# Exercise 4.3
Linear Combination of Atomic Orbitals: Planar Molecules

Planar Molecules (Bent, Trigonal Planar, etc.)

The main difference between planar molecules and linear molecules is the number of pi systems.[1]
In a linear molecule, the p_x orbitals combine to make one set of π MOs and the p_y orbitals combine to make a second set of π MOs perpendicular to the first set:

 and
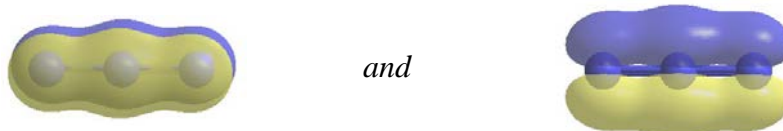
In a planar molecule, there can only be one set of π MOs because there is only one plane that passes through all the atoms in the molecule (shown as a red dashed line on the side view). So, in a planar molecule, only the p_z orbitals[2] combine to make a single set of π MOs:

top view   *side view*

A side effect of this difference is that there are two orientations of p orbitals contributing to the σ MOs. This tends to make the σ MOs of planar molecules appear more complex than the σ MOs of linear molecules.

For example, water is a bent molecule:
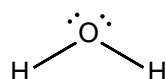
Grouping the AOs by symmetry and energy gives:
- one pi-symmetric $2p_z$ orbital from O,
- one sigma-symmetric $2s$ orbital from O that is too low in energy to mix with the other sigma-symmetric atomic orbitals,
- four more sigma-symmetric orbitals: $2p_x(O)$, $2p_y(O)$ and two $1s(H)$.

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[1] A "pi system" is a set of pi-symmetric AOs on a set of connected atoms which all share the same nodal plane and can therefore combine to make a single set of pi-symmetric MOs. So, the p_x orbitals in a linear molecule form one pi system, and the p_y orbitals form another pi system. In a planar molecule, the p_z orbitals form the only pi system.

[2] Recall the convention that p_x and p_y have the same symmetry. If one p orbital has different symmetry, it is p_z.

It is therefore easy to predict the shape of the only pi-symmetric MO (1π). It should look like the $2p_z$ orbital from O:
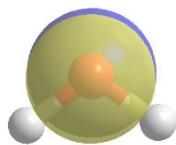
It is also easy to predict the shape of the lowest energy sigma-symmetric MO (1σ). It should look like the $2s$ orbital from O (though the modeling software calculates a small contribution from the $1s$ orbitals of H, "stretching out" the MO a little):
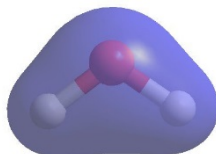
The remaining sigma-symmetric MOs are more difficult to predict but, once we see the pictures generated by modeling software, we can imagine combinations of $2p$ orbitals from O and $1s$ orbitals from both H that would generate each shape. The top image for each MO is the shape calculated using modeling software. In the bottom image of each MO, a $2p$ orbital on the oxygen atom and a $1s$ orbital on each hydrogen atom are shown with the appropriate phases to combine to give the MO in the image above. The equation in the middle describes the overlap using + to indicate constructive overlap ("in phase") and – to indicate destructive overlap ("out of phase"):

