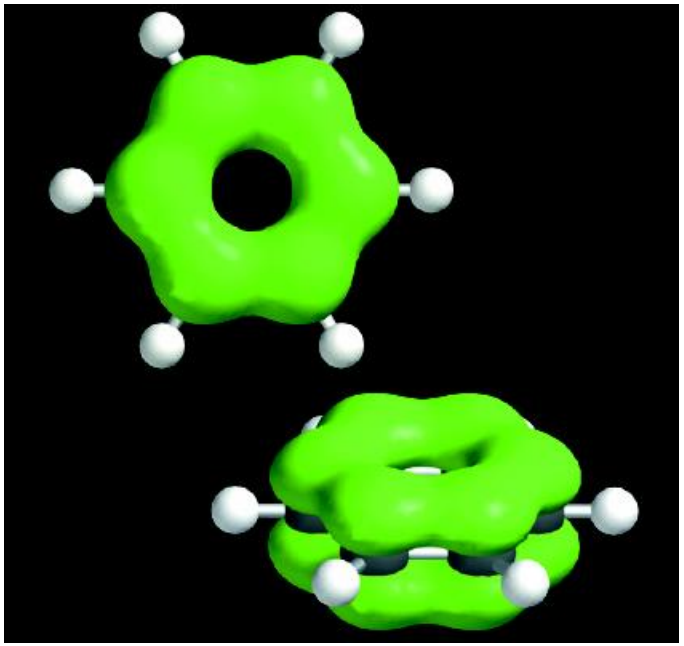
Chapter 4.4

Molecular Orbitals

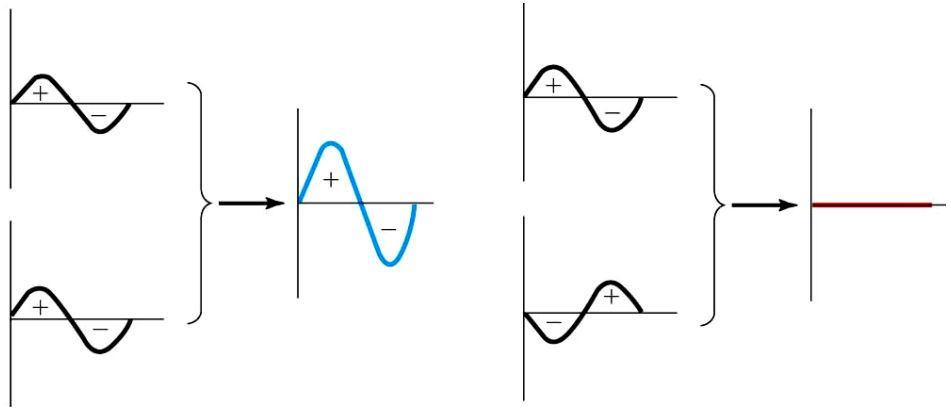


Chapter Outline

1. Molecular Orbitals
2. Molecular Orbital Energy Level Diagrams
3. Bond Order and Bond Stability
4. Homonuclear Diatomic Molecules
5. Heteronuclear Diatomic Molecules
6. Delocalization and the Shapes of Molecular Orbitals

Molecular Orbital Theory

- Combination of atomic orbitals on different atoms forms molecular orbitals (MO's) so that electrons in MO's belong to the molecule as a whole.
- Waves that describe atomic orbitals have both positive and negative phases or amplitudes.
- As MO's are formed the phases can interact constructively or destructively.



(a) In-phase overlap (add)

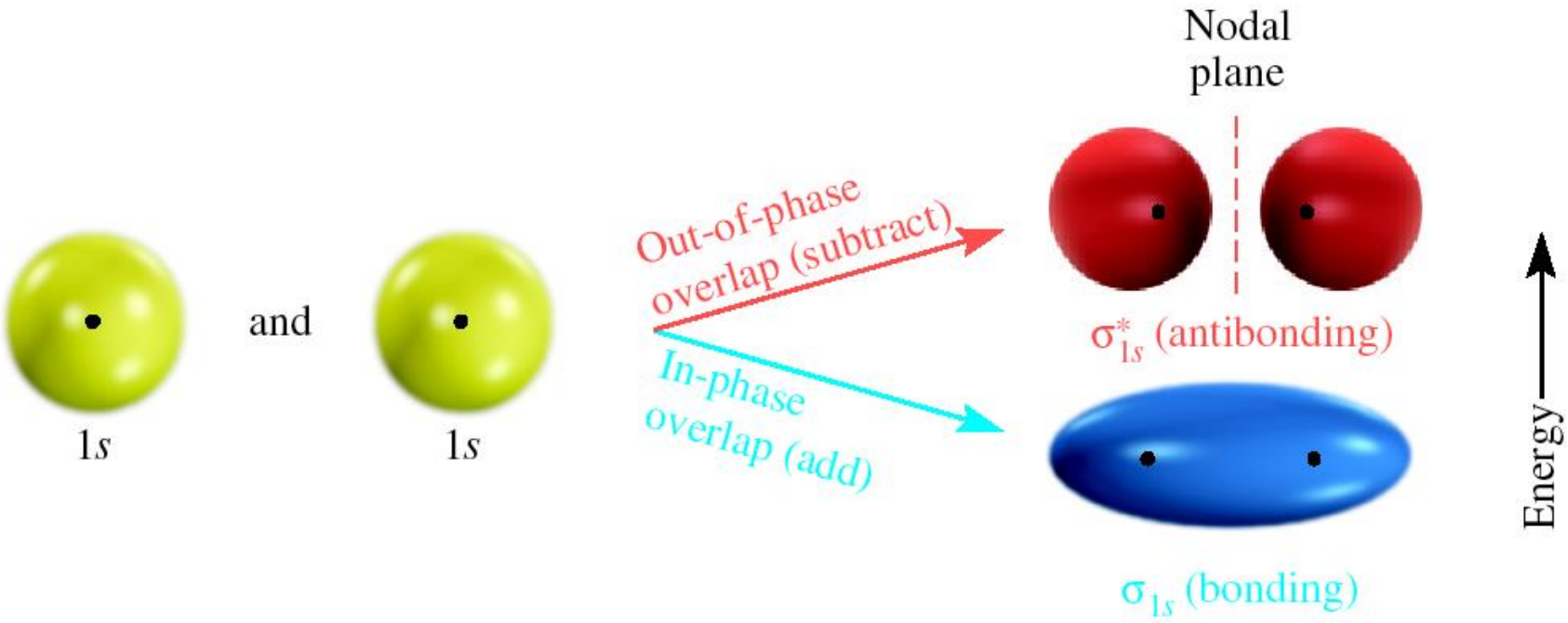
(b) Out-of-phase overlap (subtract)

Molecular Orbitals

- There are two simple types of molecular orbitals that can be produced by the overlap of atomic orbitals.
  1. Head-on overlap of atomic orbitals produces σ (sigma) orbitals.
  2. Side-on overlap of atomic orbitals produces π (pi) orbitals.
- Two 1s atomic orbitals that overlap produce two molecular orbitals designated as:
  1. σ_{1s} or bonding molecular orbital
  2. σ_{1s}^* or antibonding molecular orbital.

