Atomes et molécules

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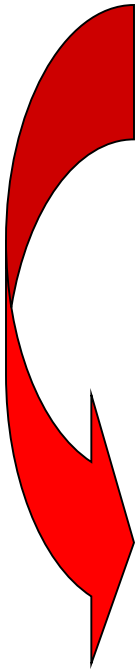
Chapter 11 : Molecular bondings in the wave model

Chapter 11 : Molecular bondings in the wave model

Lewis representation

≡

Good approach of the molecular structure



Strong or week electron density ?
(understanding the chemical reactivity)

Study of the chemical bonding
in the frame of the quantum description

Chapter 11 : Molecular bondings in the wave model

Bonding formation between 2 atoms

the system formed by both atoms stabilizes itself :

following the rules of quantum mechanic (Pauli principle)
in the state of lowest possible energy

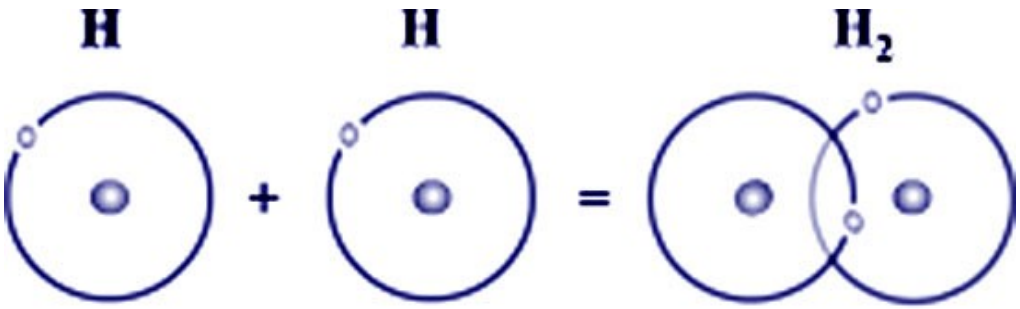
Atomic electronic structure are perturbed :

the orbitals of both atoms (≡ OA)
Interact with each other and overlap

The result is the formation of **a new molecular orbital** (**≡ OM**)
containing two electrons (electron pair bond),
which can be described by a molecular wave function

I) Molecular Orbital of H_2

Bohr orbit (H) : 0.0529 nm (0.529 Å)

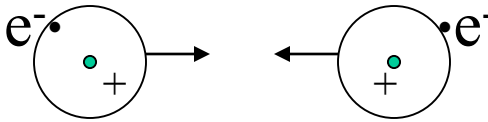


Interatomic distance of the order of 0.1 nm (or 100 pm) : d = 74 pm for H2

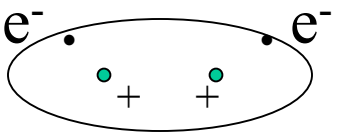
Formation of H_2 :

The molecular orbital **(OM)**, is formed when both atomic orbitals **(OA) 1s** of the H atoms overlap

Atomic orbitals are described by ψ_1 and ψ_2



The molecular wave function which describes the distribution of both electrons in the H_2 molecule is obtained by a linear combination of ψ_1 and ψ_2 : $\psi = k_1 \psi_1 + k_2 \psi_2$ (LCAO) k_1, k_2 are constants



