화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

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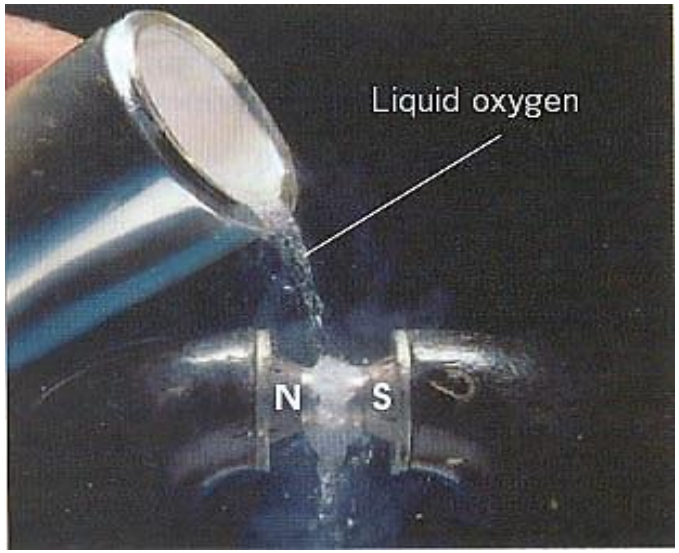
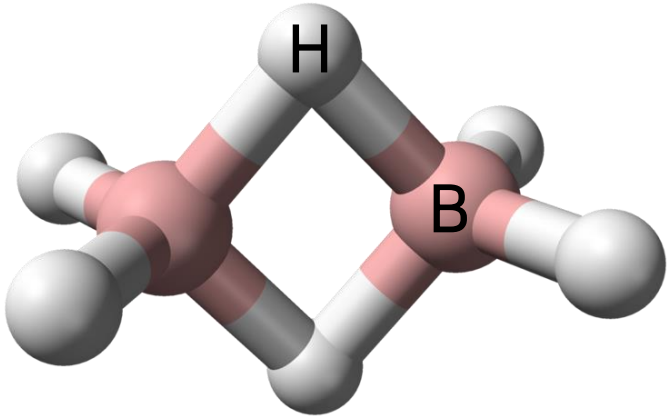
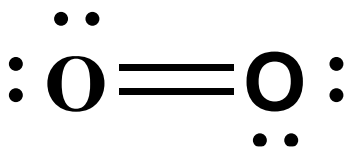
Molecular Orbital Theory

3.8. The Limitations of Lewis's Theory

How does O_2 appear paramagnetism?







How can we treat diborane (B_2H_6)?

Total # of valence electrons: 12 only!
But has 8 bondings!

Molecular Orbital Theory

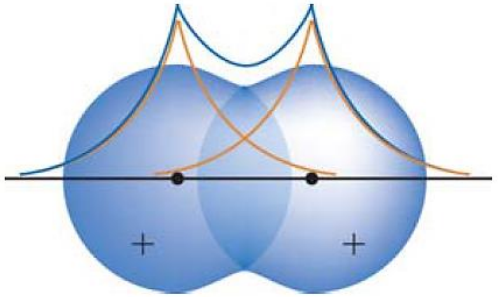
3.9. Molecular Orbitals

Valance Bond Theory:

Lone-pair (e-)s are localized on individual atoms.

Molecular Orbital: All valence (e-)s are delocalized over the whole molecule.

MOs are formed by linear combination of atomic orbital (LCAO-MO)

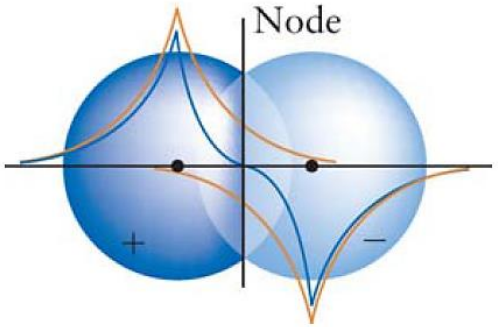


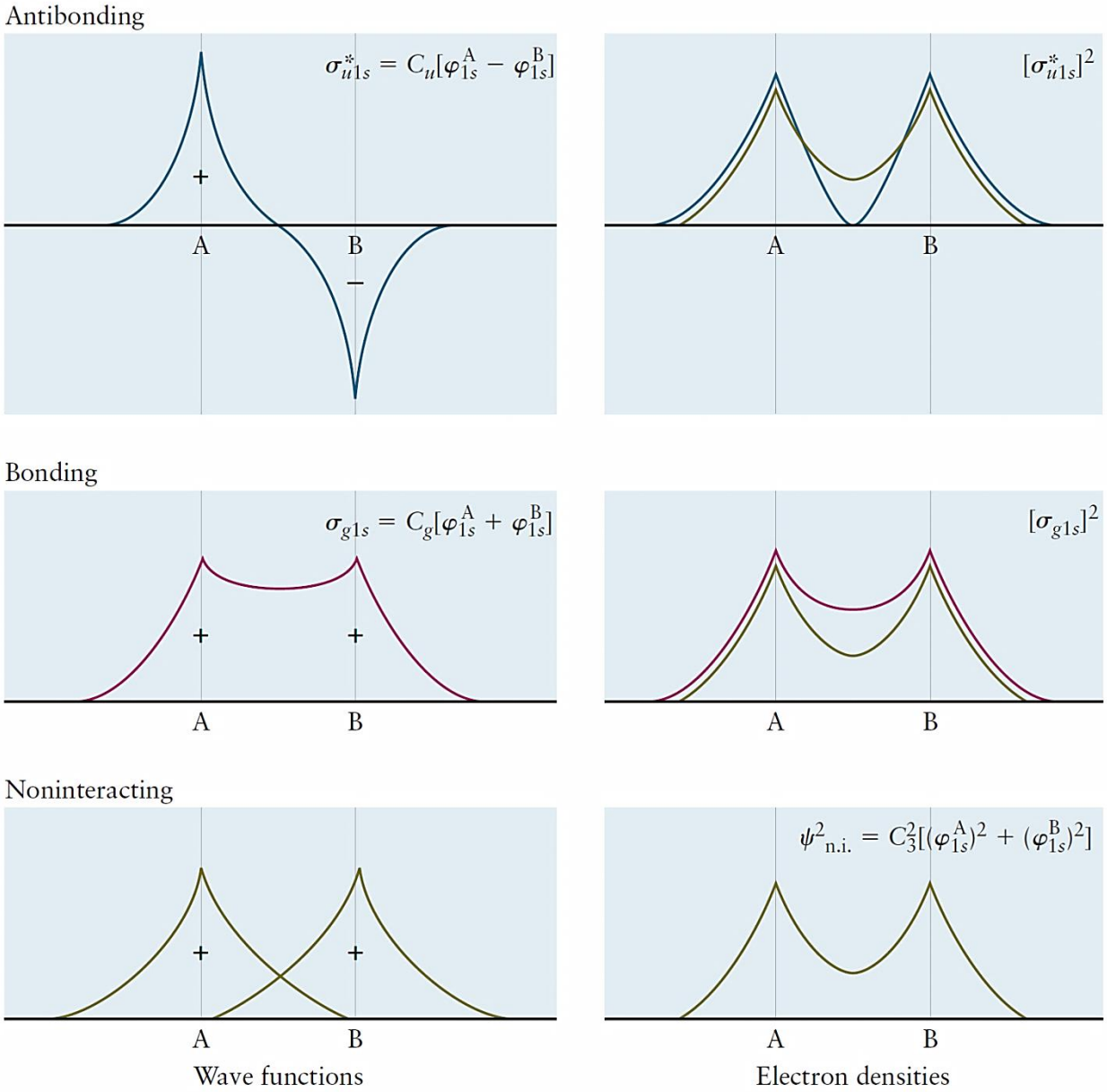
Bonding orbital (constructive interference)

$$\psi = \psi_{A1s} + \psi_{B1s}$$

Anti-bonding orbital (destructive interference)

$$\psi = \psi_{A1s} - \psi_{B1s}$$





Anti-bonding orbital

$\psi = \psi_{A1s} - \psi_{B1s}$

Overall raising of E

bonding orbital

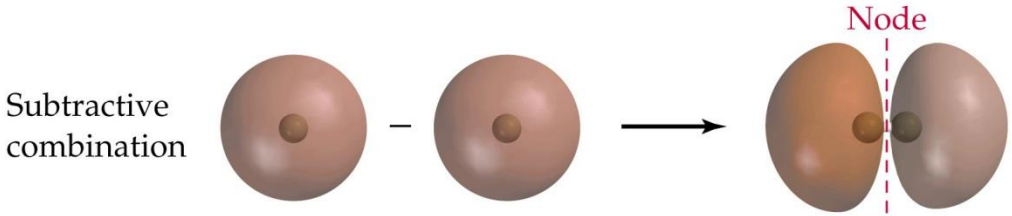
$\psi = \psi_{A1s} + \psi_{B1s}$

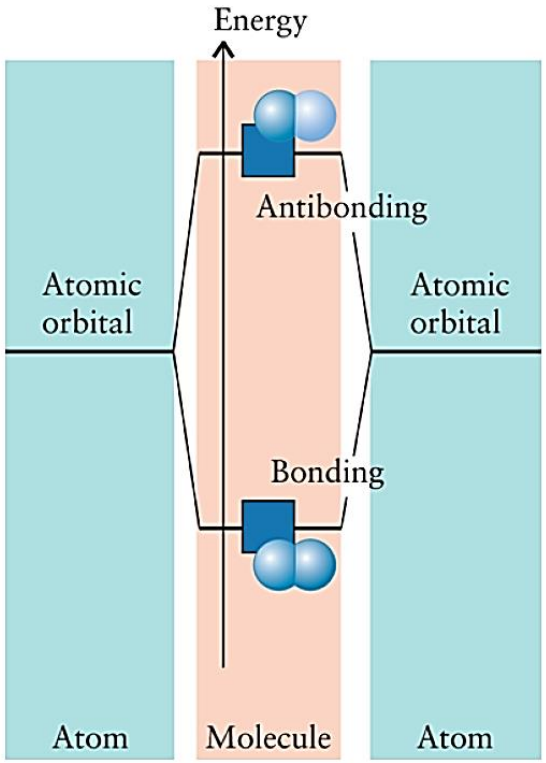
Overall lowering of E

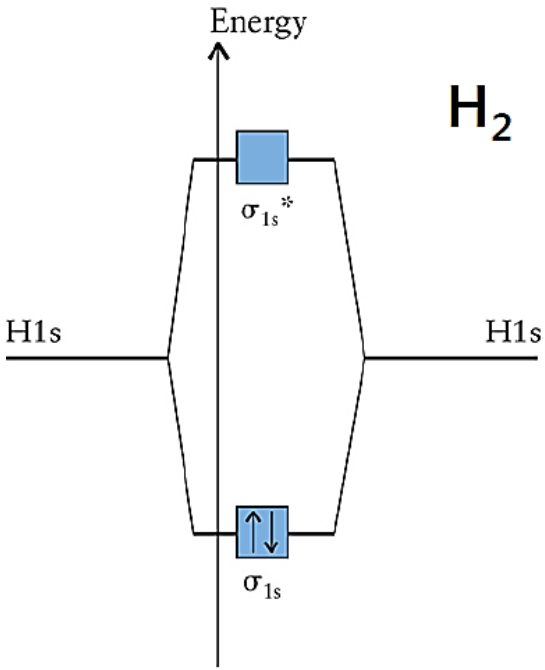
Non-bonding orbital

No interaction btw.

atomic orbital





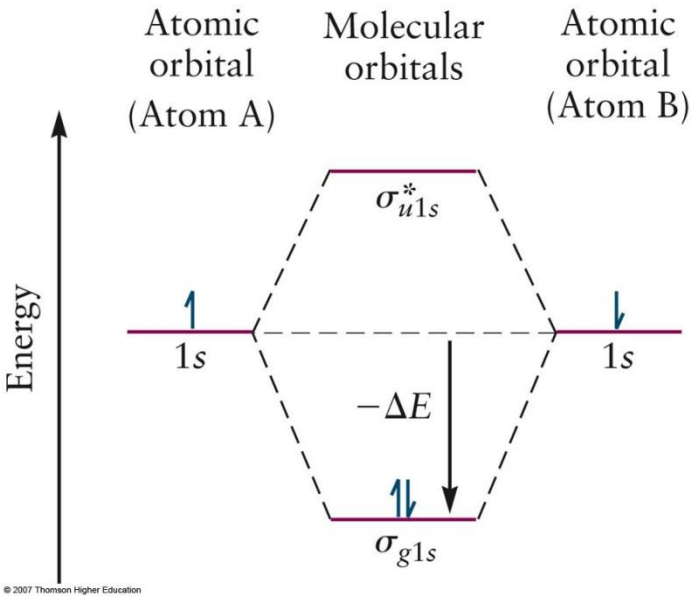


Bond order = (2-0)/2= 1

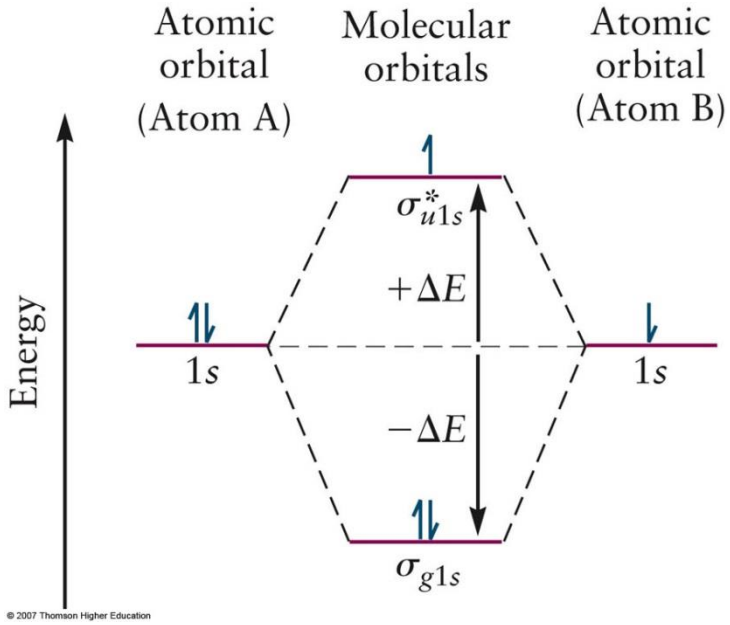
How can we explain H_2^+ and H_2^-?