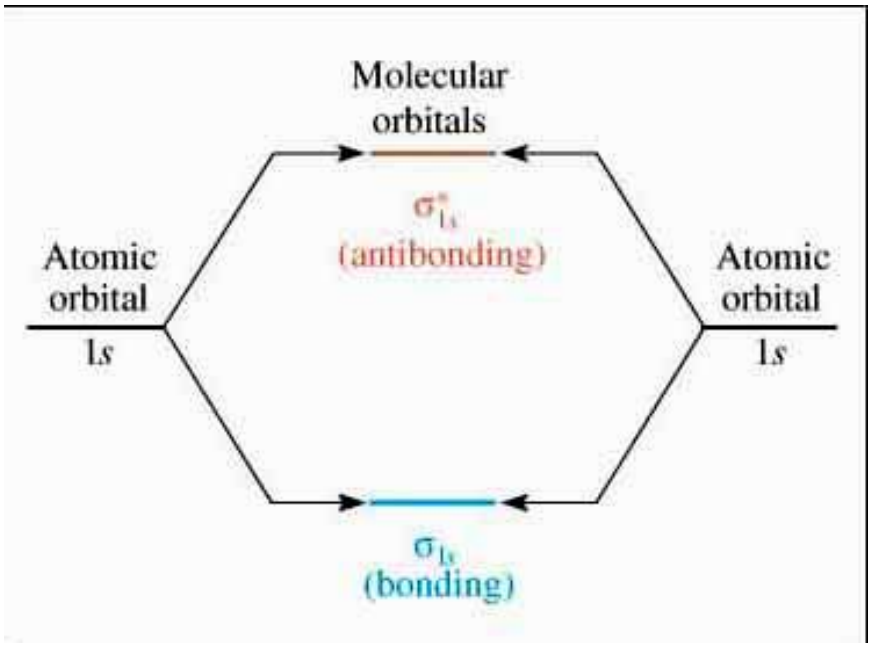
Molecular Orbitals

- Graphically these two orbitals look like this:



Molecular Orbitals

- Energetically, the molecular orbitals split.
  1. The σ_{1s} lies lower in energy.
  2. The σ_{1s}^* is higher in energy.

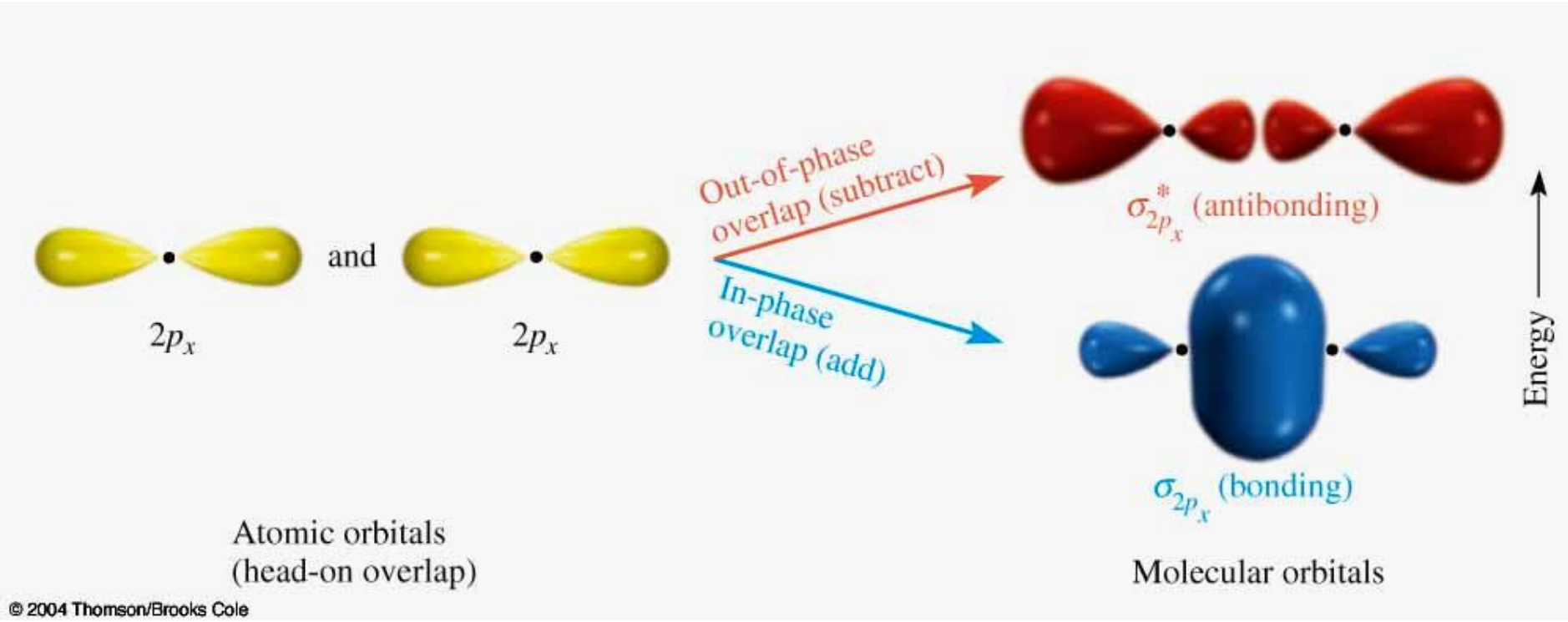


Molecular Orbitals

- The head-on overlap of two corresponding p atomic orbitals on different atoms, say $2p_x$ with $2p_x$ produces:
  1. σ_{2p_x} bonding orbital
  2. $\sigma^*_{2p_x}$ antibonding orbital

Molecular Orbitals

- Graphically, these orbitals look like this:

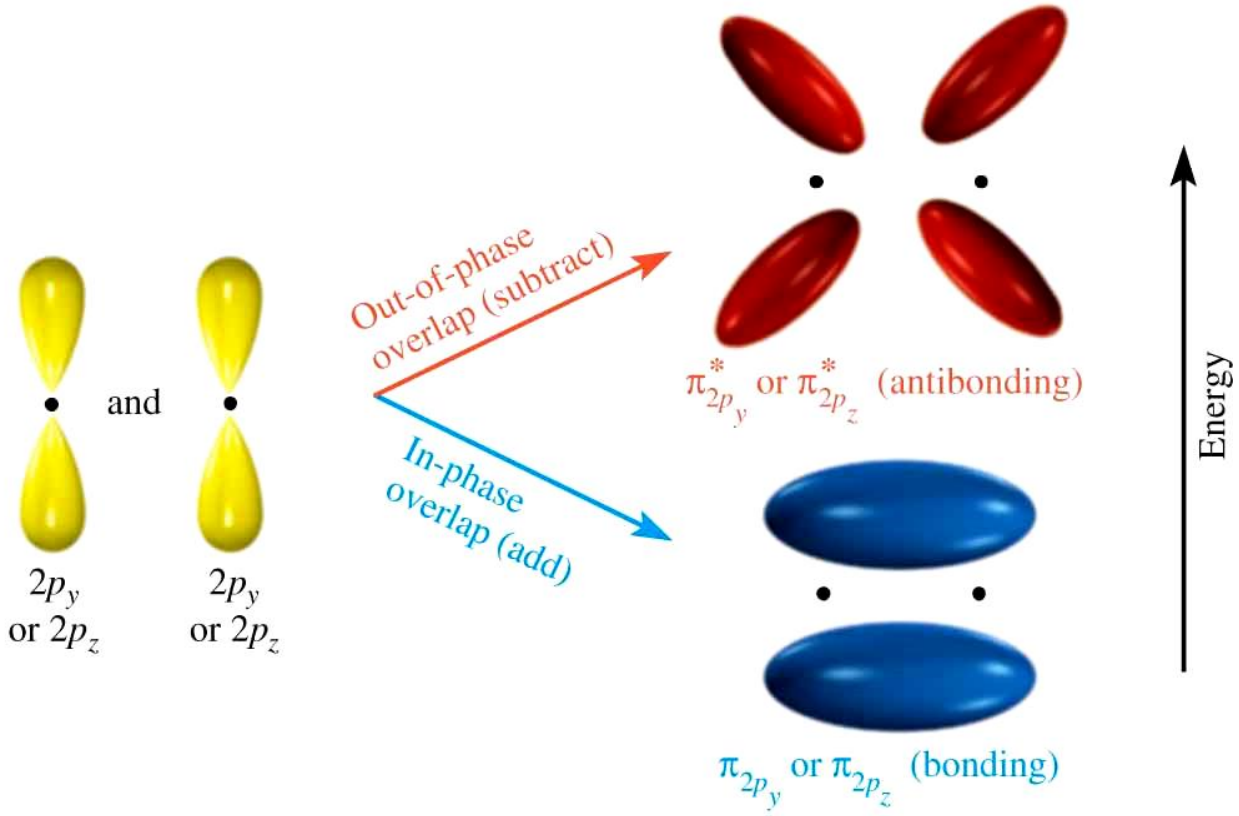


Molecular Orbitals

- Side-on overlap of two corresponding p atomic orbitals on different atoms (say $2p_y$ with $2p_y$ or $2p_z$ with $2p_z$) produces:
  1. π_{2p_y} or π_{2p_z} (both are bonding orbitals)
  2. $\pi^*_{2p_y}$ or $\pi^*_{2p_z}$ (both are nonbonding orbitals)

