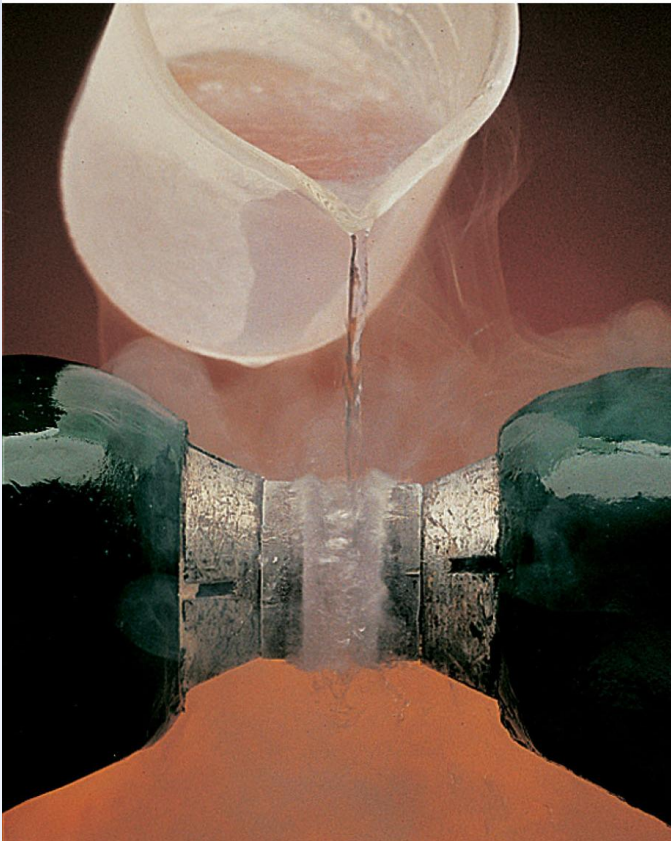


# *Molecular Orbital Theory*



Paramagnetic properties of O<sub>2</sub>

# Covalent Bonding Theory

- **Valence Bond Theory**
  - useful for deriving shapes/polarity
  - simple but inaccurate/deficient
- **Molecular Orbital Theory**
  - more complex/more accurate
  - all valence electrons are delocalized

# Molecular Orbital Theory

- The goal of molecular orbital theory is to describe molecules in a similar way to how we describe atoms, that is, in terms of **orbitals, orbital diagrams, and electron configurations**

# Orbitals

- space to find out the electron with the highest possibility.
- Atomic Orbital
- Hybrid Orbital
- Molecular Orbital

# • Atomic orbital

- Pure orbital of an atom
- Immixing orbital with other atomic orbital
- Characteristic for one atom
  - $1s^1$  → characteristic of hydrogen atomic orbital
  - $1s^2$  → characteristic of helium atomic orbital

# • Hybrid orbital

- Mixing of atomic orbitals to form a new set of orbitals
- The properties and the energy of hybrid orbitals are intermediate of non-hybrid orbitals
  - $sp$  → 50% of s orbital & 50% of p orbital
  - $sp^2$  → 33.3% of s orbital & 66.7% of p orbitals

- Molecular orbital

- Result of the **overlapping** of orbitals and the **mixing** of different atomic orbitals in the molecule

- Electrons belong to the molecule as a whole

- $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$



# Orbitals

- Atomic orbitals
  - $1s^2, 1s^2 2s^2 2p^1$
- Hybrid orbitals
  - $sp, sp^2, sp^3, dsp^2$
- Molecular orbitals
  - $(\sigma_{1s})^2, (\sigma^*_{1s})^2$



# Molecular Orbital

- Bonding orbital
- Antibonding orbital
- Nonbonding orbital

- Bonding orbital

- The electron density localized between the two nuclei

- Has higher stability and lower energy than the origin atomic orbital

- $\Psi_b = \Psi_A + \Psi_B$  ( $\Psi_b = \Psi$  bonding)

# • Antibonding orbital

– The electron density = zero (nodal plane)

– Has lower stability and higher energy than the origin atomic orbital

$$-\Psi_{ab} = \Psi_A - \Psi_B \quad (\Psi_{ab} = \Psi \text{ antibonding})$$

# • Nonbonding orbital

- The electron localized to each atomic orbital
- Electrons in nonbonding lobe repel to those in bonding lobe
- Influent the geometry shape of the molecule

# Orbitals Interaction

- Interactions of the atomic orbitals
  - In-phase interaction
  - Out-of-phase interaction

# • In-phase interaction

- Intensity of the negative charge >>>
- Negative charge between 2 nuclei >>>
- plus-minus attraction between the electron charge and the nuclei >>>
- Potential energy <<<
- Stability of the molecule >>>

# • Out-of-phase interaction

- **intensity** of the negative charge <<<
- **negative charge** between the nuclei <<<
- **plus-minus attraction** between the electron charge and the nuclei <<<
- **Potential energy** >>>
- **Stability** of the molecule <<<



The lower the potential energy, the more stable the molecule

The higher the potential energy, the less stable the molecule

# 2 types of overlap of the atomic orbitals

1. Head-on overlap (end-on overlap) of atomic orbital

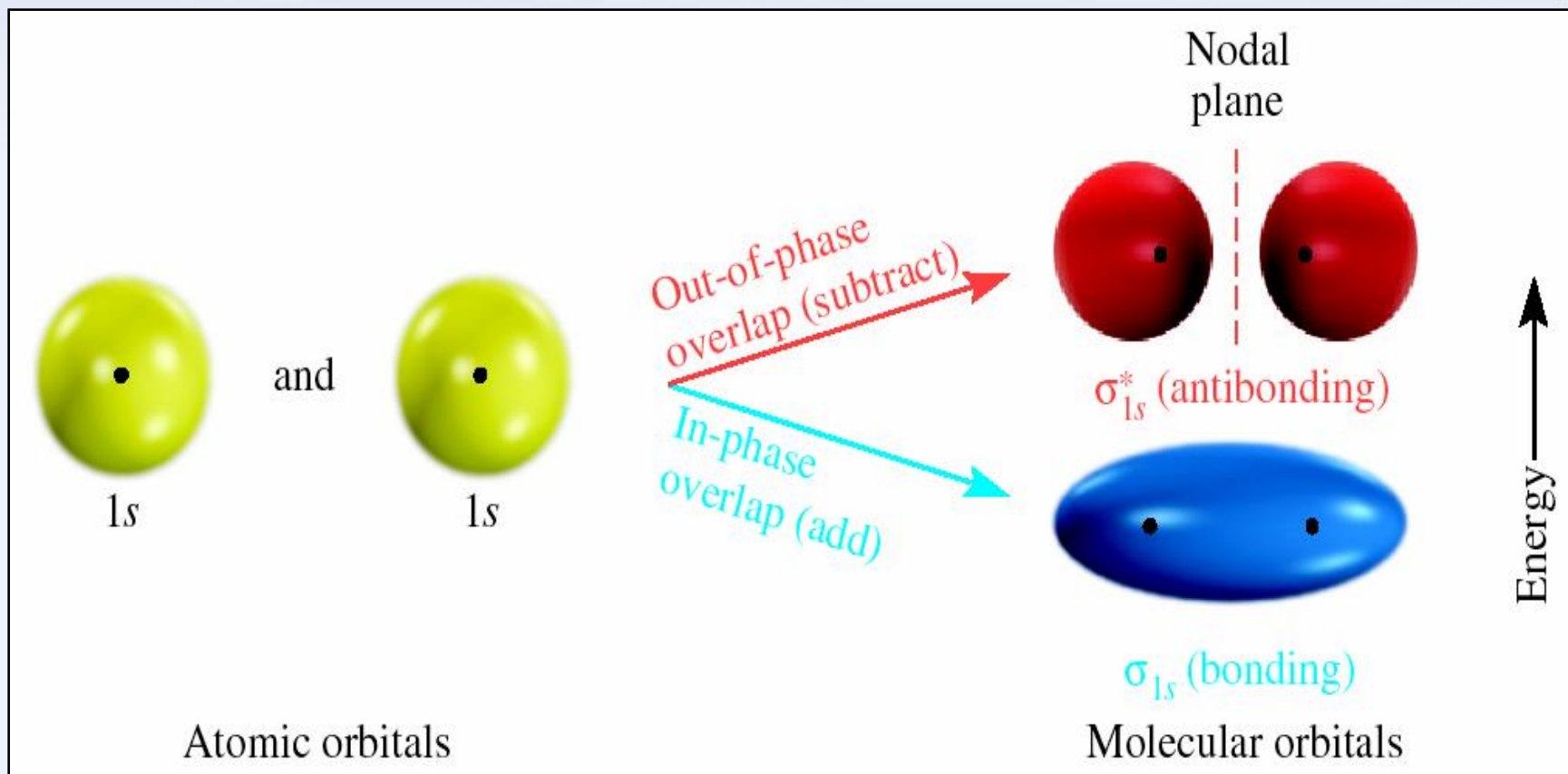
→ produces  $\sigma$  (sigma) orbitals.