$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

H_2



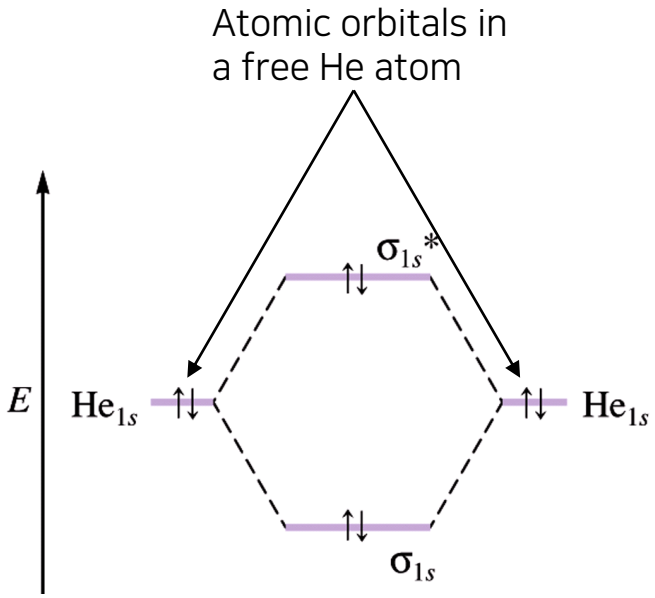
H_2^-



Electrons placed in anti-bonding MO destabilizes the bonding.

H_2^- : $\frac{2-1}{2} = \frac{1}{2}$ Half- bond

Connection with single, and double bonds



$$\text{Bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

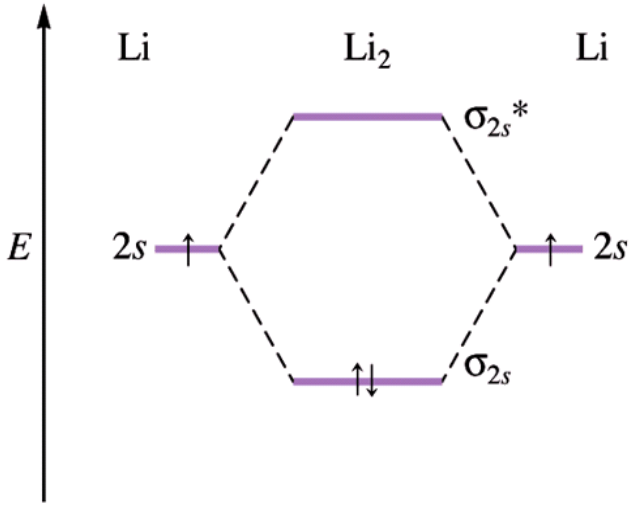
H_2 : $\frac{2-0}{2} = 1$ Single bond

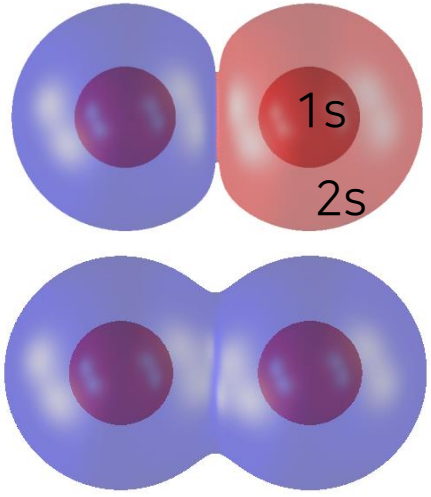
H_2^- : $\frac{2-1}{2} = \frac{1}{2}$ Half- bond

He_2 : $\frac{2-2}{2} = 0$ No-chemical bond

Li + Li → Li_2

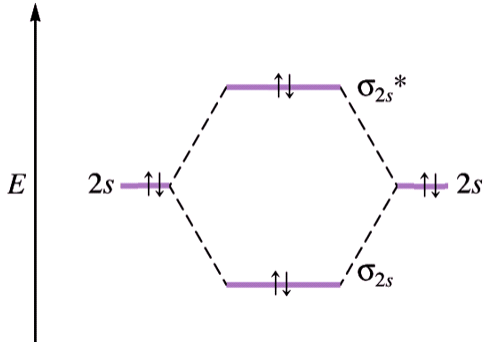
Core-electrons are not involved in bonding
We only count valence electrons





