CHEM F111 : General Chemistry
Semester II: AY 2017-18
Lecture-12, 07-02-2018

Notice: Extra class

EXTRA CLASS NOTICE
TUTORIAL SECTION 6

DATE: Wednesday, 7th Feb 2018   TIME: 5.00pm
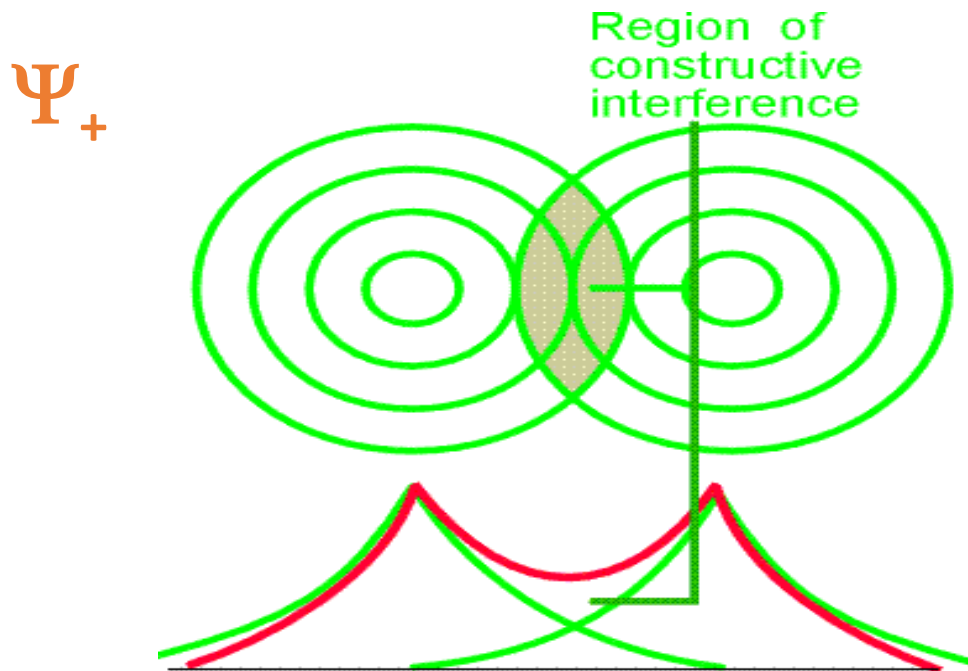VENUE: Room No. 3249

Notice: Extra class

EXTRA CLASS NOTICE
TUTORIAL SECTION 11

DATE: Wednesday, 7th Feb 2018   TIME: 5.30pm
VENUE: Room No. 6103

Summary of lecture 11

Ψ_+

Region of constructive interference

$\Psi_- = 1s_{HA}(1)\ 1s_{HB}(2) - 1s_{HA}(2)\ 1s_{HB}(1)$

→ between the two nuclei, Ψ_- changes sign → $|\Psi_-|^2 = 0$ → creation of a σ^* bond described by a "*antibonding molecular orbital*".
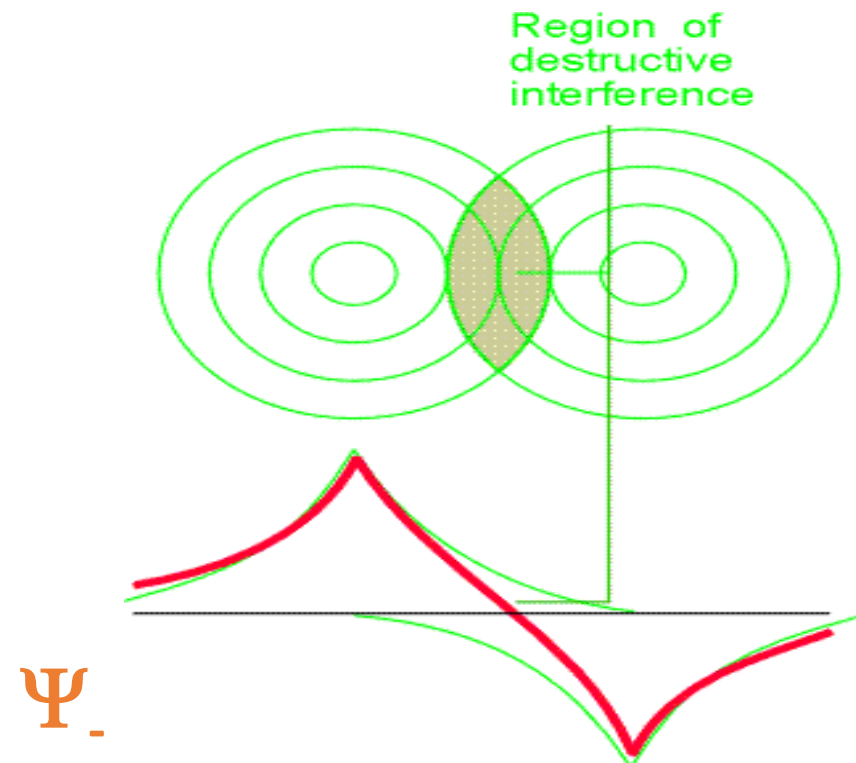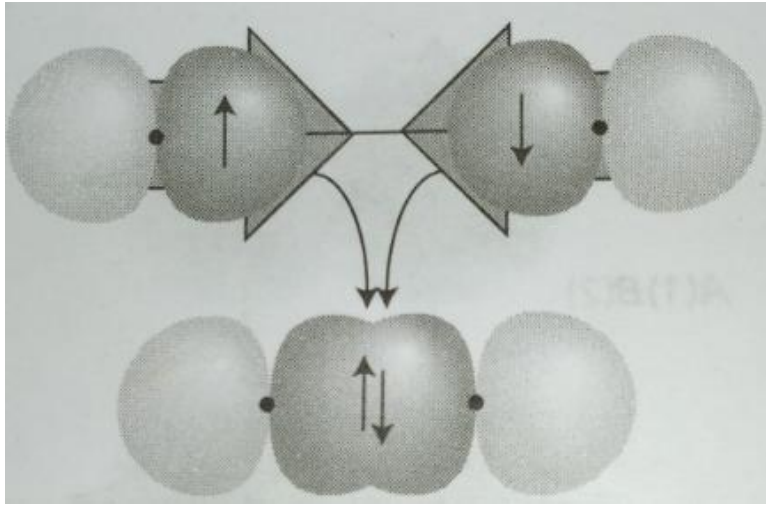
$\Psi_+ = 1s_{HA}(1)\ 1s_{HB}(2) + 1s_{HA}(2)\ 1s_{HB}(1)$

→ between the two nuclei: $|\Psi_+|^2 > 0$ creation of a σ bond described by a "*bonding molecular orbital*"

Region of destructive interference

Ψ_-

EC of N: $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$
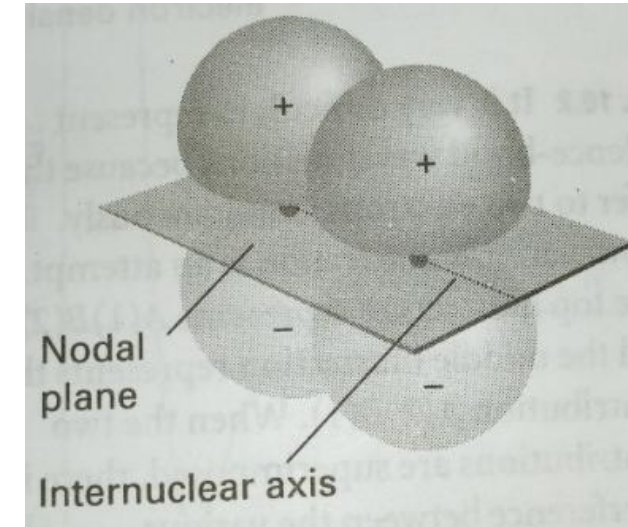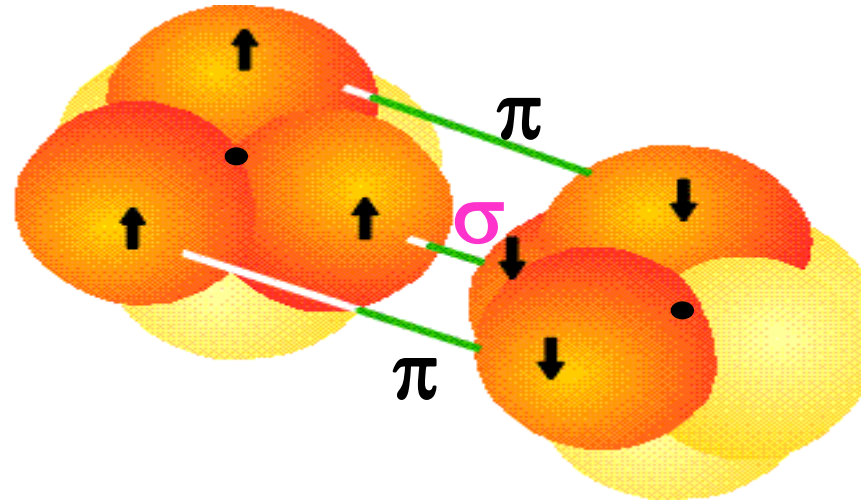