2. Side-on overlap (parallel overlap) of atomic orbital

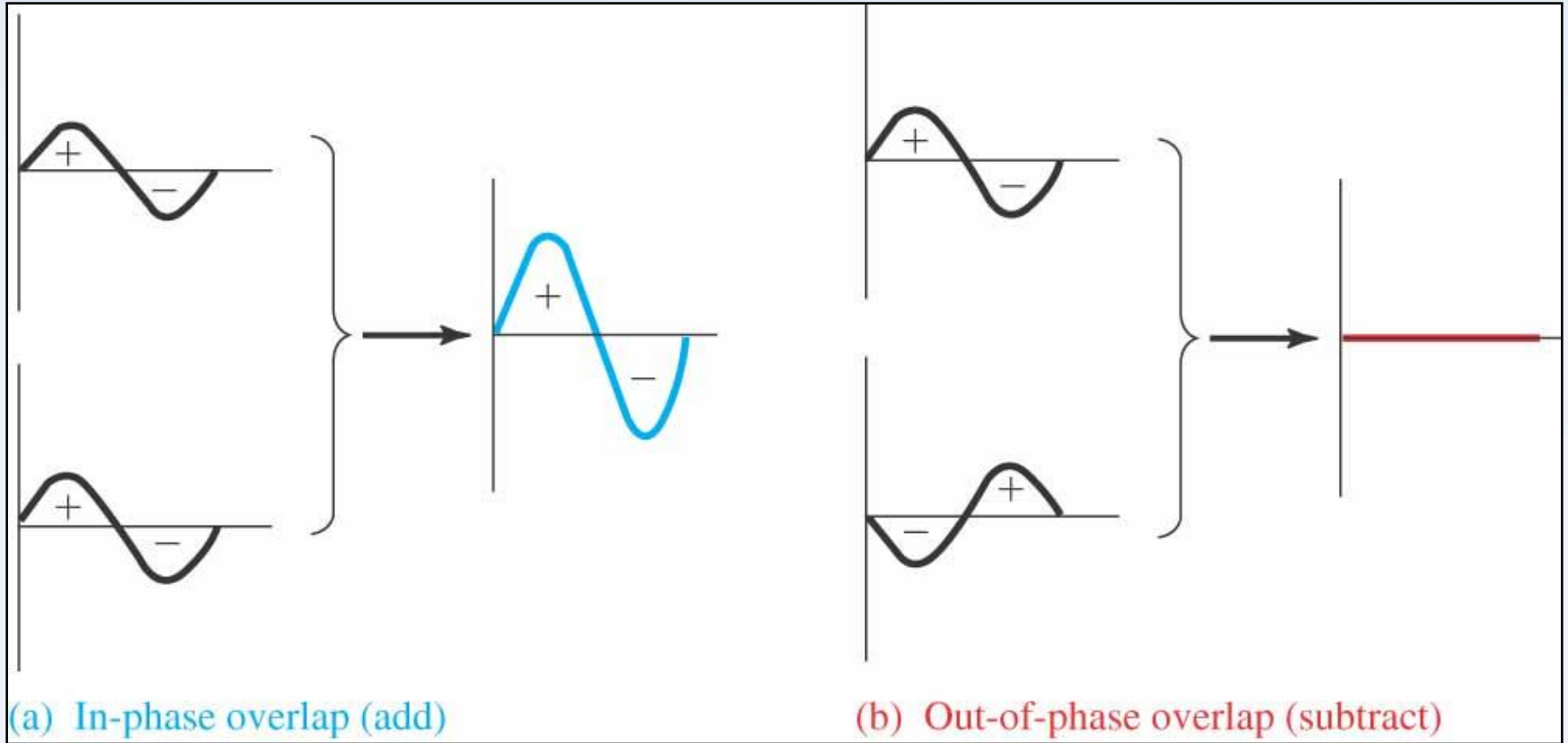
→ produces  $\pi$  (pi) orbitals.

# Head-on-overlap of two 1s orbitals

- Two 1s atomic orbitals that overlap produce two molecular orbitals designated as:
  1.  $\sigma_{1s}$  bonding molecular orbital
  2.  $\sigma^*_{1s}$  antibonding molecular orbital



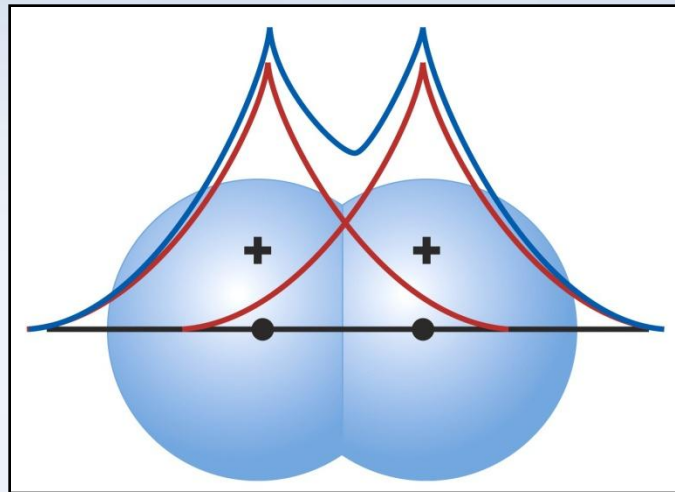
# Overlap of Wave functions of two s orbitals



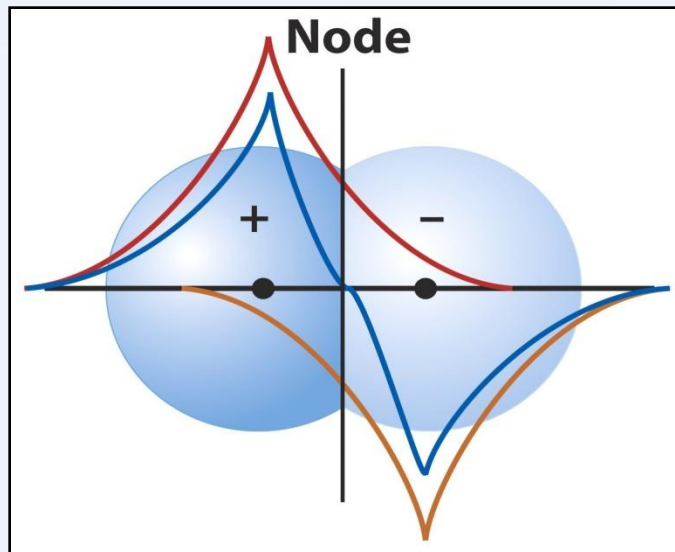
(a) In-phase overlap (add)

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

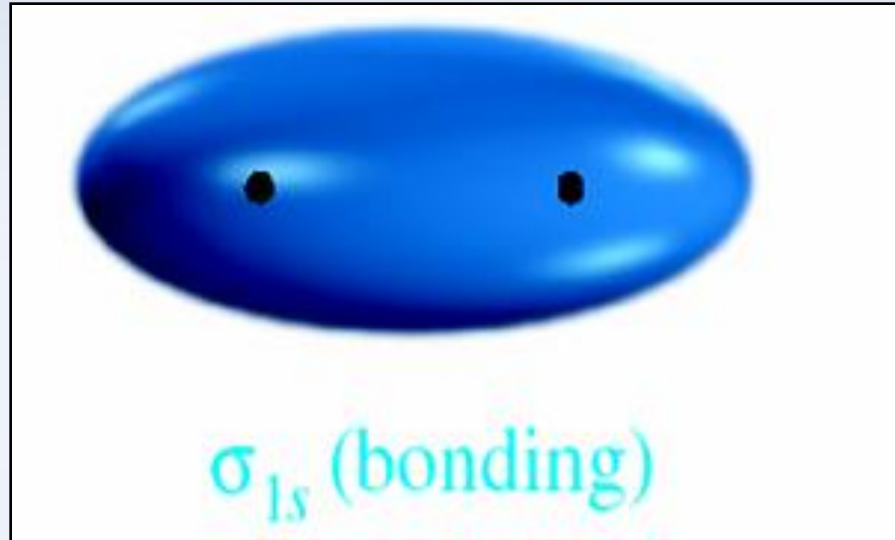
Constructive  
Overlap  
of two 1s orbitals



Destructive  
Overlap of two  
1s orbitals



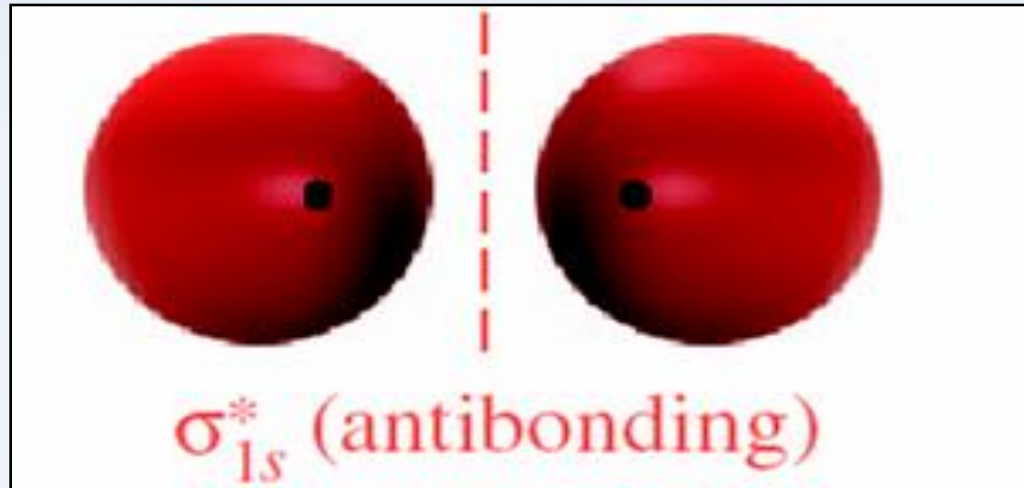
# Bonding orbital



- Lower energy
- Stable
- Favorable for electrons
- Electrons exist between nuclei



# Anti-bonding orbital

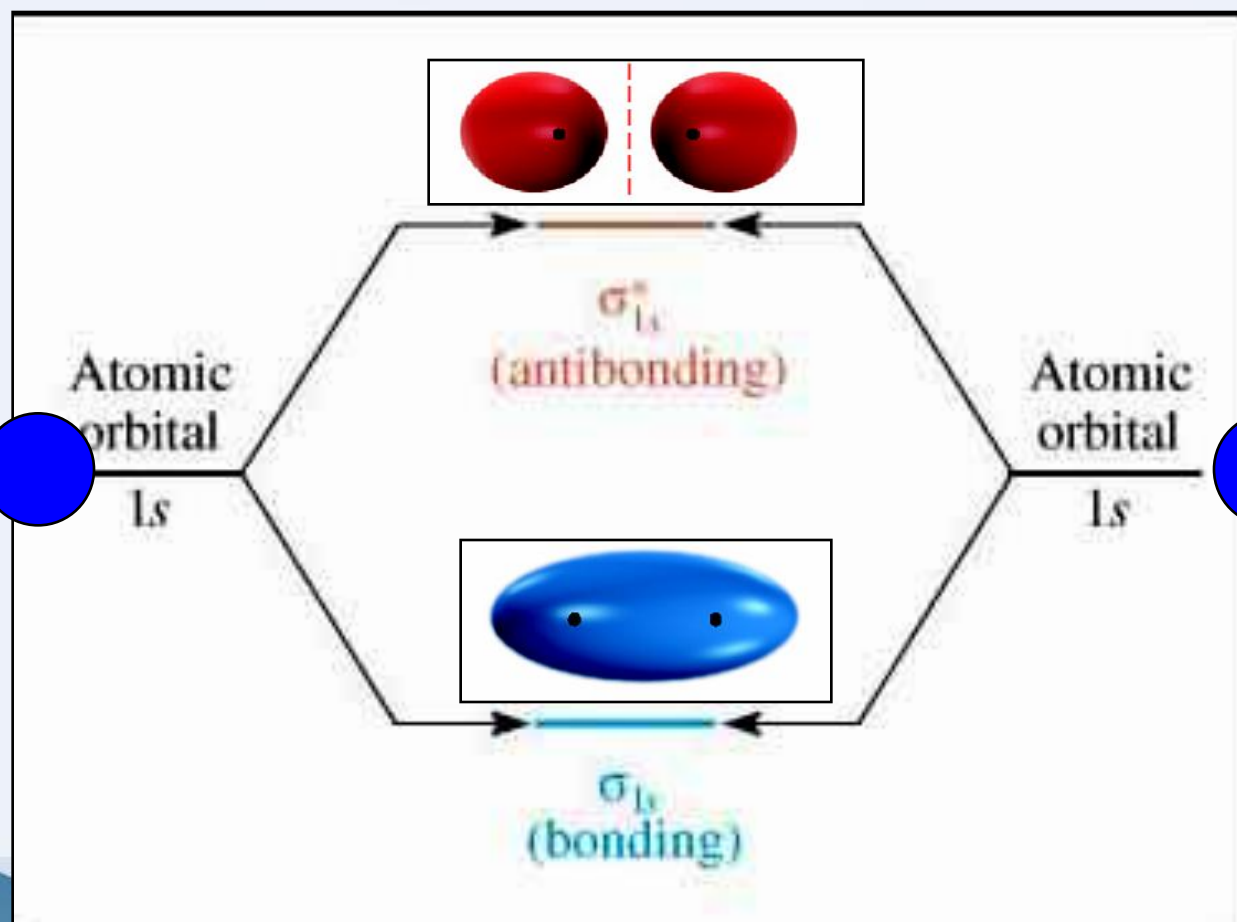


- Higher energy
- Unstable
- Unfavorable for electrons
- Electrons exist outside

Energetically, the molecular orbitals split.