$$\text{Bond order} = \frac{2-0}{2} = 1 \quad \text{(stable)}$$

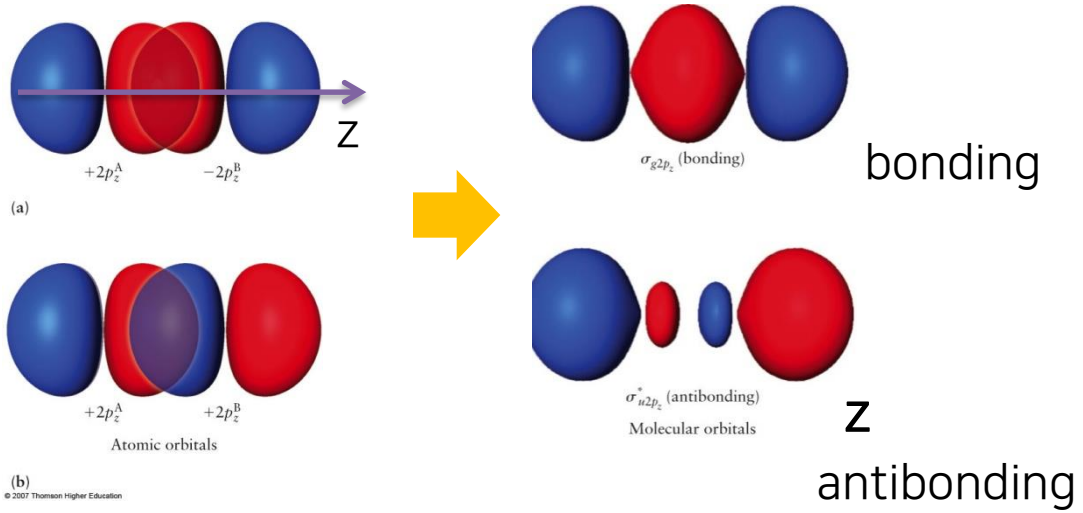
Be + Be → No chemical bonding

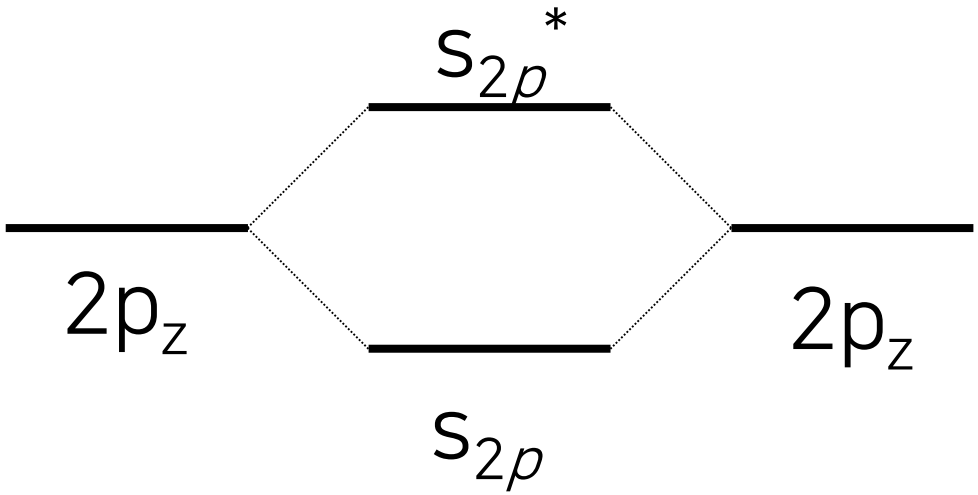


$$\text{Bond order} = \frac{2-2}{2} = 0$$

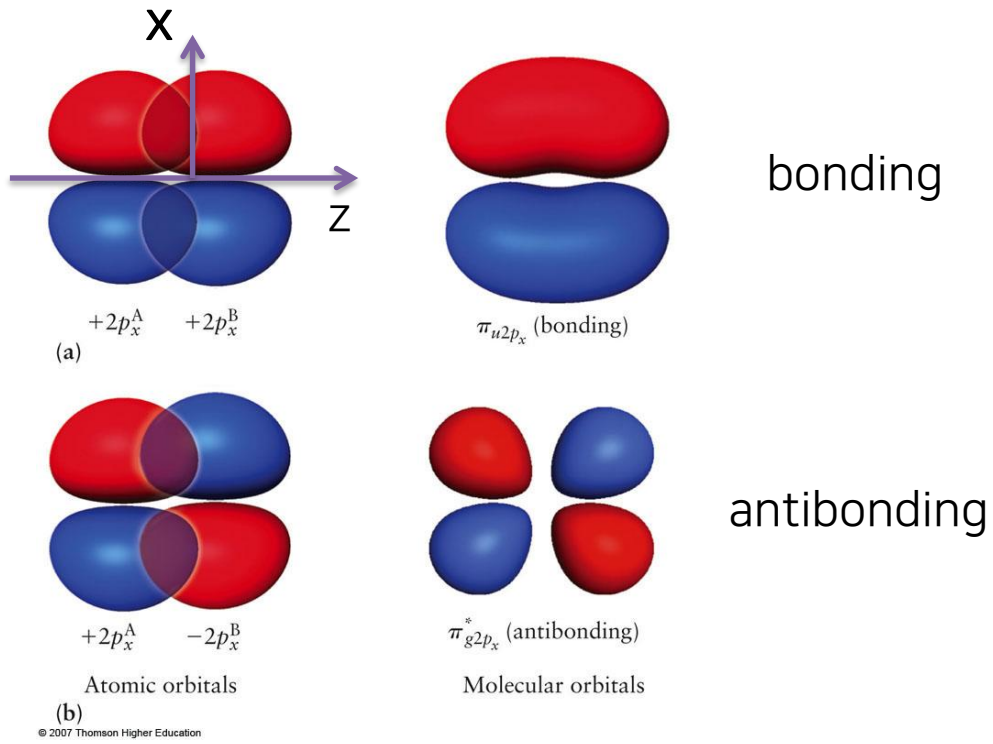
s-bonding in $2p_z$-$2p_z$

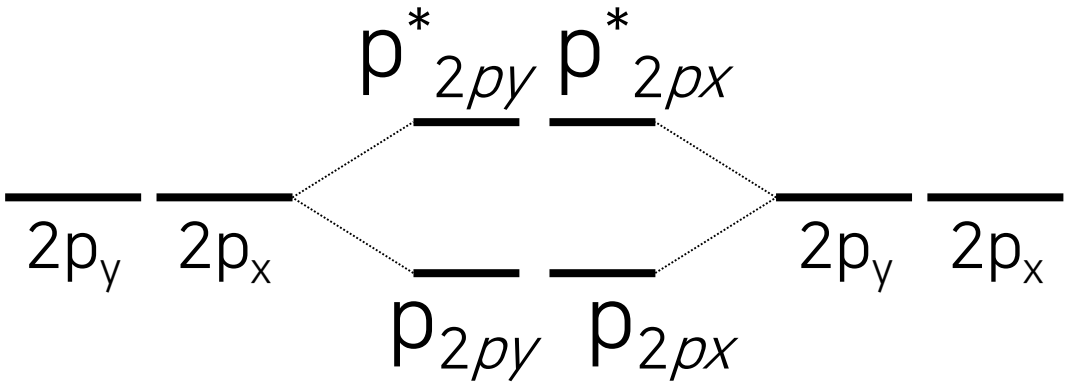
Typo! ☹





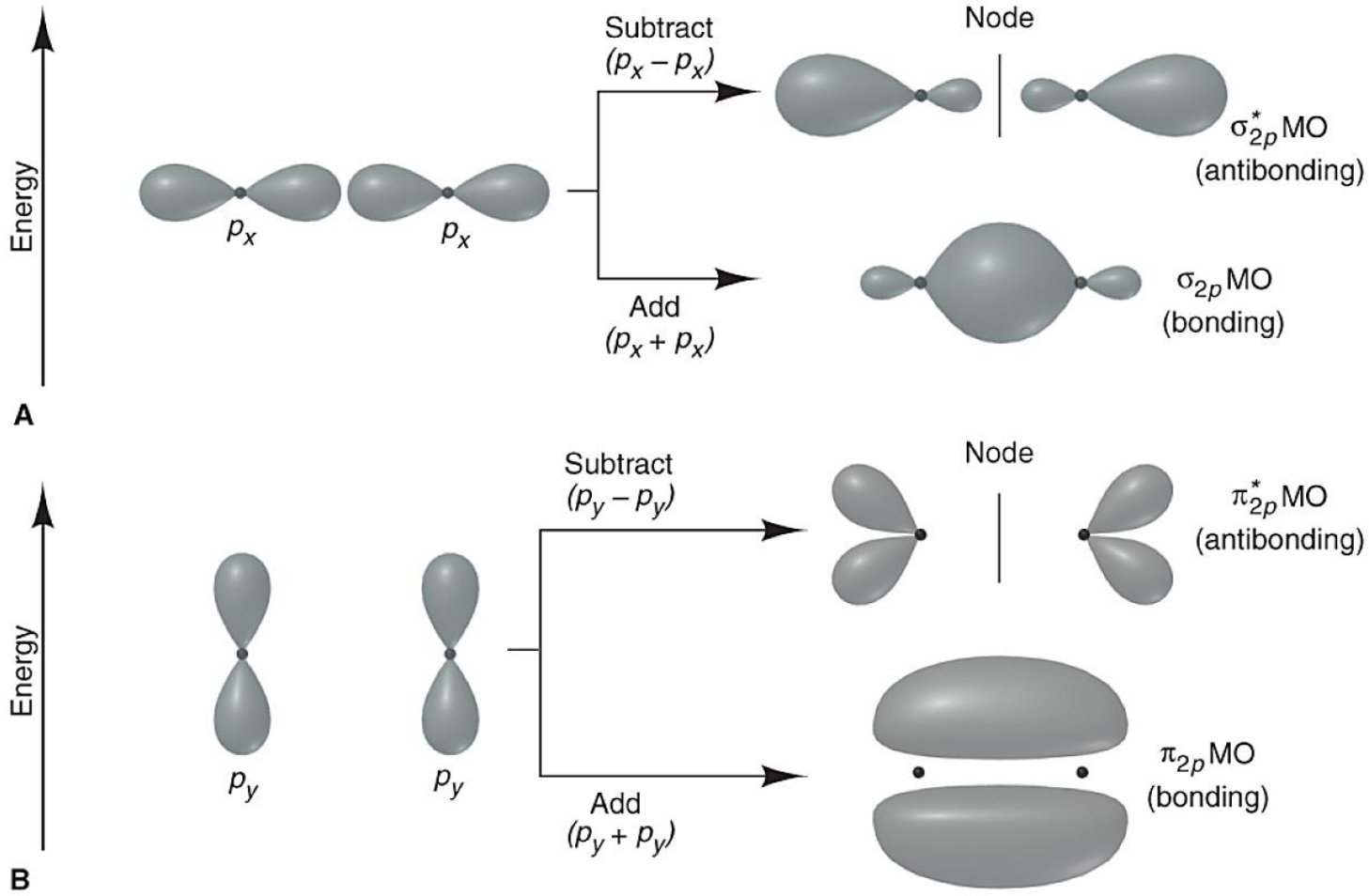
p-bonding in $2p_x$-$2p_x$ and $2p_y$-$2p_y$
* weaker than s-bond; Doubly degenerate

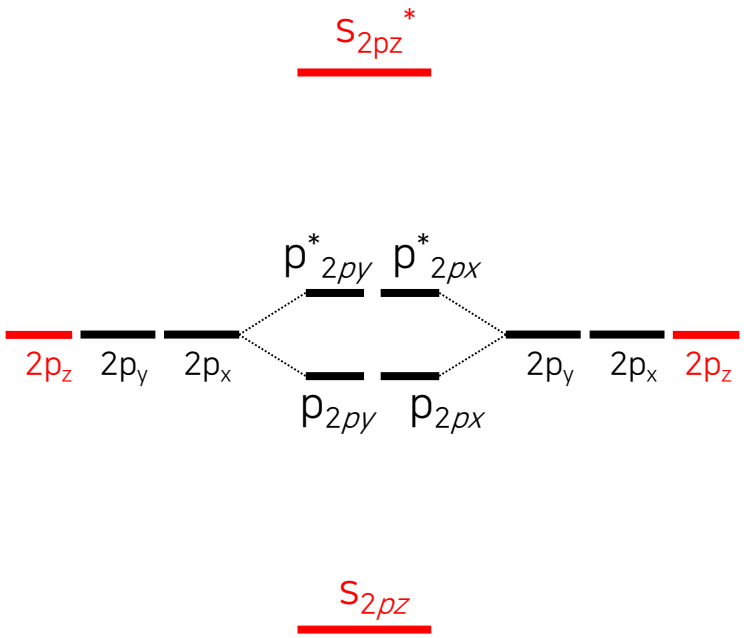


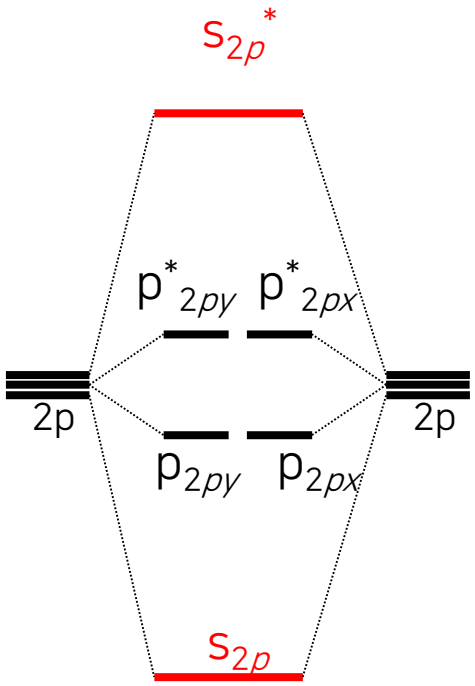


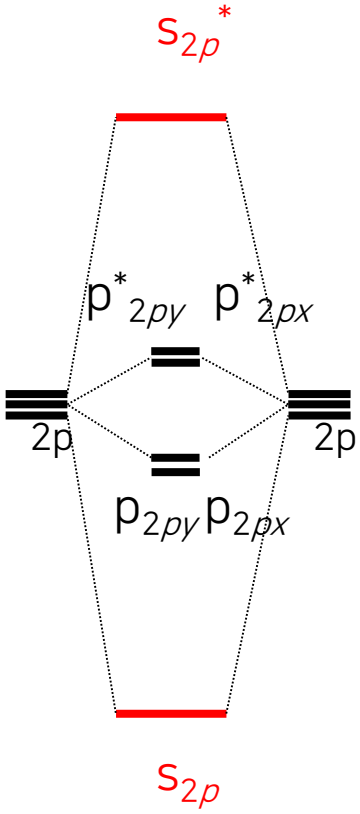
3.10. (e-) Configurations of Diatomic Molecules

For homonuclear diatomic molecules of period 2 atoms,

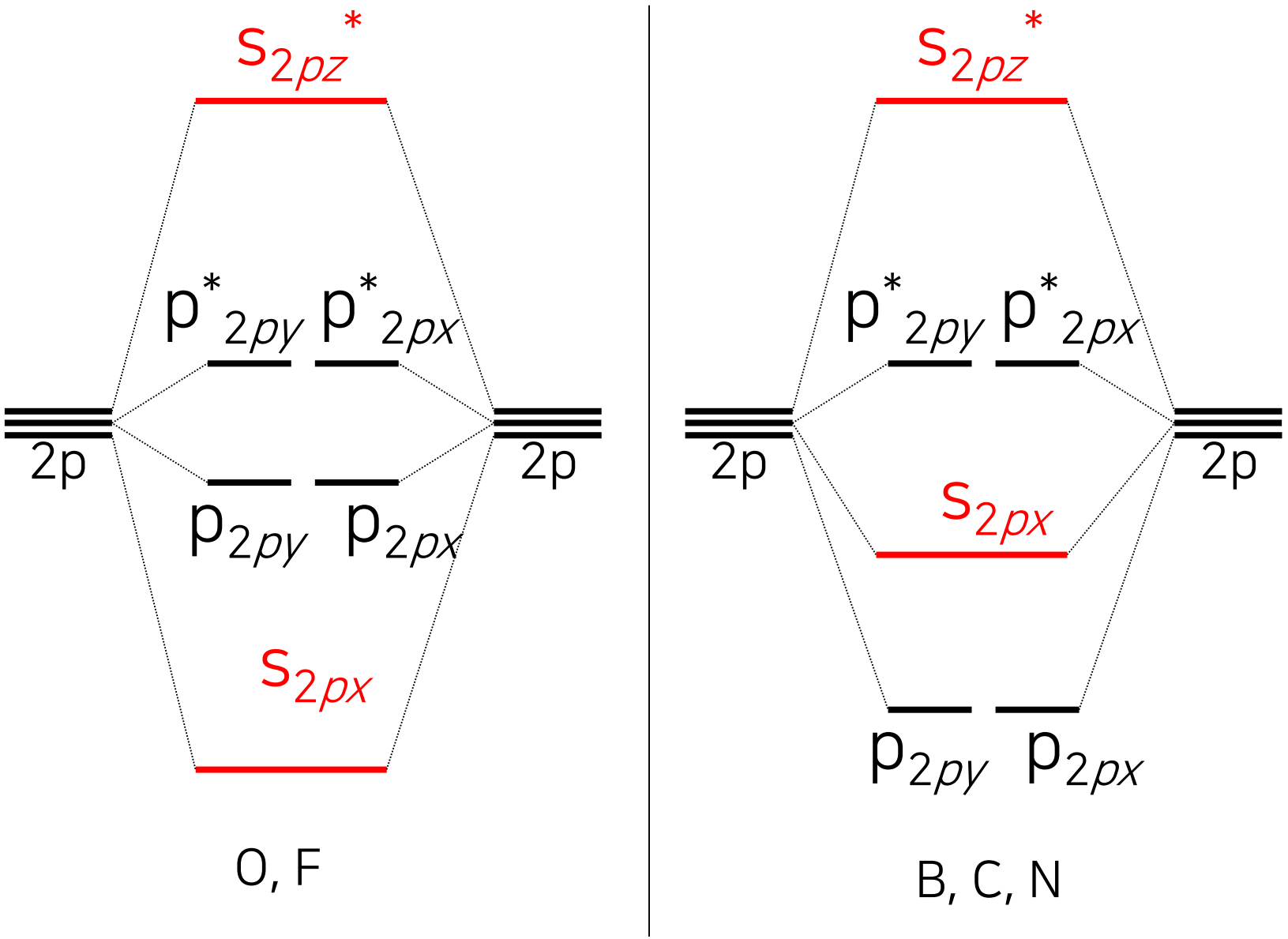



σ^*_{2pz}
π^*_{2py} π^*_{2px}
$2p_z$ $2p_y$ $2p_x$ $2p_y$ $2p_x$ $2p_z$
π_{2py} π_{2px}
σ_{2pz}

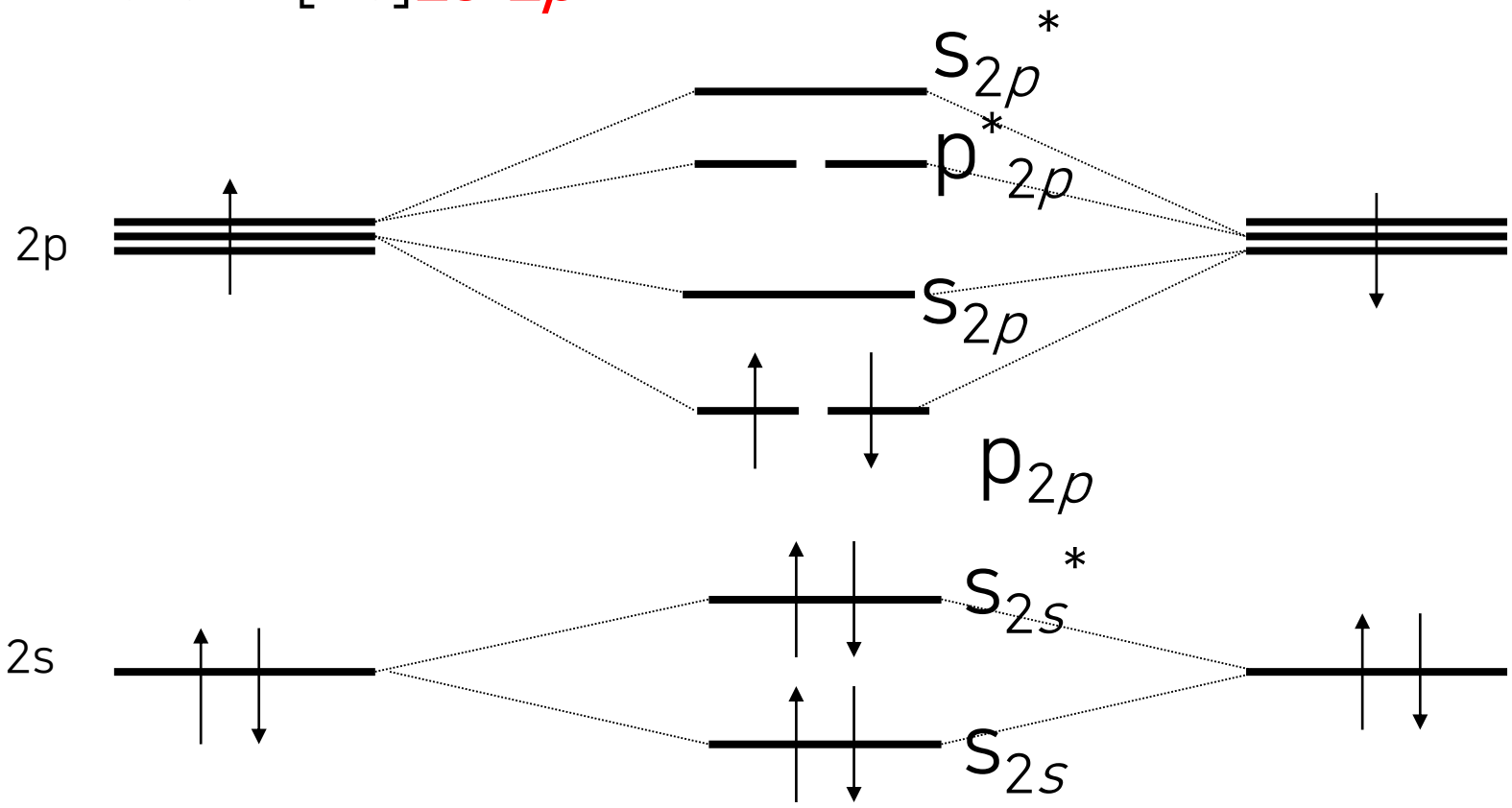

σ^*_{2p}
π^*_{2py} π^*_{2px}
2p 2p
π_{2py} π_{2px}
σ_{2p}


σ^*_{2p}
π^*_{2py} π^*_{2px}
2p 2p
π_{2py} π_{2px}
σ_{2p}

Often, pi and sigma bonding order is reversed !!!