σ Bond (2p$_z$)

π Bond (2p$_x$ & p$_y$)

The remaining N2p orbitals can't merge to give σ bonds as they don't have ***cylindrical symmetry*** around the internuclear axis

N$_2$: 3 bonds are formed by combining the 3 different 2p orbitals of the 2 nitrogen atoms. This is possible because of the symmetry and the position of those 2p orbitals wrt each other. **N$_2$** has sp hybridization.
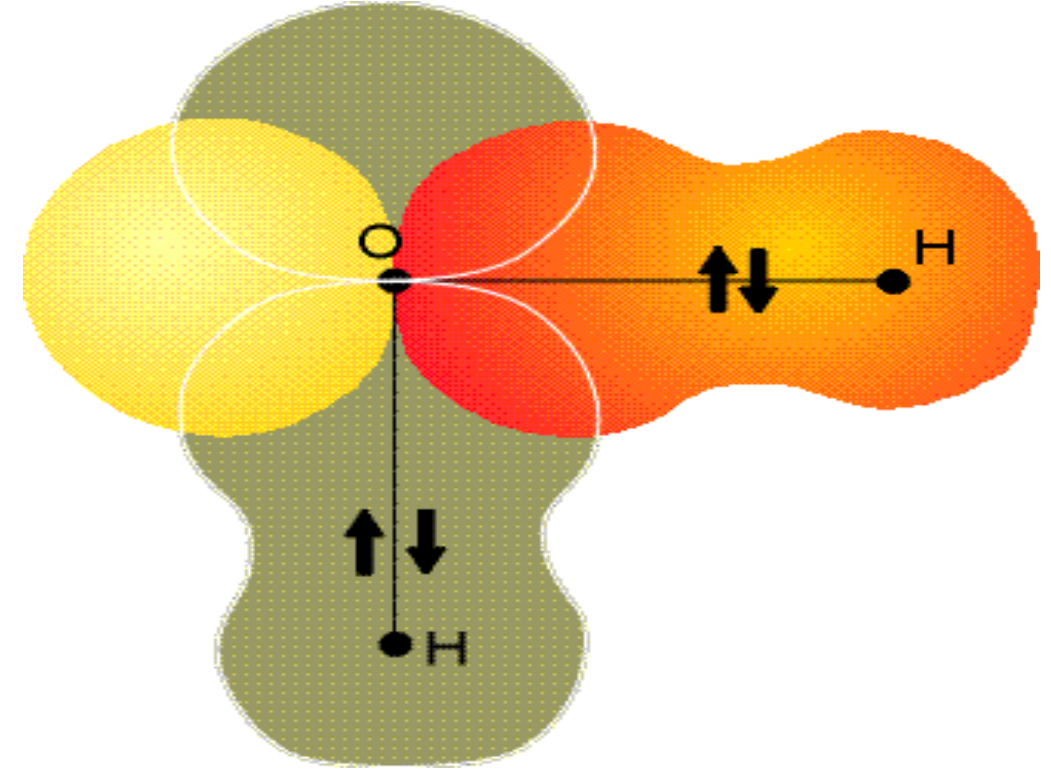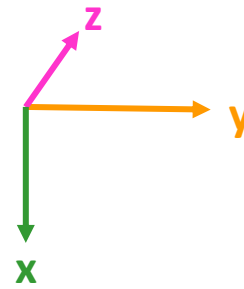
Polyatomic molecules (H_2O)

EC of O: $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

EC of H: $1s^1$

H_2O should be an angular molecule, which it is. However, the theory predicts a bond angle between the $\sigma_{(O-H)}$ bonds is $90°$, whereas the *actual bond angle is 104.5°.*
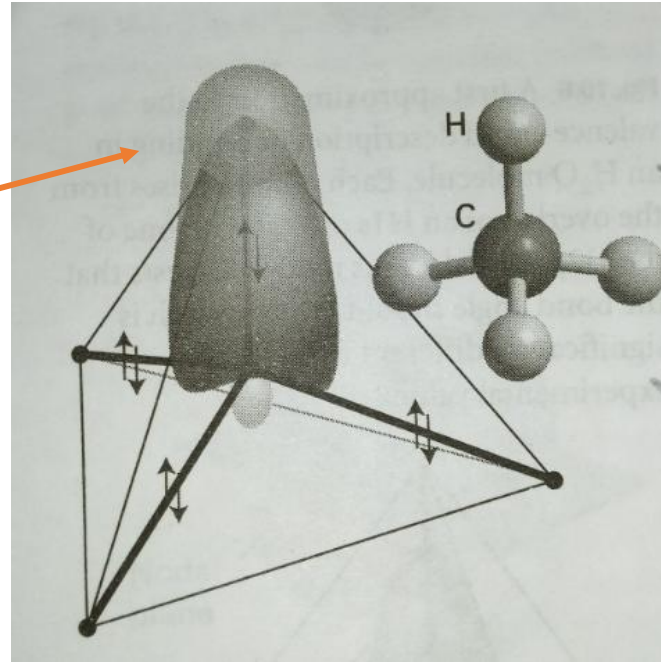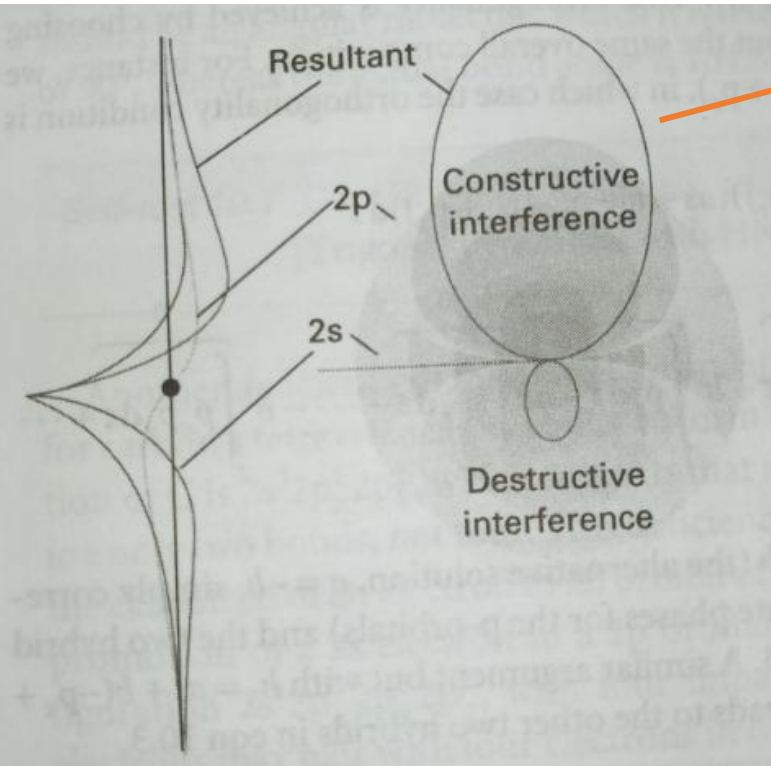
Hybridization

➢ Poor prediction of bond angles.

➢ Number of bonds that an atom may participate in, for example the tetravalency of C.

Consider first the example of methane, with four equivalent C-H bonds.

• Ground state: $1s^2 2s^2 2p_x^1 2p_y^1$

• Promote one electron to get $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

• Quantum mechanics permits the same electron distribution to be described in different ways. Construct a set of four equivalent linear combinations, i.e., form hybrid orbitals

sp³ Hybridization

An orthonormal set of hybrid orbitals is created by applying a transformation on the orthonormal hydrogenic orbitals. The sp³, sp² or sp hybrid orbitals are <u>linear combinations of the AO's</u>, they appear as the resulting interference between s and p orbitals.


$$sp^3$$
$$h_1 = s + p_x + p_y + p_z$$
$$h_2 = s - p_x + p_y - p_z$$
$$h_3 = s - p_x - p_y + p_z$$
$$h_4 = s + p_x - p_y - p_z$$

Each hybrid atomic orbital has the same energy and can be occupied by one electron of the promoted atom ➔ CH_4 has 4 similar bonds.
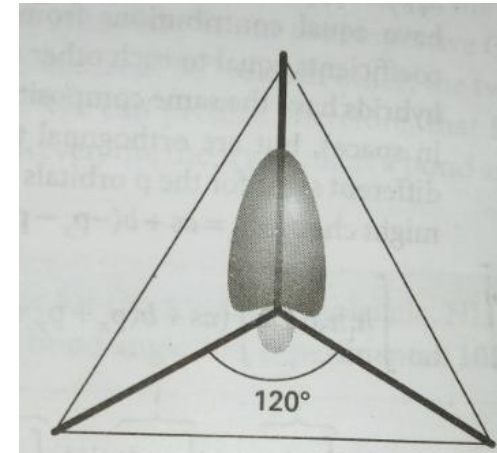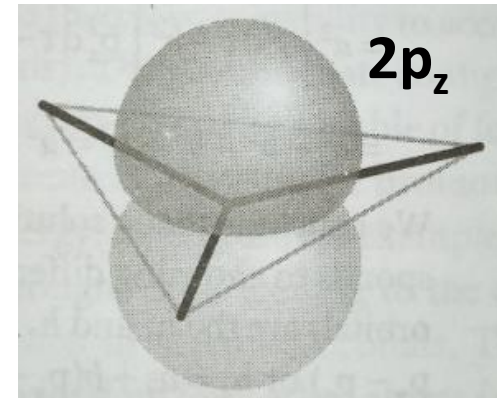
sp² Hybridization

◆ The sp² hybrid atomic orbitals lie in a plane and points towards the corners of an equilateral triangle.