1. The  $\sigma_{1s}$  is **lower** in energy.
2. The  $\sigma^*_{1s}$  is **higher** in energy.

Molecular orbital diagram for the union of two s orbitals

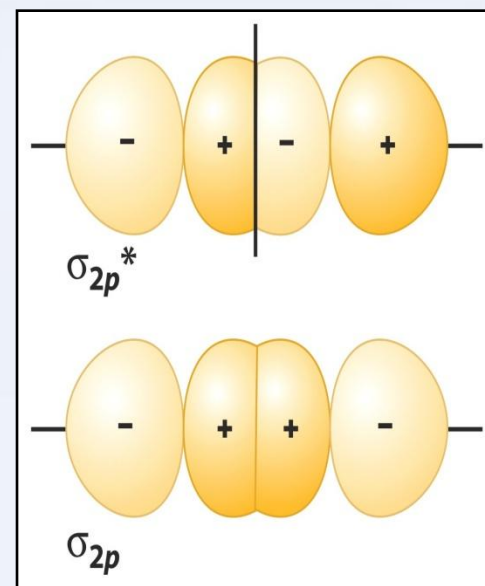
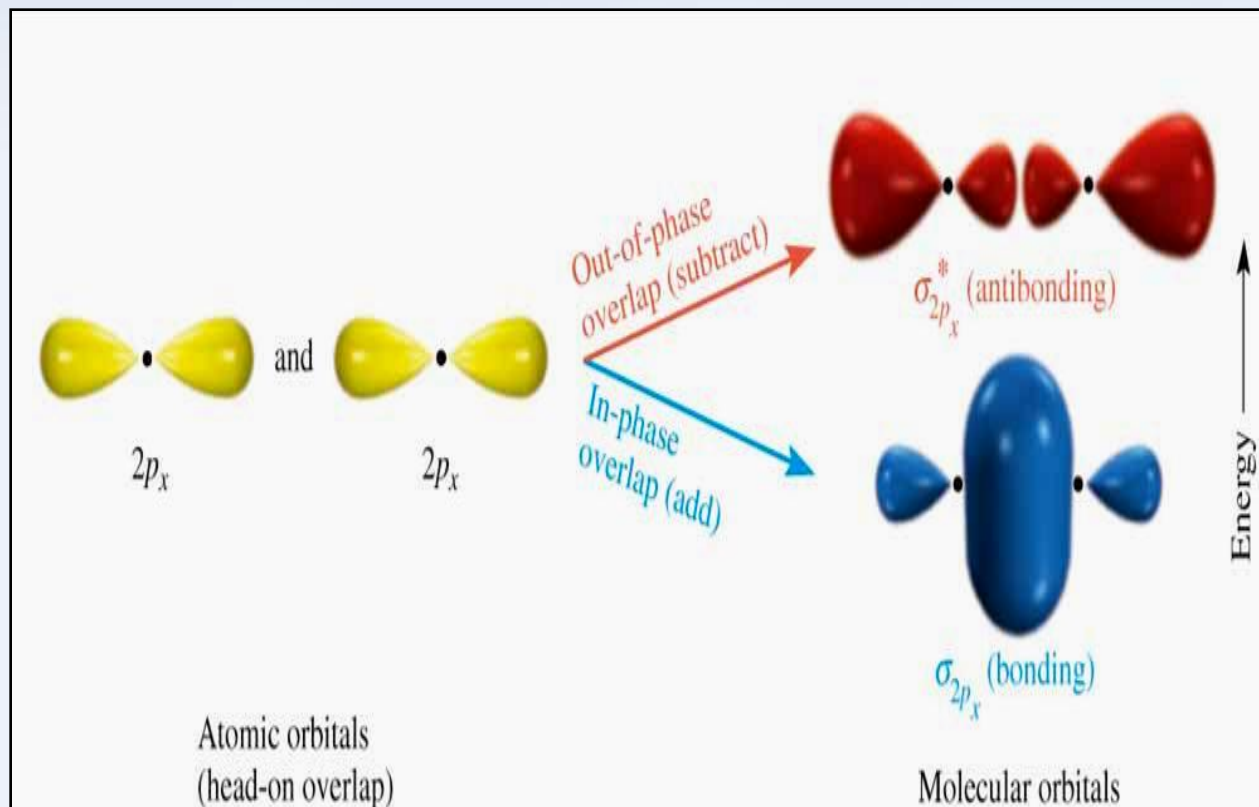


# Head-on-overlap of two $2p_x$ orbitals

- **Head-on (end-on) overlap** of **two p atomic orbitals** on different atoms, such as  $2p_x$  with  $2p_x$ , produces:

1.  $\sigma_{2px}$       **bonding** molecular orbital

2.  $\sigma^*_{2px}$       **antibonding** molecular orbital

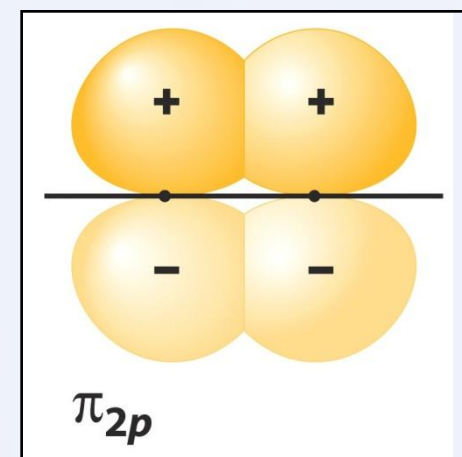
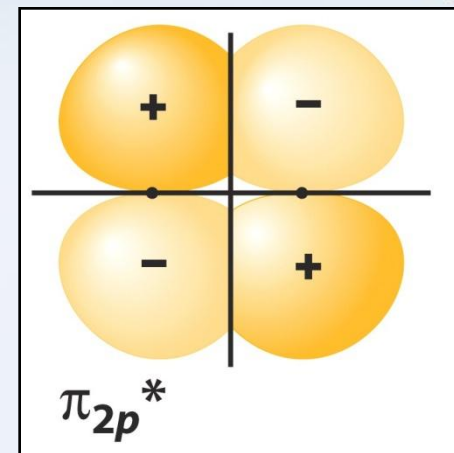
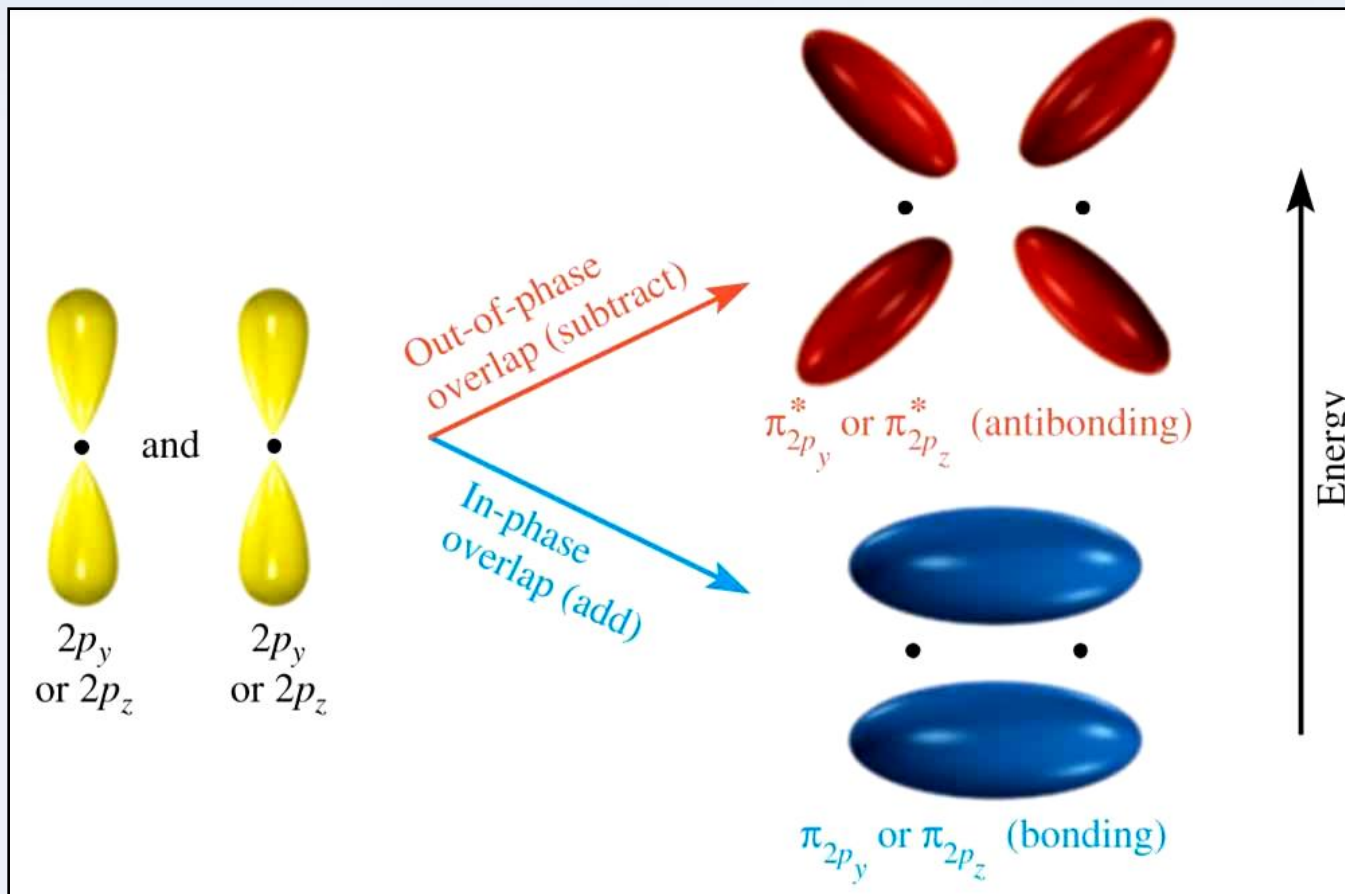


# Side-on-overlap of two $2p_y$ or $2p_z$ orbitals

- **Side-on (parallel) overlap** of two p atomic orbitals on different atoms (such as  $2p_y$  with  $2p_y$  or  $2p_z$  with  $2p_z$ ) produces:

1.  $\pi_{2p_y}$  or  $\pi_{2p_z}$  (both are bonding orbitals)

2.  $\pi^*_{2p_y}$  or  $\pi^*_{2p_z}$  (both are antibonding orbitals)





- How many molecular orbitals are formed when
  - two 1s orbitals interact?
  - two 2p orbitals interact?