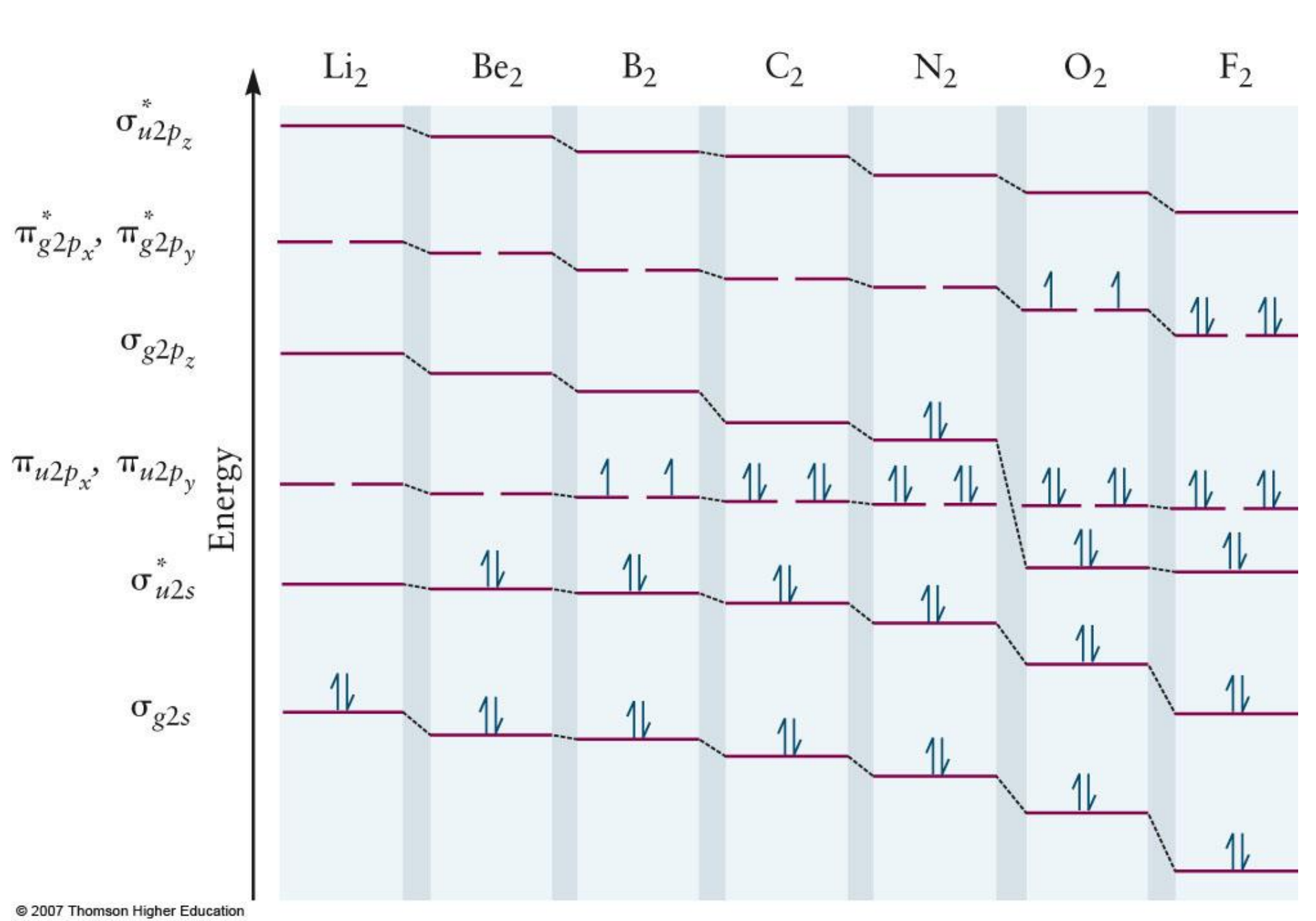


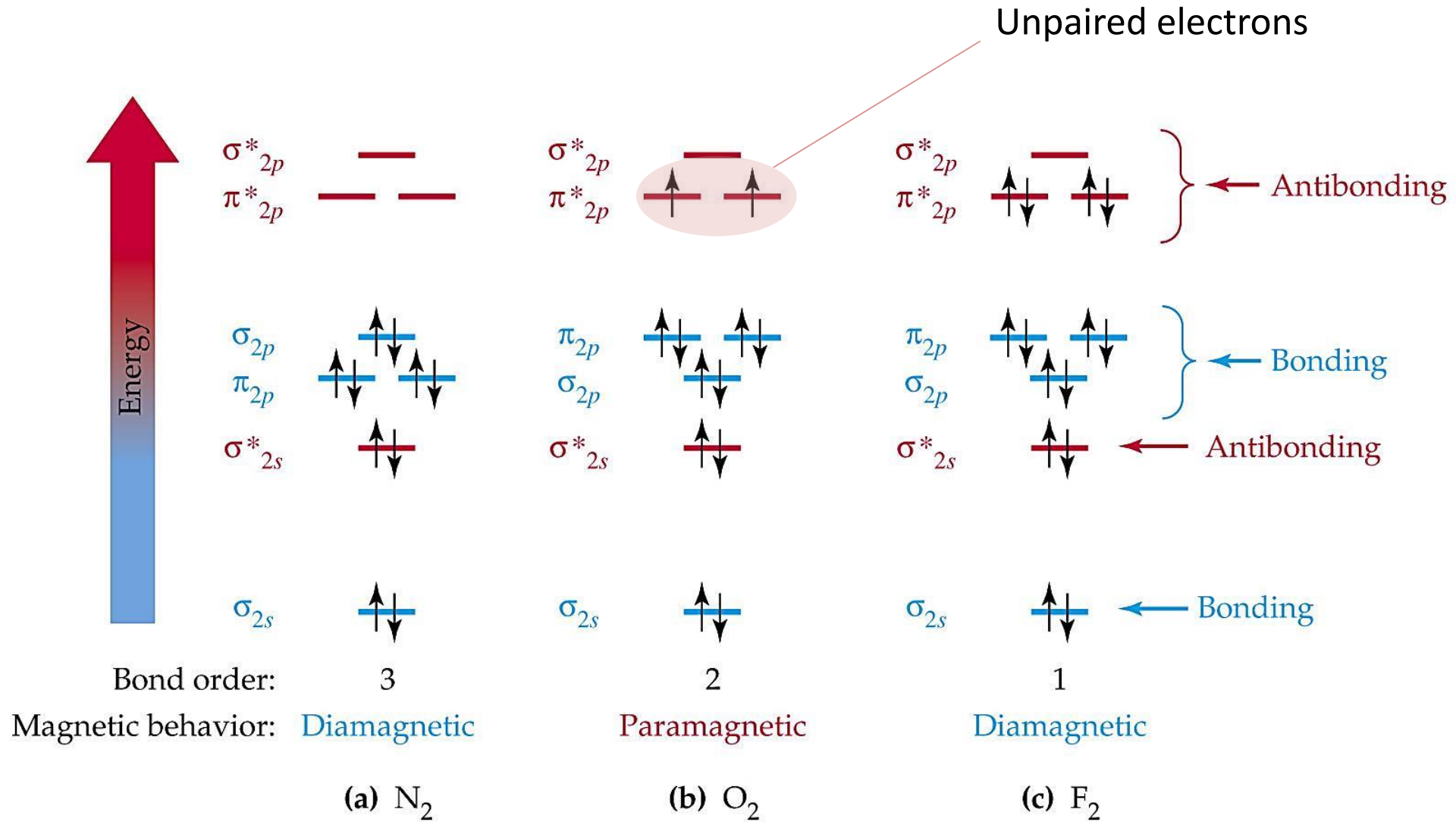
B atom: [He]$2s^2 2p^1$

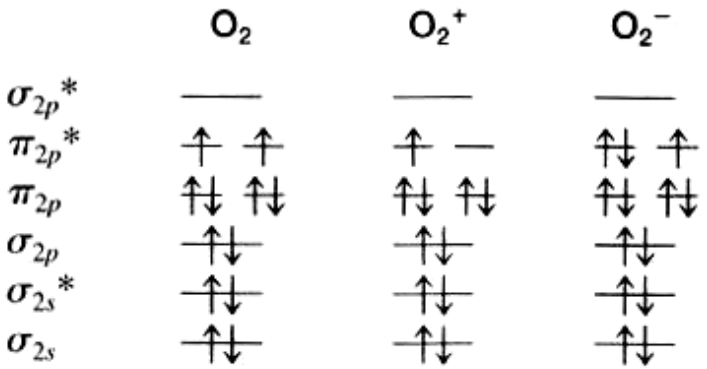


$(s_{2s})^2(s^*_{2s})^2\ (p_{2p})^2$

Bond order = [(bonding electron) – (anti-bonding electron)]/2
= (4-2)/2 = 1




Unpaired electrons
Energy
σ*2p
π*2p
σ2p
π2p
σ*2s
σ2s
Antibonding
Bonding
Antibonding
Bonding
Bond order: 3 2 1
Magnetic behavior: Diamagnetic Paramagnetic Diamagnetic
(a) N2
(b) O2
(c) F2



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

Bond order

$$O_2: \quad \frac{8-4}{2} = 2 \qquad O_2^+: \quad \frac{8-3}{2} = 2.5 \qquad O_2^-: \quad \frac{8-5}{2} = 1.5$$

O_2^+ has the strongest bond.

Key aspects of MO-theory:

Electrons are delocalized; Anti-bonding electrons weaken bonds

Heteronuclear Diatomic Molecules

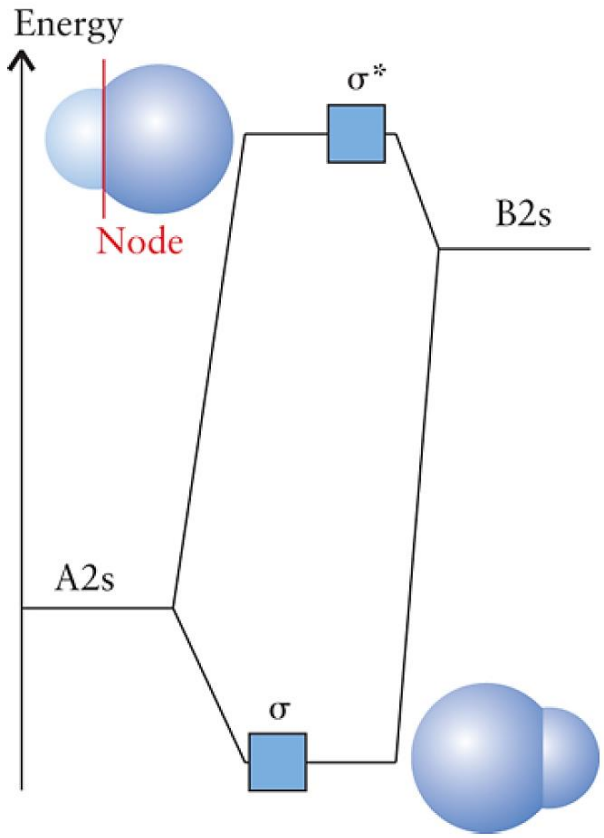
$$\psi = C_A \psi_A + C_B \psi_B$$

Unequal contribution of individual atoms → C_A, C_B

→ In a **nonpolar covalent** bond, $C_A^2 = C_B^2$

→ In an **ionic** bond, C_A or $C_B \sim 0$

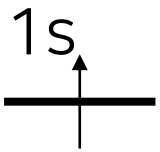
→ In a **polar covalent** bond, more electronegative atom has the larger contribution to the lowest energy (bonding) orbital. The contribution to the highest-energy orbital is greater for the higher-energy AO, which belongs to the less electronegative atom.



When two atoms have significantly different energy levels:

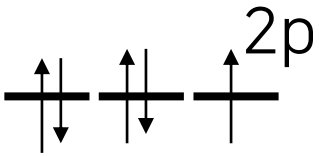
Ex) HF: F-atom likes electrons
→ lower energy levels than H-atom

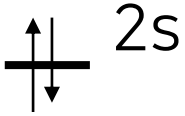
H



?

