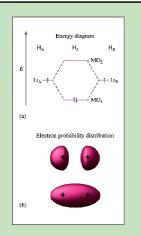
Molecular Orbital Theory

- For example, when two hydrogen atoms bond, a σ_{1s} (bonding) molecular orbital is formed as well as a σ_{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 H₂ molecule.
(b) The shapes of the molecular orbitals are obtained by squaring the wave functions for MO₁ and MO₂.



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

Factors that determine orbital interaction:

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

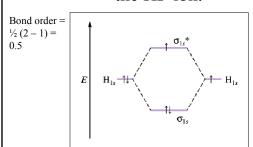
For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large

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.

bond order =
$$\frac{1}{2}$$
 ($n_b - n_a$)

Figure 9.29: The molecular orbital energy-level diagram for the H₂ ion.



Electron Configurations of Diatomic Molecules of the Second Period

- Homonuclear diatomic molecules such as Li₂ utilize only σ orbitals. For filled K shell bonding and antibonding orbitals use KK designation.
- 2. Be₂ = KK(σ_{2s})²(σ_{2s} *)² Bond order = 1/2 (2-2) = 0 So Be₂ is unstable
- For remaining elements, molecular orbitals must also be formed using p orbitals

Figure 9.32: The molecular orbital energy-level diagram for the Li₂ molecule.

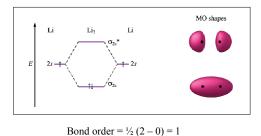
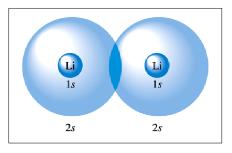


Figure 9.31: The relative sizes of the lithium 1*s* and 2*s* atomic orbitals.



- •The overlap of "p" orbitals results in **two sets of \Pi** orbitals (two bonding and two antibonding) and **one set of G 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 N_2 and O_2 . For Li $_2$ through C_2 , 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 9.33: (a) The three mutually perpendicular 2*p* orbitals on two adjacent boron atoms. Two pairs of parallel *p* orbitals can overlap as shown in (b) and (c), and the third pair can overlap head-on as shown in (d).

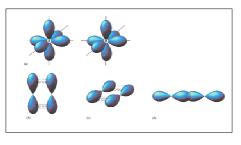


Figure 9.34: (a) The two p orbitals on the boron atom that overlap head-on produce two s molecular orbitals, one bonding and one antibonding. (b) Two p orbitals that lie parallel overlap to produce two p molecular orbitals, one bonding and one antibonding.

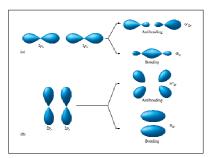


Figure 9.35: The expected molecular orbital energy-level diagram resulting from the combination of the 2p orbitals on two boron atoms.

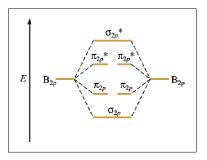
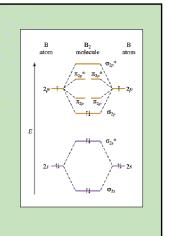


Figure 9.36: The expected molecular orbital energy-level diagram for the B₂ molecule.

Problem: B₂ is paramagnetic!



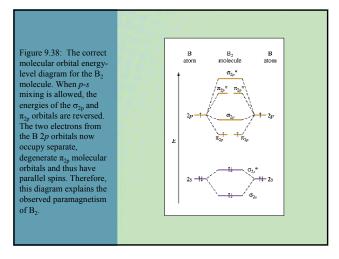
Diamagnetism

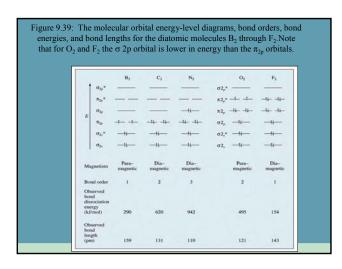
- paired electrons
- prepelled from induced magnetic field
- much weaker than paramagnetism

Paramagnetism

- unpaired electrons
- sattracted 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 Sample tube will appear heavier when the electromagnet is turned on because the sample is attracted into the inducing Electromagnet magnetic field.

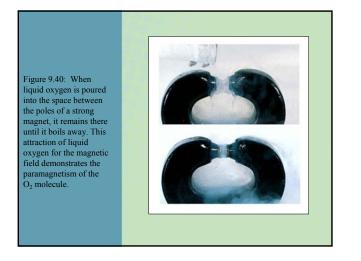


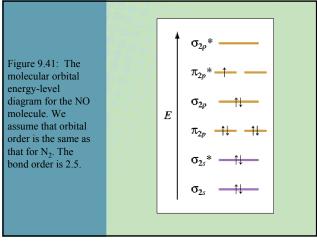


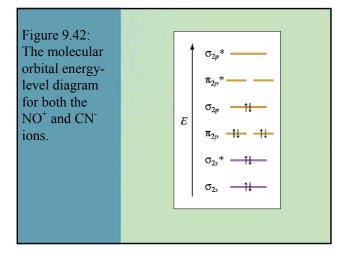
3. O_2 has 12 valence electrons. Its MO configuration is:

 $O_2 = KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^2(\pi_{2p})^2(\pi_{2p}^*)(\pi_{2p}^*)$ with one electron in each of the π_{2p}^* orbitals spin aligned (Hund's rule) and,

bond order for $O_2 = 1/2(8-4) = 2$







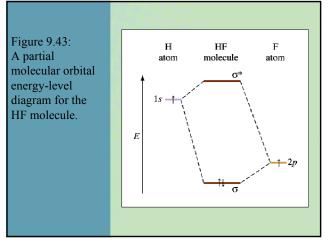


Figure 9.44: The electron probability distribution in the bonding molecular orbital of the HF molecule.

Note the greater electron density close to the fluorine atom.

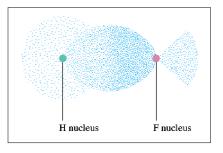


Figure 9.45: The resonance structures for O_3 and NO_3 . Note that it is the double bond that occupies various positions in the resonance structures.

Figure 9.49: (a) The p orbitals used to form the π bonding system in the NO₃ ion. (b) A representation of the delocalization of the electrons in the π molecular orbital system of the NO₃ ion.

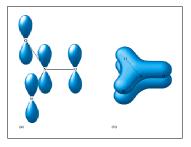


Figure 9.46: (a) The benzene molecule consists of a ring of six carbon atoms with one hydrogen atom bound to each carbon. (b) Two of the resonance structures for the benzene molecule.

Figure 9.47: The σ bonding system in the benzene molecule.

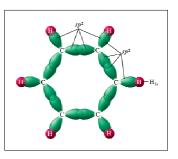
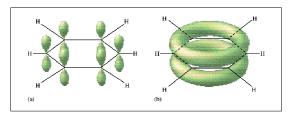


Figure 9.48: (a) The p molecular orbital system in benzene is formed by combining the six p orbitals from the six sp^2 hybridized carbon atoms. (b) The electrons in the resulting p molecular orbitals are delocalized over the entire ring of carbon atoms, giving six equivalent bonds. A composite of these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



Outcomes of MO Model

- 1. As <u>bond order</u> increases, bond energy increases and bond length decreases.
- 2. Bond order is not absolutely associated with a particular bond energy.
- 3. N₂ has a triple bond, and a correspondingly high bond energy.
- 4. O₂ is paramagnetic. This is predicted by the MO model, not by the LE model, which predicts diamagnetism.

Combining LE and MO Models

- σ bonds can be described as being localized.
- π bonding must be treated as being delocalized.