Molecular Orbitals

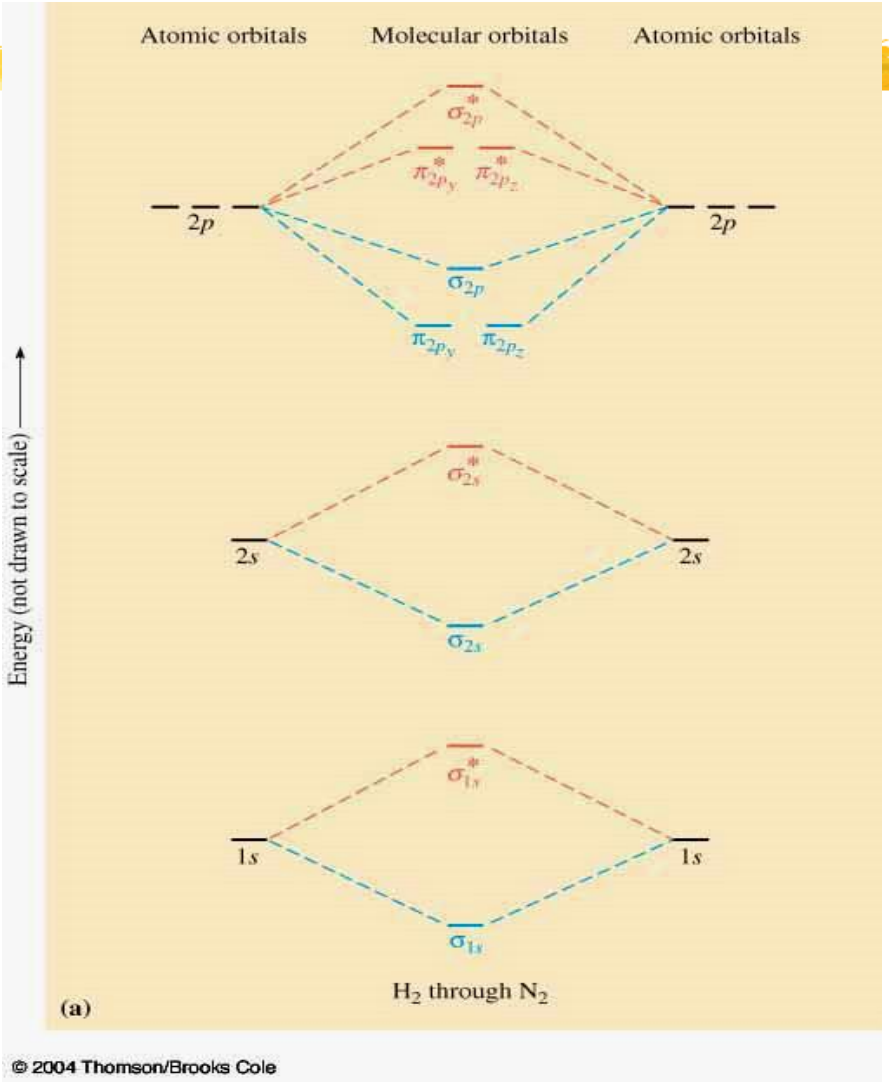
- Graphically these orbitals look like this:



Molecular Orbital Energy Level Diagram

- Now that we have seen what these MO's look like and a little of their energetics, how are the orbitals filled with electrons?
- Order of filling of MO's obeys same rules as for atomic orbitals.
  - Including
    1. Aufbau principle
    2. Hund's Rule
  - Thus the following energy level diagram results for the homonuclear diatomic molecules H_2 through N_2.

Molecular Orbital Energy level Diagram



Bond Order and Bond Stability

- Once the energy level diagram has been filled with the appropriate number of electrons, how do we determine the molecular stability?
- Bond order (bo) of a molecule is defined as half the number of electrons in bonding orbitals minus half the number of electrons in antibonding orbitals

$$bo = \frac{\left(\#\, e^{-} \text{ in bonding orbitals}\right) - \left(\#\, e^{-} \text{ in antibonding orbitals}\right)}{2}$$

Bond Order and Bond Stability

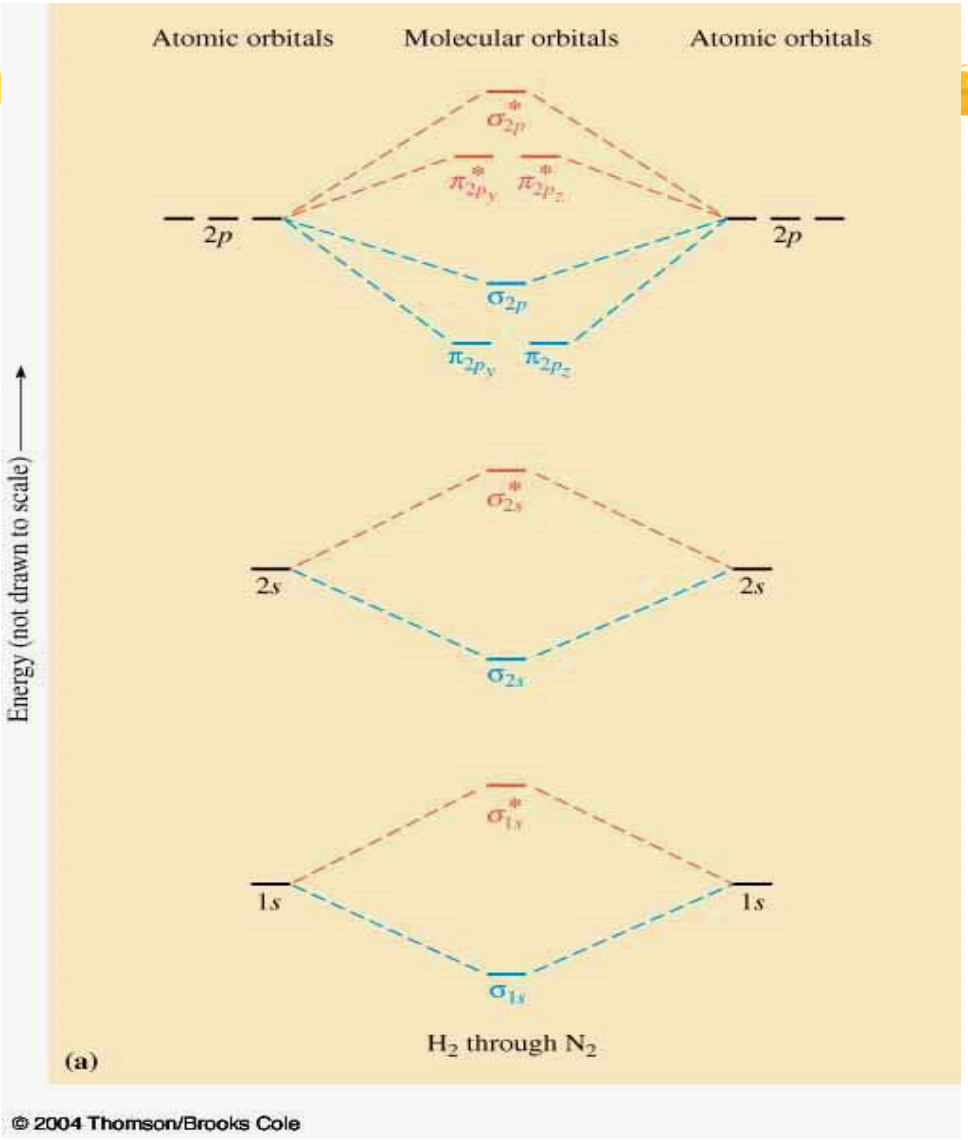
- The larger the bond order, the more stable the molecule or ion is.
- Bond order = 0 implies there are equal numbers of electrons in bonding and antibonding orbitals.
  - ~ same stability as separate atoms
- Bond order > 0 implies there are more electrons in bonding than antibonding orbitals.
  - Molecule is more stable than separate atoms.
- The greater the bond order, the shorter the bond length and the greater the bond energy.