F

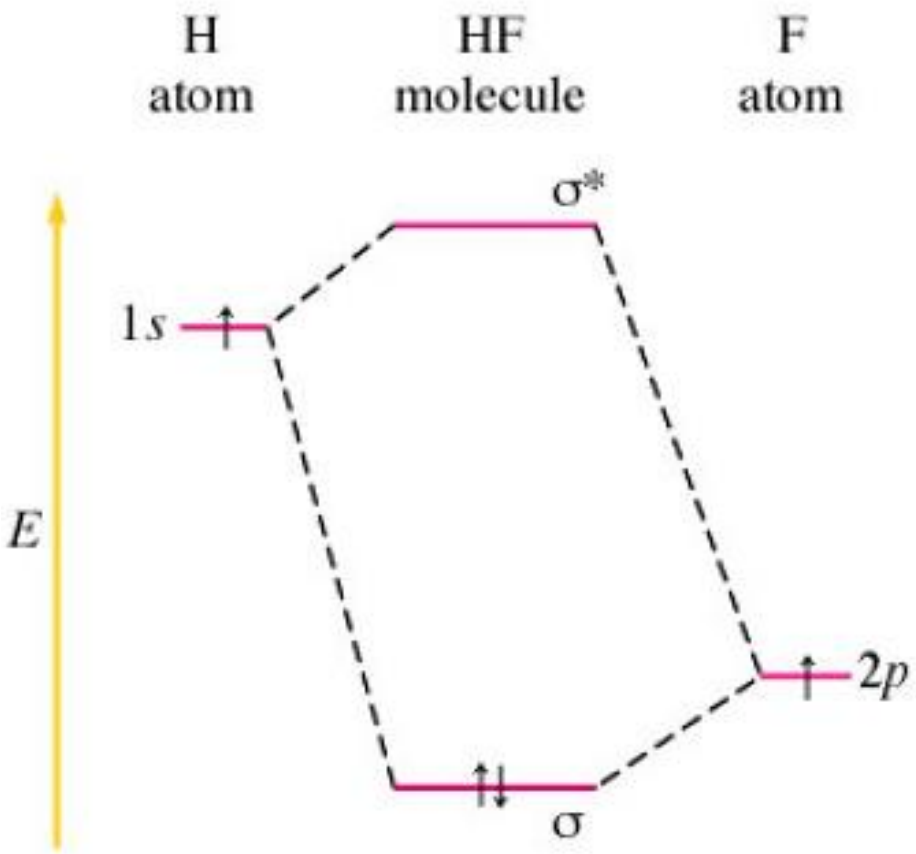




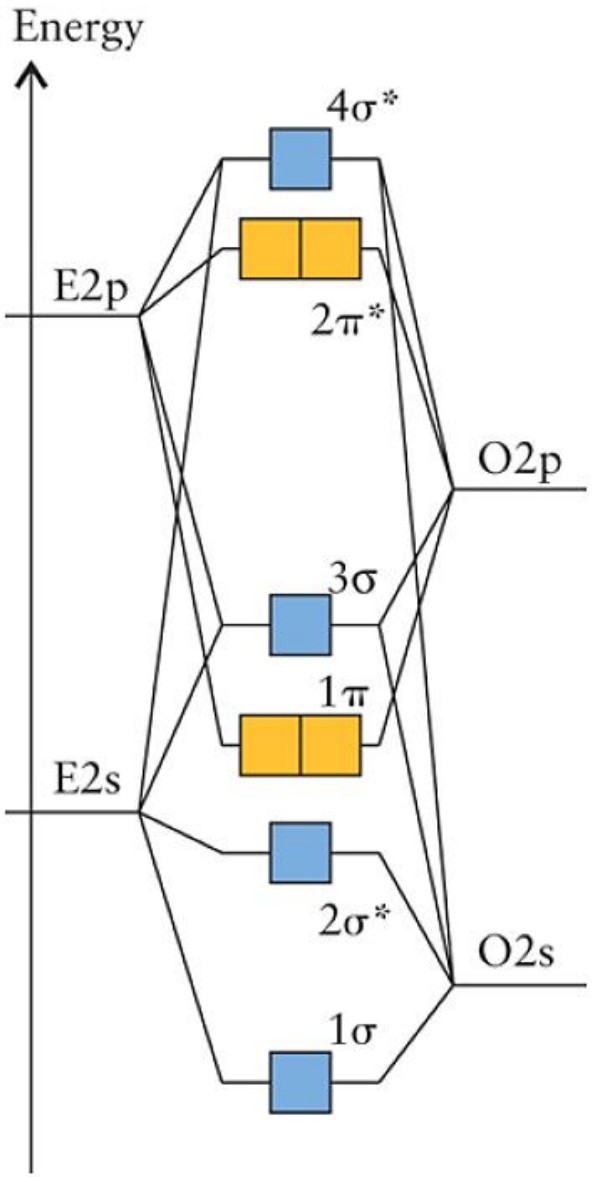
Rules of forming MO from AO

- Only the orbitals with similar energy interact each other. Orbitals with large energy difference DO NOT interact each other.
- The orbitals should spatially overlap with each other
- Orbitals should have correct symmetry.