# $\sigma$ and $\pi$ orbitals

- Overlap in  $\pi \lll \sigma$
- Electron charge enhancement between the nuclei in  $\pi \lll \sigma$
- Electron charge between the nuclei in  $\pi \lll \sigma$
- Nuclei-electron attraction in  $\pi \lll \sigma$
- Stabilization of  $\pi \lll \sigma$
- Potential energy of  $\pi \ggg \sigma$

# $\sigma^*$ and $\pi^*$ orbitals

- Less overlap leads to less shift of electron charge between the nuclei.
- Overlap in  $\pi^* \lll \sigma^*$
- Shift of Electron charge between the nuclei in  $\pi^* \lll \sigma^*$
- Electron charge in  $\pi^* \ggg \sigma^*$
- Nuclei-electron attraction in  $\pi^* \ggg \sigma^*$
- Stabilization of  $\pi^* \ggg \sigma^*$
- Potential energy of  $\pi^* \lll \sigma^*$

How are the orbitals filled  
with the electrons ?

Note: you consider all the  
electrons of each atom, not just  
the valence electrons!

!!!

# Molecular Orbital (MO)

Orbital filled by electrons based on

# LCAO

(Linear Combination of Atomic Orbitals)

# Keep these in mind!!!

1. Molecular orbitals are formed from the **overlap** of atomic orbitals.
2. Only atomic orbitals of about **the same energy interact** to a significant degree.

# Keep these in mind!!!

3. The number of MO = the number of combined AO
4. When two atomic orbitals overlap, and two molecular orbitals are formed, a bonding MO and an antibonding MO

# Keep these in mind!!!

5. The filling of the orbitals by electrons in molecular orbital like to those in atomic orbitals
  - Aufbau Principle
  - Hund's Rule
  - Pauli Exclusion Principle



# The Uses of Molecular Orbital

- Predicting:
  - The **stability** of the molecule
  - The **magnetism** of the molecule

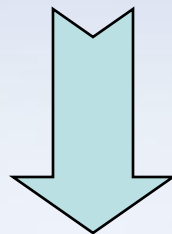
# Stability of the Molecule

- Molecule stability determined by its **BOND ORDER (BO)**

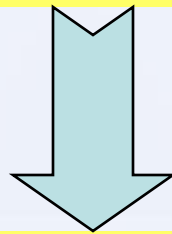
$$BO = \frac{(\sum e^- \text{ in bonding orbitals}) - (\sum e^- \text{ in antibonding orbitals})}{2}$$

- Bond order reflects the bond strength
  - $BO = 0$ , the molecule is **unstable** (there are equal numbers of electrons in bonding and antibonding orbitals)
  - $BO > 0$ , suggests a **stable** molecule (there are more electrons in bonding than antibonding orbitals)

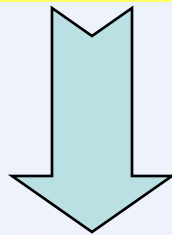
Bond Order >>>



Bond Length <<<



Bond energy >>>



Stability of the molecule >>>

# Magnetism of the Molecule

- Paramagnetic
  - compounds that are weakly attractive in magnetic fields
  - unpaired electrons
- Diamagnetic
  - compounds that are not attractive in magnetic fields
  - all electrons are paired
  - no unpaired electrons

- Amplitude

- Quadrate of wave functions

- Electron density

- The highest possibility to find the electron

- bonding  $\psi_b^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$

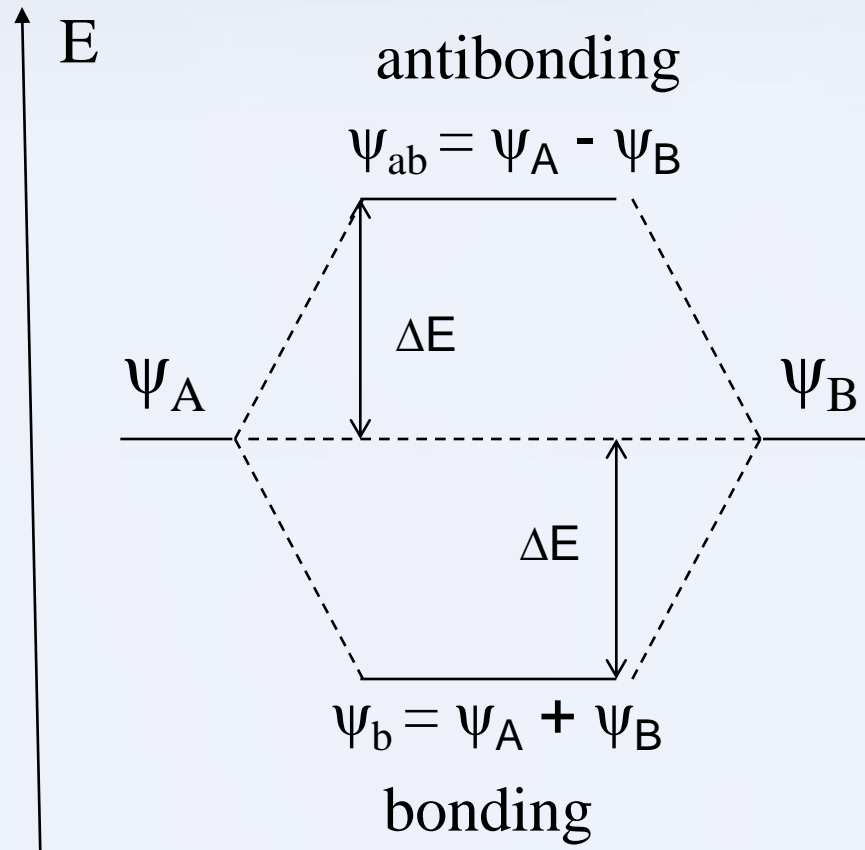
- antibonding  $\psi_{ab}^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$

# Energy Level Diagram

- 2 types of energy level diagram:
  - **Homonuclear** diatomic molecules
  - **Heteronuclear** diatomic molecules