Homonuclear Diatomic Molecules

- Consider the overlap of the atomic orbitals of two nitrogen atoms to form an N_2 molecule.

- Each N atom has 7 electrons thus the N_2 molecule has 14 electrons.
  - Obey the Aufbau principle and Hund's rule to place the 14 electrons in the energy level diagram.

Homonuclear Diatomic Molecules



Homonuclear Diatomic Molecules

- In shorthand notation we represent this configuration as

$$N_2 \; \sigma_{1s}^2 \; \sigma_{1s}^{*2} \; \sigma_{2s}^2 \; \sigma_{2s}^{*2} \; \pi_{2p_y}^2 \; \pi_{2p_y}^{*2} \; \sigma_{2p}^2$$

Homonuclear Diatomic Molecules

- The greater the bond order of a bond the more stable we predict it to be.
- For N_2 the bond order is

$$bo = \frac{10 - 4}{2}$$

$$= \frac{6}{2}$$

$$= 3 \text{ corresponding to a triple bond in VB theory}$$

Homonuclear Diatomic Molecules

- MO treatment can also be applied to ions.
  - Ions are charged and that charge affects the stability as well as the bond order.

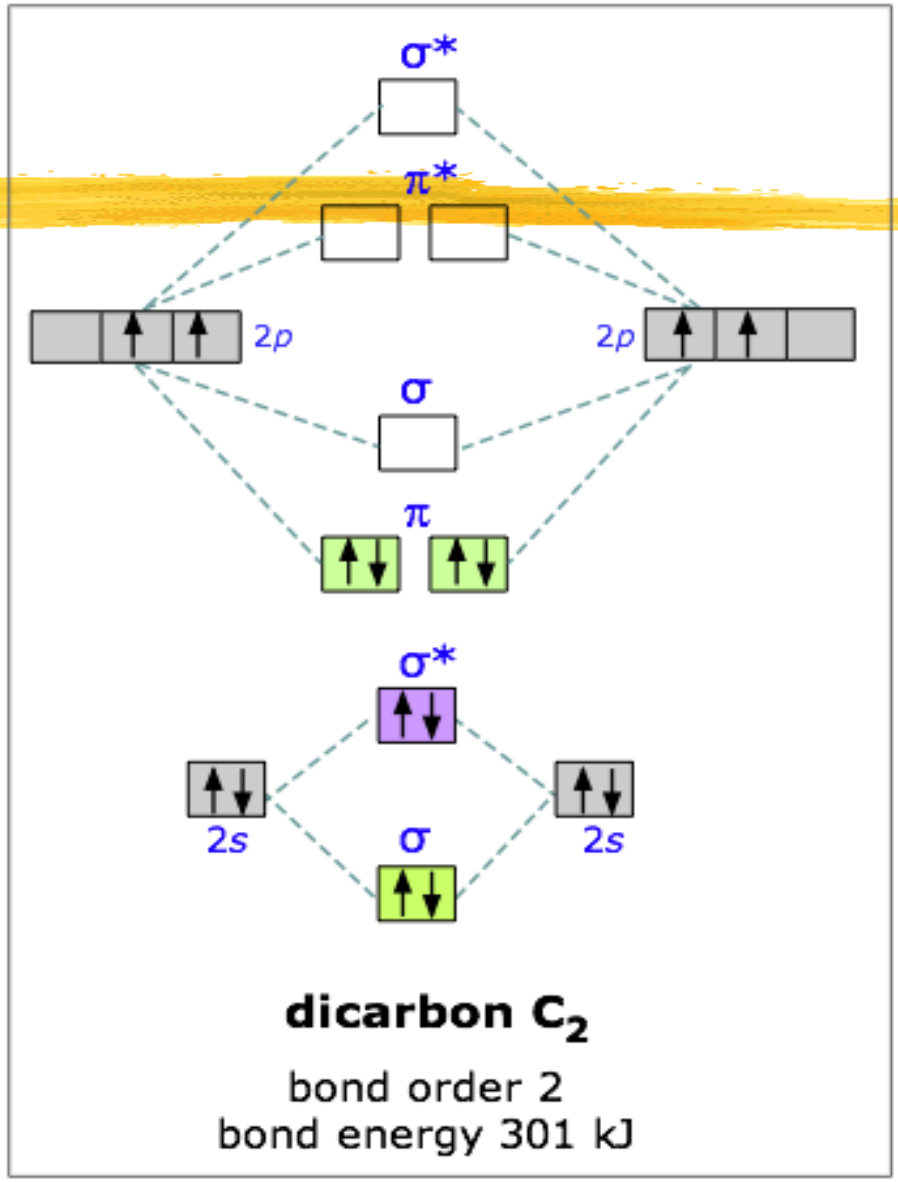
- Example 9-1: Write out the electron configuration of the N_2^+ ion in abbreviated notation ($\sigma_{1s}^2\ \sigma_{1s}^{*2}$.....). What is the bond order?

You do it!

Homonuclear Diatomic Molecules

Carbon has 4 valence electron, $2s^2 2p^2$

For two carbon atoms, we have a total of eight electrons, which can be accommodated in the first four molecular orbitals. The lowest two are the 2*s*-derived bonding and antibonding pair, so the "first" four electrons make no net contribution to bonding.



Homonuclear Diatomic Molecules

- Example 9-2: Write out the electron configuration of the O_2 molecule in abbreviated notation. What is the bond order? Is the molecule paramagnetic or diamagnetic?