◆ $2p_z$ is not involved in the hybridization, and its axis is perpendicular to the plane of the triangle.

$$h_1 = s + 2^{1/2} p_y$$
$$h_2 = s + (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$$
$$h_3 = s - (3/2)^{1/2} p_x - (1/2)^{1/2} p_y$$

120°

2p_z
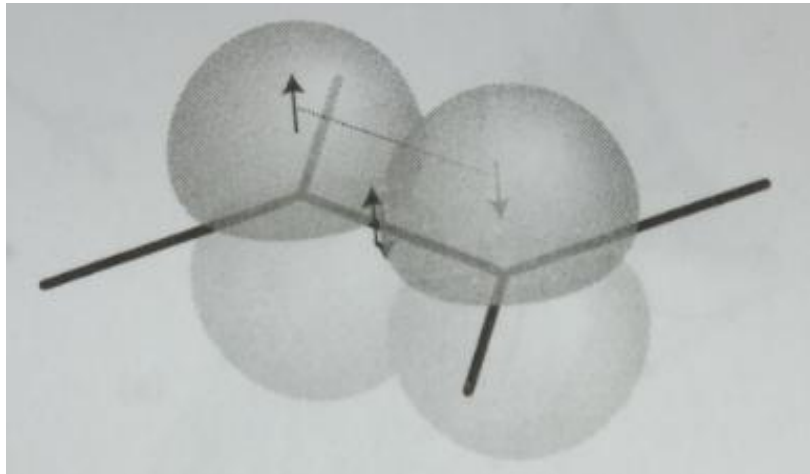
◆ $CH_2=CH_2$: the hybrid atomic orbitals of each C atom create the backbone of the molecule via 3σ bonds (2 C-H and 1 C-C).

◆ The remaining $2p_z$ of the 2 C atoms create a π bond preventing internal rotation.
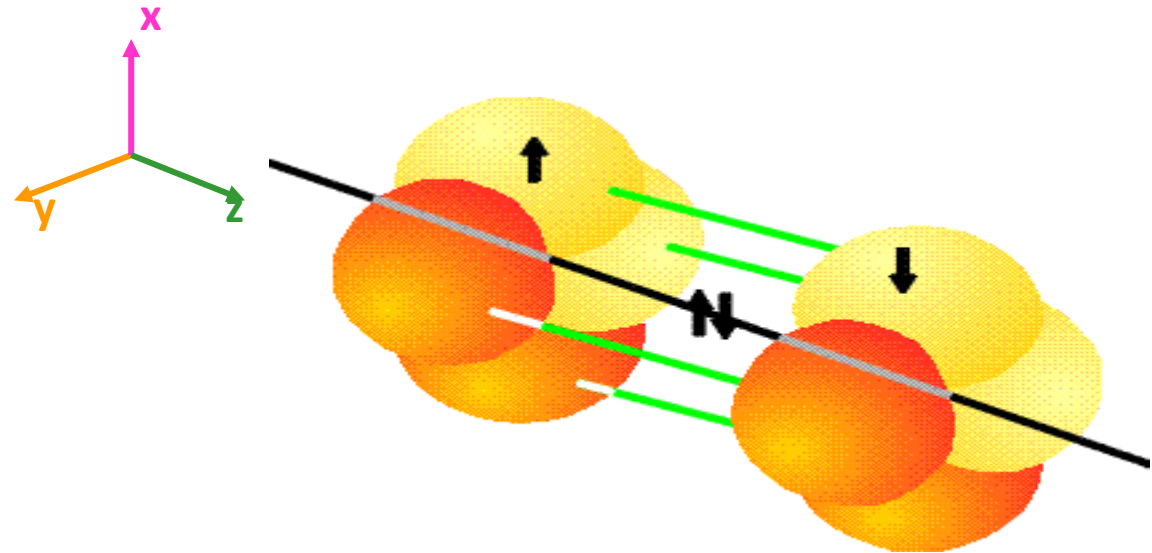
sp Hybridization

In ethyne, HC≡CH: Formation of 2 σ bonds (with C and H) using the 2 hybrid atomic orbitals h_1 and h_2.

The remaining $2p_x$ and $2p_y$ can form two π bonds between the two carbon atoms.

$h_1 = s + p_z$

$h_2 = s - p_z$

Resonance

- The superposition of the wavefunctions representing different electron distributions in the same nuclear framework.

- Consider the VB description of a <u>purely covalently bonded HCl molecule</u>

$$\psi_{H\text{-}Cl}(1,2) = \psi_H(1)\psi_{Cl}(2) + \psi_H(2)\psi_{Cl}(1)$$

But H^+Cl^- is ionic also, the wavefunction for this form

$$\psi_{H+Cl\text{-}}(1,2) = \psi_{Cl}(1)\psi_{Cl}(2) \text{ (this wavefunction alone is unrealistic)}$$

Therefore, ψ for HCl is as superposition of both, $\psi_{HCl} = \psi_{H\text{-}Cl} + \lambda\psi_{H+Cl\text{-}}$ (λ = nu. co.)

or, $\psi = \psi_{covalent} + \lambda\psi_{ionic}$

λ^2 represents relative proportion of the ionic contribution.

Re-visit VBT

The language of valence bonding:

1. The nature of bond types: σ and π bonds are formed by spin pairing
2. Promotion: valence electron may be promoted to empty orbitals if overall that results in a lowering of energy
3. Hybridization: atomic orbitals may be hybridized
4. Resonance: the superposition of individual structures

Drawbacks of VBT
- ✓ This theory does not discuss energies of electrons.
- ✓ The assumptions about the electrons being localized to specific locations

Need of MOT

1. Molecular orbitals are obtained by combining the atomic orbitals on the atoms in the molecule.

2. This theory takes s, p, and d-orbitals of central atom into account for study.

3. It explains σ, π, and δ bond formation.

4. MOT predicts bond order, stability, bond strength, and the existence of the molecule

5. MOT can explain: N_2, O_2, HCl, CO, $[CoCl_4]^{2-}$, $[Co(NH_3)_6]^{3+}$ etc.
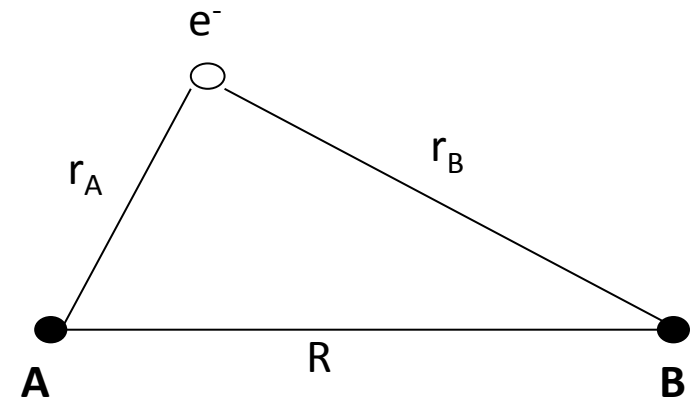
LCAO-Molecular Orbital (MO) theory

The individual orbitals of separate atoms combine to make orbitals that span the entire molecules

By using linear variation theory; we can construct the MO by taking linear combinations of the occupied atomic orbital.

The hydrogen molecule-ion: H-H⁺
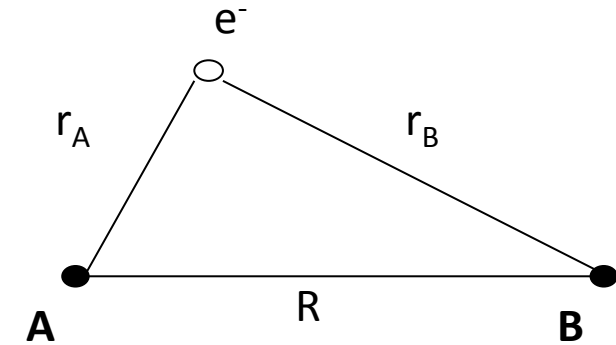
LCAO-Molecular Orbital (MO) theory

The electron can be found in an atomic orbital (AO) belonging to atom A (*i.e.;* 1s of H) and also in an atomic orbital belonging to B (*i.e.;* 1s of H$^+$)

➡ The total wavefunction should be a superposition of the 2 AO and it is called ***molecular orbital*** LCAO-MO.

