Molecular Orbital Theory

- For example, when two hydrogen atoms bond, a $\sigma_{1s}$ (bonding) molecular orbital is formed as well as a $\sigma_{1s}^*$ (antibonding) molecular orbital.
- The following slide illustrates the relative energies of the molecular orbitals compared to the original atomic orbitals.
- Because the energy of the two electrons is lower than the energy of the individual atoms, the molecule is stable.

Figure 9.26: (a) The molecular orbital energy-level diagram for the H$_2$ molecule. (b) The shapes of the molecular orbitals are obtained by squaring the wave functions for MO$_1$ and MO$_2$.

Factors that determine orbital interaction:

- energy difference between the interacting orbitals
- magnitude of their overlap

For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large

- In order to participate in MOs, atomic orbitals must overlap in space. (Therefore, only valence orbitals of atoms contribute significantly to MOs.)
**Bond Order**

- The term **bond order** refers to the number of bonds that exist between two atoms.
- The bond order of a diatomic molecule is defined as one-half the difference between the number of electrons in bonding orbitals, \( n_b \), and the number of electrons in antibonding orbitals, \( n_a \).

\[
\text{bond order} = \frac{1}{2} (n_b - n_a)
\]

**Electron Configurations of Diatomic Molecules of the Second Period**

1. Homonuclear diatomic molecules such as Li\(_2\) utilize only \( \sigma \) orbitals. For filled K shell bonding and antibonding orbitals use KK designation.

2. Be\(_2\) = KK(\( \sigma_{2\pi} \))\(^2\) (\( \sigma_{2\pi}^* \))^2  Bond order = \( \frac{1}{2} (2-2) = 0 \)
   So Be\(_2\) is unstable

3. For remaining elements, molecular orbitals must also be formed using p orbitals

**Figure 9.29:** The molecular orbital energy-level diagram for the H\(_2^-\) ion.

**Figure 9.32:** The molecular orbital energy-level diagram for the Li\(_2\) molecule.
The overlap of “p” orbitals results in two sets of π orbitals (two bonding and two antibonding) and one set of σ orbitals (one bonding and one antibonding).

The next slide illustrates the relative energies of these molecular orbitals for homonuclear diatomic molecules composed of 2nd period elements. Note that the relative energies of the σ and π bonding orbitals changes between N₂ and O₂. For Li₂ through C₂, interactions between the σ orbitals formed from the 2s and 2p atomic orbitals cause an increase in the energy of the σ 2p MO’s.
Figure 9.35: The expected molecular orbital energy-level diagram resulting from the combination of the 2p orbitals on two boron atoms.

Figure 9.36: The expected molecular orbital energy-level diagram for the B₂ molecule.

Problem: B₂ is paramagnetic!

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Diamagnetism

- paired electrons
- repelled from induced magnetic field
- much weaker than paramagnetism

Paramagnetism

- unpaired electrons
- attracted to induced magnetic field
- much stronger than diamagnetism
Figure 9.37: Diagram of the kind of apparatus used to measure the paramagnetism of a sample. A paramagnetic sample will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing magnetic field.

Figure 9.38: The correct molecular orbital energy-level diagram for the B₂ molecule. When p-s mixing is allowed, the energies of the σ₂p and π₂p orbitals are reversed. The two electrons from the B 2p orbitals now occupy separate, degenerate π₂p molecular orbitals and thus have parallel spins. Therefore, this diagram explains the observed paramagnetism of B₂.

Figure 9.39: The molecular orbital energy-level diagrams, bond orders, bond energies, and bond lengths for the diatomic molecules B₂ through F₂. Note that for O₂ and F₂, the σ 2p orbital is lower in energy than the π₂p orbitals.

3. O₂ has 12 valence electrons. Its MO configuration is:

\[ O₂ = KK(σ_{2s})^2(σ_{2s}^*)^2(σ_{2p})^2(σ_{2p})^2(π_{2p})^2(π_{2p}^*) \]

with one electron in each of the π₂p orbitals spin aligned (Hund’s rule) and,

bond order for O₂ = \( \frac{1}{2}(8-4) = 2 \)
Figure 9.40: When liquid oxygen is poured into the space between the poles of a strong magnet, it remains there until it boils away. This attraction of liquid oxygen for the magnetic field demonstrates the paramagnetism of the O₂ molecule.

Figure 9.41: The molecular orbital energy-level diagram for the NO molecule. We assume that orbital order is the same as that for N₂. The bond order is 2.5.

Figure 9.42: The molecular orbital energy-level diagram for both the NO⁺ and CN⁻ ions.

Figure 9.43: A partial molecular orbital energy-level diagram for the HF molecule.
Figure 9.44: The electron probability distribution in the bonding molecular orbital of the HF molecule. Note the greater electron density close to the fluorine atom.

Figure 9.45: The resonance structures for O₃ and NO₃⁻. Note that it is the double bond that occupies various positions in the resonance structures.

Figure 9.46: (a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon. (b) Two of the resonance structures for the benzene molecule.
Figure 9.47: The $\sigma$ bonding system in the benzene molecule.

Figure 9.48: (a) The $p$ molecular orbital system in benzene is formed by combining the six $p$ orbitals from the six $sp^2$ hybridized carbon atoms. (b) The electrons in the resulting $p$ molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these orbitals is represented here.

Outcomes of MO Model

1. As bond order increases, bond energy increases and bond length decreases.
2. Bond order is not absolutely associated with a particular bond energy.
3. $N_2$ has a triple bond, and a correspondingly high bond energy.
4. $O_2$ is paramagnetic. This is predicted by the MO model, not by the LE model, which predicts diamagnetism.

Combining LE and MO Models

- $\sigma$ bonds can be described as being localized.
- $\pi$ bonding must be treated as being delocalized.