Homonuclear Diatomic Molecules

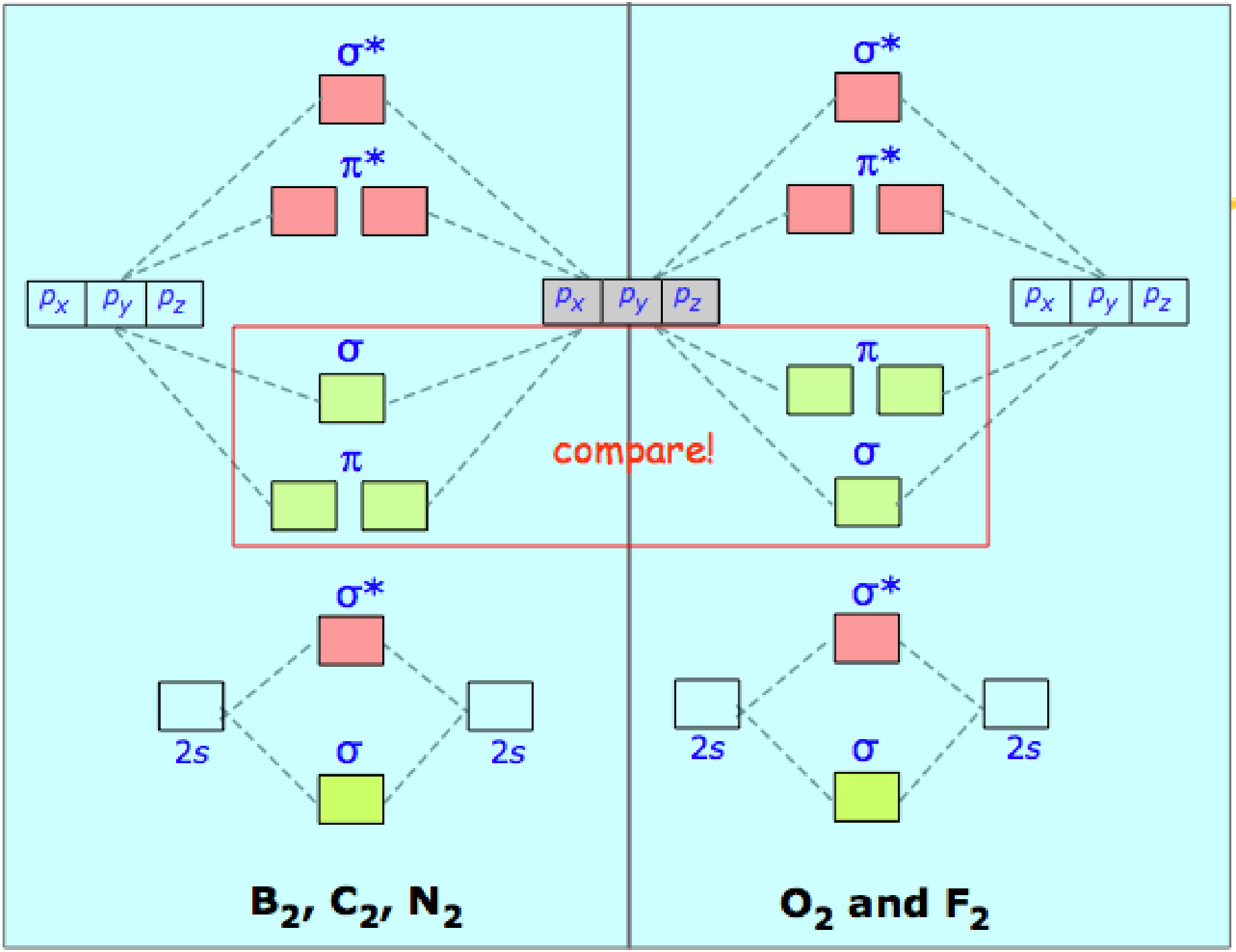
$$O_2\ \sigma_{1s}^2\ \sigma_{1s}^{*2}\ \sigma_{2s}^2\ \sigma_{2s}^{*2}\sigma_{2p_x}^2\ \pi_{2p_y}^2\ \pi_{2p_z}^2\ \pi_{2p_y}^{*1}\ \pi_{2p_z}^{*1}$$

$$\text{bo} = \frac{10-6}{2} = 2$$

2 unpaired e^- $\therefore$ paramagnetic

Valence Bond theory predicts that O_2 is diamagnetic

experimentally - O_2 is paramagnetic


σ*
π*
p_x p_y p_z
σ
π
compare!
σ*
2s
σ
2s
B_2, C_2, N_2
σ*
π*
p_x p_y p_z
π
σ
σ*
2s
σ
2s
O_2 and F_2

Homonuclear Diatomic Molecules

- Example 9-3: Write out the electron configuration of the Be_2 molecule in abbreviated notation. What is the bond order? Would you predict that the molecule exists?

You do it!

Homonuclear Diatomic Molecules

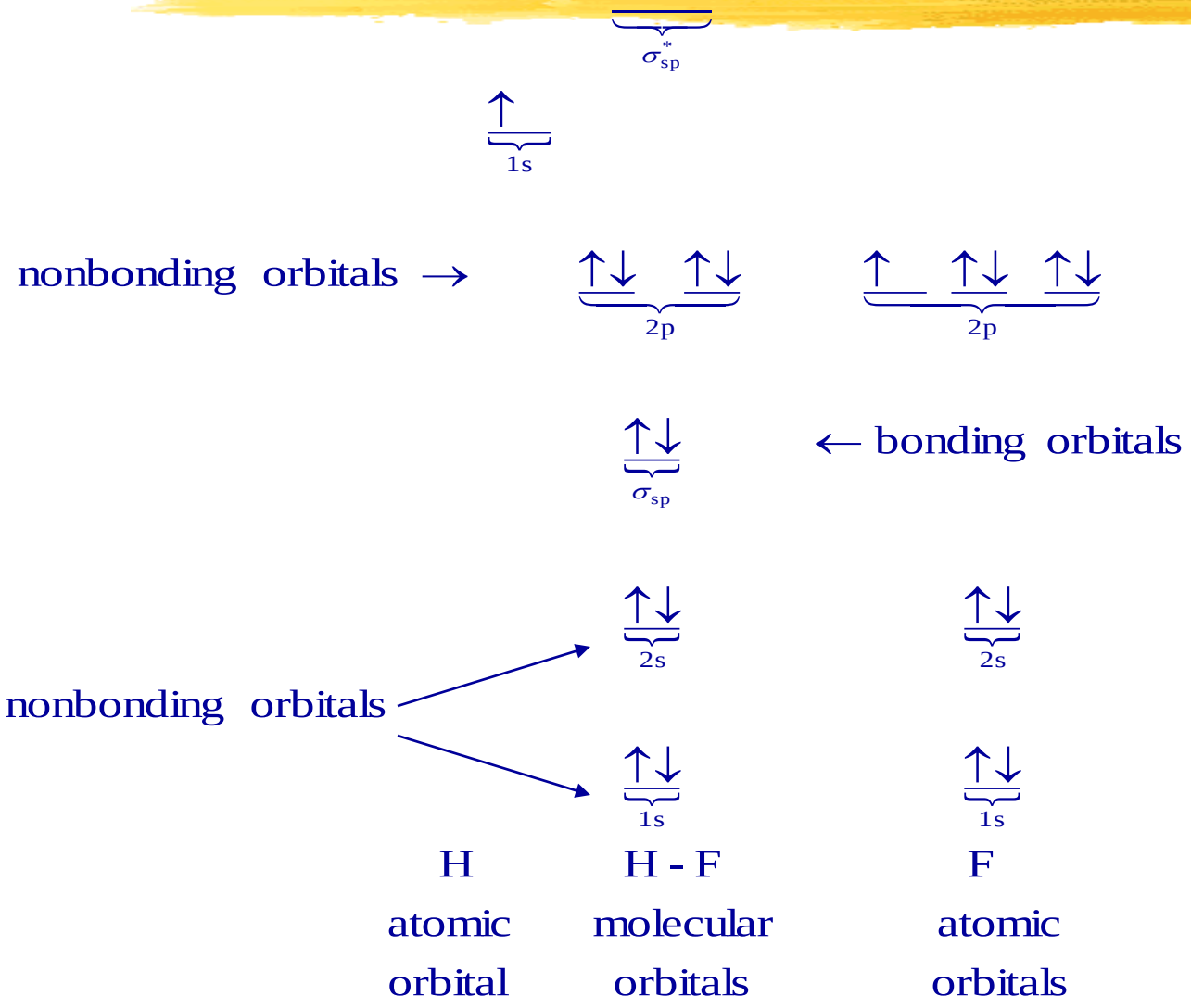
Homonuclear Diatomic Molecules

- Example 9-4: Write out the electron configuration for F_2. In this molecule the σ_p molecular orbital is lower than the π_p molecular orbitals. What is the bond order? Is F_2 paramagnetic?

