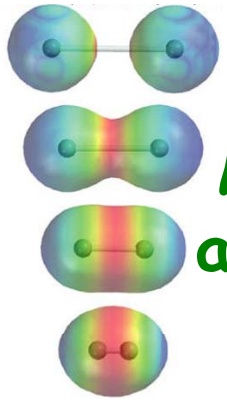
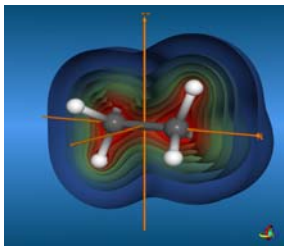


Chapter 9

Bonding II:

Molecular Geometry and Bonding Theories



Molecular Orbital Theory

- ***Molecular orbital theory*** : Atomic orbitals (AO) combine to form new molecular orbitals (MO) which are spread out over the entire molecule.
- Molecular orbitals (MO) describe the properties of the entire molecule, and not the properties of individual atoms.
- Molecular orbitals (wave functions) result from adding and/or subtracting atomic orbitals (wave functions).

Chapter 9 Section 6

Molecular Orbital Theory

- Molecular orbitals:
  - have specific shapes and energies.
  - can have a maximum of two electrons with opposite spins.
  - are equal to the number of atomic orbitals they have been composed from "the number of orbitals is conserved".
- Our study about MO theory is restricted to diatomic molecules.

Chapter 9 Section 6

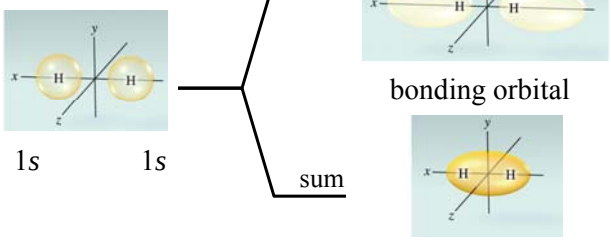
Molecular Orbitals from *s* Atomic Orbitals

Hydrogen molecule

$H + H \rightarrow H\text{-}H$

$1s^1 \quad 1s^1 \qquad \sigma_{1s}^2$

antibonding orbital

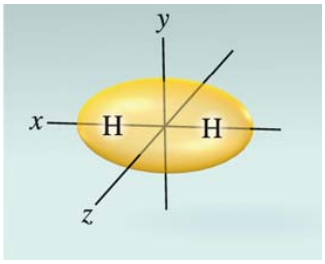


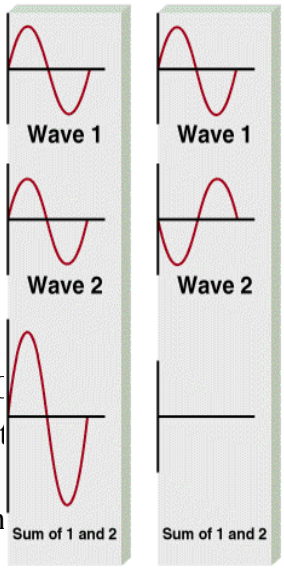
H atomic orbitals ⇨ **H_2 molecular orbitals**

Chapter 9 Section 6

σ_{1s} Molecular Orbital

Hydrogen molecule



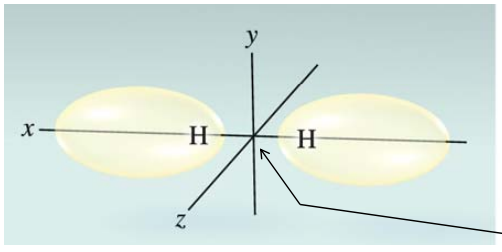


- "***Bonding***" molecular orbital.
- Constructive combination of "***ns***" AO
- High electron density "high probabilit the two nuclei.
- Lower energy and more stable than th were added.

Chapter 9 Section 6

σ^*_{1s} Molecular Orbital

Hydrogen molecule

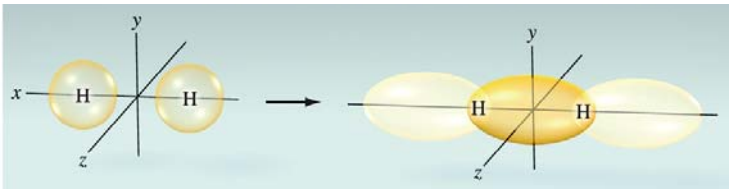


- "***Antibonding***" molecular orbital.
- Destructive combination of "***ns***" AOs.
- Very low electron density "low probability" between the two nuclei. The electron density pulls the two nuclei in opposite directions.
- Higher energy and less stable than the AOs that were subtracted.