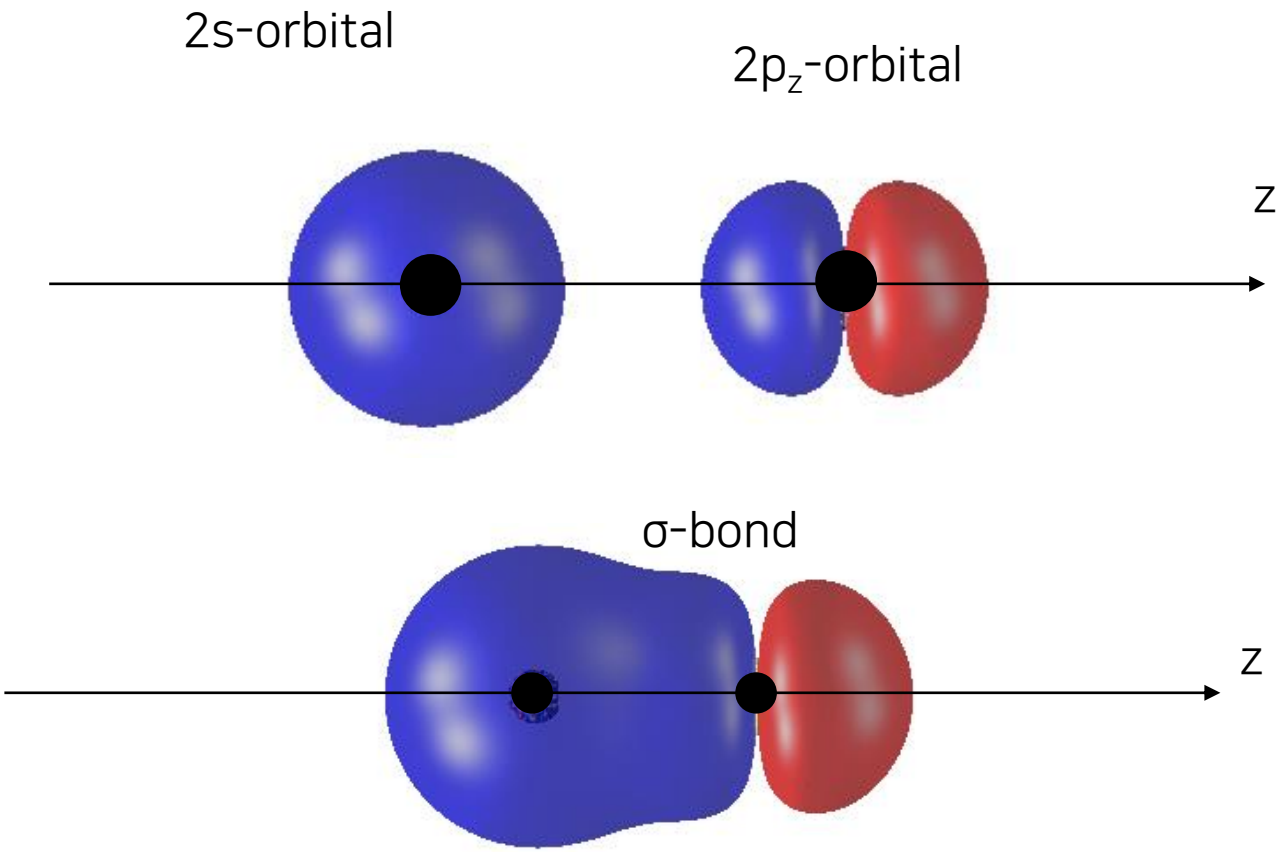
Example I: HF



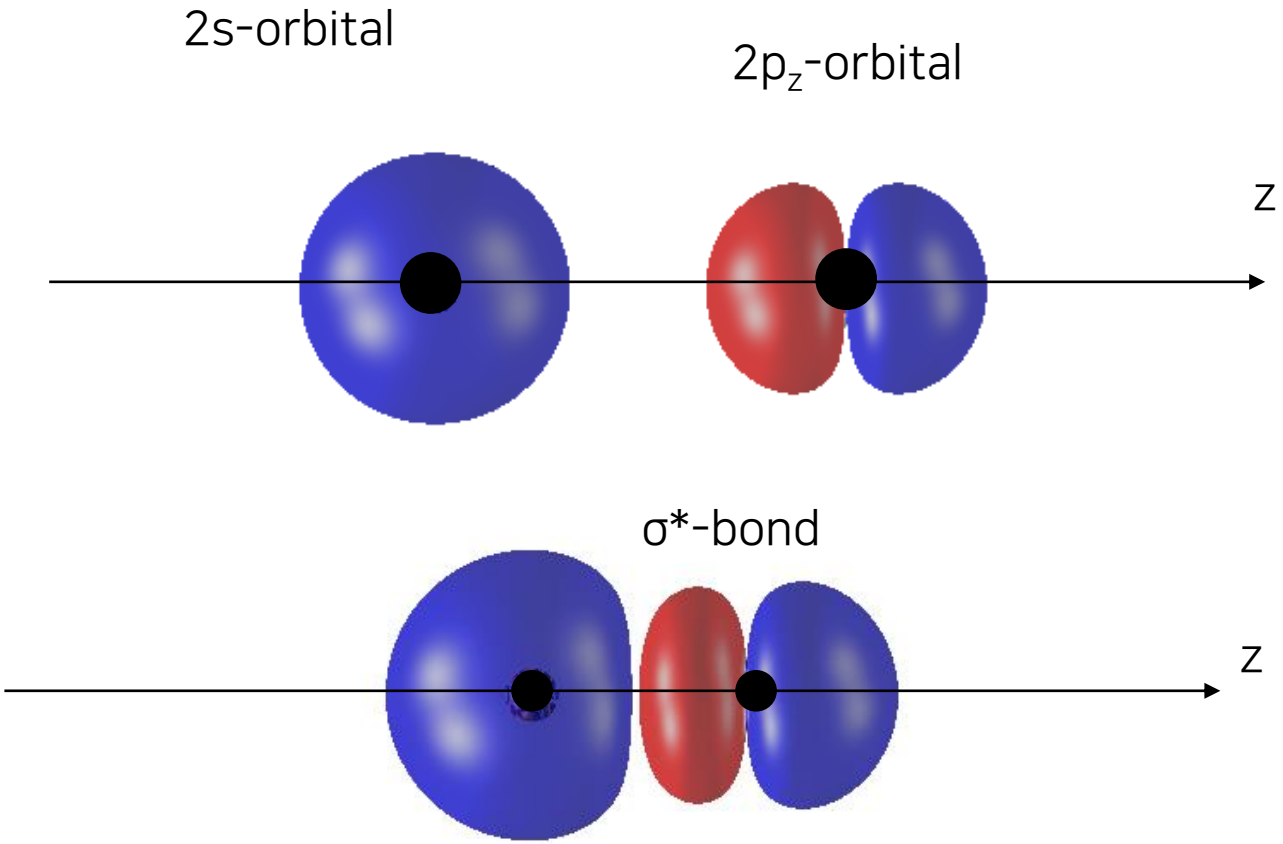
Example 2: CO & NO



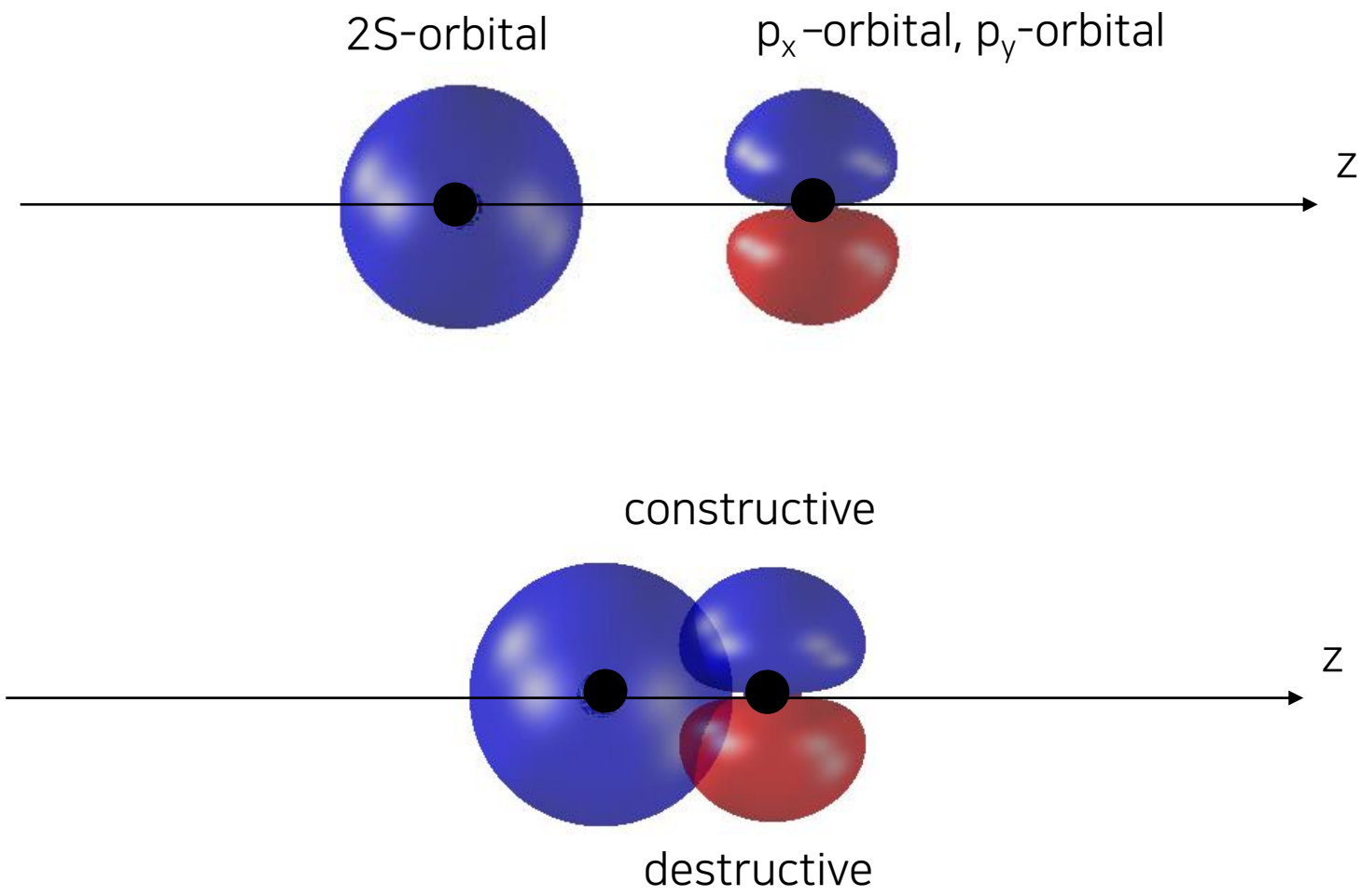
σ-bonding between s and p-orbitals



σ*-anti-bonding between s and p-orbitals

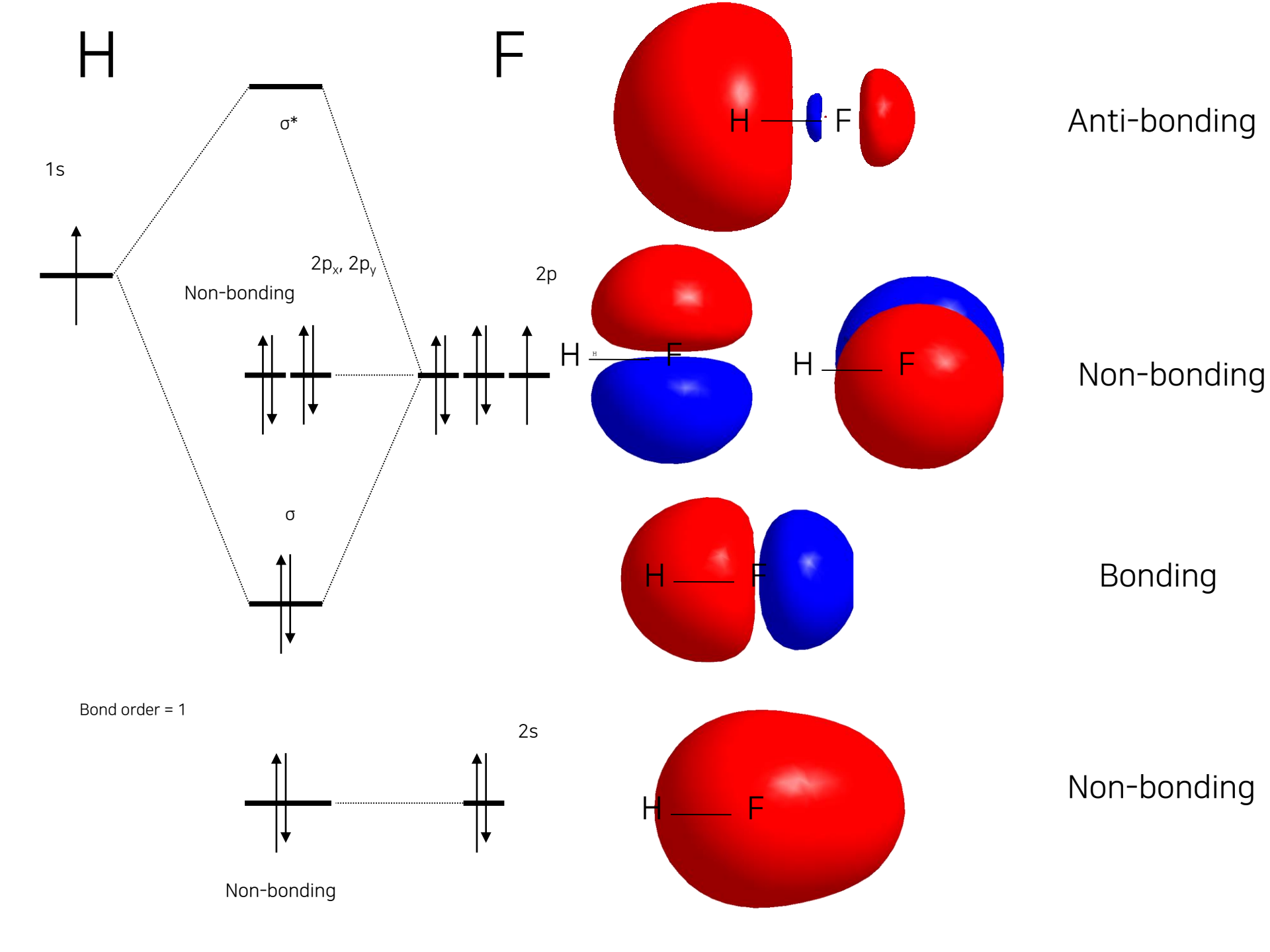


non-bonding:



Wrong symmetry; no spatial overlap; large energy difference

MO of non-bonding = AOs of participating atoms

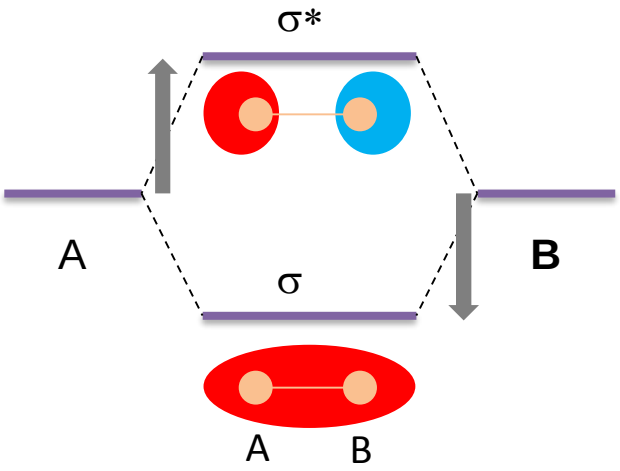

H
F
σ*
1s
2p
x
, 2p
y
Non-bonding
σ
Bond order = 1
2s
Non-bonding
H
F
Anti-bonding
H
F
Non-bonding
H
F
Bonding
H
F
Non-bonding

Relative energy of AOs and the resulting MO

If energy (A) = energy (B):

$\psi_{\sigma^*} = \phi_A - \phi_B$

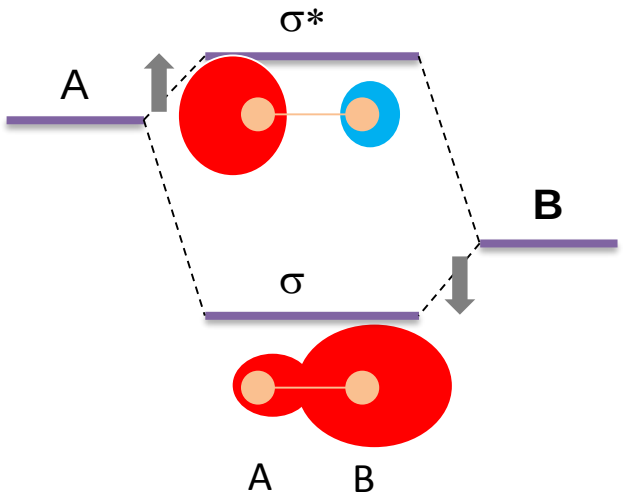
$\psi_{\sigma} = \phi_A + \phi_B$



If energy (A) > energy (B):

$\psi_{\sigma^*} = C\phi_A - c\phi_B$

$\psi_{\sigma} = c\phi_A + C\phi_B$



Both the bonding and anti-bonding MOs = equal mixture of A and B AOs

Anti-bonding MO is similar to electro-phositive AO

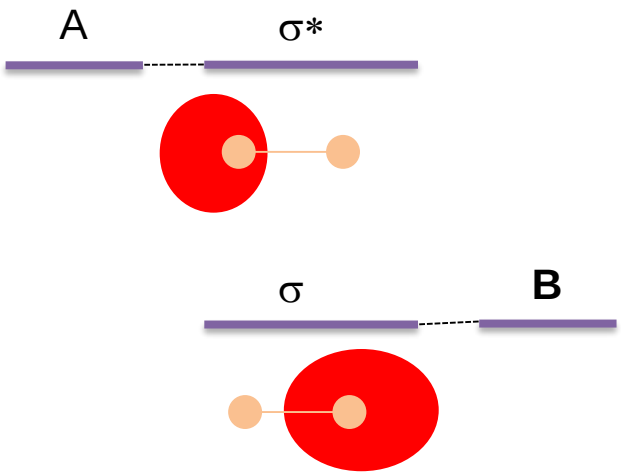
bonding MO is similar to electro-negative AO

Relative energy of AOs and the resulting MO

If energy (A) >> energy (B):

$\psi_{\sigma^*} = \phi_A$

$\psi_{\sigma} = \phi_B$



They form non-bonding orbitals

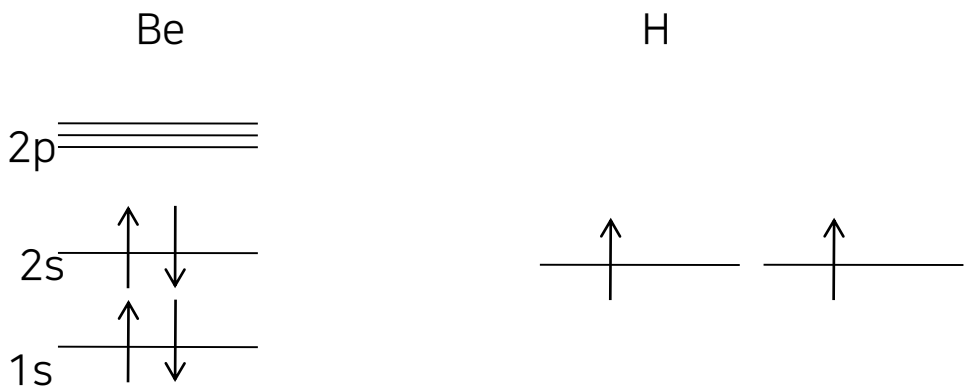
MO of Polyatomic Molecules

AO's form MO when:

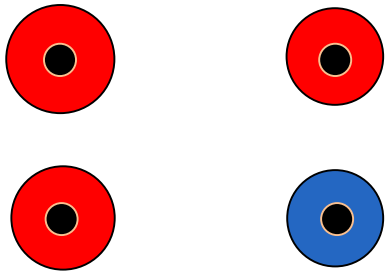
1. AOs should have similar energies
2. Physical overlap
3. Symmetry
4. The MO follows the symmetry of molecular shape:
   -the wave function can be symmetric or anti-symmetric
   but it cannot be asymmetric

BeH_2

For Be and H atoms, 2p (Be) and 2s (Be) orbitals have similar energy with 1s(H).



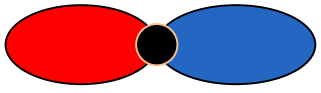
Symmetric and anti-symmetric AO of 2H



1s+

1s-

2p of Be



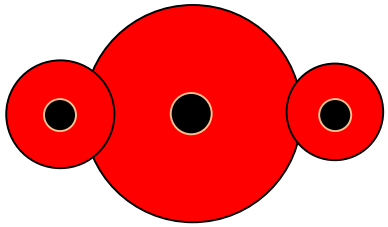
p_z

p_x and p_y

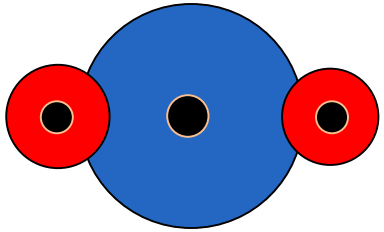
2s

Total of 6 AO ➔ 6 MO

2s(Be) and 1s(H)

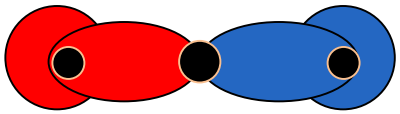


$\sigma(s)$

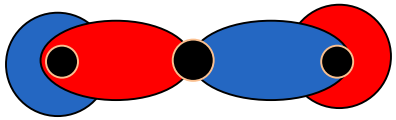


$\sigma^*(s)$

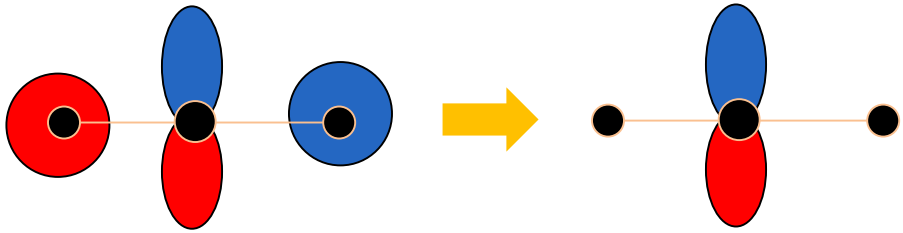
2p(Be) and 1s(H)