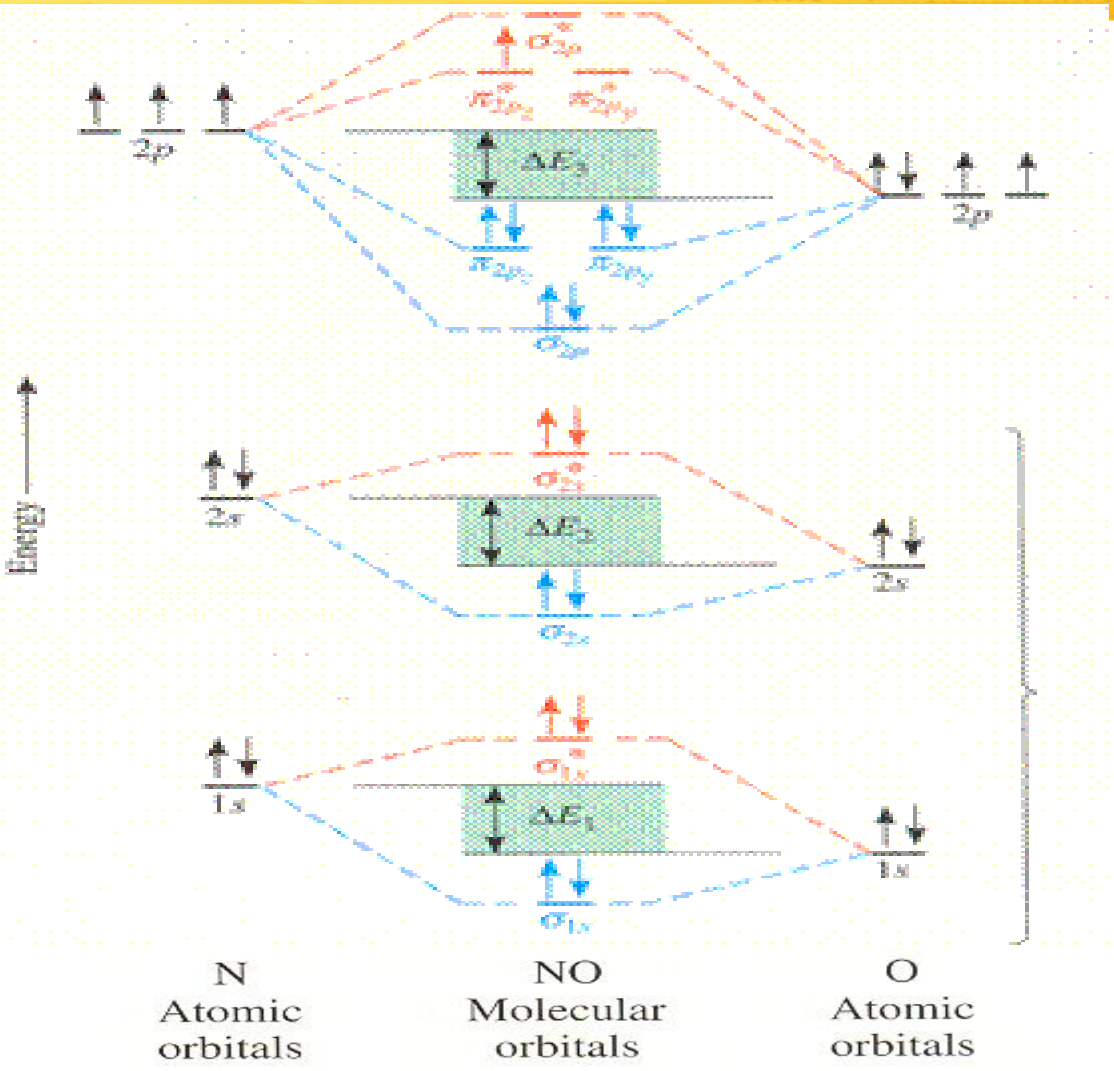
Heteronuclear Diatomic Molecules

- Molecular orbital diagrams for heteronuclear molecules have skewed energies for the combining atomic orbitals to take into account the differing electronegativities.
- The more electronegative elements are lower in energy than those of the less electronegative element.
- Use HF as an example.

Heteronuclear Diatomic Molecules



For molecule NO:
Draw molecular orbital energy level diagram.



ii. Determine bond order.

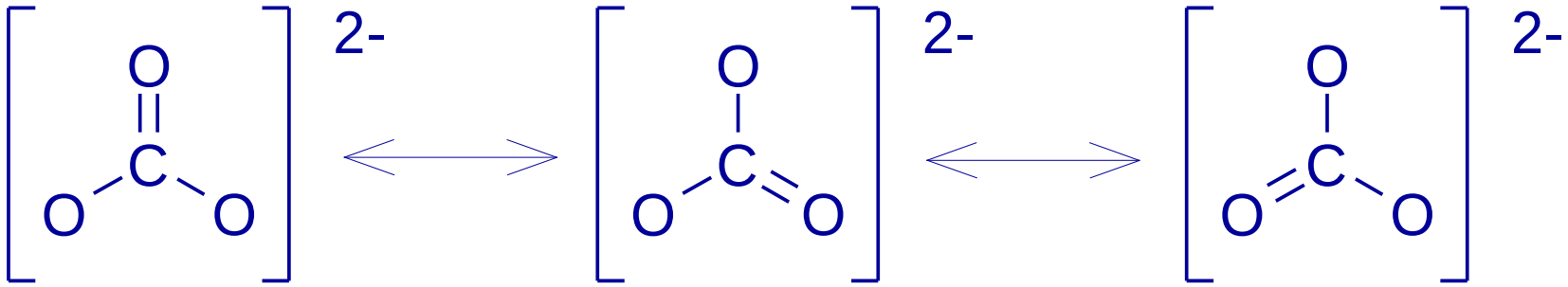
Bond order = (10-5)/2 = 2.5

iii. Predict the molecule magnetism.

paramagnetic

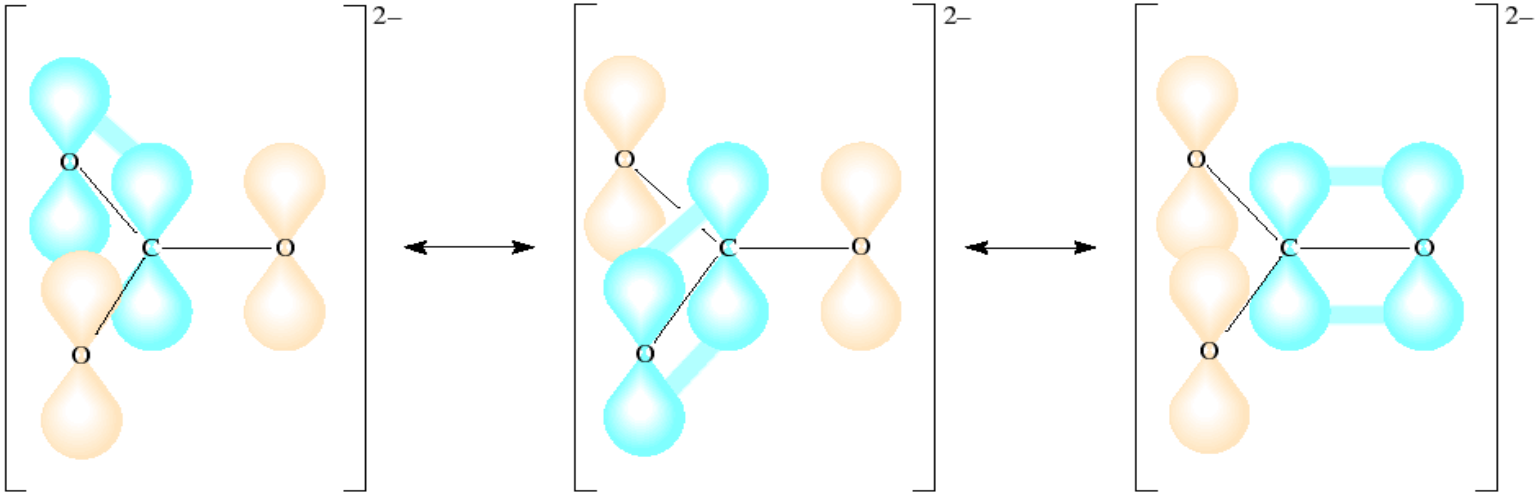
Delocalization and Shapes of Molecular Orbitals

- Valence bond theory discusses resonance formulas.
  - Carbonate ion (CO_3^{2-}) is an example.