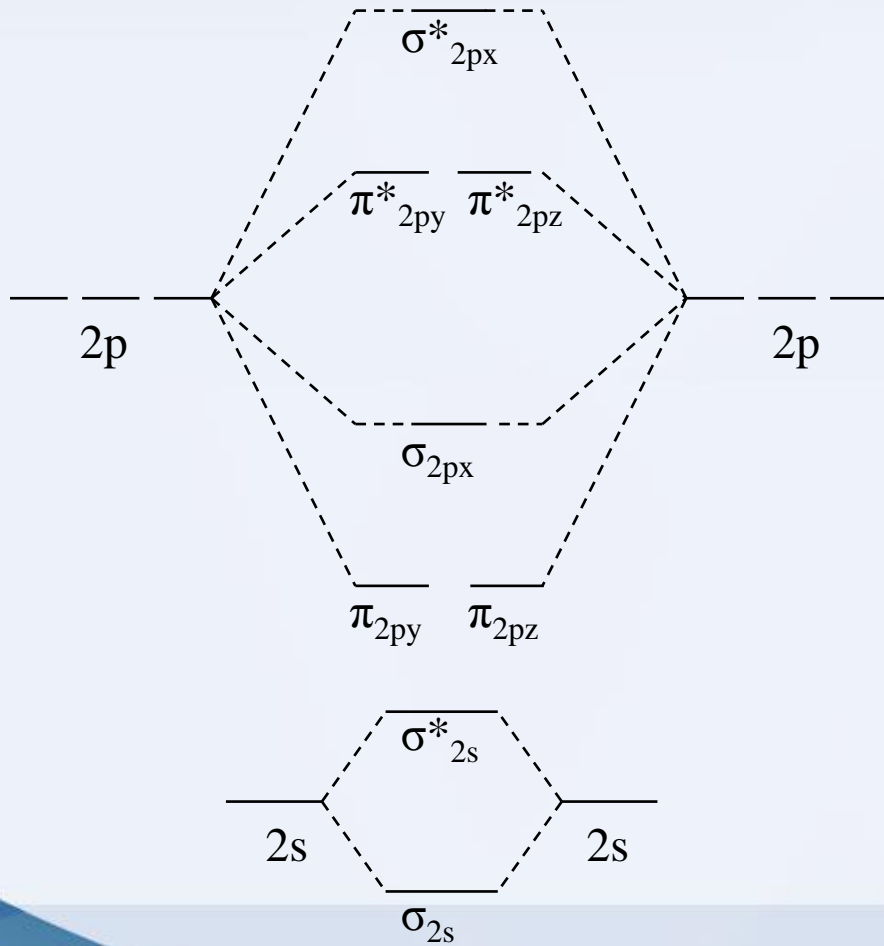
# Homonuclear Diatomic Molecules



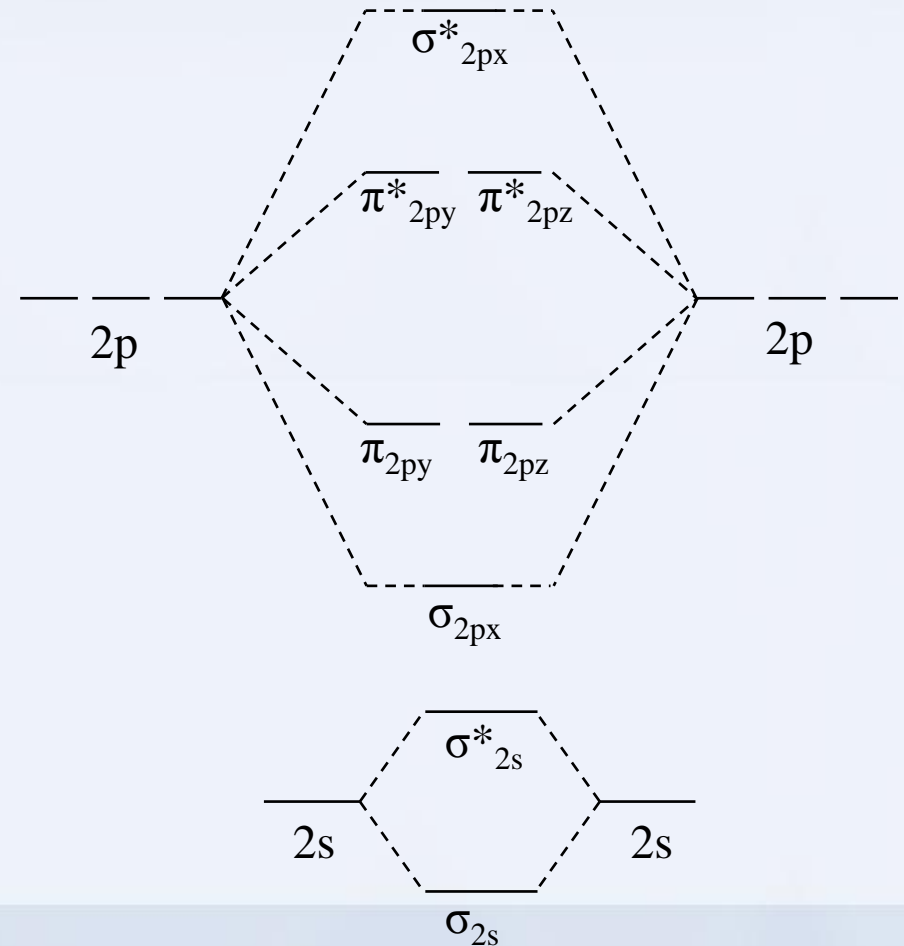
- Electronegativity of  $A = B$
- Energy of  $A = B$

# Energy Level Diagram

$\text{Li}_2 - \text{N}_2$



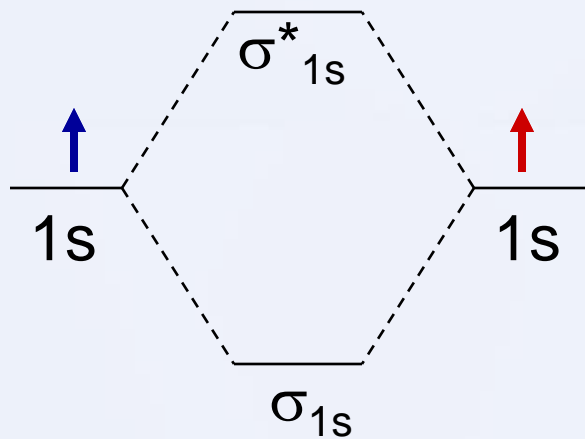
$\text{O}_2 - \text{Ne}_2$



# Energy Level Diagram of H<sub>2</sub> Molecule



AO H    MO H<sub>2</sub>    AO H



$$\text{BO} = \frac{\sum e^-_{\text{bonding}} - \sum e^-_{\text{antibonding}}}{2}$$

$$\text{BO} = \frac{2 - 0}{2} = 1 \rightarrow \text{STABLE}$$

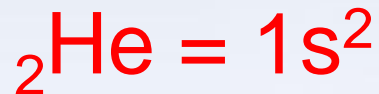
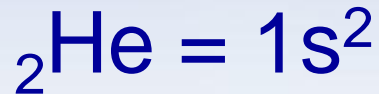
No unpaired  
electron



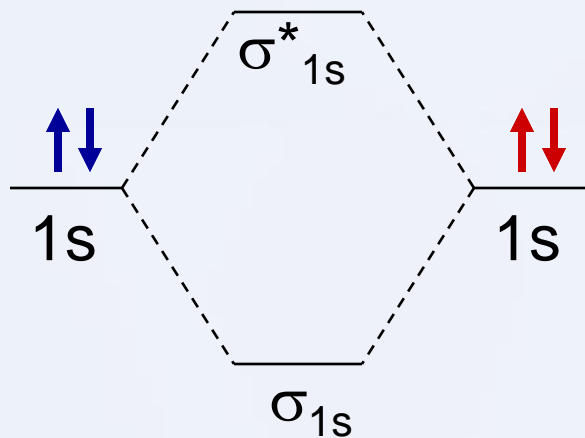
**DIAMAGNETIC**

Molecular Electronic Configuration =  $(\sigma_{1s})^2$

# Energy Level Diagram of He<sub>2</sub> Molecule



AO He      MO He<sub>2</sub>      AO He



$$\text{BO} = \frac{\sum e^-_{\text{bonding}} - \sum e^-_{\text{antibonding}}}{2}$$

$$\text{BO} = \frac{2 - 2}{2} = 0 \rightarrow \text{UNSTABLE}$$

No unpaired  
electron



DIAMAGNETIC

Molecular Electronic Configuration =  $(\sigma_{1s})^2 (\sigma^*_{1s})^2$

## Problem 1:

Molecule of  $N_2$  (atomic number 7)

- Sketch the energy level diagram
- Determine the magnetism
- Determine the stability of the molecule
- Write the molecular electronic configuration

Answer:

Molecule of N<sub>2</sub>:

- Homonuclear diatomic molecule
- Has the same electronegativity
- Has the same energy level for both atom

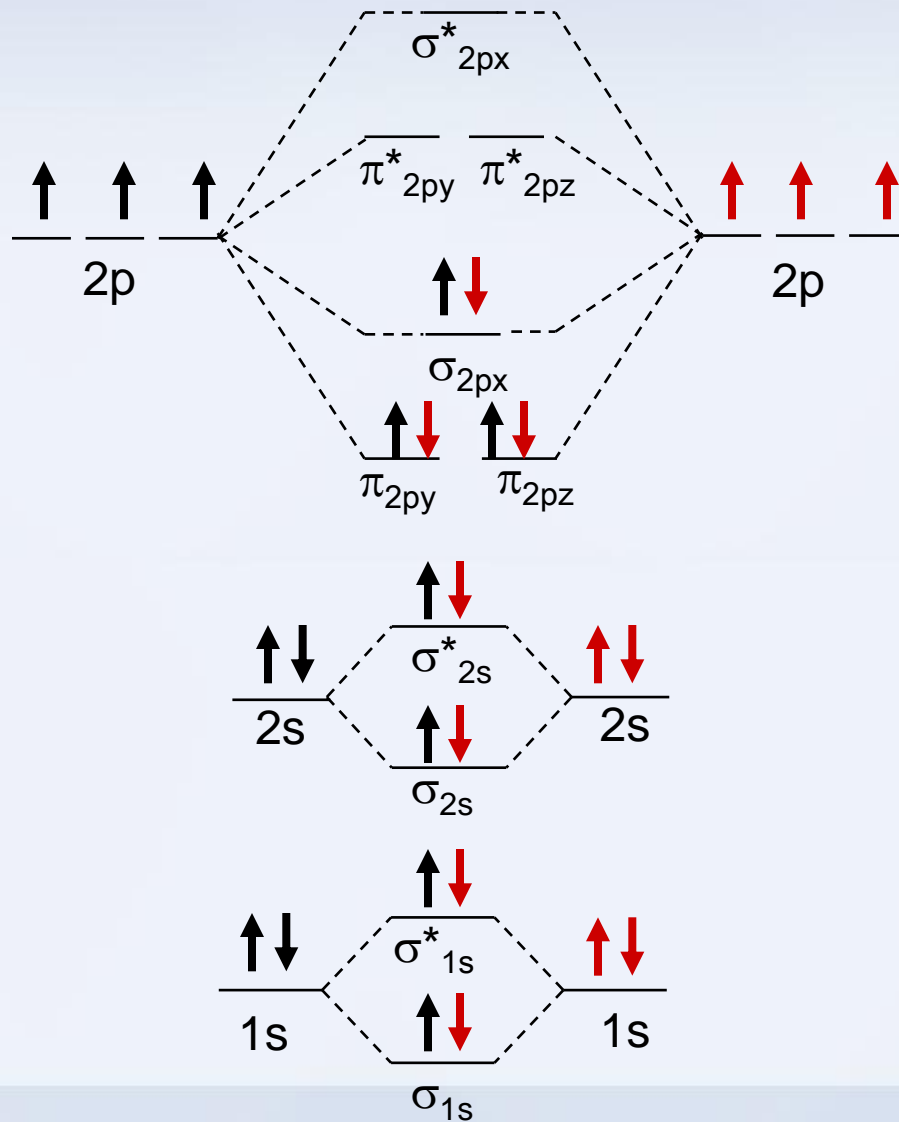


AO N

MO N<sub>2</sub>

AO N

Energy

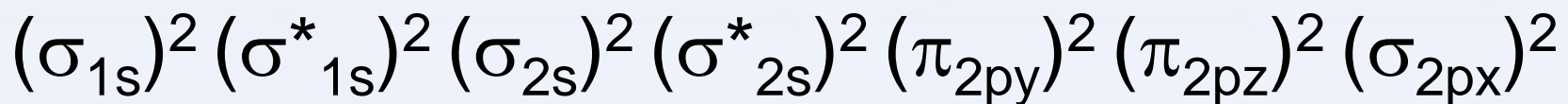




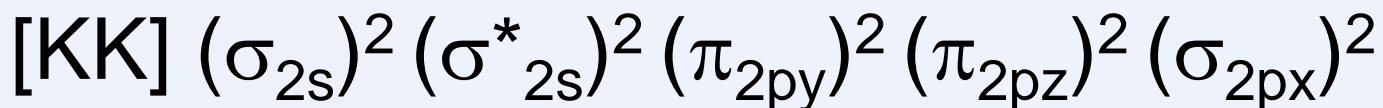
$$BO = \frac{10 - 4}{2} = 3 \quad \text{OR} \quad \frac{6 - 0}{2} = 3 \rightarrow \text{STABLE}$$

No unpaired electron  $\rightarrow$  DIAMAGNETIC

Molecular Electronic Configuration =



OR



## Problem 2:

Molecule of  $O_2$  (atomic number 8)

