Exercise 2.2
Linear Combination of Atomic Orbitals: Homonuclear Diatomics

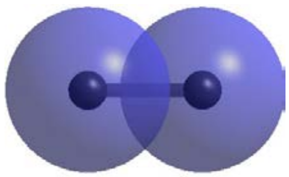
Using Linear Combination of Atomic Orbitals to Draw Molecular Orbitals

Molecular orbitals are built from atomic orbitals using a method called “linear combination of atomic orbitals” which is often abbreviated as LCAO. The atomic orbitals being combined must all have the same type of symmetry (all sigma or all pi)

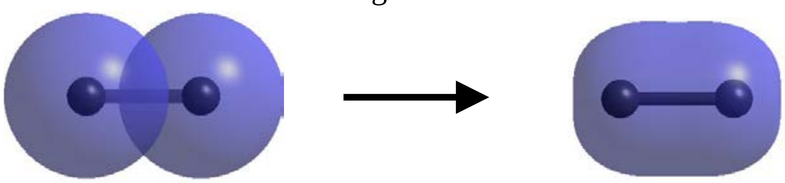
To draw a molecular orbital using LCAO:

1. Draw the molecule so that you know where the nuclei are.

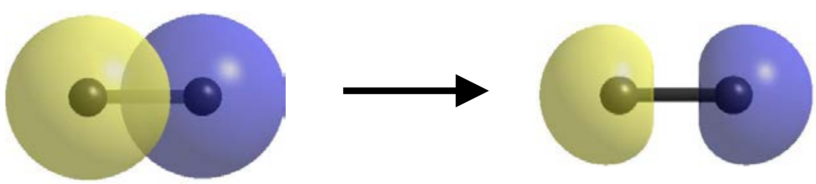
2. Draw each atomic orbital that you will be using to build the molecular orbital. Draw each orbital on the correct nucleus. Valence atomic orbitals should be drawn large enough so that they appear to overlap.



3. On a new picture of the molecule, draw the combination.
    a. In any region where the two atomic orbitals overlap with the same phase, there is “constructive overlap” and you should represent that by making the molecular orbital look like the lobes of the two atomic orbitals merged into one bigger lobe. Orbitals are really waves and, when two waves are added in-phase, the combination is larger than either of the two starting waves.

    b. In any region where the two atomic orbitals overlap with opposite phases, there is “destructive overlap” and you should represent that by making the molecular orbital look like the two atomic orbitals partially canceled out, leaving a node between them. Orbitals are really waves and, when two waves are added out-of-phase, the combination is smaller than either of the two starting waves.

With enough practice, you’ll be able to skip the first “draw the atomic orbitals” steps and draw the molecular orbital directly; however, you should not do this until you are very confident in your ability to do so correctly. If you’re still drawing the atomic orbitals first at the end of CHEM 2000, that’s fine!

Constructive Overlap and Destructive Overlap Both Happen

Whenever atomic orbitals are combined to make molecular orbitals, THE TOTAL NUMBER OF ORBITALS MUST BE PRESERVED!

So, if two atomic orbitals are combined to make a molecular orbital, there must be a second molecular orbital produced at the same time. Similarly, if three atomic orbitals are combined, they must make three molecular orbitals. If four atomic orbitals are combined, they must make four molecular orbitals. And so on…

If two atomic orbitals combine to make two different molecular orbitals, there must be two different ways to combine them. If you refer back to the diagrams at the bottom of the previous page, you'll see those two ways: constructive overlap (where the two atomic orbitals have the same phase in the overlap region) and destructive overlap (where the two atomic orbitals have opposite phases in the overlap region).

In diatomic molecules, constructive overlap gives a bonding molecular orbital (which is lower in energy than either atomic orbital from which it was made) while destructive overlap gives an antibonding molecular orbital (which is higher in energy than either atomic orbital from which it was made). In larger molecules, the situation is a little more complicated than that, but the general principle still applies.

1. Draw the two molecular orbitals that are formed from each pair of atomic orbitals in a second period homonuclear diatomic molecule. Label each molecular orbital as sigma or pi. Label each molecular orbital as bonding or antibonding.

