

Chemistry 2000 Slide Set 5: Molecular orbitals for polyatomic molecules

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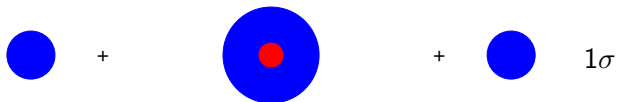
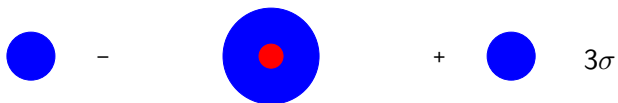
LCAO-MO theory for polyatomic molecules

- LCAO-MO theory can of course be used for molecules of any size.
- This becomes difficult to do qualitatively with many nuclei or complex geometries, but we can do symmetric triatomic molecules by hand, as well as some aspects of larger, highly symmetric molecules.
- Symmetry is an important principle.
- If all else fails, use a computer!

BeH_{2(g)}

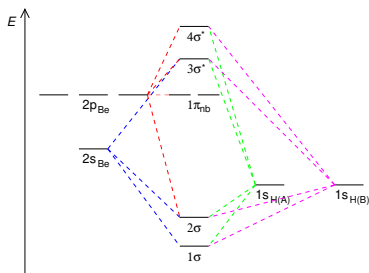
- BeH₂ in the gas phase is a linear molecule.
- The Be 2s and 2p orbital energies are similar to the H 1s orbital energy.
- Because of the symmetry of the molecule, MOs can either be symmetric or anti-symmetric about the centre (so that the electron density is always symmetric).
- The Be 2p_x and 2p_y become nonbonding π orbitals of BeH₂.

- Possible bonding and antibonding σ linear combinations:



Important:
The molecular orbitals are
delocalized
over the whole molecule.

- Valence MO diagram (not all tie-lines drawn):



- Ground-state electron configuration: $(1\sigma)^2(2\sigma)^2$
- Bond order = ?

HOMO, LUMO, and Lewis acidity

HOMO: Highest Occupied Molecular Orbital

LUMO: Lowest Unoccupied Molecular Orbital

Frontier orbitals: HOMO and LUMO

- BeH_2 is a Lewis acid, i.e. an electron-pair acceptor.
- A donated electron pair goes into the LUMO of the acceptor.
- Where is the LUMO for BeH_2 ?
How does this relate to the Lewis electron pushing diagrams?
- The HOMO-to-LUMO gap is also important because it represents the lowest-energy electronic transition and is typically responsible for absorption in the UV or visible range.

CO₂

Valence atomic orbitals available:

From C: 2s, 2p

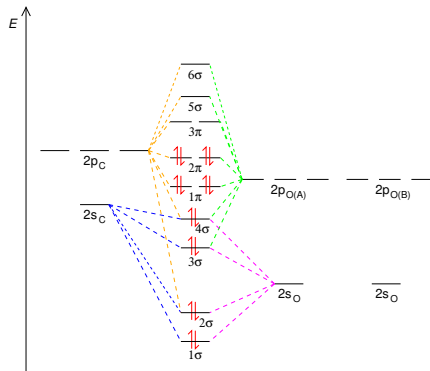
From each O: 2s, 2p

Valence σ -type AOs: $2s_C$, $2p_{z,C}$, $2s_{O(A)}$, $2s_{O(B)}$, $2p_{z,O(A)}$, $2p_{z,O(B)}$
 \therefore 6 valence σ MOs

Valence π -type MOs: $2p_{x,C}$, $2p_{y,C}$, $2p_{x,O(A)}$, $2p_{y,O(A)}$, $2p_{x,O(B)}$, $2p_{y,O(B)}$
 \therefore 6 (3 pairs) valence π MOs

That's a lot of orbitals!

A peek at the result, and an observation



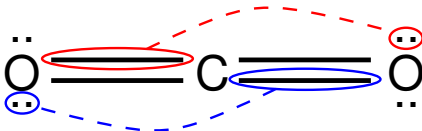
- Notice that the frontier orbitals are π orbitals.

π orbitals as frontier orbitals

- For molecules with “nice” Lewis diagrams (octet rule satisfied) that have multiple bonds, the frontier orbitals are very frequently π orbitals.
- Because the σ and π orbitals arise from independent LCAOs, we can build the π orbital energy diagram independently of the σ orbitals.

Counting π electrons

- π electrons can be counted from the Lewis diagram.
- Double and triple bonds contain π electrons, but so do **some** lone pairs.
- Rules:
 - In a double bond, **one pair** of electrons are part of the π system.
 - In a triple bond, **two pairs** of electrons are part of the π system.
 - When there is at least one lone pair on an atom one bond away from a π bond, count **one** of the lone pairs as π electrons.
 - CO₂ has **8** π electrons:



π MOs of nonlinear molecules

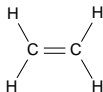
- So far, we have focused on linear molecules.
- The principles are the same for nonlinear molecules.
- Again, we will focus on the frontier π orbitals.