Chapter 9 Section 6

σ_{1s} and σ^*_{1s} Molecular Orbitals

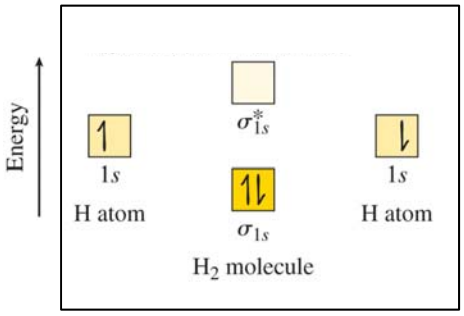
Hydrogen molecule

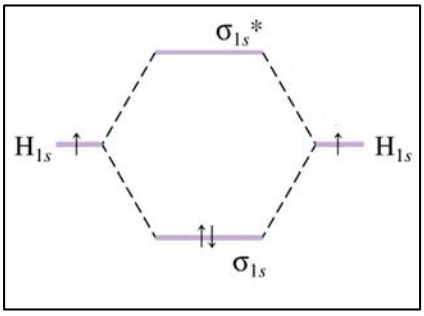


- Showing all the MOs in a molecule can result in a complicated picture.
- Energy diagrams / energy levels are often used to represent MOs in the molecule.

Chapter 9 Section 6

MOs in the Hydrogen Molecule



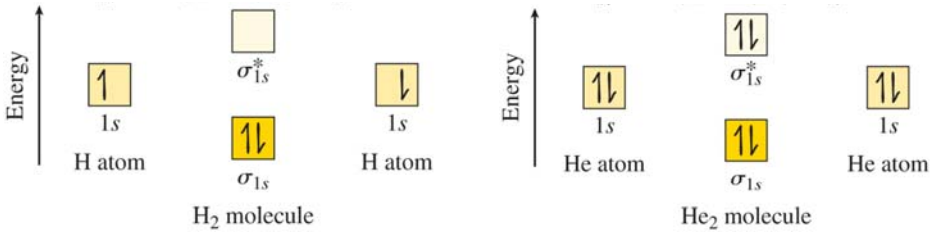


- Energy diagrams / energy levels are often used to represent MOs in the molecule.

Chapter 9 Section 6

Bond Order

$$\text{bond order} = \frac{\text{number of electrons in bonding molecular orbitals} - \text{number of electrons in antibonding molecular orbitals}}{2}$$



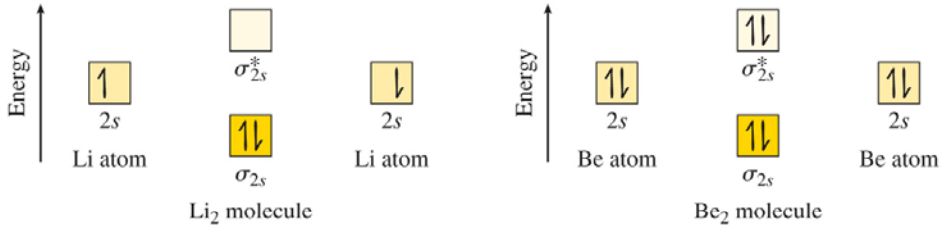
bond order = 1/2 (2 – 0) = 1
single bond

bond order = 1/2 (2 – 2) = 0
no bond

Chapter 9 Section 6

Bond Order

- The higher the value of the bond order, the more stable the molecule and the stronger the bond.



bond order = 1/2 (2 – 0) = 1
single bond

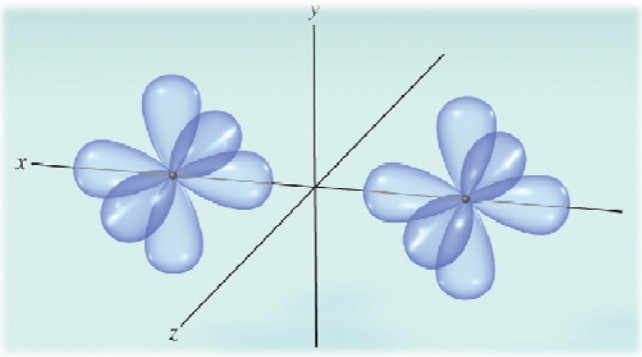
bond order = 1/2 (2 – 2) = 0
no bond

- MO theory predicts Li_2 to be a stable molecule whereas Be_2 to be not.