   "Homonuclear diatomic" means that both atoms in the molecule are of the same element. "Second period" means that the element is in the second row of the periodic table.

(a) $2p_z + 2p_z$ (constructive overlap) $2p_z - 2p_z$ (destructive overlap)

(b) $2p_x + 2p_x$ (constructive overlap) $2p_x - 2p_x$ (destructive overlap)

(c) $2p_y + 2p_y$ (constructive overlap) $2p_y - 2p_y$ (destructive overlap)

2. Draw the two molecular orbitals that are formed from each pair of atomic orbitals in a third period homonuclear diatomic molecule. Label each molecular orbital as sigma or pi. Label each molecular orbital as bonding or antibonding.

(a) $3s + 3s$ (constructive overlap) $3s - 3s$ (destructive overlap)

(b) $3p_z + 3p_z$ (constructive overlap) $3p_z - 3p_z$ (destructive overlap)

(c) $3p_x + 3p_x$ (constructive overlap) $3p_x - 3p_x$ (destructive overlap)

(d) $3p_y + 3p_y$ (constructive overlap) $3p_y - 3p_y$ (destructive overlap)

3. Draw the two molecular orbitals that are formed from each pair of atomic orbitals in a fourth period homonuclear diatomic molecule. Label each molecular orbital as sigma or pi. Label each molecular orbital as bonding or antibonding.

(a) $3d_{z^2} + 3d_{z^2}$ (constructive overlap) $3d_{z^2} - 3d_{z^2}$ (destructive overlap)

(b) $3d_{xz} + 3d_{xz}$ (constructive overlap) $3d_{xz} - 3d_{xz}$ (destructive overlap)

(c) $3d_{yz} + 3d_{yz}$ (constructive overlap) $3d_{yz} - 3d_{yz}$ (destructive overlap)

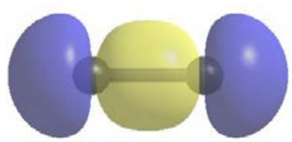
When More Than Two Atomic Orbitals Combine…

When atomic orbitals on neighboring atoms have energies within 1 Ry of each other and have the same type of symmetry, they will combine to make molecular orbitals. In some atoms, the $2s$ and $2p$ atomic orbitals have energies within 1 Ry of each other. As such, all four sigma-symmetric atomic orbitals ($2s$ and $2p_z$ on each atom) combine to make four sigma-symmetric molecular orbitals. This is the case for B_2, C_2, N_2 and their ions.

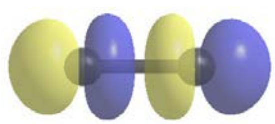
When dealing with cases in which more than two atomic orbitals combine, it can be helpful to use nodes to help you predict the shape of the molecular orbitals. While you would get similar answers to the question below by pretending that the $2s$ and $2p$ atomic orbitals did not interact, the technique will be useful for dealing with larger molecules. As such, it's a good idea to get familiar with the technique using a relatively simple case.

The easiest strategy is to identify the lowest energy (fewest nodes therefore "most bonding") combination of atomic orbitals first. Then identify the highest energy (most nodes therefore "most antibonding") combination of atomic orbitals. Finally, predict the number of nodes for each of the other molecular orbitals and draw the corresponding shapes. You ought to be able to imagine a set of atomic orbitals within every molecular orbital you have drawn. Also, in symmetrical molecules, every molecular orbital must be either symmetric or antisymmetric.

When a symmetric molecular orbital is reflected through the middle of the molecule, the shapes and phases match perfectly:



When an antisymmetric molecular orbital is reflected through the middle of the molecule, the shapes match perfectly but the phases are opposite:



4. Consider a homonuclear diatomic molecule in which the $2s$ and $2p_z$ atomic orbitals all combine to give a set of four sigma-symmetric molecular orbitals.

(a) Draw the lowest energy combination of atomic orbitals (the combination that gives fewest nodes) and the resulting molecular orbital. How many nodes does it have?

(b) Draw the highest energy combination of atomic orbitals (the combination that gives most nodes) and the resulting molecular orbital. How many nodes does it have?

(c) Two molecular orbitals remain. How many nodes must each have? Use that information to draw the remaining two molecular orbitals.