➡ Let's write the atomic orbitals on the two atoms by the letters A and B.

$\Psi_\pm$**= N(A $\pm$ B)**

N is the ***normalization constant***

The hydrogen molecule-ion: H-H$^+$

LCAO-Molecular Orbital (MO) theory

The hydrogen molecule-ion: H-H⁺

Example for Ψ_+ = N(A + B):

$$\int \psi^* \psi \, d\tau = N^2 \left[\int A^2 \, d\tau + \int B^2 \, d\tau + 2\int AB \, d\tau \right] = 1$$

$$= N^2(1 + 1 + 2S) = 1$$

$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

$S = \int AB \, d\tau$ is the ***overlap integral*** related to the overlap of the 2 AO
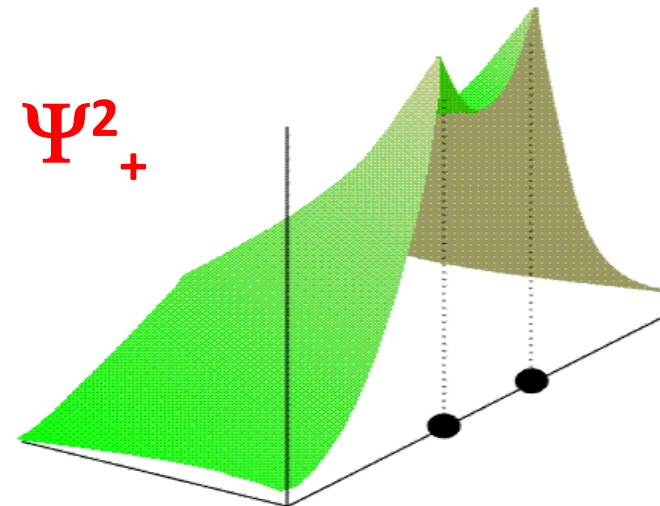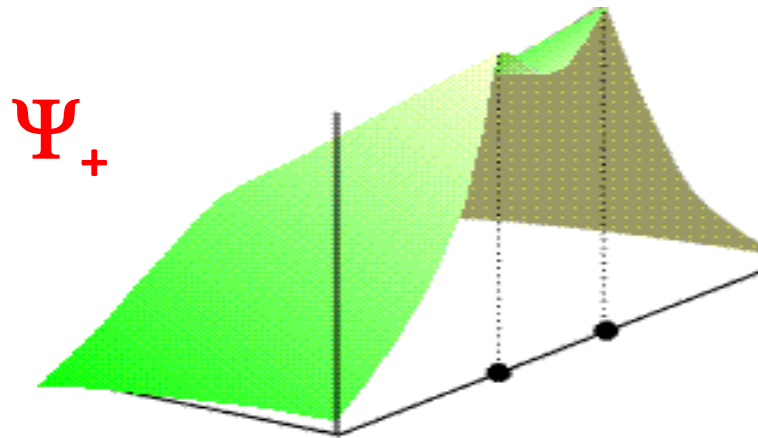
Bonding orbital

$$\Psi_+ = \{2(1+S)\}^{-1/2}(A + B), \text{ with } A=1s, B=1s \text{ of } H$$

Probability density: $\Psi^2_+ = \{2(1+S)\}^{-1}(A^2 + B^2 + 2AB)$

A^2 and B^2 = probability density to find the e^- in the atomic orbital A and B

2AB = the *overlap density* represents an enhancement of the probability density to find the e^- in the internuclear region: *the electron accumulates in regions where AO's overlap and interfere constructively*; which creates a *bonding orbital (σ)* with one electron.
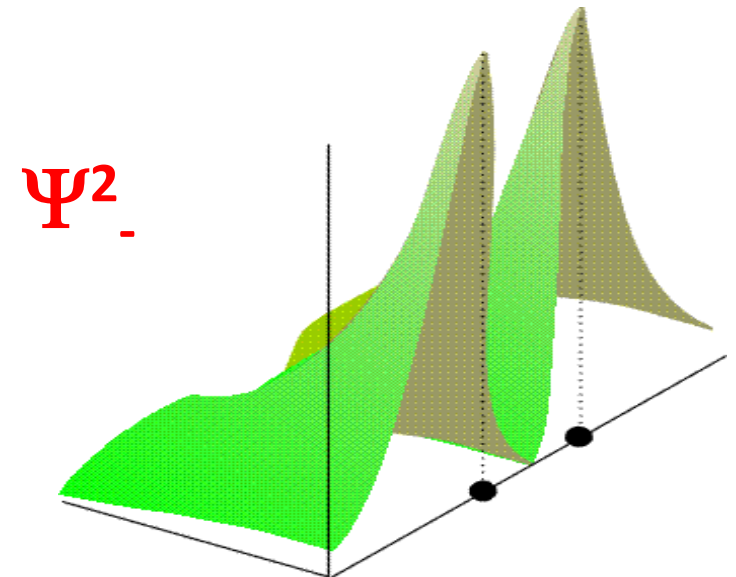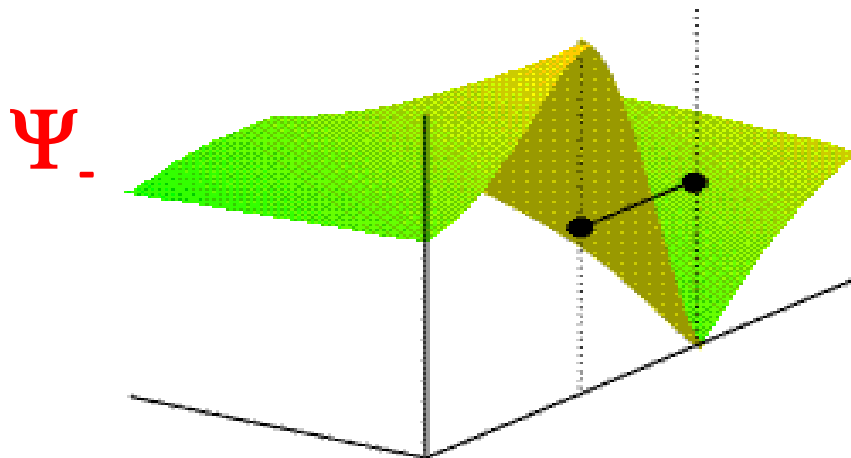
Antibonding orbital
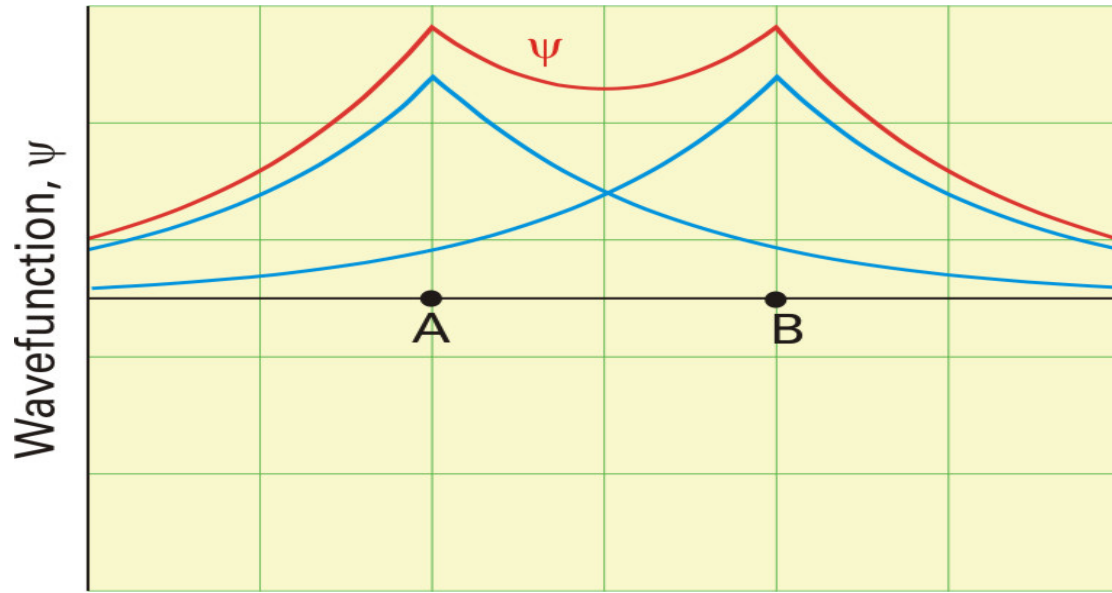
$$\Psi_- = \{2(1-S)\}^{-1/2}(A - B)$$