Chapter 9 Section 6

Molecular Orbitals from *p* Atomic Orbitals

- Some molecules, such as B_2, combine their *p* AOs to generate new MOs. (B: $1s^2 2s^2 2p^1$).
- Recall the shape of the 2*p* orbitals.

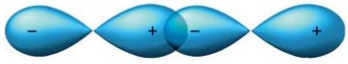


Chapter 9 Section 6

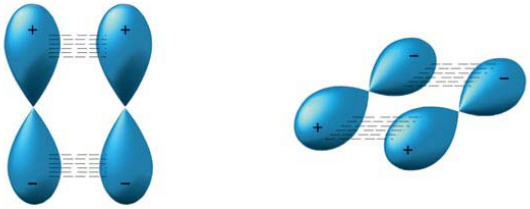
Molecular Orbitals from *p* Atomic Orbitals

- Two pairs of parallel *p* orbitals can overlap ***sideways***, and the third pair can overlap ***head-on***.

σ_{2p}

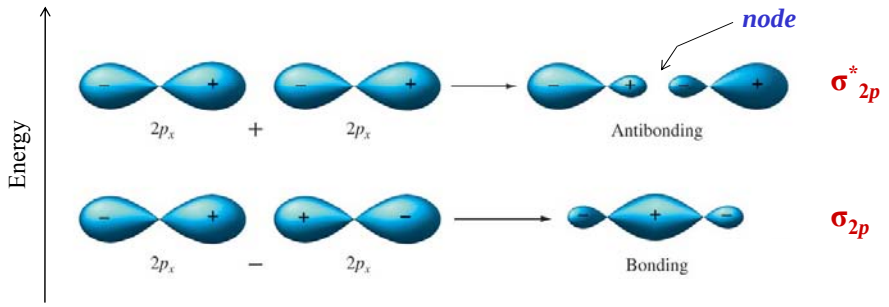


π_{2p}



Chapter 9 Section 6

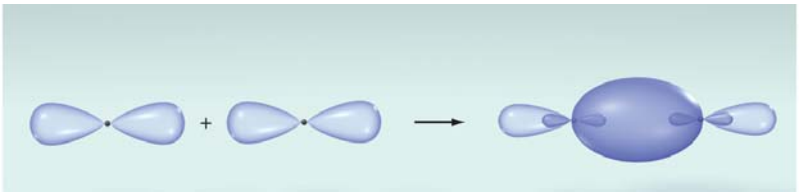
Head-On Overlap for *p* MOs



- The two *p* orbitals that overlap head-on produce two σ MOs:
  - one ***bonding***, σ_{2p} (constructive combination), and
  - one ***antibonding***, σ^*_{2p}, (destructive combination).

Chapter 9 Section 6

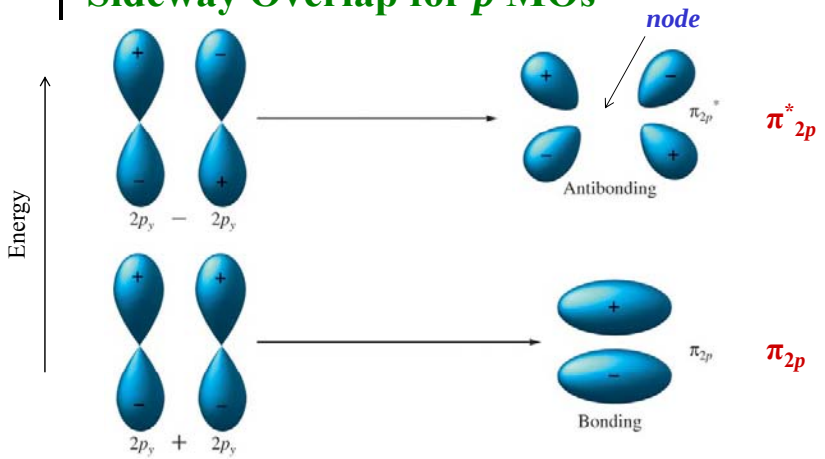
Head-On Overlap for *p* MOs



- Both ***bonding*** σ_{2p} and ***antibonding*** σ^*_{2p} MOs can be shown together in one diagram. They would look kind of complicated.