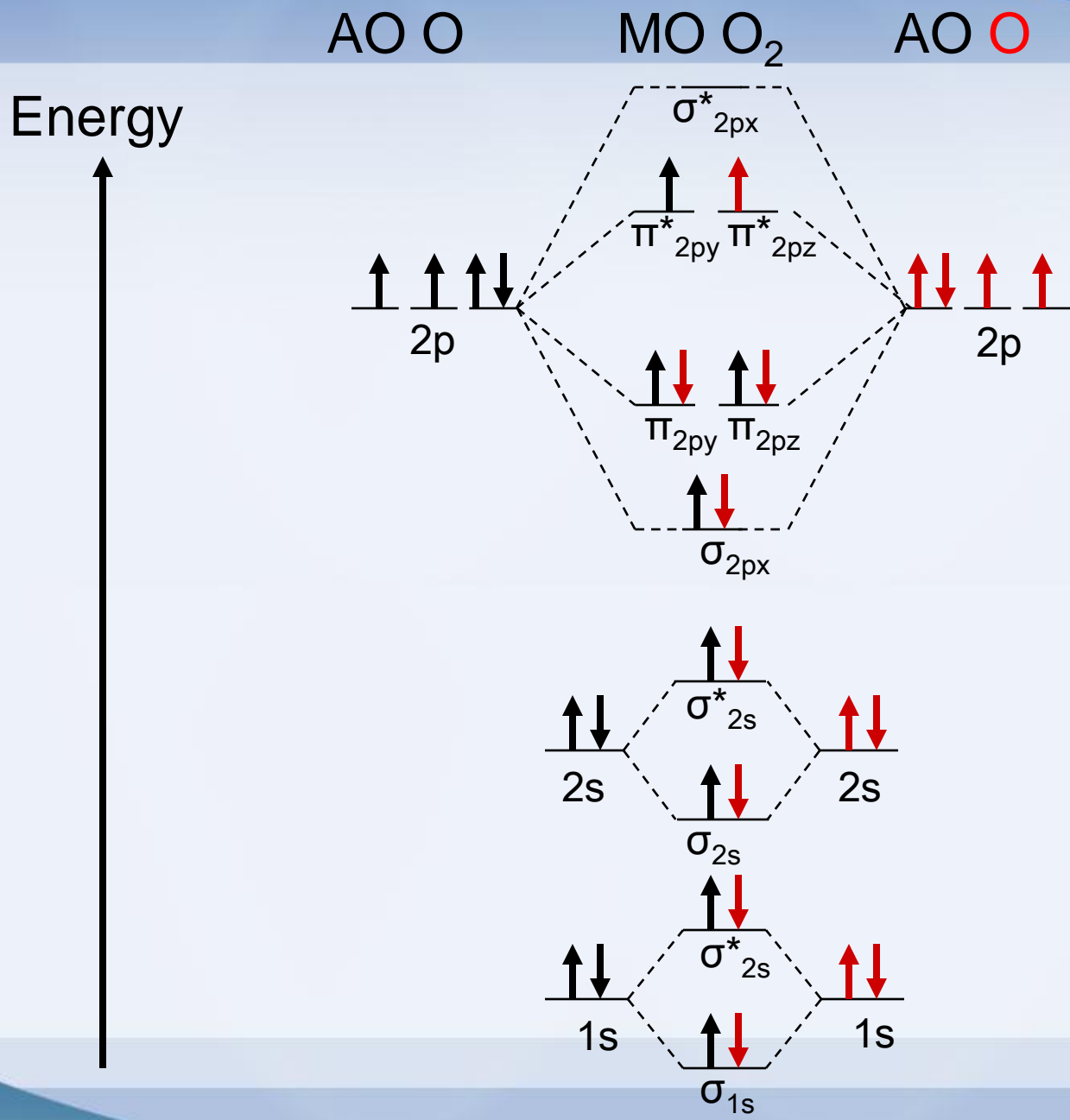
- Sketch the energy level diagram
- Determine the magnetism
- Determine the stability of the molecule
- Write the molecular electronic configuration

Answer:

Molecule of O<sub>2</sub>:

- Homonuclear diatomic molecule
- Has the same electronegativity
- Has the same energy level for both atom

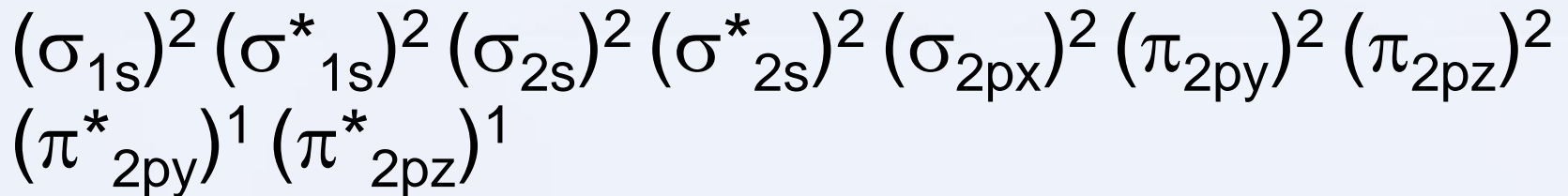




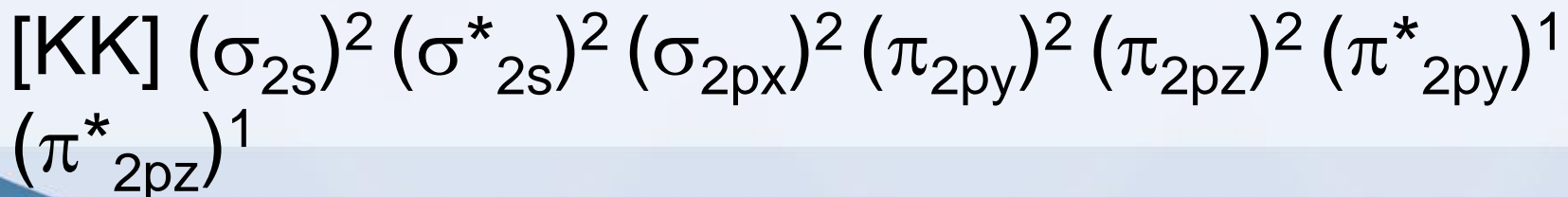
$$BO = \frac{10 - 6}{2} = 2 \quad \text{OR} \quad \frac{6 - 2}{2} = 2 \rightarrow \text{STABLE}$$

