Exercise 4.1
Linear Combination of Atomic Orbitals: Linear Polyatomic Molecules

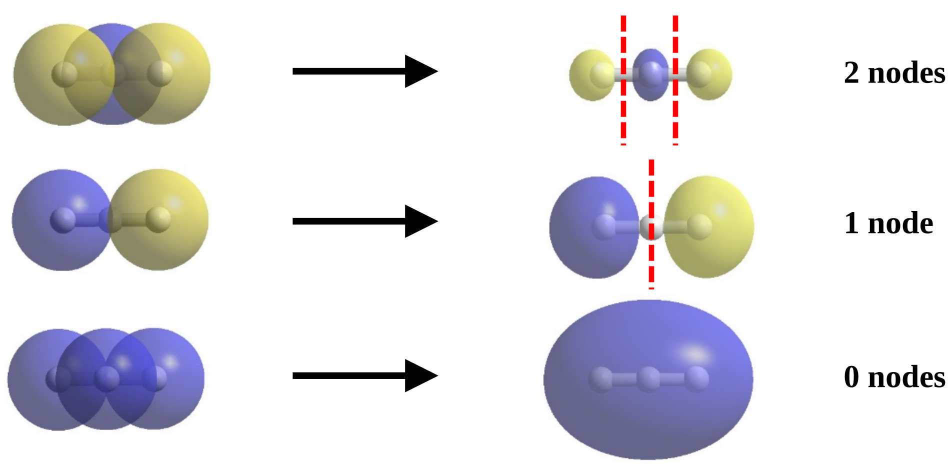
Linear Combination of More Than Two Atomic Orbitals

Linear Combination of Atomic Orbitals (LCAO) is not limited to situations where there are only two atoms. All the same principles apply in polyatomic molecules. Orbitals must have the same symmetry to interact, and they must have similar energies. We tend to use 1 Ry as an easy to remember cut-off for "close enough in energy to interact", but it is important to realize that interaction simply gets weaker as the AO energies get farther apart. There is no significant difference between an energy gap of 0.99 Ry and an energy gap of 1.01 Ry.

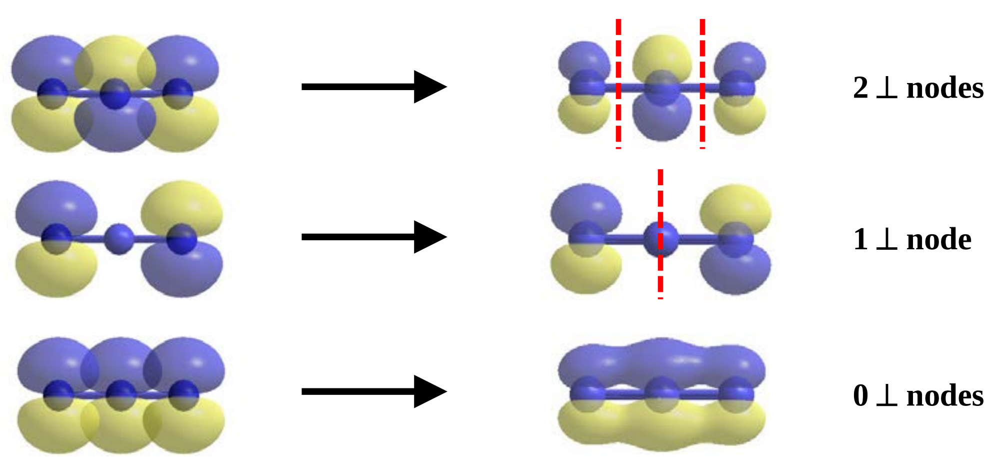
The number of molecular orbitals (MOs) produced from LCAO is **always** equal to the number of AOs combined, and the MOs produced must have the same symmetry as the AOs.

It is usually easiest to start by finding the most in-phase interaction (to make the "most bonding" MO) and the most out-of-phase interaction (to make the "most antibonding" MO). Count the number of nodes in each of those MOs. Then work out the "in the middle" MOs based on the knowledge that the number of nodes tends to increase with energy.

For example, LCAO of three *s* orbitals produces three σ-symmetric MOs. There are no nodes in the "most bonding" MO. There are two nodes in the "most antibonding" MO. So, logically, there should be one node in the middle MO. If the molecule or ion is symmetric, that one node will go through the middle of the molecule. Nodes are shown with dashed red lines:



The same is true for LCAO of three *p* orbitals to produce three π-symmetric MOs:



1. Draw the set of four σ-symmetric MOs that would be produced from LCAO of four *s* orbitals in a linear molecule containing four atoms of the same element.

   Rank the MOs from lowest to highest energy, and label them accordingly.

2. Draw the set of four π-symmetric MOs that would be produced from LCAO of four *p* orbitals in a linear molecule containing four atoms of the same element.

   Rank the MOs from lowest to highest energy, and label them accordingly.

3. Draw the set of six σ-symmetric MOs that would be produced from LCAO of three $2s$ orbitals and three $2p_z$ orbitals in a linear molecule containing three atoms of the same element.

Rank the MOs from lowest to highest energy, and label them accordingly.

Assume that all six AOs are close enough in energy that you don't need to worry about polarization of the MOs.

4. There are ten valence MOs in ethyne ($H - C \equiv C - H$).

Assume that all AOs are close enough in energy that you don't need to worry about polarization of the MOs.

(a) List the ten AOs which can be combined to make these ten MOs. Clearly indicate which AOs come from each atom.

(b) Which of these AOs are π-symmetric? Can they all combine, or do they need to be divided into groups according to orientation?

(c) Which of these AOs are σ-symmetric?

(d) Draw the four π-symmetric MOs that can be produced from LCAO of the four π-symmetric AOs. Rank the MOs from lowest to highest energy, and label them accordingly.

(e) Draw the six σ-symmetric MOs that can be produced from LCAO of the six σ-symmetric AOs. Rank the MOs from lowest to highest energy, and label them accordingly.