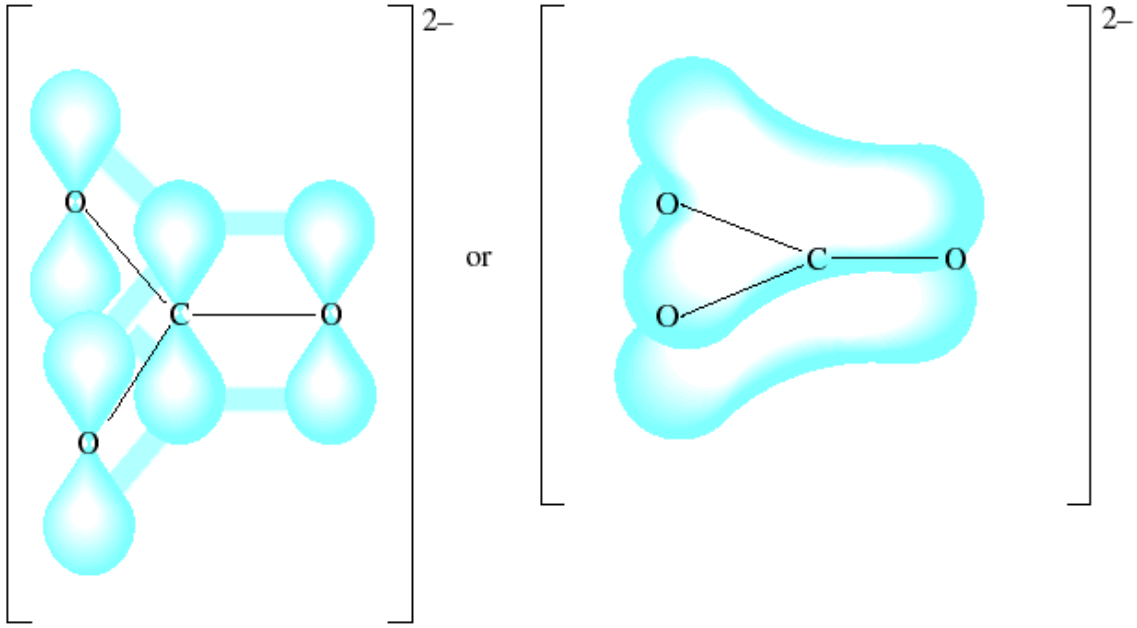
Delocalization and Shapes of Molecular Orbitals

- Molecular orbital theory describes shapes in terms of *delocalization of electrons*.
  - Again carbonate ion (CO_3^{2-}) is a good example.



Delocalization and Shapes of Molecular Orbitals

- Molecular orbital theory describes shapes in terms of *delocalization of electrons*.
  - Again carbonate ion (CO_3^{2-}) is a good example.



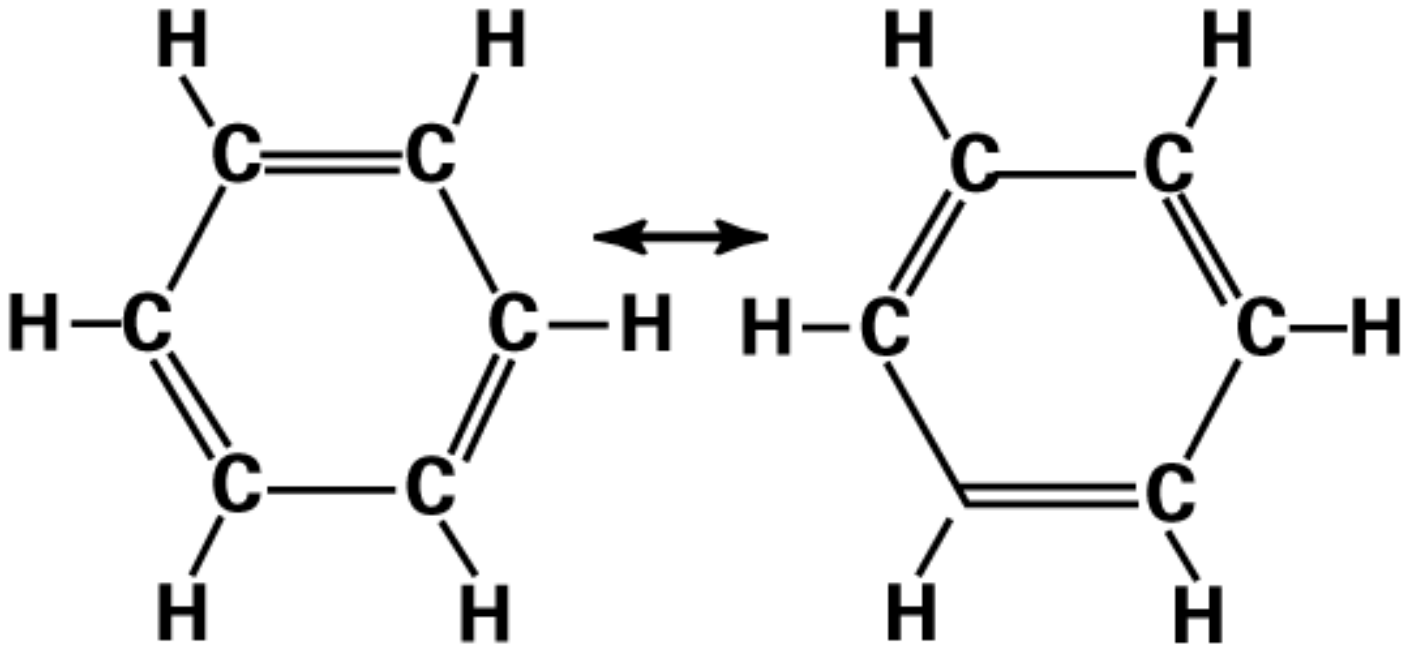
Delocalization and Shapes of Molecular Orbitals

- The structure of benzene is described well by molecular orbital theory.

Delocalization and Shapes of Molecular Orbitals

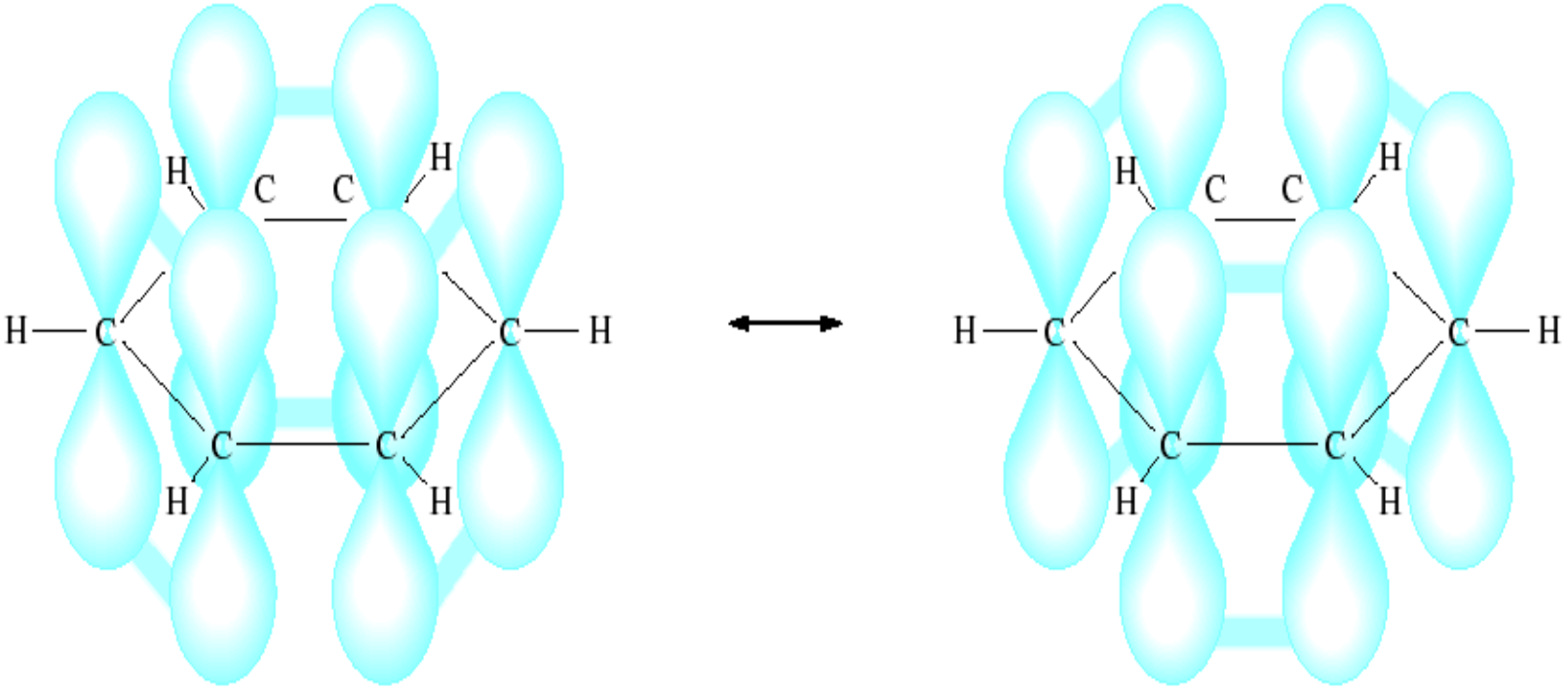
- Resonance structure - VB theory.