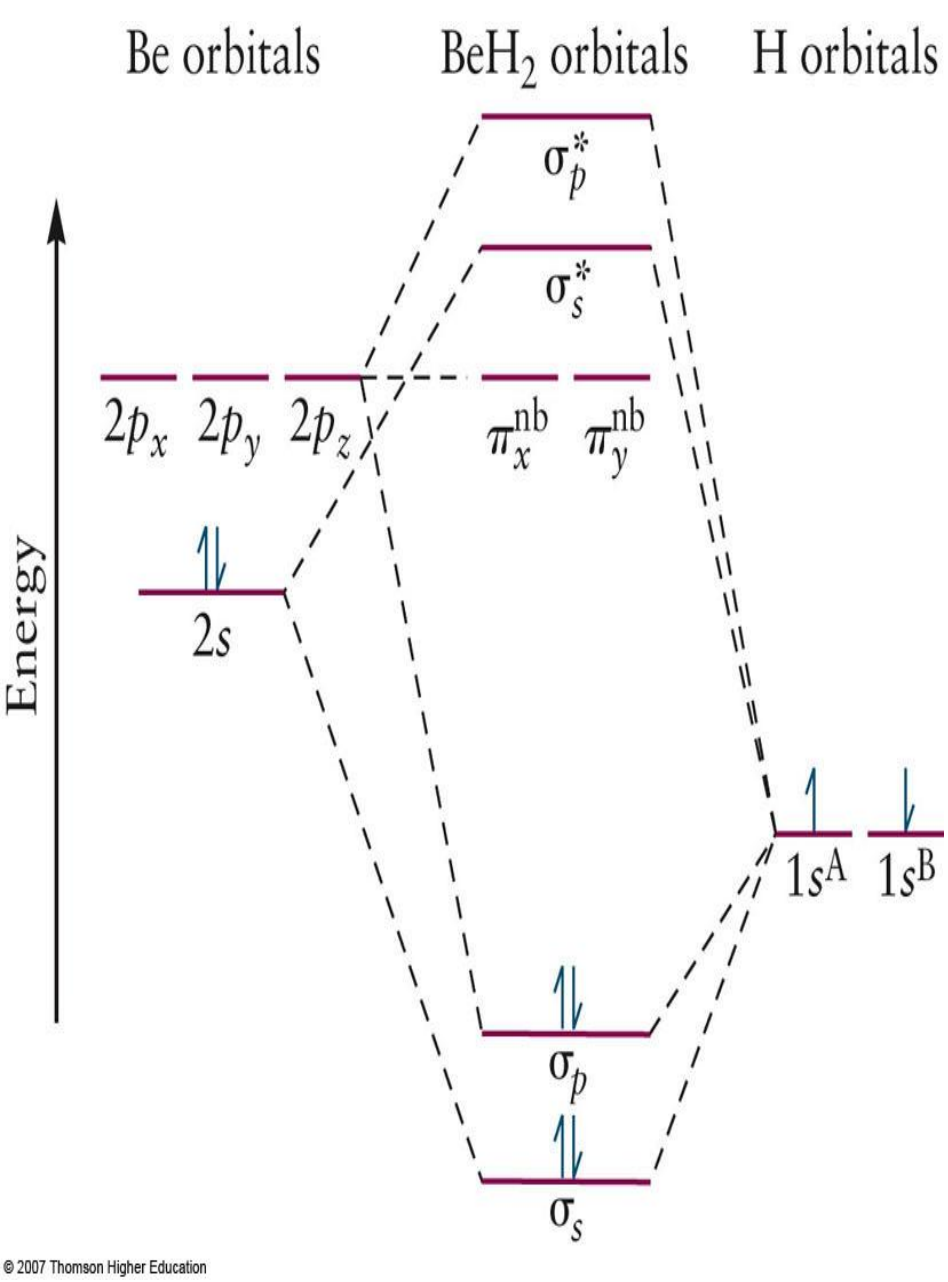
$\sigma(p_z)$

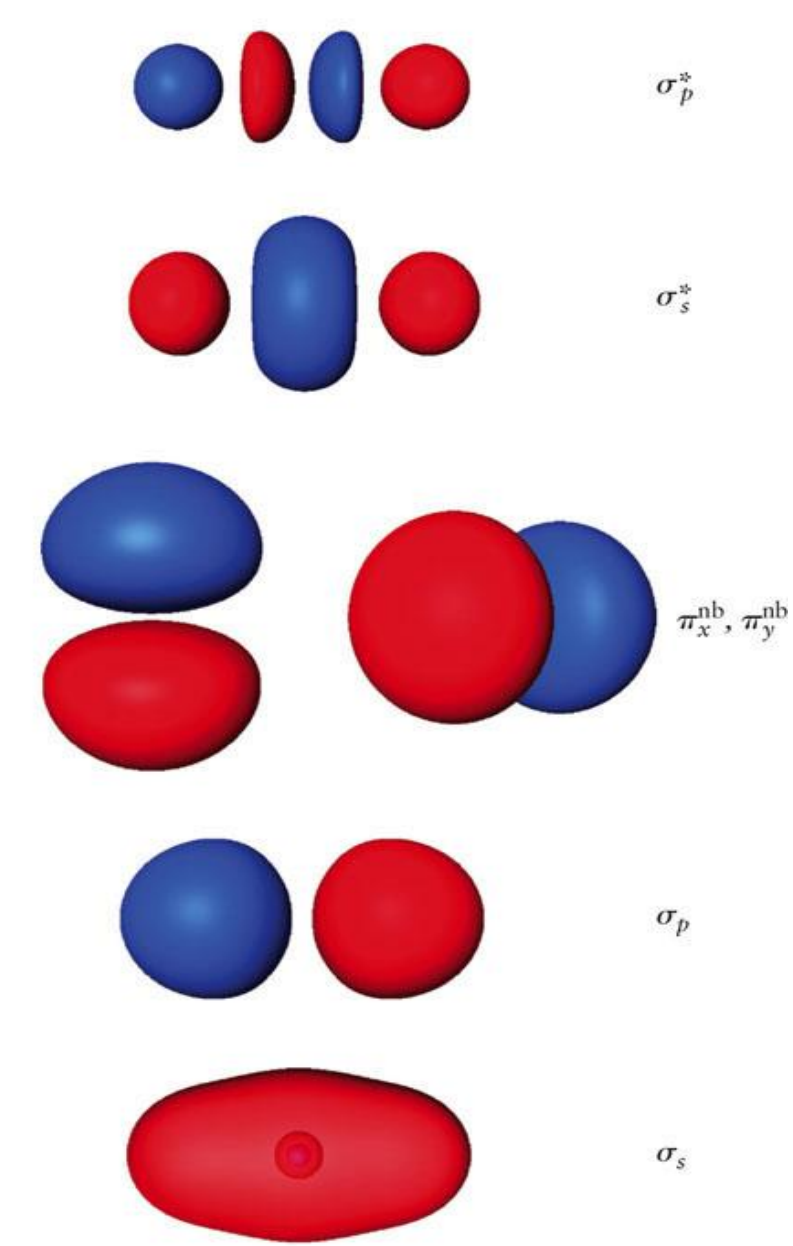


$\sigma^*(p_z)$



$\pi_x(nb)$ $\pi_y(nb)$



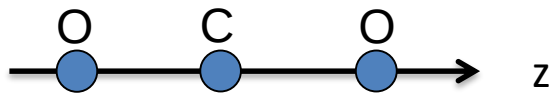


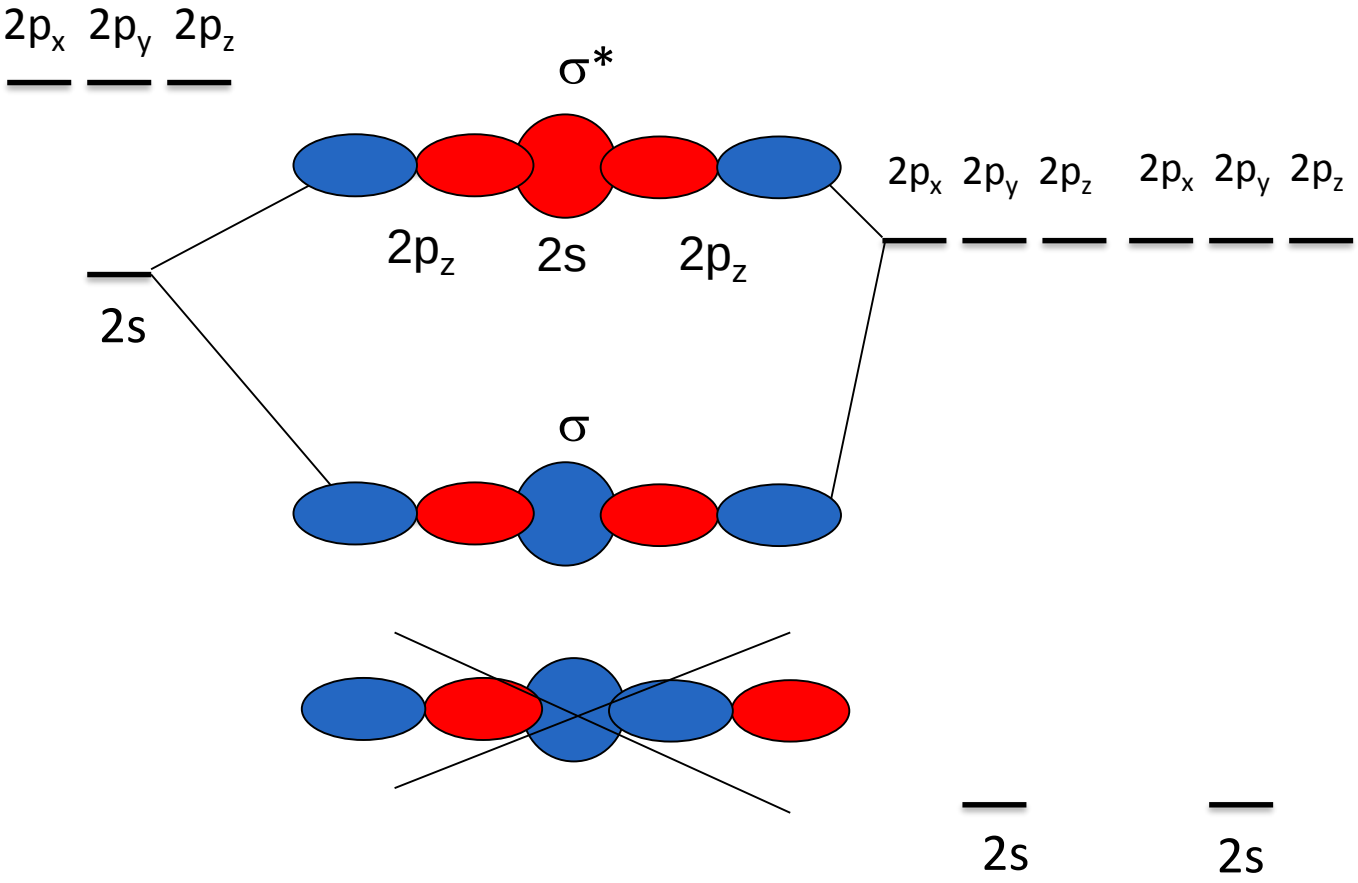
What is the bond order?

Molecular orbitals of CO_2

C: 1s, 2s, $2p_x$, $2p_y$, $2p_z$

O: 1s, 2s, $2p_x$, $2p_y$, $2p_z$





Molecular orbitals of CO_2

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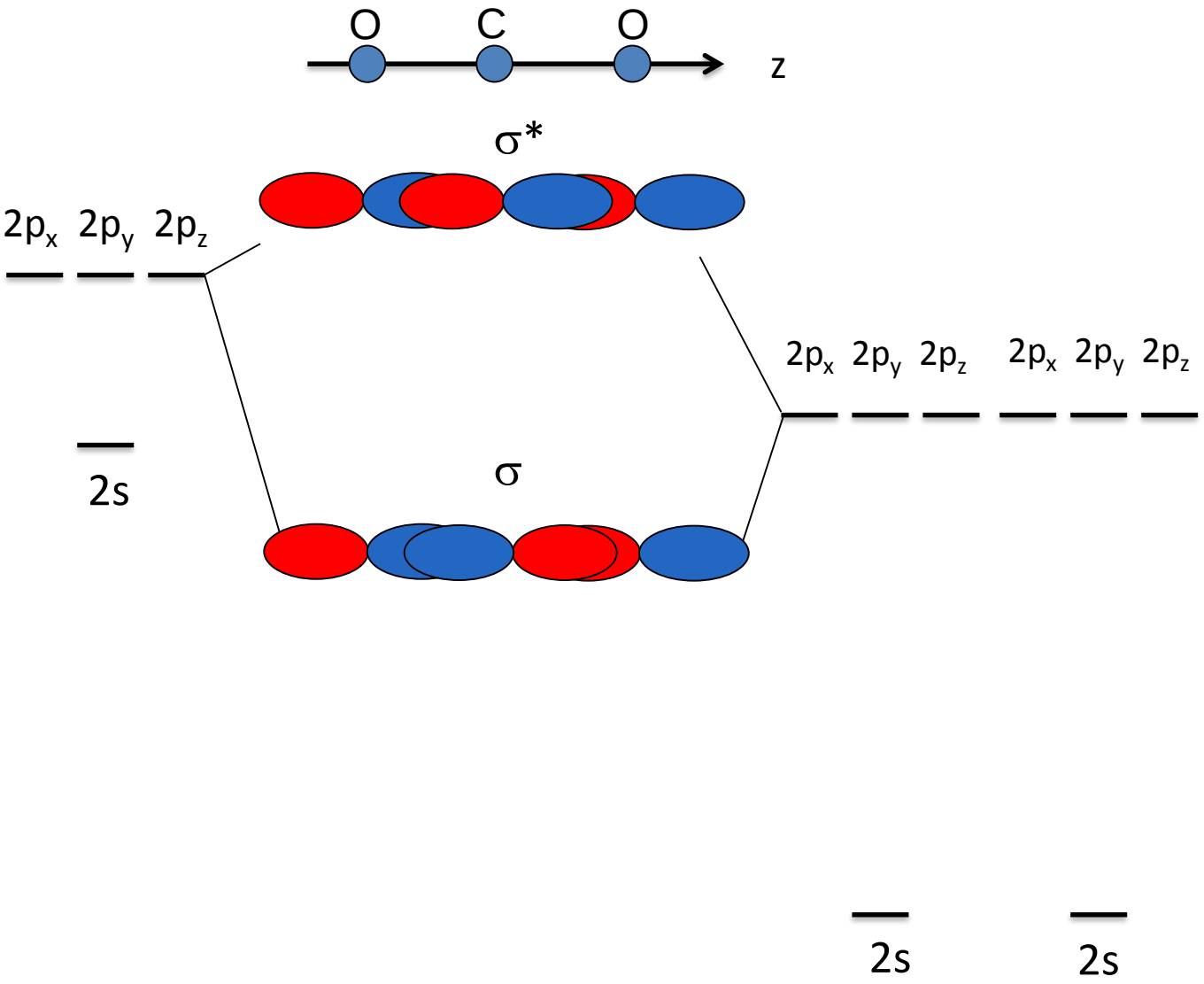