Definition: The nodal plane of a π MO contains the molecule.

- Technically, only planar molecules can have true π MOs.
- Linear molecules have degenerate π MOs because the molecule lies in **two** orthogonal planes.
- Planar (nonlinear) molecules need not have degenerate π MOs.

Ethene

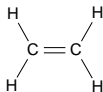
What we know and don't know from VSEPR



- From VSEPR theory, we know that there should be a trigonal planar arrangement around each carbon atom.
- VSEPR does **not** tell us how these two planar structures are oriented relative to each other.
 - The molecule could be completely flat.
 - The two CH₂ groups could be twisted 90° relative to each other.

Ethene

MO treatment



- For each carbon atom, the s , p_x and p_y orbitals are available to form σ bonds. These are needed to form the two bonds to the hydrogen atoms, and the carbon-carbon bond.
- There would therefore be **one** p orbital left over on each carbon, the p_z , oriented perpendicular to the trigonal plane.
- The p_z orbital on one carbon atom can only combine with the p_z orbital on the other, forming a π bond, if they are oriented identically, i.e. **only if the molecule is flat**.

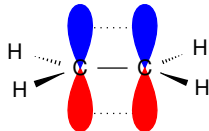
Ethene

MO treatment (continued)

- The two p_z orbitals combine to give one bonding and one antibonding π orbital.
- There are two π electrons which therefore occupy the bonding orbital, giving a π bond order of 1 and an overall carbon-carbon bond order of 2.

Ethene

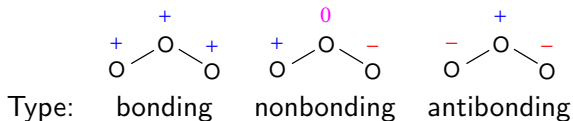
- LCAO construction of bonding π orbital:

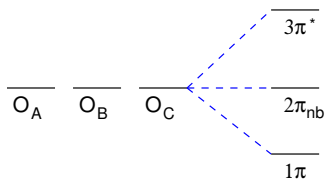


- Note that the π bond **enforces planarity** since twisting about the bond axis would destroy the overlap between the p orbitals.

Ozone

- Ozone is planar, so there will be one p orbital from each oxygen atom perpendicular to the plane of the molecule.
- With three p orbitals, we can make three MOs.
- Represent the orientation of a p orbital making up an MO by a + or - (e.g. + if the phase of the lobe of the p orbital sticking up is positive).
- Possible arrangements:



Ozone π MO diagram

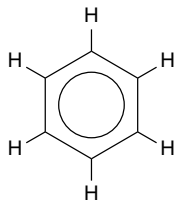
- Resonance structures of ozone:



Note: Use **one** resonance structure to count π electrons.

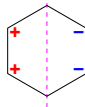
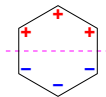
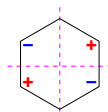
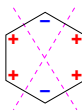
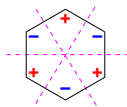
- Determine the bond order using the MO diagram.

Benzene



- Again, there is one p orbital available for π bonding per carbon atom, so six π orbitals.
- There are six electrons in these π orbitals.

Highest energy



Lowest energy

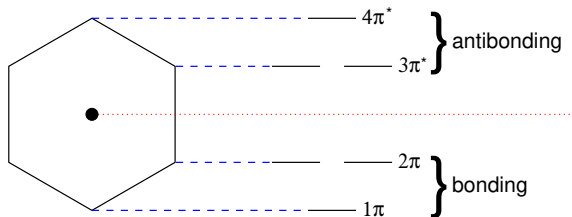


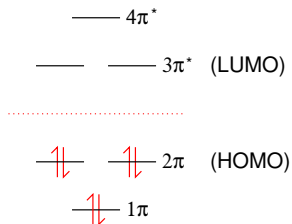
Observation: More nodal planes = higher energy

Note: The bottom three are bonding orbitals.
The top three are antibonding.

Energy levels of monocyclic planar hydrocarbons

- There is a simple trick for generating the π MO diagram of a planar monocyclic hydrocarbon (like benzene).
- Draw the polygonal carbon cycle with one of the points down.
- Mark the centre of the polygon.
- The heights of the points are the π orbital energies.
- The centre divides the bonding from the antibonding orbitals.
- For benzene:





- π orbital occupancy in benzene: $(1\pi)^2(2\pi)^4$
- Bond order ($\sigma + \pi$): $1 + \frac{3}{6} = \frac{3}{2}$