the AOs have different energies, we measure (de)stabilization from the closest AO. Looking at the diagram, we see E(AO on A) < E(AO on B), so we measure <u>stabilization</u> of the BMO from the AO on A, and <u>destabilization</u> of the ABMO from the AO on B. The diagram shows that |stabilization| < |destabilization|. The consequence of this rule is that if both AOs had been filled with electrons, both MOs would have been filled as well. In that case, the molecule's energy would have been much higher than the energy of the separated atoms. Antibonding orbitals destabilize electrons.

Rule #3 - the degree of (de)stabilization depends on AO-AO overlap

When the AO on A overlaps strongly with the AO on B, the BMO is highly stabilized and the ABMO is highly destabilized. When overlap is weak, the BMO is only slightly stabilized (if that) and the ABMO is only slightly destabilized. This rule explains why we choose hybridizations to fit experimental bond angles. We know bonds are strong so we choose a hybridization that is consistent with this, i.e., one that predicts strong overlap and strong bonds.

These three rules are enough to get us started, but we will add more ideas about molecular orbitals as we go along.

Tips for Further Study

Here is what I expect you to know and know how to do when it comes to atomic, hybrid, and molecular orbitals:¹

- Define
 - Orbital energy, atomic orbital, hybrid orbital (sp, sp^2, sp^3) , atom hybridization
 - o molecular orbital, bonding orbital, antibonding orbital
 - o orbital energy diagram, orbital mixing diagram
 - o sigma orbital, pi orbital, orbital overlap, sigma overlap, pi overlap
- Use bond angles to choose an appropriate hybrid orbital model
 - Describe %s and %p content of sp, sp^2 , sp^3 hybrid orbitals
 - Describe the four orbitals that appear in the sp, sp^2 , sp^3 hybrid orbital models
 - Draw (cartoons) of the orbitals in the sp, sp^2 , sp^3 hybrid orbital models that show appropriate angles for the orbital symmetry axes
- Starting with a structural formula, describe an appropriate MO model for each electron pair
 - Describe atom hybridizations
 - Describe atomic/hybrid orbitals that overlap to create bonding, antibonding orbitals
 - Describe MOs as either sigma or pi
 - o Describe nonbonding orbitals
 - Use orbital overlap to predict relative strengths of different bonds

Read: Sorrell 2.5-2.7

Comments: You have read some of this material before. This time make sure that you understand how the hybrid and molecular orbital models fit together with the material that you have already learned.

Practice exercises:

- MO models*: Ex. 2.5-2.12, 2.25, 2.26
- Lewis \rightarrow VSEPR \rightarrow hybridization: Ex. 2.15
- Sigma v. Pi MOs: Ex. 2.16

Comments: The list of "MO models" problems is long for a reason: different molecules require different MO models. Therefore you need to practice constructing and drawing models for a wide variety of structures. It's not unusual for certain models to pose more problems than others. <u>Note the ones that cause you trouble and discuss them with me</u>.

*Sorrell refers to "MO models" as "valence bond representations." This wording is incorrect. I will say "Draw the MO model for ...," when I want you to do the thing that Sorrell is looking for in these problems.

¹ Reminder: these learning objectives refer to material covered by the lecture on Day 5. <u>Add them</u> to the learning objectives listed for previous days.