$$1s(H) + 2p_x(O) + 1s(H) \qquad 1s(H) + 2p_y(O) + 1s(H) \qquad 1s(H) - 2p_y(O) - 1s(H) \qquad 1s(H) - 2p_x(O) - 1s(H)$$
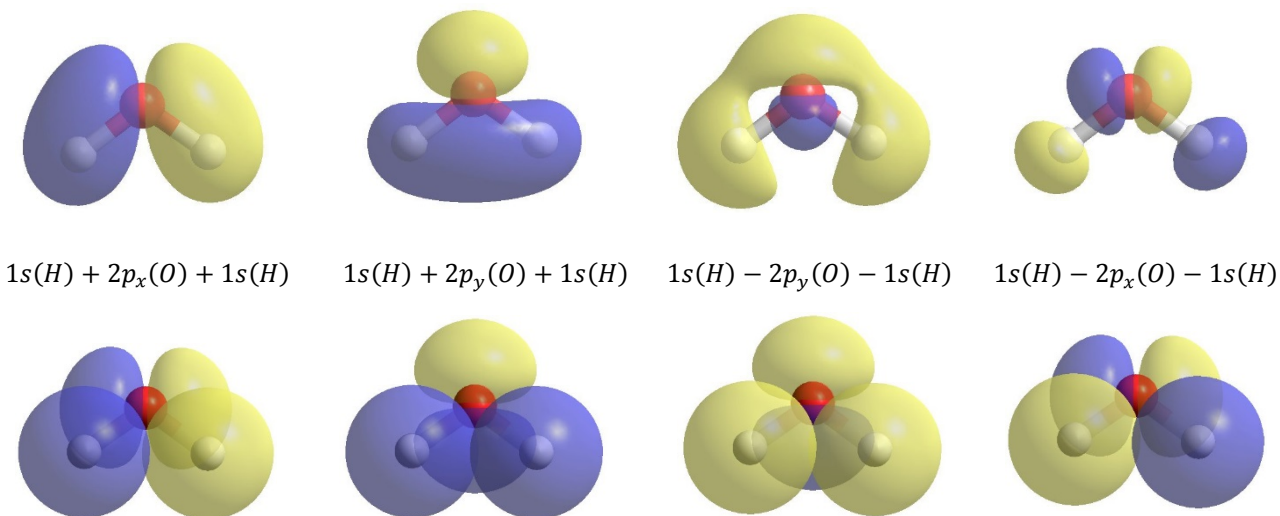
Because of the symmetry of the water molecule, each of these MOs is either symmetric or antisymmetric. If you reflect the MO left-to-right, the shape will not change; the phases of each lobe either all remain the same or all switch. Any MO made from a $1s$ orbital on one H is also made from a $1s$ orbital on the other H. This behavior is formalized in "group theory", a topic typically taught in senior courses.

In CHEM 2000, you are **not** expected to predict the shapes of the σ MOs of planar molecules without guidance. You are, however, expected to recognize the AOs that form them, recognize that they have sigma symmetry, and categorize them as bonding, antibonding or nonbonding. You can also be asked to interpret a molecular orbital energy level diagram that has been provided.

1. How many pi systems does each of the following species have?
    List the atomic orbitals contributing to each pi system.
    Hint: You will have to draw Lewis diagrams and apply VSPER to answer this question.

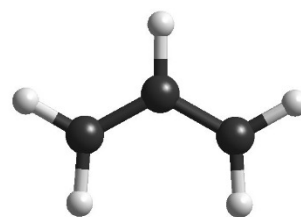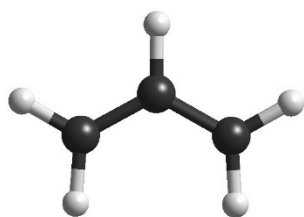(a) CO_2 (b) CH_2O (c) O_3
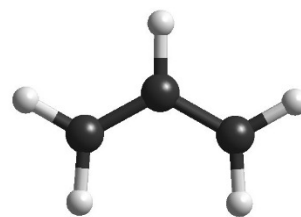
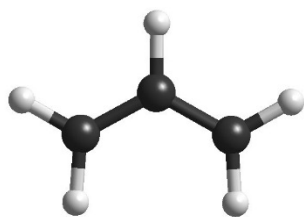(d) NO_2^- (e) NO_3^- (f) NO_2^+

2. The images below show the geometry of the allyl cation $(C_3H_5^+)$ in which each carbon atom is trigonal planar. For each π MO of the allyl cation, draw the AOs which combine to make it (on the image on the left) and the MO itself (on the image on the right).

$3\pi^*$

$2\pi_{nb}$

1π