Chapter 9 Section 6

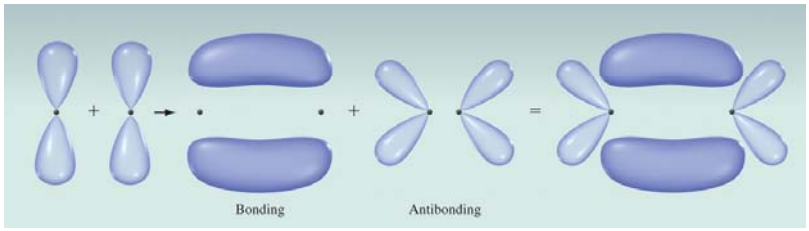
Sideway Overlap for *p* MOs



- Two *p* orbitals that lie parallel overlap to produce two π MOs:
  - one ***bonding*** , π_{2p} (constructive combination), and
  - one ***antibonding***, π^*_{2p} (destructive combination).

Chapter 9 Section 6

Sideway Overlap for *p* MOs

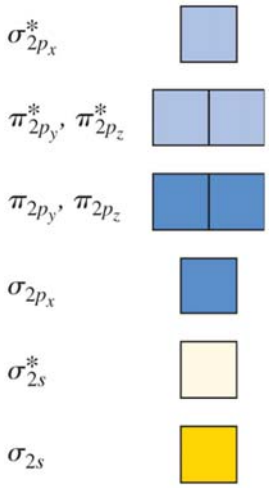


- The ***Bonding*** π_{2p} and ***antibonding***, π^*_{2p} MOs can be shown together in one diagram. They would look kind of complicated.
- Remember that you have ***two Bonding*** π_{2p} MOs (along the *y* and *z*-axes) and ***two antibonding***, π^*_{2p} MOs (also along the *y* and *z*-axes), giving ***four*** π MOs in total.

Chapter 9 Section 6

Molecular Orbital Diagram

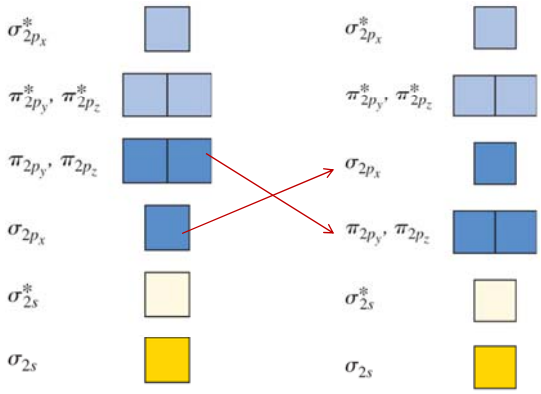
- MOs generated from the combination of ***p*** AOs are always ***higher*** in energy than MOs generated form the combination of ***s*** AOs.
- Antibonding MOs are ***higher*** in energy than bonding MOs.



Chapter 9 Section 6

Molecular Orbital Diagram

- The order of MO energies assumes no interaction taking place between *p* and *s* orbitals.
- In atoms of smaller nuclear charges (Li, B, C and N) the *s* orbitals are held less tightly by the nucleus and some *s*-*p* interaction takes place.



s and p orbitals do **not** interact

O_2, F_2, Ne_2

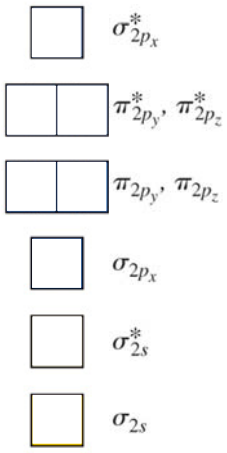
s and p orbitals do interact

Li_2, B_2, C_2 , N_2

Chapter 9 Section 6

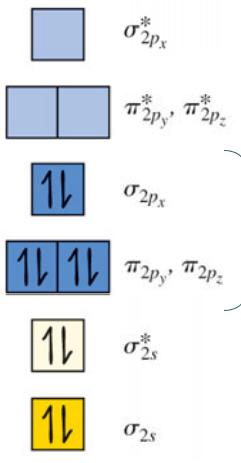
Molecular Orbital Diagram of O_2

- When filling the MO levels, you have to:
  - Count the number of valence electrons,
  - Start with the lower energy orbitals first,
  - Follow Hund's rule, and
  - Put not more than two electrons in one MO.