Probability density: $\Psi^2_- = \{2(1-S)\}^{-1}(A^2 + B^2 - 2AB)$

-2AB = reduction of the probability density to find the e$^-$ in the internuclear region: there is a *destructive interference* where the two AO overlap, which creates an *antibonding orbital σ^*.*
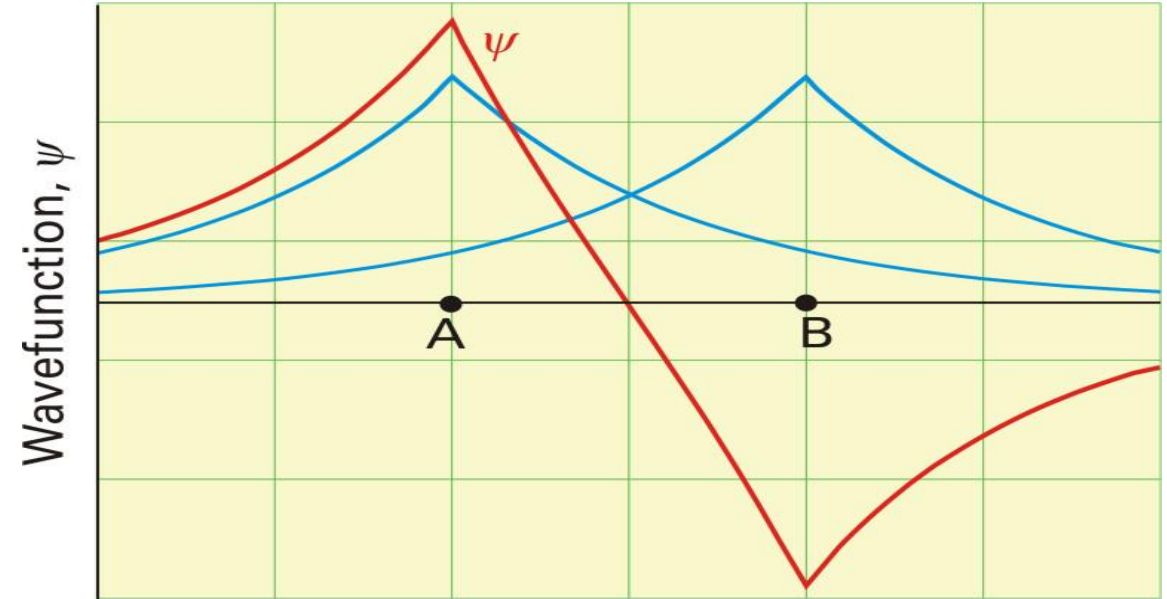
➔ Nodal plane between the 2 nuclei

Ψ_-
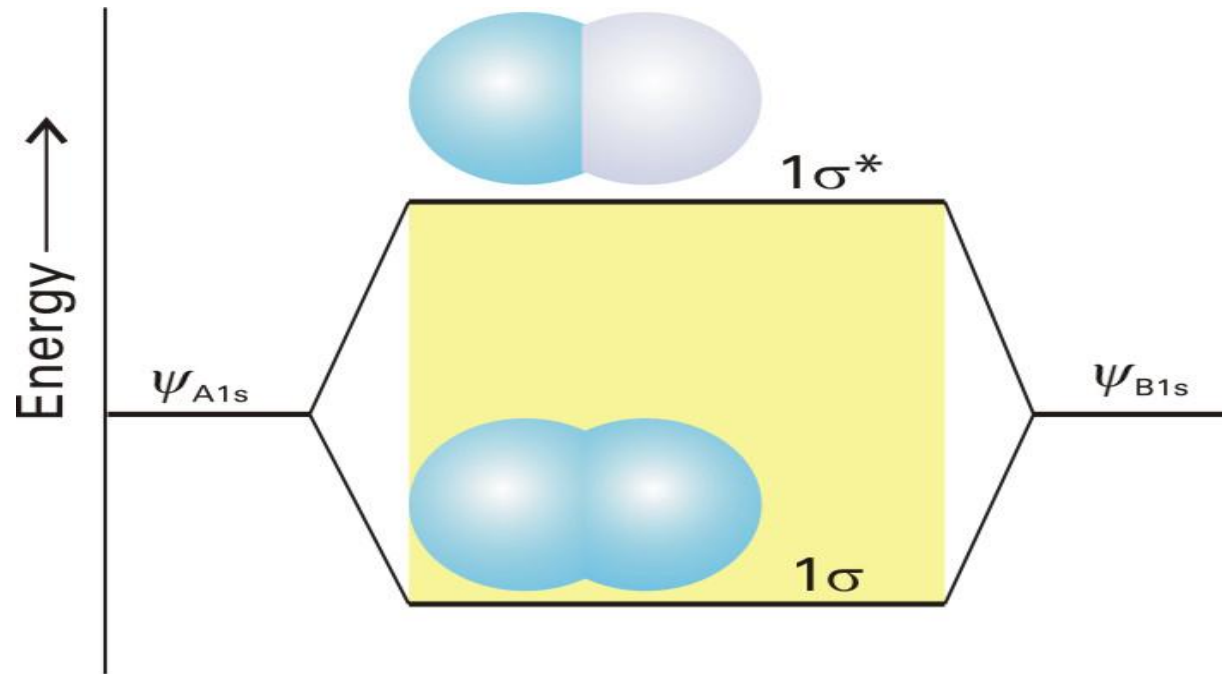
Ψ^2_-

Bonding and antibonding MO's
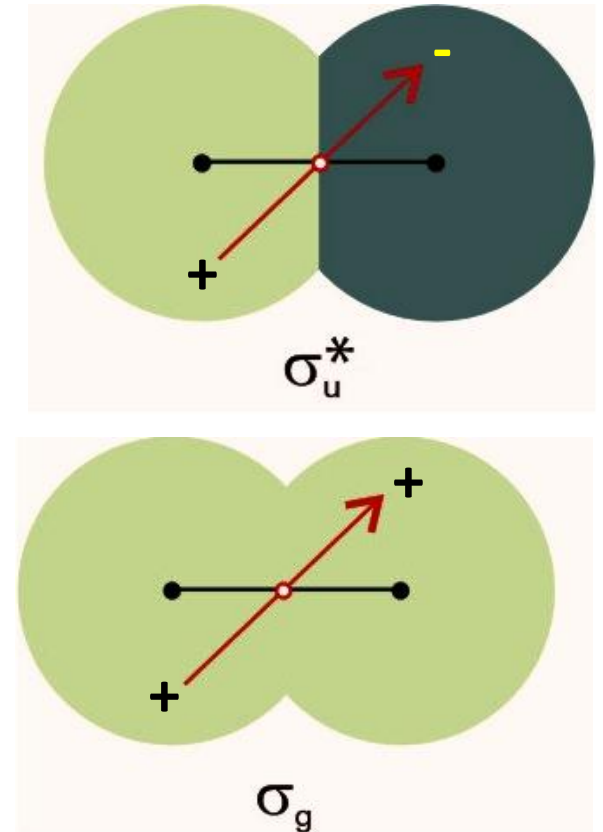

Bonding

Antibonding

Variation of the molecular orbitals along the internuclear axis: increased electron density between nuclei in bonding case, and the node midway between nuclei in antibonding case
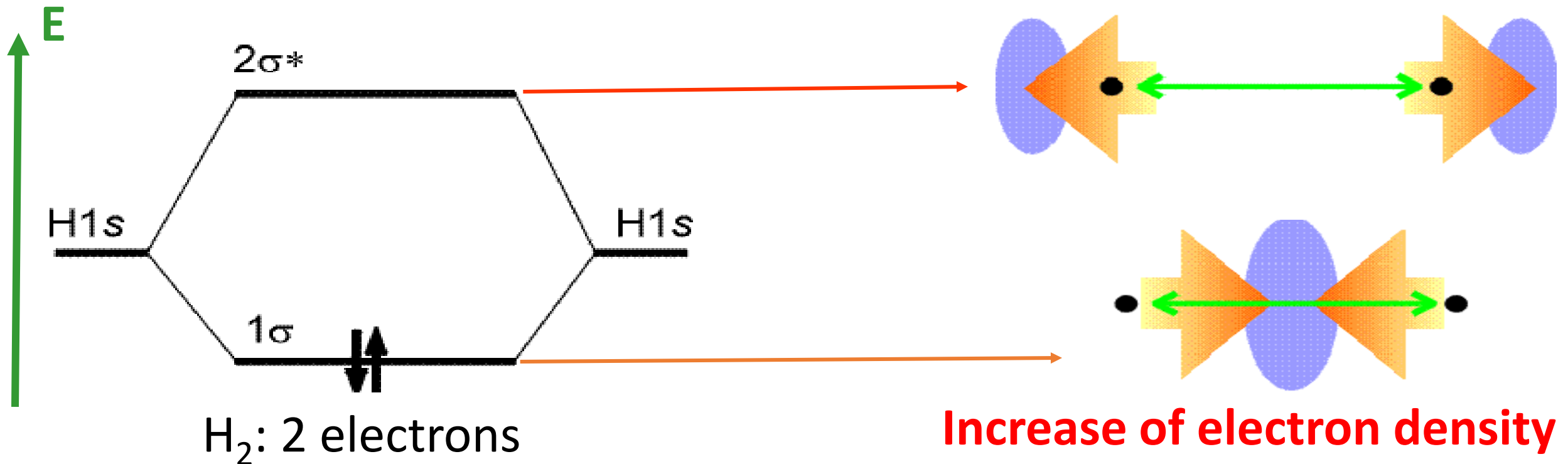
LCAO MOs of H_2^+

MO's characterized by
- Energy - Bonding / Antibonding character(*)
- Transformation under inversion – symmetric (g), antisymmetric (u). (homonuclear)

Structure of H₂ molecule

Now, we use the molecular orbitals ($\sigma= \Psi_+$ and $\sigma*= \Psi_-$) found for H$_2$ molecule; in order to describe many-electron diatomic molecules.