2 unpaired electron  $\rightarrow$  PARAMAGNETIC

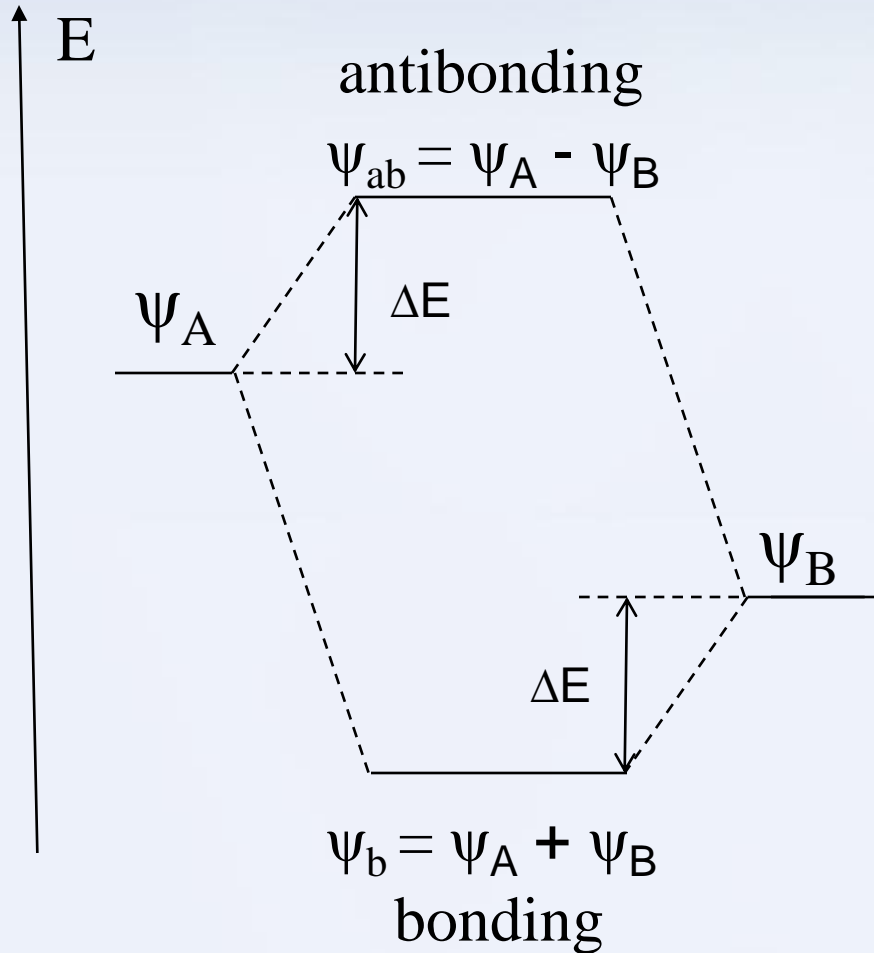
Molecular Electronic Configuration =



OR



# Heteronuclear Diatomic Molecules

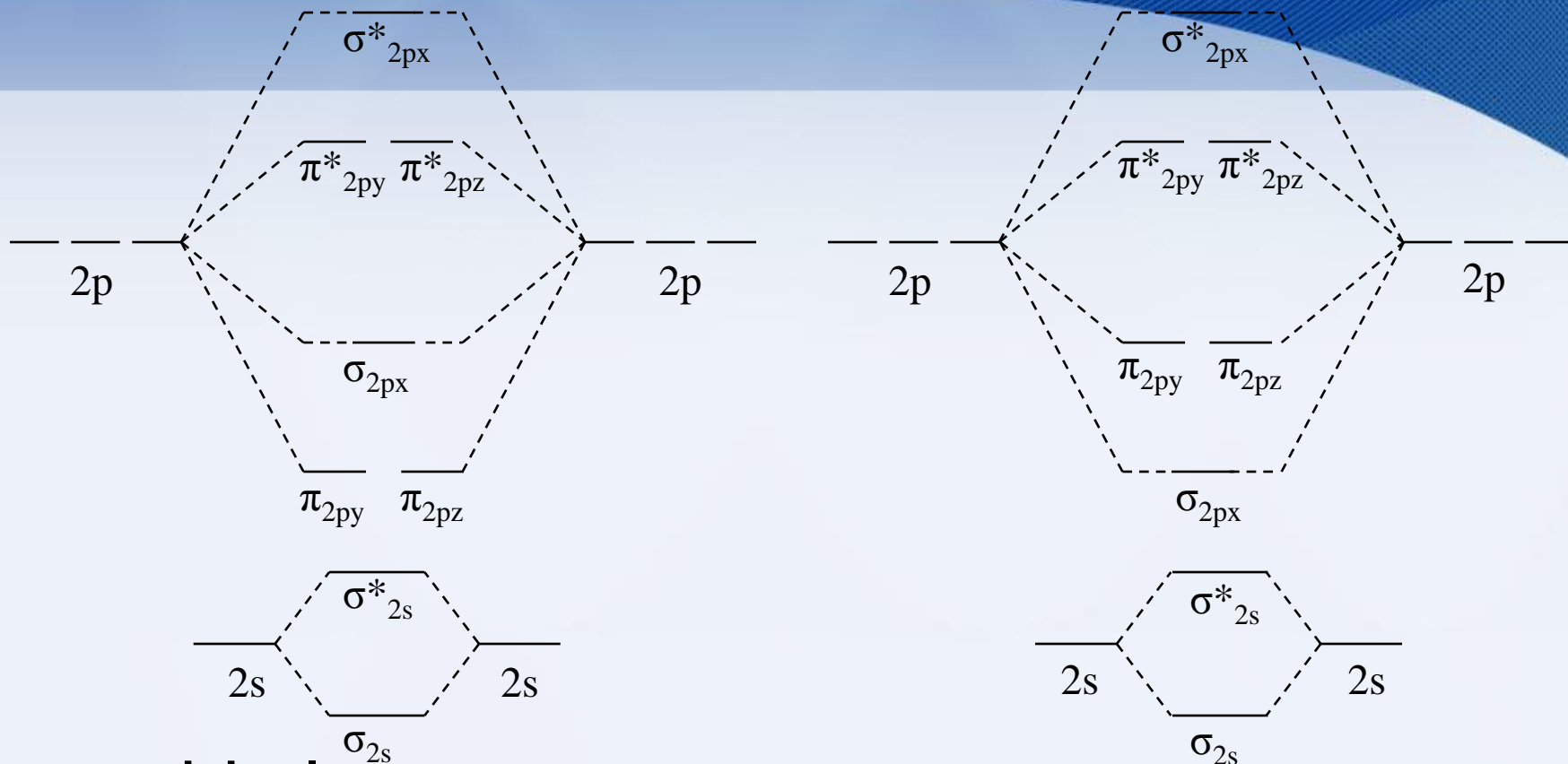


- Electronegativity of  $A < B$
- Energy of  $A > B$
- The more electronegative the atom, the lower the energy.

## Problem 3

- Sketch the energy level diagram of CO molecule.
- What type energy level diagram must be adopted?
  - $\text{Li}_2$  –  $\text{N}_2$  type?
  - OR
  - $\text{O}_2$  –  $\text{Ne}_2$  type?





- p orbital:

- Li<sub>2</sub>–N<sub>2</sub> type : 2π, 1σ, 2π\*, 1σ\* or

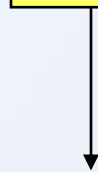
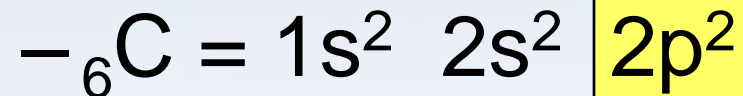
2121

- O<sub>2</sub>–Ne<sub>2</sub> type : 1σ, 2π, 2π\*, 1σ\* or

1221

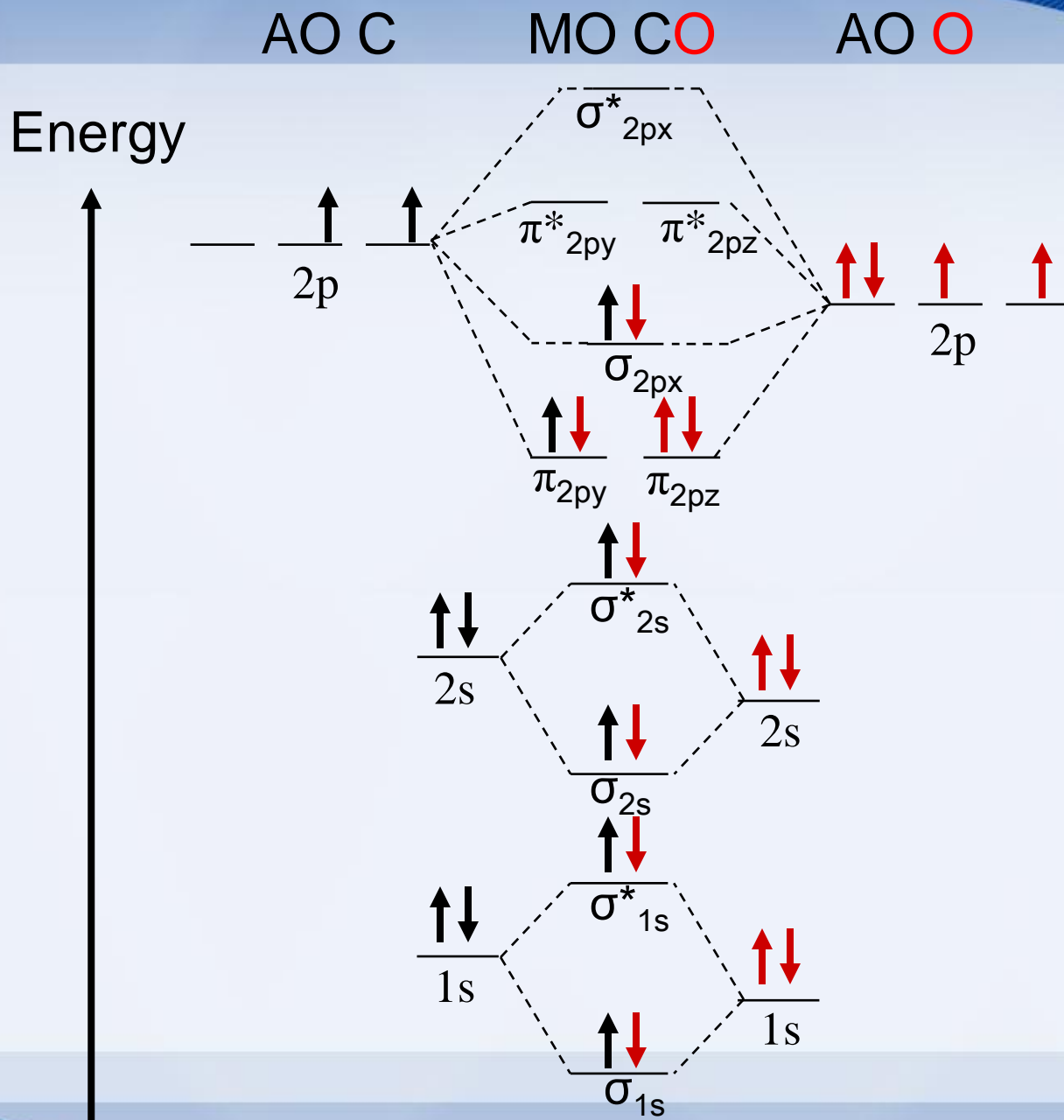
- Use
  - 2121 type when the total  $e^-$  in p orbital less than or equal to  $\frac{1}{2}$  filled
  - 1221 type when the total  $e^-$  in p orbital more than  $\frac{1}{2}$  filled
- Remember:
  - Maximum  $e^-$  in p orbital = 12  $e^-$
- So:
  - 2121 type when total  $e^-$  in p orbital  $\leq 6 e^-$
  - 1221 type when total  $e^-$  in p orbital  $> 6 e^-$

- CO molecule:



6 e<sup>-</sup> → 2121 type

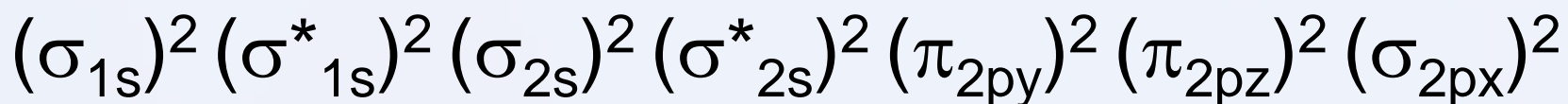
- Electronegativity of O > C
- O has lower energy than C



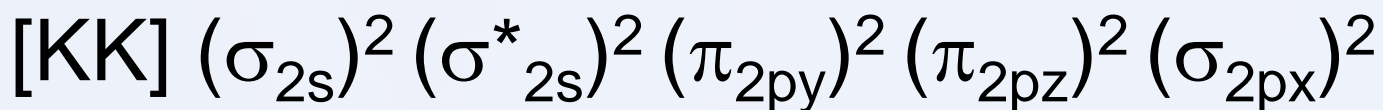
$$\text{BO} = \frac{10 - 4}{2} = 3 \quad \text{OR} \quad \frac{6 - 0}{2} = 3 \rightarrow \text{STABLE}$$

No unpaired electron  $\rightarrow$  DIAMAGNETIC

Molecular Electronic Configuration =



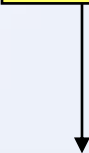
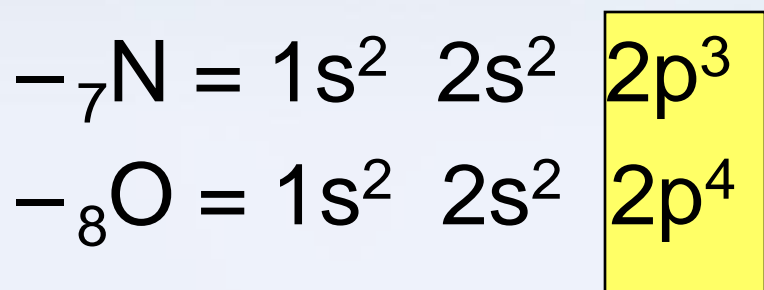
OR



## Problem 4

- Sketch the energy level diagram of  $\text{NO}^-$  ion.
- Determine the stability and magnetism of  $\text{NO}^-$  ion.
- Write down the molecular electronic configuration.