Lewis formulas



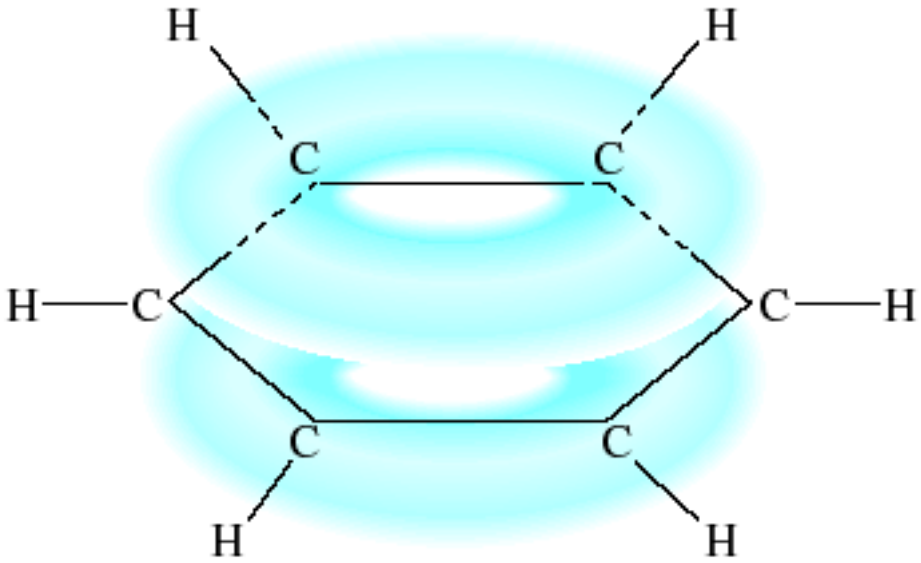
Delocalization and Shapes of Molecular Orbitals

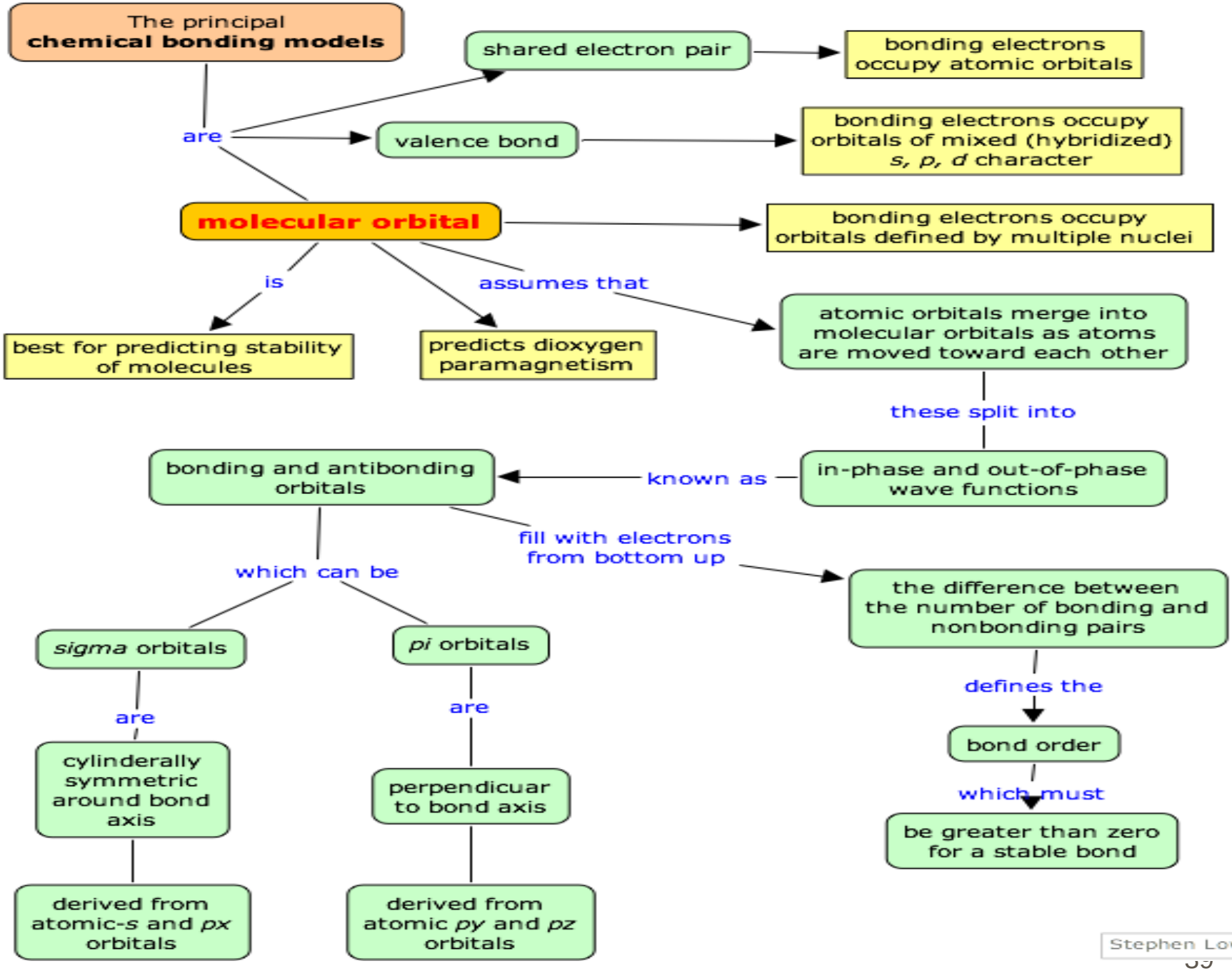
- Molecular orbital theory



Delocalization and Shapes of Molecular Orbitals

- Molecular orbital theory




The principal chemical bonding models
are
shared electron pair
bonding electrons occupy atomic orbitals
valence bond
bonding electrons occupy orbitals of mixed (hybridized) s, p, d character
molecular orbital
bonding electrons occupy orbitals defined by multiple nuclei
is
best for predicting stability of molecules
predicts dioxygen paramagnetism
assumes that
atomic orbitals merge into molecular orbitals as atoms are moved toward each other
these split into
in-phase and out-of-phase wave functions
known as
bonding and antibonding orbitals
fill with electrons from bottom up
the difference between the number of bonding and nonbonding pairs
defines the
bond order
which must
be greater than zero for a stable bond
which can be
sigma orbitals
are
cylinderally symmetric around bond axis
derived from atomic-s and px orbitals
pi orbitals
are
perpendicuar to bond axis
derived from atomic py and pz orbitals
Stephen Lower