Chapter 9 Section 6

Molecular Orbital Diagram of N_2



The order of these two MOs are switched

Chapter 9 Section 6

Paramagnetism and Diamagnetism

- ***Paramagnetism*** causes the substance to be attracted to a magnetic field.

  Diamagnetism causes the substance to be repelled from a magnetic field.

- ***Paramagnetism*** is associated with ***unpaired*** electrons.

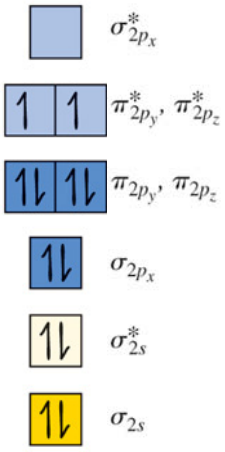
  Diamagnetism is associated with ***paired*** electrons.

Liquid oxygen, $O_2(l)$, is attracted to the poles of a magnet because O_2 is paramagnetic.

Chapter 9 Section 6

Molecular Orbital Diagram

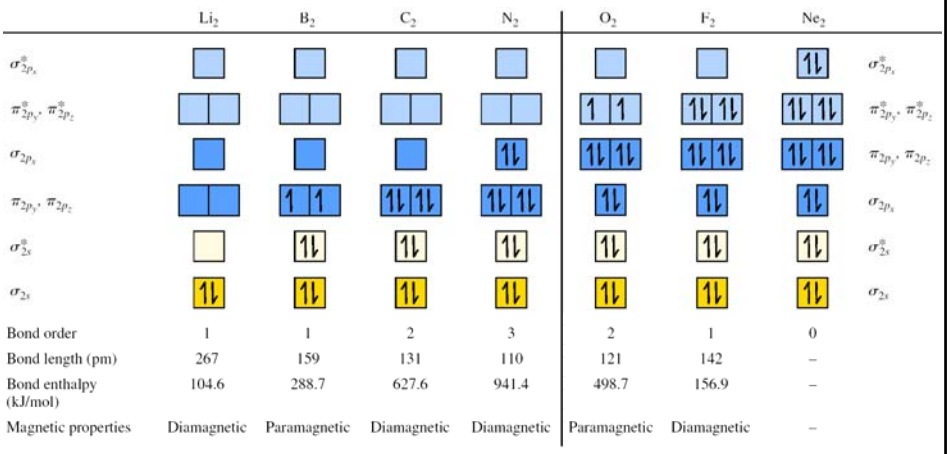
- Molecular orbital theory helps you predict several important properties of the substance.
  - Bond order (bond length and bond strength).
  - Bond enthalpy (bond energy)
  - Magnetic properties.



MO diagram of O_2

Chapter 9 Section 6

Molecular Orbital Diagrams

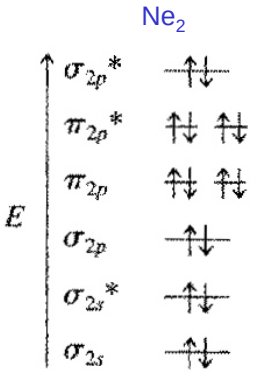


	Li_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	1	2	3	2	1	0
Bond length (pm)	267	159	131	110	121	142	–
Bond enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	–
Magnetic properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	–

Chapter 9 Section 6

Exercises

- Predict the bond order and magnetism of Ne_2.

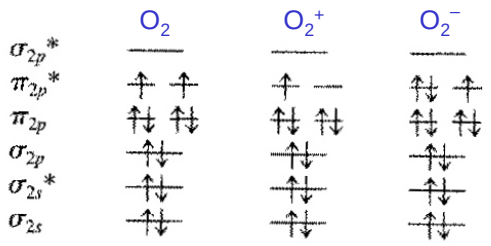


- Bond order
  = (8 – 8) / 2 = 0
  According to the MO theory, Ne_2 doesn't exist.

