Dr M. Mehrdad
University of Guilan, Department of Chemistry, Rasht, Iran
**Methyl Chloride**

Methyl chloride is considered as a prototype of an organic molecule singly bonded to an electronegative element. Instead of constructing a complete mixing diagram, we will concentrate on the C-Cl bond.

Clearly, the C-Cl bond is formed by the mixing of $\sigma$(out) of the CH$_3$ with a chlorine p orbital.

The mixing diagram is shown as Figure 11. The chlorine AO’s, as predicted, are lower in energy than the $\sigma$(out) orbital of carbon.

Thus the polarizations have the bonding MO polarized towards Cl, whereas the antibonding MO is polarized towards C.

**Figure 1.19**

Orbital mixing diagram for CH$_3$Cl, with computed orbitals shown. $\sigma$(out) + $p$ is the bonding orbital. $\sigma$(out) – $p$ is the LUMO, $\sigma^*$ antibonding orbital.
The most interesting MO is the LUMO, which is the prototype $\sigma^*$ orbital.

It is C-Cl antibonding, with the orbital density accentuated at the carbon end of the molecule, with a very large density on the “backside” of the carbon.

The drawing below perhaps better represents this situation:

![Diagram of the $\sigma^*$ C-Cl orbital](image-url)
Butadiene

The $\pi$-system of 1,3-butadiene is examined in Figure 12, as an example of how conjugated $\pi$-systems can be treated by orbital mixing.

For the most part, in so doing, one is primarily interested in the mixing of the $\pi$ and $\pi^*$ group orbitals, which upon mixing give four MO’s as shown.

Note that the simple schematic mixing of the ethylene $\pi$ and $\pi^*$ orbitals does not predict the relative extent to which the individual $p$-orbitals on each carbon contribute to each of the MO’s.

However, the simple mixing properly predicts the impact on orbital energies and upon the nodal properties of the MO’s.
More extended $\pi$-systems

When constructing MO diagrams of extended $\pi$ systems, it is generally satisfactory to simply consider the mixing of the $p$-orbitals of the system, with particular emphasis upon the nodal properties and their relative energies, as shown below for 1,3,5-hexatriene,

which mixes 6 conjugated $p$-orbitals and produces 6 MO’s, three bonding and three antibonding, as shown in Figure 13:

**Figure 13.** $\pi$-Molecular Orbital diagram for 1,3,5-hexatriene
This Figure presents the MOs of benzene, both in symbolic form and as produced by an accurate quantum mechanical calculation.
"HOMO" of benzyl—that is, the singly occupied orbital of benzyl radical, the empty orbital of benzyl cation, and the doubly occupied HOMO of benzyl anion.
The Allyl System

It is a useful exercise to form the MO’s of the allyl system using an orbital mixing strategy, and such an analysis is shown below in Figure 14.

Figure 14. Mixing diagram for the allyl $\pi$–system
Whether one is talking about an allyl cation, radical or anion (2, 3 or 4 $\pi$ electrons, the energies and symmetries (nodal properties) of the three $\pi$-MO’s depicted in Figure 14 will not vary significantly.

Specifically, it should be noted that allyl molecular orbital $\pi_2$ is the LUMO for the cation, the SOMO for the radical and the HOMO for the carbanion, which is in each case the reactive orbital of the respective species.

This is consistent with the VB (resonance) approach to understanding the nature of these species.

For allyl, it is simplest to first mix C1 and C3.

We can form the in-phase and out-of-phase combinations of p orbitals, but to a good approximation, these nonadjacent orbitals do not overlap significantly, so there is no energy split.

Now we bring in C2. It can mix only with the in-phase combination of C1 and C3, because it lies on the node of the combination.
Empty in allyl cation
Half-filled in allyl radical
Filled in allyl anion
For allyl, it is simplest to first mix C1 and C3. We can form the in-phase and out-of-phase combinations of \( p \) orbitals, but to a good approximation, these nonadjacent orbitals do not overlap significantly, so there is no energy split.

Now we bring in C2. It can mix only with the in-phase combination of C1 and C3, because it lies on the node of the combination.