E

2σ*

H1s   H1s

1σ

H₂: 2 electrons

Increase of electron density

Bond order calculation

Bond order: $b = \frac{1}{2}(n-n^*)$

➔ The greater the bond order between atoms of a given pair of elements, the shorter is the bond and the <u>greater is the bond strength</u>.

n= number of electrons in the bonding orbital
n*= number of electrons in the antibonding orbital

Other diatomic molecule

Period 2 diatomic molecules

➤ According to molecular orbital theory, σ orbitals are built from all orbitals that have the <u>appropriate symmetry</u>.

➤ In homonuclear diatomic molecules of Period 2, that means that two 2s and two $2p_z$ orbitals should be used. From these four orbitals, four molecular orbitals can be built:

Four σ MO
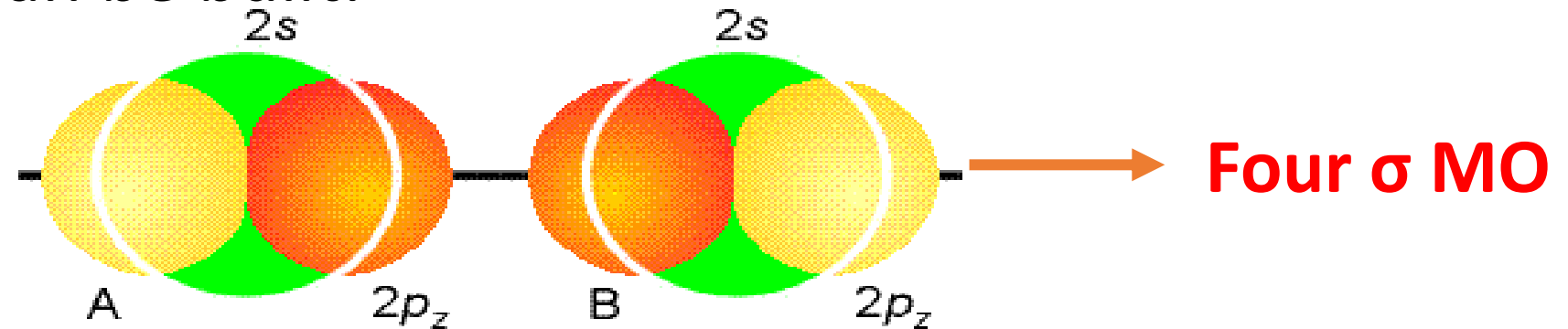
With N atomic orbitals ➔ the molecule will have N molecular orbitals, which are combinations of the N atomic orbitals.

MO using p atomic orbital
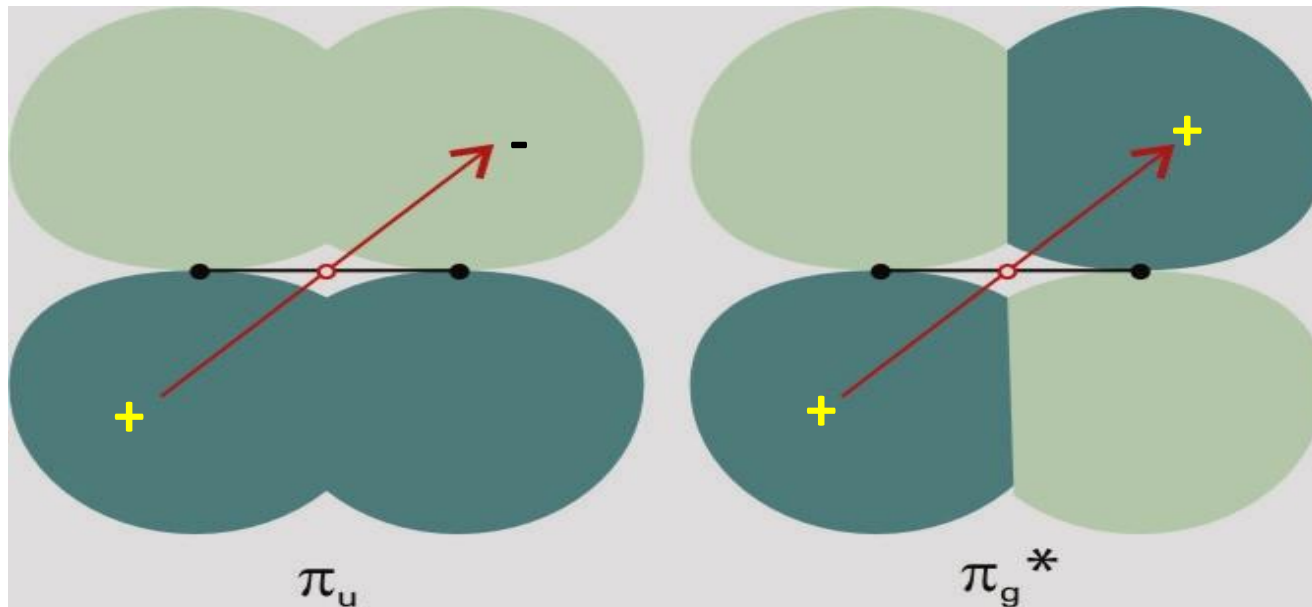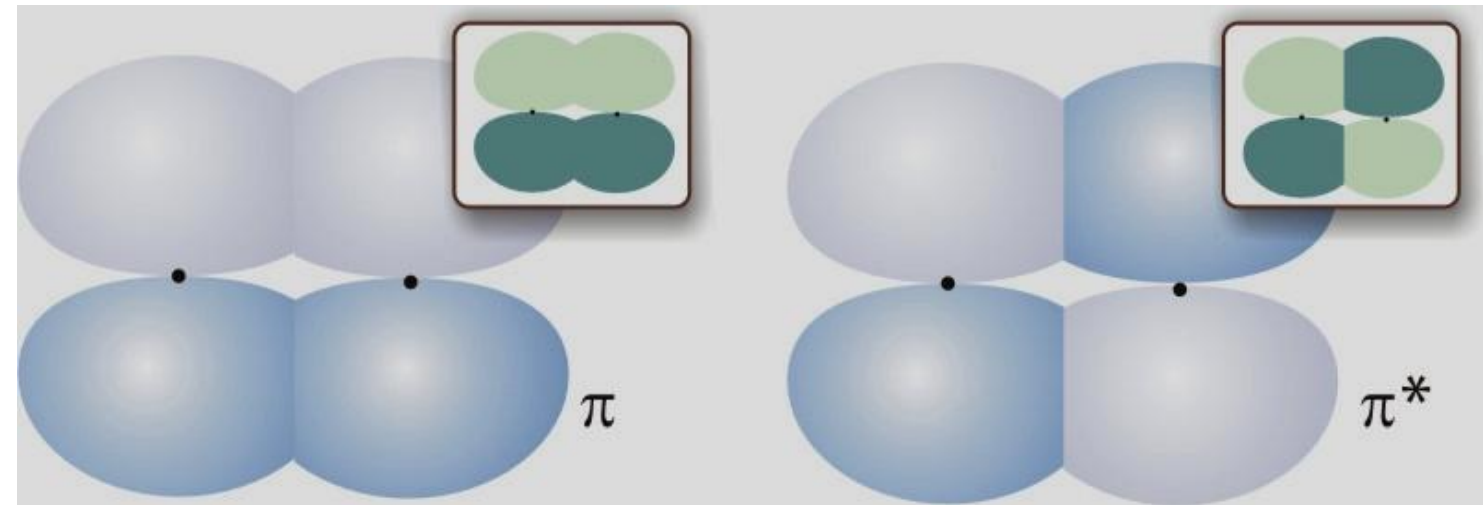
σ and $\sigma*$ from the p_z orbitals
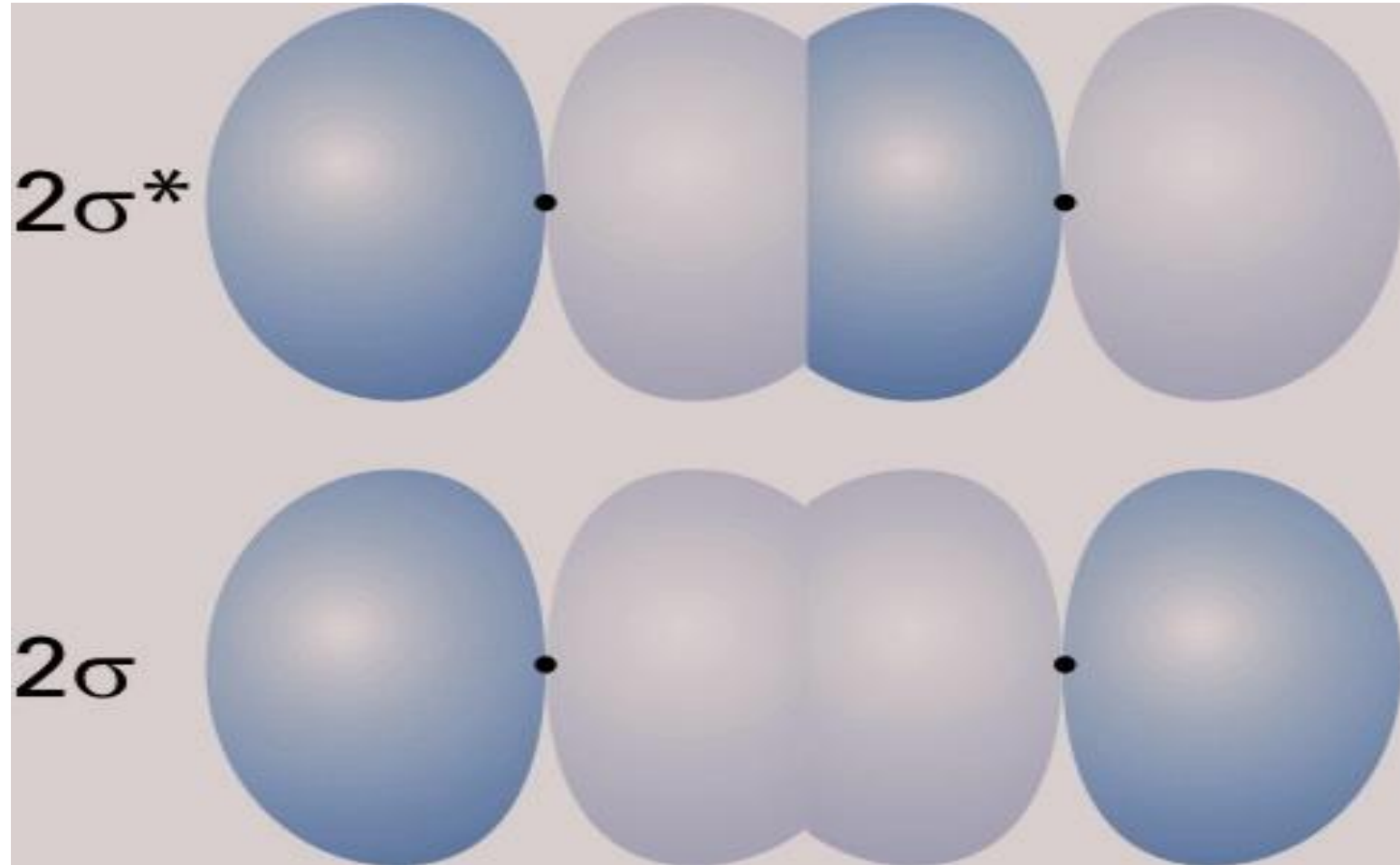
π orbitals