Chapter 9 Section 6

Exercises

- Give the electron configurations and bond orders for O_2, O_2^+, and O_2^-.



For O_2: $\frac{8-4}{2} = 2$

For O_2^+: $\frac{8-3}{2} = 2.5$

For O_2^-: $\frac{8-5}{2} = 1.5$

O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$

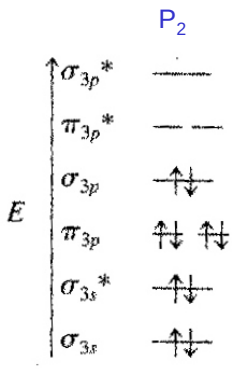
O_2^+: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$

O_2^-: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$

Chapter 9 Section 6

Exercises

- Predict the bond order and magnetism of P_2.

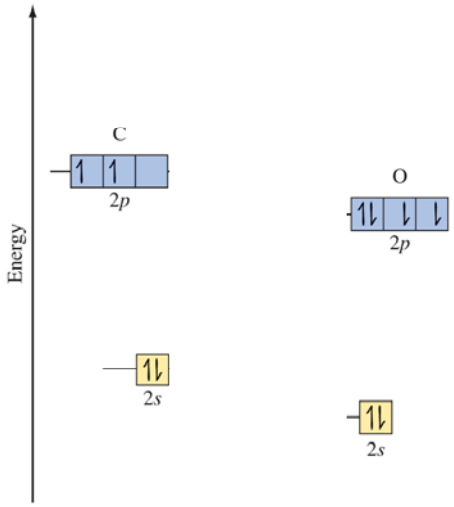


- Bond order
  = (8 – 2) / 2 = 3
  According to the MO theory, P_2 exists and it is diamagnetic.

Chapter 9 Section 6

Bonding in Heteronuclear Diatomic Molecules

- MO model can be expanded to diatomic molecules with two different nuclei whose electronic natures are not so different.
- Carbon monoxide (CO) is expected from MO theory to be diamagnetic and to have a bond order of:
  (8 – 2) / 2 = 3

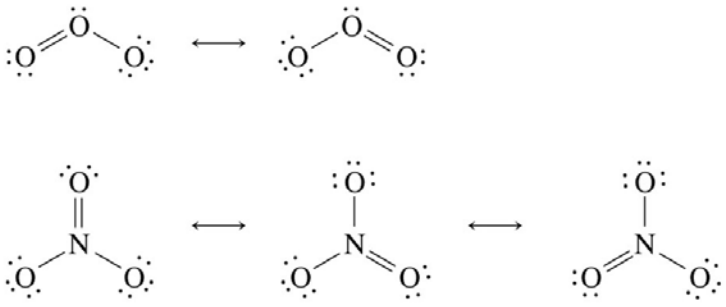


The MO energy-level diagram of the CO molecule

Chapter 9 Section 7

Descriptions of Molecules with Delocalized Bonding

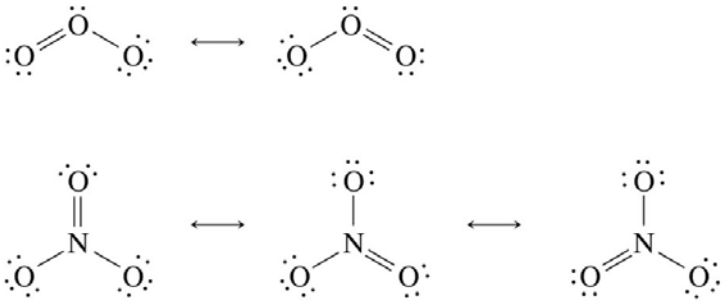
- Localized electron model assumes that the bonding electron pair is being shared between two atoms (***localized***).
- In several cases, such as O_3 and NO_3^-, the π-electron bonding pairs are ***delocalized*** and are **not** present at a specific location in the molecule.



Chapter 9 Section 7

Descriptions of Molecules with Delocalized Bonding

- In molecules with resonance structures,
  - σ bonds can be viewed to be localized, and
  - π bonds can be considered to be delocalized.



Chapter 9 Section 7

Example: Benzene (C_6H_6)

Each C atom has 3 electron domains

Hybridization: sp^2