- $\text{NO}^-$  molecule:



$7 e^- \longrightarrow 1221 \text{ type}$

- Electronegativity of  $\text{O} > \text{N}$
- Energy of  $\text{O} < \text{N}$

# Choosing of 2121 or 1221 type

- Left behind the total charge of the molecule to choose 2121 or 1221 type.
- Total charge of the molecule belongs to molecule ( $\text{NO}^-$ ) as a whole, not to single atom
- Add the total charge of the molecule to the new molecular orbital

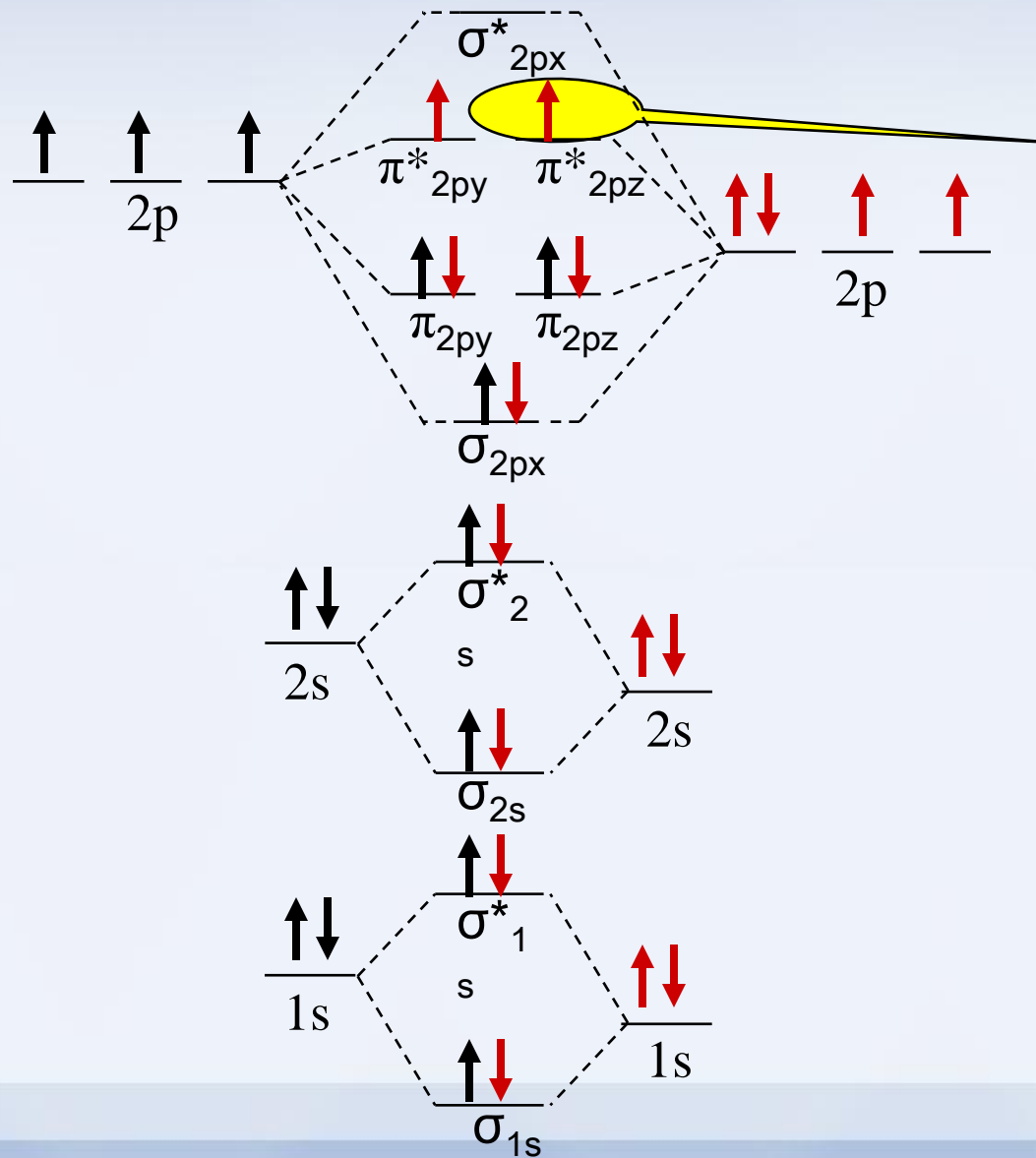


AO N

MO NO<sup>-</sup>

AO O

Energy

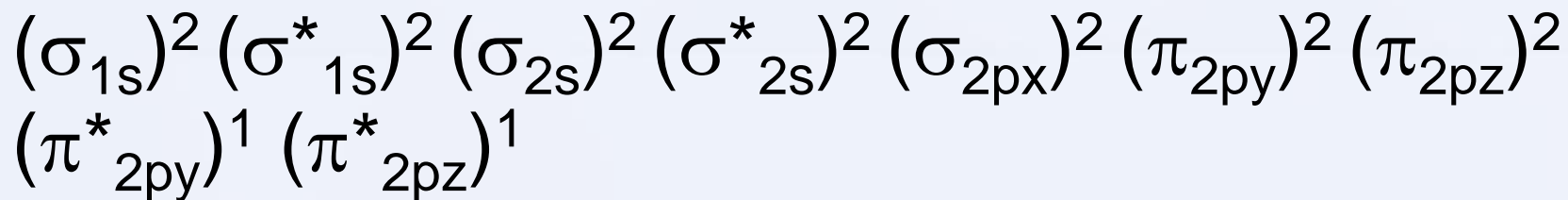


+ 1 e<sup>-</sup>  
from the  
total  
charge of  
the NO<sup>-</sup>  
molecule

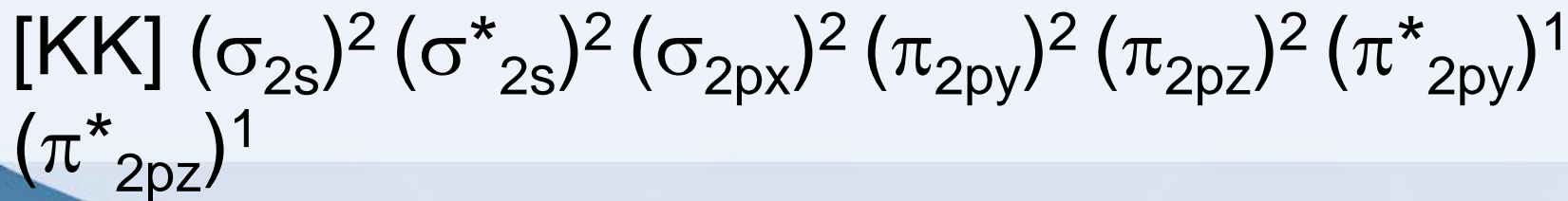
$$BO = \frac{10 - 6}{2} = 2 \quad \text{OR} \quad \frac{6 - 2}{2} = 2 \rightarrow \text{STABLE}$$

2 unpaired electron  $\rightarrow$  PARAMAGNETIC

Molecular Electronic Configuration =



OR

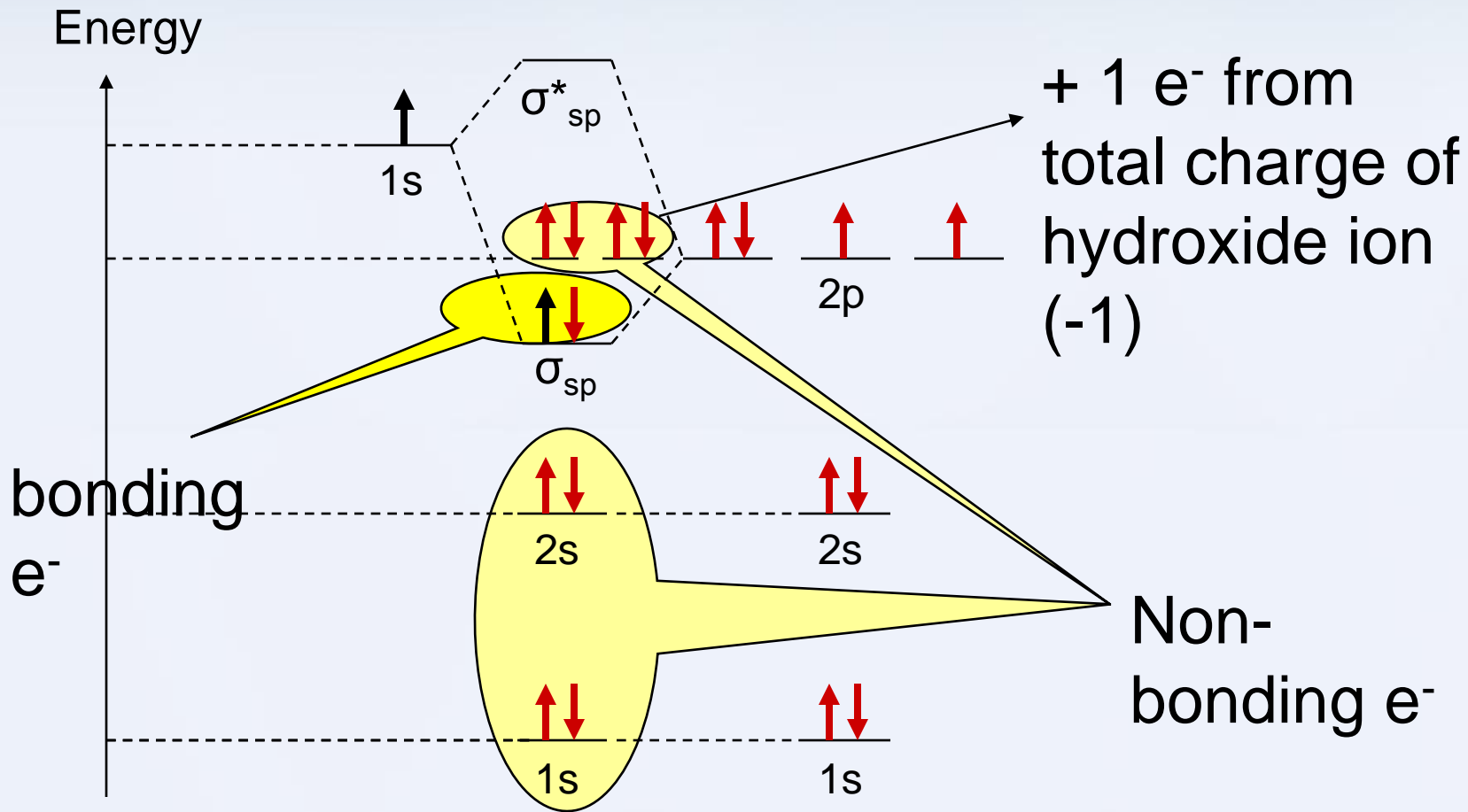


## Problem 5

- Sketch the energy level diagram of  $\text{OH}^-$  ion.
- Determine the stability and magnetism of  $\text{OH}^-$  ion.
- Write down the molecular electronic configuration.

- ${}_1\text{H} = 1s^1$
- ${}_8\text{O} = 1s^2 2s^2 2p^4$
- Remember:
  - (-1) charge of hydroxide ion belongs to the molecule as a whole, not to single atom (neither H nor O)
  - Electronegativity of O > H
  - Energy of O < H
  - Bond occur between the electron in 1s orbital of H atom and 2p orbital of O atom

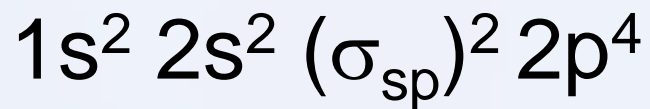
AO H    MO OH<sup>-</sup>    AO O



$$BO = \frac{2 - 0}{2} = 1 \rightarrow \text{STABLE}$$

No unpaired electron  $\rightarrow$  DIAMAGNETIC

Molecular Electronic Configuration =



The end of the discussion  
of  
Molecular Orbital Theory

**Thanks for the attention**