The 2p_x and 2p_y orbitals lead to a pair of π and a pair of π* orbitals

π

π^*

π_u

π_g^*

Inversion symmetry of π orbital

Construction of molecular orbital

- Use all available valence orbitals from atoms

- Classify according to symmetry (σ/π) with respect to axis

- From N_σ AO's, build N_σ MO's of σ symmetry

- Similarly N_π MO's of π symmetry. These occur in degenerate pairs

- In general, the energy of each type of orbital increases with the number of inter-nuclear nodes
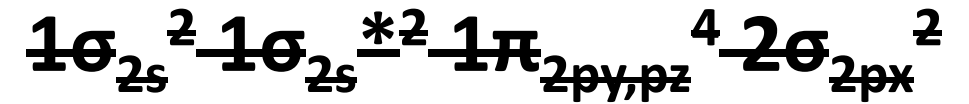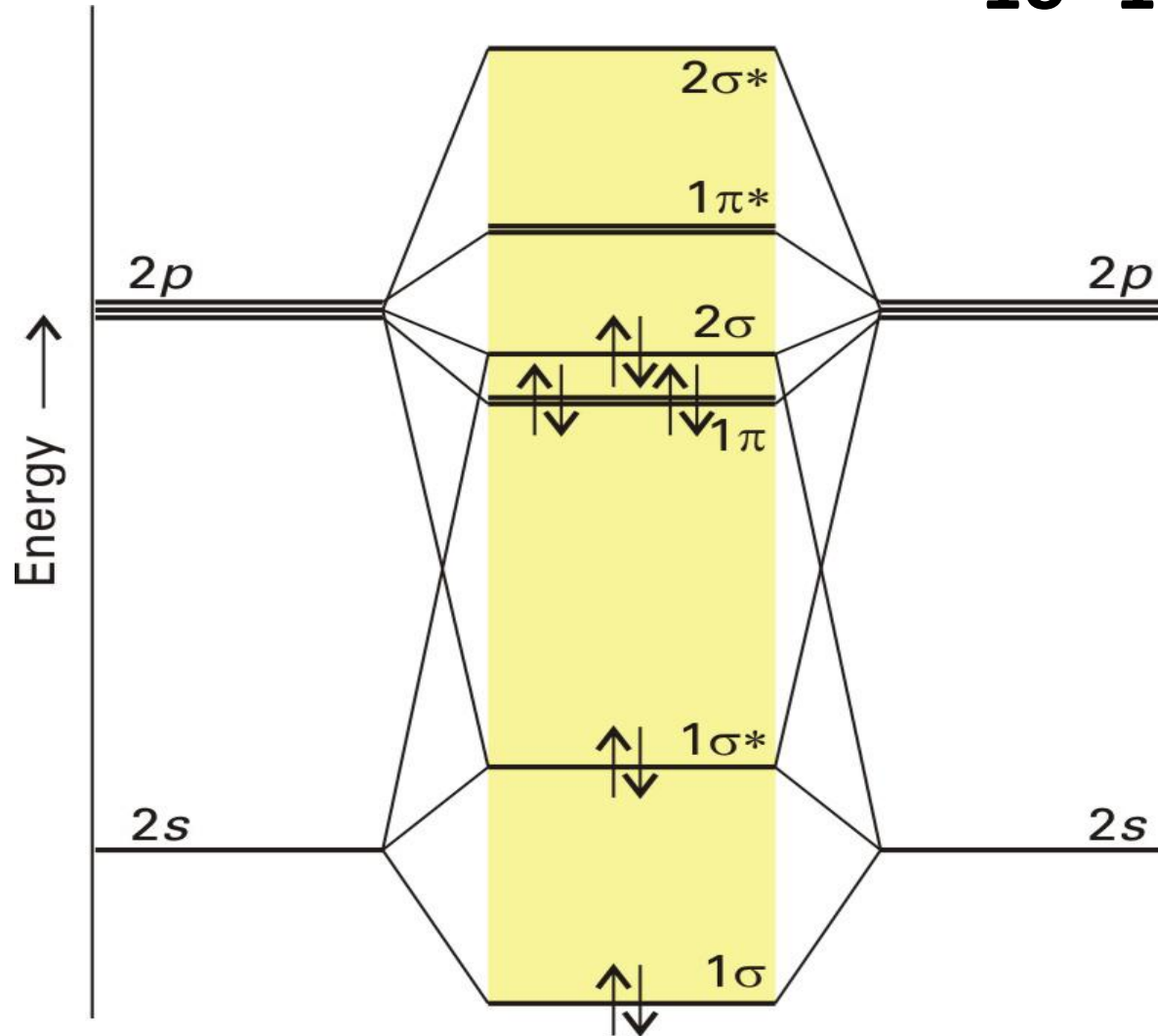
Filling of molecular orbitals

Certain rules are to be followed while filling up molecular orbitals with electrons in order to write correct molecular configurations:

Aufbau Principle – This principle states that those molecular orbital which have the lowest energy are filled first.

Pauli's Exclusion Principle – According to this principle each molecular orbital can accommodate maximum of two electrons having opposite spins.

Hund's Rule – This rule states that in two molecular orbitals of the same energy, the pairing of electrons will occur when each orbital of same energy consist one electron.

