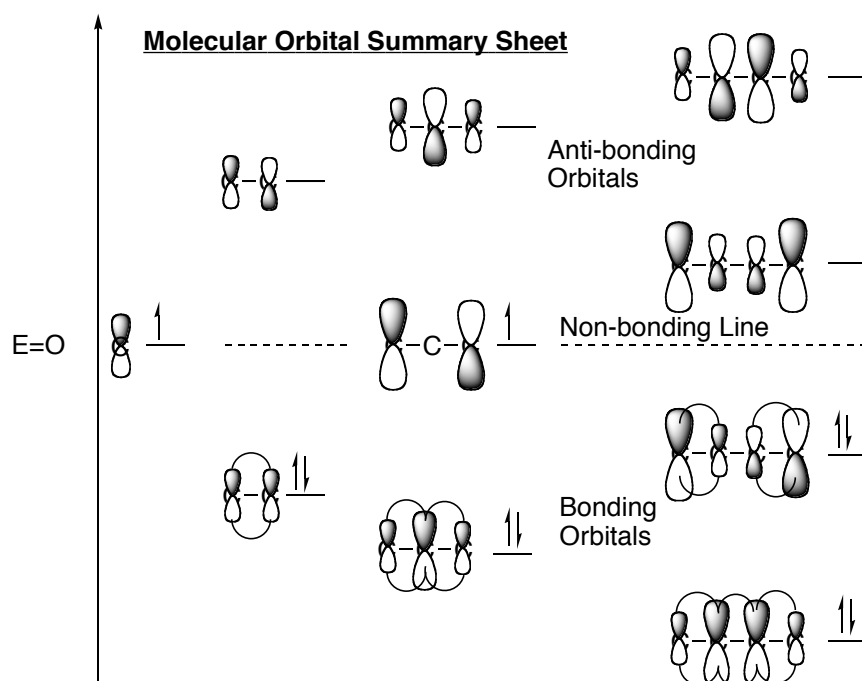
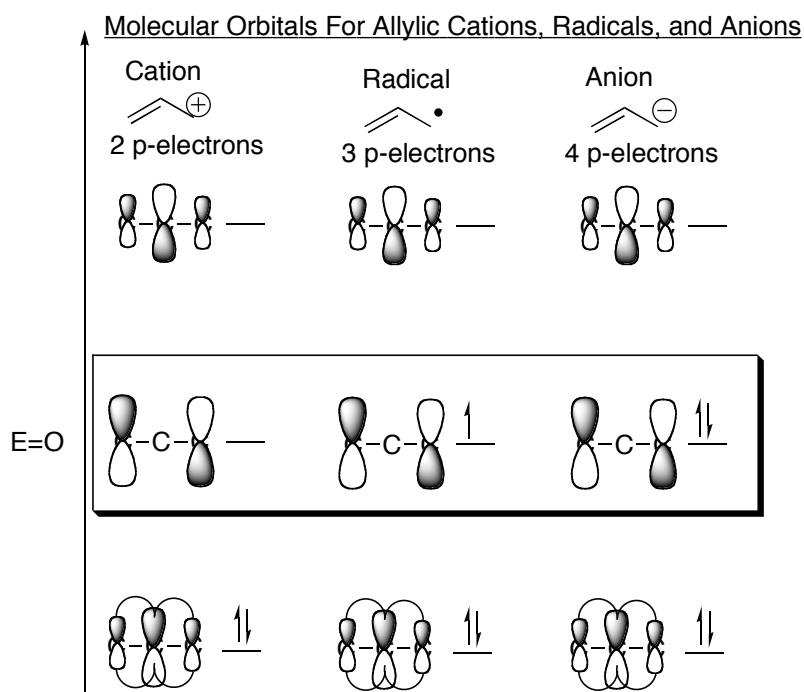


Sections 15.3, 8, 9 Molecular Orbitals and Conjugation



Observations:

1. Shown is an isolated radical, a double bond, an allyl radical, and butadiene.
2. "**MO**" = "**M**olecular **O**rbital"
3. MO's lower/stabler in energy than the non-bonding line are referred to as "bonding MO's", while those that are higher (less stable) in energy are called "antibonding MO's"
4. The number of π MO's equals the number of contributed π (p) orbitals. (One p in gives one MO. Two p's in gives two MO's. Three p's in gives three MO's. Four p's in gives four MO's. Etc.)
5. Any bonding MO is mirrored by an antibonding MO, whose energy is as high above nonbonding as the bonding MO is above it.
6. Thus the sum energies of the MO's (ignoring electron occupancy) equals 0.
7. However, not all MO's are occupied by electrons. Electron occupancy proceeds from the lowest MO's up. And it's the energies of the electrons that determine the molecular energy. Thus explains why it's energetically profitable for a molecule to be conjugated.
CONJUGATING THE P ORBITALS LOWERS THE ENERGIES OF THE ELECTRONS AND THUS IS STABILIZING.
8. The highest occupied molecular orbital is called the "**HOMO**", and the lowest unoccupied molecular orbital is called the "**LUMO**". These are also referred to as the Frontier Molecular Orbitals (**FMO**'s). The frontier molecular orbitals are the orbitals involved as nucleophiles or electrophiles in reactions. If electrons are donated (nucleophile), they will come from the HOMO. If electrons are accepted (electrophile), they will go to the LUMO. Thus the energies and shapes of the HOMO/LUMO are really important.
9. The lowest MO keeps getting lower and lower (more and more stable). But, the energy level of the HOMO does **not** get progressively lower. Notice that the diene HOMO is higher than the simple alkene HOMO.
10. Notice that not all atoms have the same sized p-orbitals in the FMO's. When reactions happen, atoms with the big p-lobes are the ones that react.



11. For allylic systems, notice that the energies and shapes of the MO's stay the same.
12. However, the occupancy does change. An allylic cation has two π -electrons, an allylic radical has three, and an allylic anion has four. Thus the key reactive middle MO goes from empty (strongly electrophilic) to full (strongly nucleophilic) across the series.
13. The MO picture tells the same story that resonance pictures show: there is no reactivity on the central carbon, but the outside carbons are the ones that react, whether in an allylic cation, radical, or anion.
 - MO theory explains this with the orbital lobes
 - Resonance theory explains this with $\text{CH}_2=\text{CH}-\text{CH}_2^+ \longleftrightarrow ^+\text{CH}_2-\text{CH}=\text{CH}_2$
14. Sometimes MO can explain things that the simpler resonance theory can't.