

Method to Generate MOs for Sigma Systems

- 1) Draw a geometry of the molecule or molecular fragment that you want to analyze.
- 2) Use only the s and p orbitals on heavy atoms (not hydrogen) from the periodic table.
- 3) Draw these orbitals with their phasing on the heavy atoms, and then simply draw the phasing of the hydrogen to match the phasing of the s and p orbitals on the heavy atoms.
- 4) Whenever you place the hydrogens in phase to make constructive (bonding) interactions, also draw at much higher energy the out-of-phase interaction.
- 5) If the highest bonding orbital has a symmetry element in common with the lowest anti-bonding orbital (usually a C_n axis) and they are formed primarily from different orbitals on the heavy atom, then mix (add and subtract) these two orbitals.
- 6) You have now drawn cartoons of the molecular orbitals of the sigma system.
- 7) Populate the orbitals with electrons to get bonds that are delocalized across the entire sigma-system.
- 8) The population of electrons in the orbital diagram where two geometries are being compared (a Walsh diagram) will lead you to a prediction of the most stable geometry.