MO of N$_2$ molecule

$1\sigma^2\ 1\sigma^{*2}\ 1\pi^4\ 2\sigma^2$ or $1\sigma_g^2\ 1\sigma_u^2\ 1\pi_u^4\ 2\sigma_g^2$

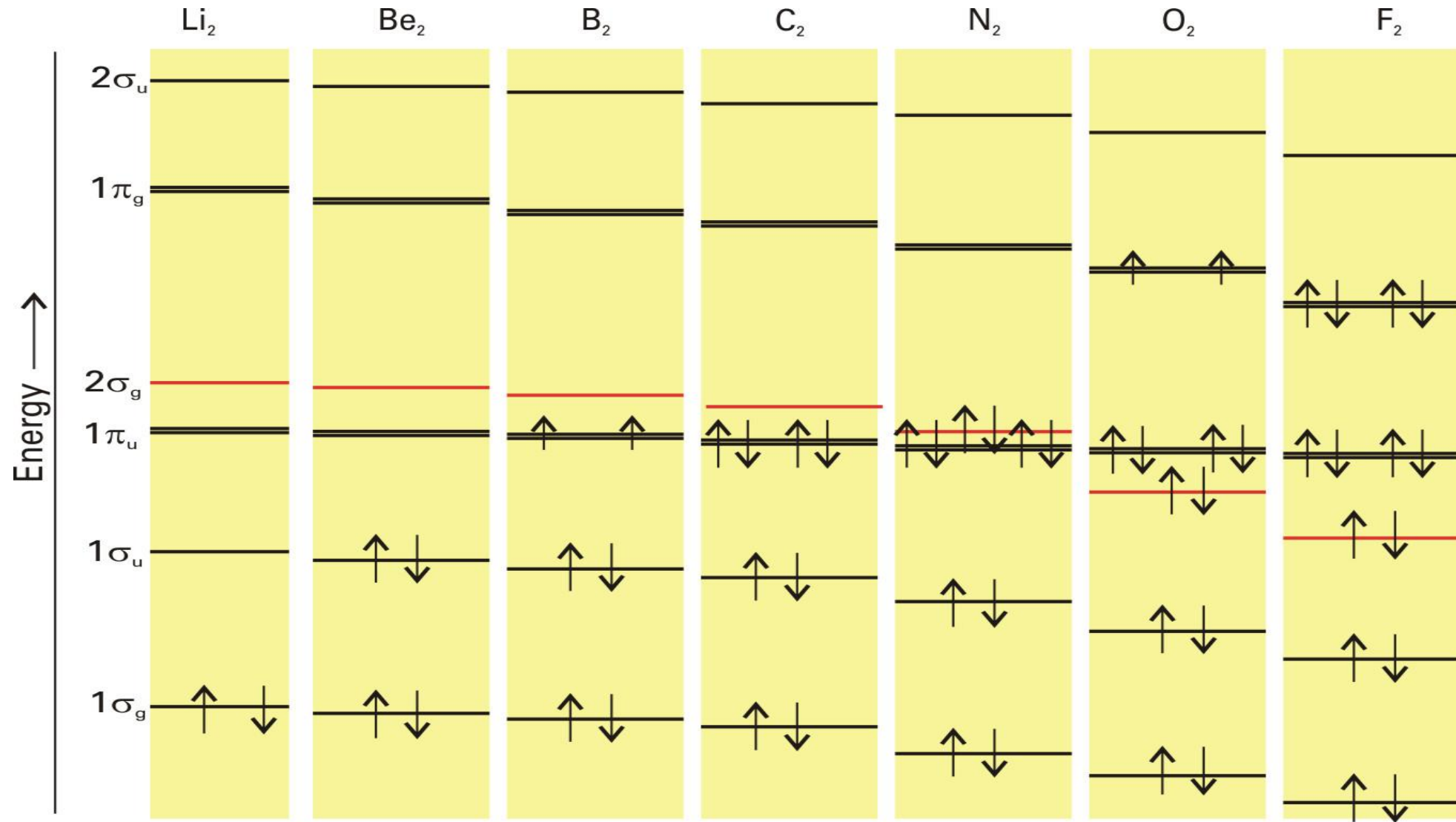~~$1\sigma_{2s}^2\ 1\sigma_{2s}^{*2}\ 1\pi_{2py,pz}^4\ 2\sigma_{2px}^2$~~

Bond order of N$_2$ = 3
Note σ and σ* of mixed 2s and 2p character

Variation of orbital energies

Discussed topics......

- ✓ Hybridization and Resonance

- ✓ LCAO-MO theory

- ✓ Bonding and antibonding orbital

- ✓ Bond order calculation

- ✓ π-orbital and inversion symmetry of π orbital

- ✓ Construction of molecular orbital for various diatomic molecule

Q. Write the <u>ground state electronic configurations of C_2</u> and compare the relative stabilities of C_2 and C_2^- systems based on molecular orbital theory.

Ans. Ground state electronic configuration of C_2 is $1\sigma_b^2 1\sigma_a^2 1\pi_b^4$ (or ~~σ $2s^2$, $\sigma*2s^2$, $[\pi 2p_x^2 = \pi 2p_y^2]$~~)

~~σ 2s, σ *2s, $[\pi 2p_x = \pi 2p_y]$, σ 2p$_z$, $[\pi *2p_x = \pi *2p_y]$, $\sigma*2p_z$~~
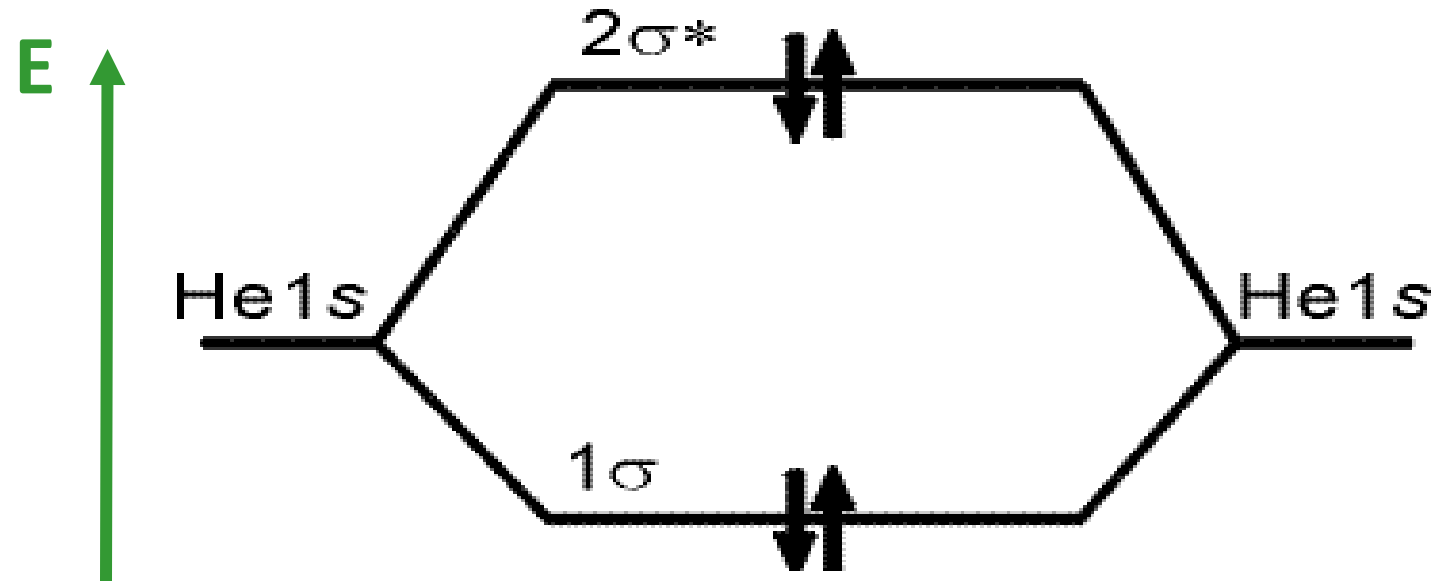
Bond order of C_2 = 2 and that of C_2^- = 2.5

Therefore, C_2^- more stable than C_2

He$_2$: 4 electrons

Bond order = 0

He$_2$ is not stable and does not exist

1. In propene (CH_3-CH_2=CH_2), the first carbon has sp^3 hybrid orbitals and the second carbon has sp^2 hybrid orbitals. These orbitals interact to make a σ bond. <u>Prove that these hybrid orbitals are not orthogonal</u>? The corresponding hybrid orbitals are η_{sp3} = $1/2(s + p_x + p_y + p_z)$ and η_{sp2} = $(1/\sqrt{3})\ s + (\sqrt{2}/\sqrt{3})\ p_z$, respectively.

Cylindrical symmetry (supporting slide)

In cylindrical symmetry, there is only one axis of rotation, and it is always vertical.

Cylindrical symmetry is commonly found in towers, columns, & domes.