Molecular orbitals of CO_2

C: 1s, 2s, $2p_x$, $2p_y$, $2p_z$
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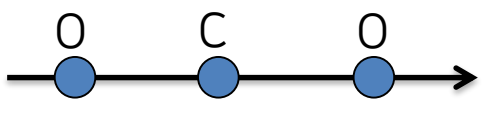
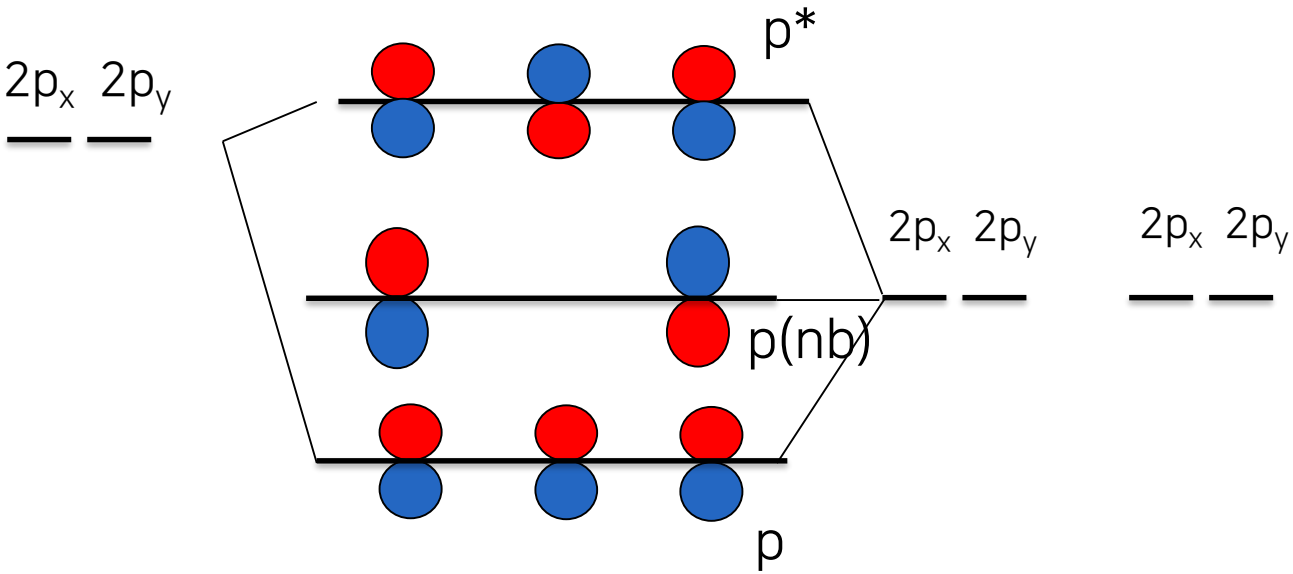
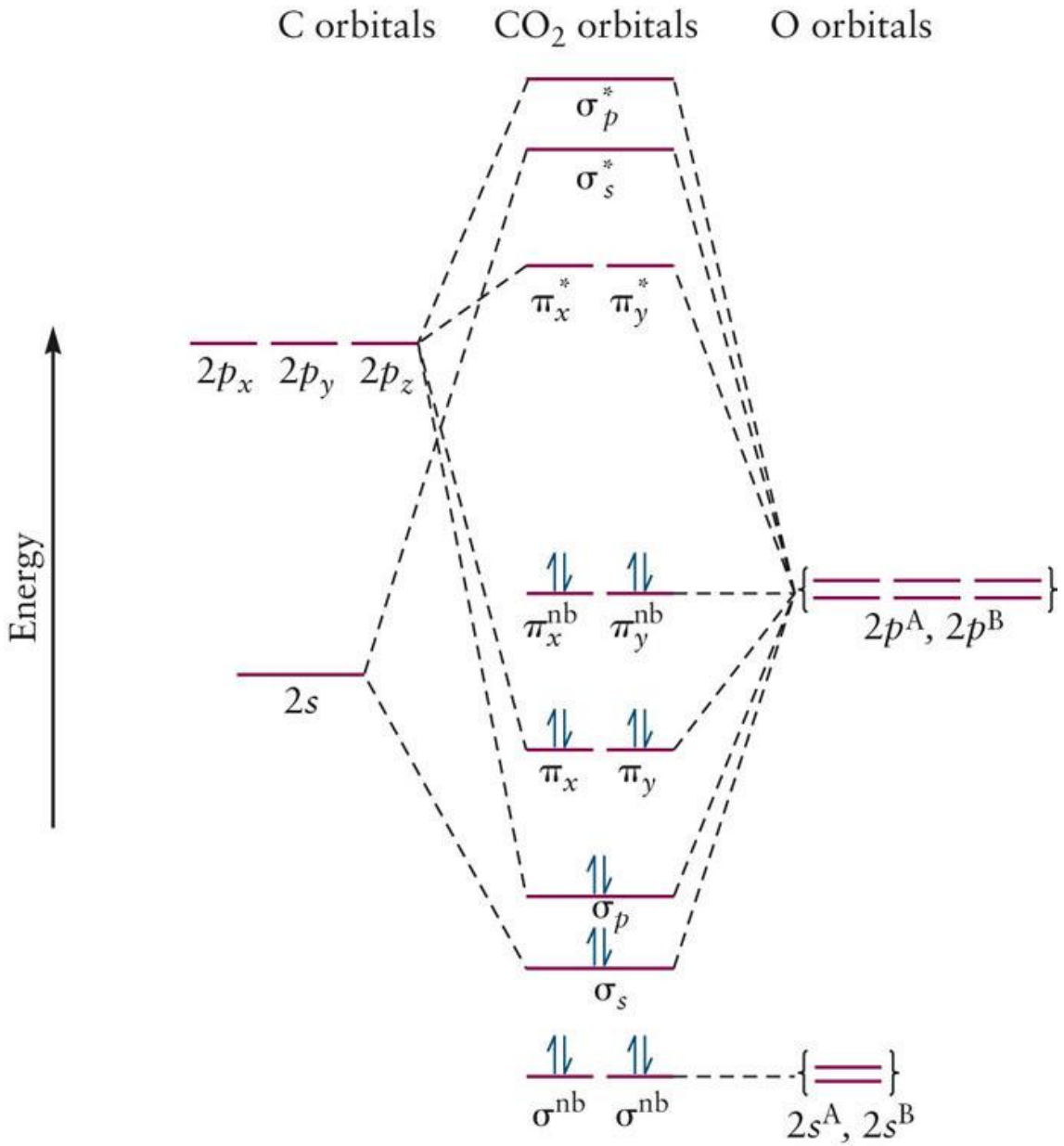
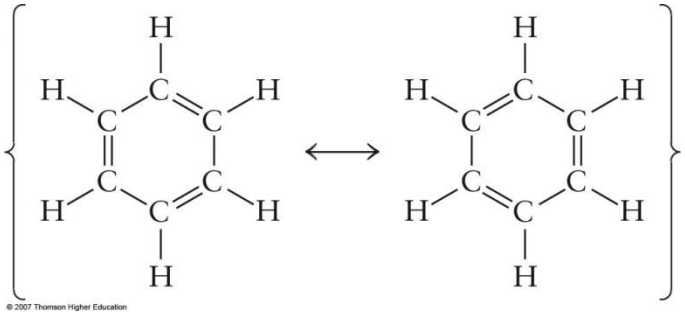
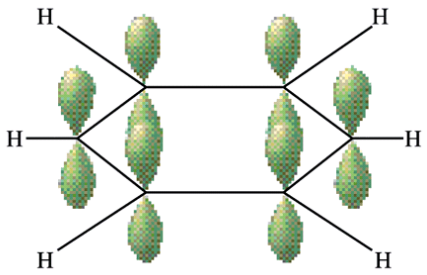






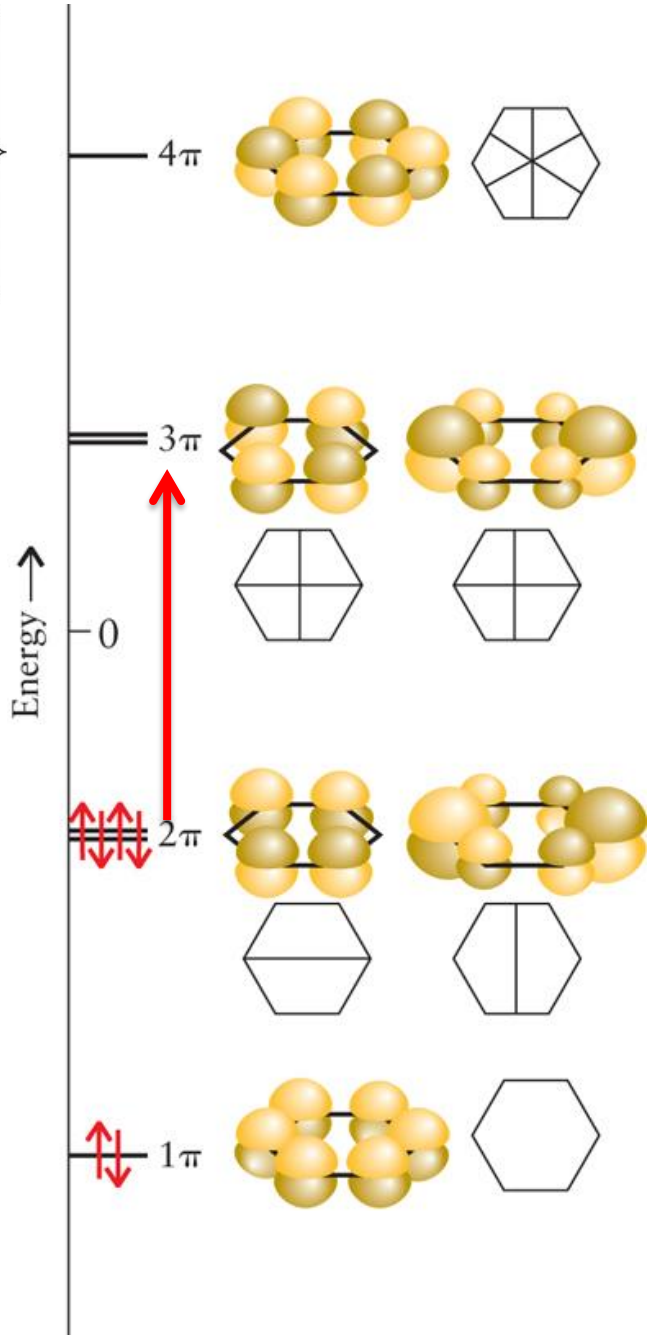
Benzene





LUMO
=lowest unoccupied molecular orbital

HOMO
=highest occupied molecular orbital



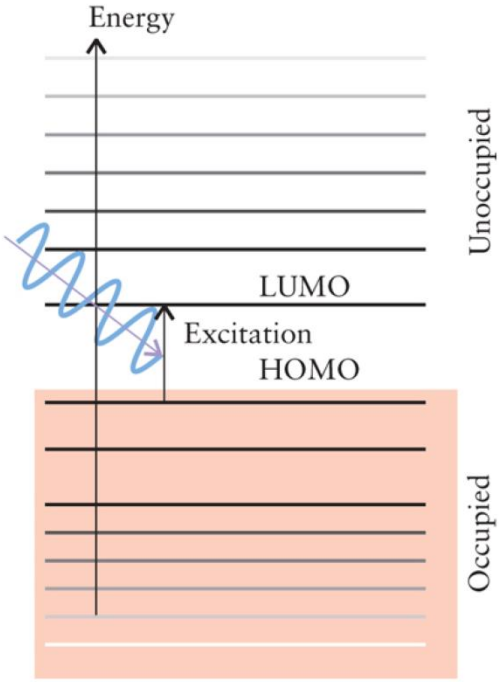
Light absorption occurs with:

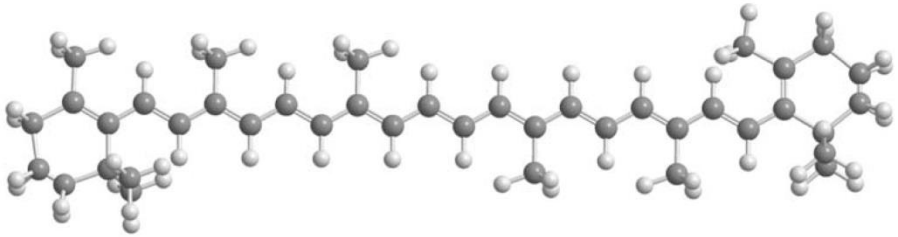
hv = HOMO-LUMO energy difference

3.11. Colors of Materials

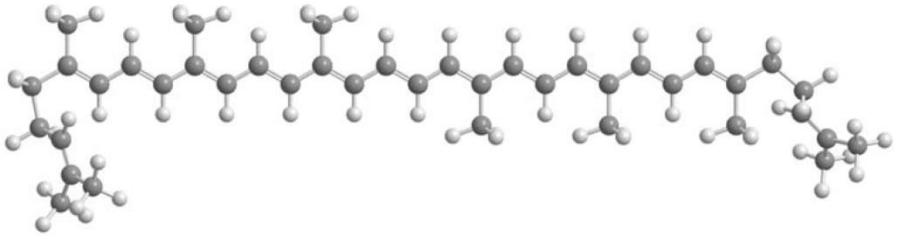
- **highest occupied molecular orbital (HOMO)**
- **lowest unoccupied molecular orbital (LUMO)**

→ excited an electron from a HOMO to a LUMO, by the photons with the energy of visible light





47 β-Carotene, $C_{40}H_{56}$



48 Lycopene, $C_{40}H_{58}$