2 different molecular wave functions ψ are possible

$$\psi(d) = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$$

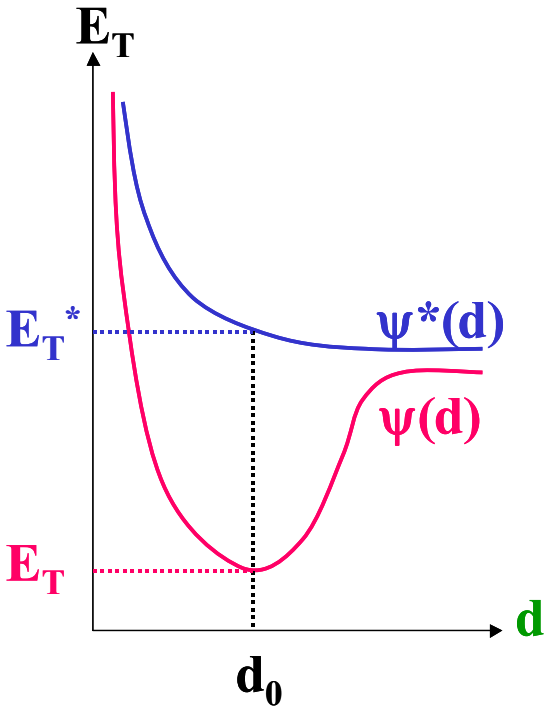
$$\psi*(d) = \frac{1}{\sqrt{2}}(\psi_1 - \psi_2)$$

depending on d :
distance between both nuclei

Introducing $\psi(d)$ et $\psi^*(d)$ in the Schrödinger equation, one can find the associated energy depending on internuclear distance d

$$\psi(d) \Leftrightarrow E_T(d)$$
$$\psi^*(d) \Leftrightarrow E_T^*(d)$$

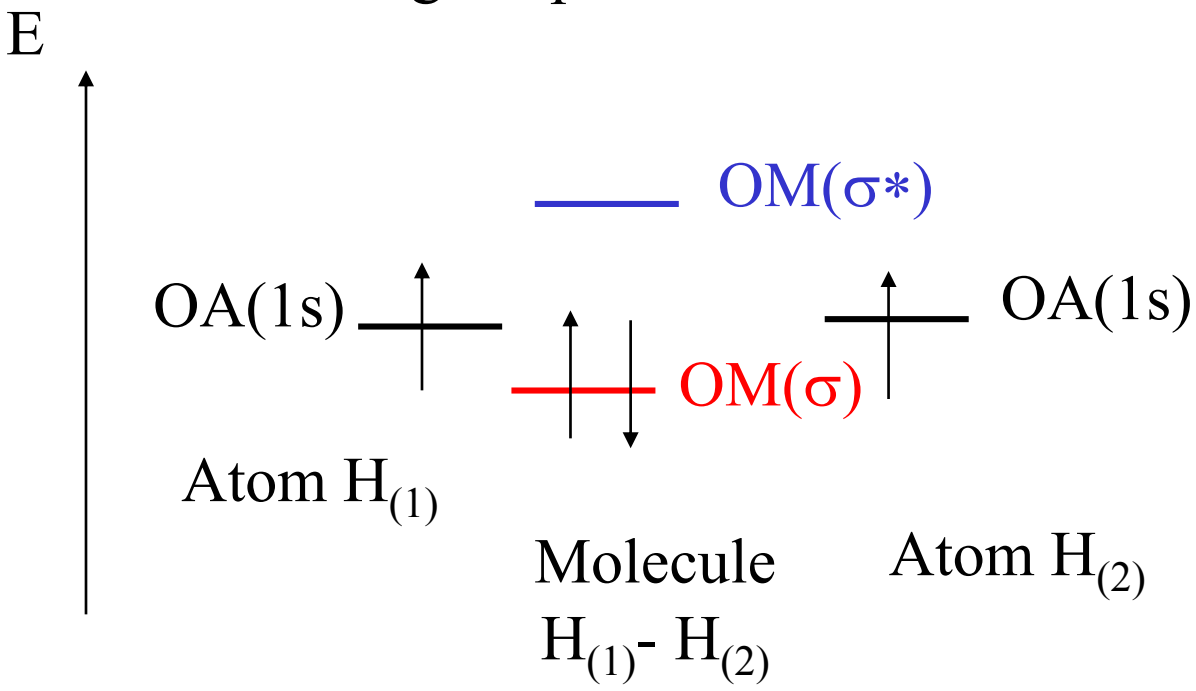
$E_T(d)$ and $E_T^*(d)$ are total energies for the molecular system and solutions to the Schrödinger equation

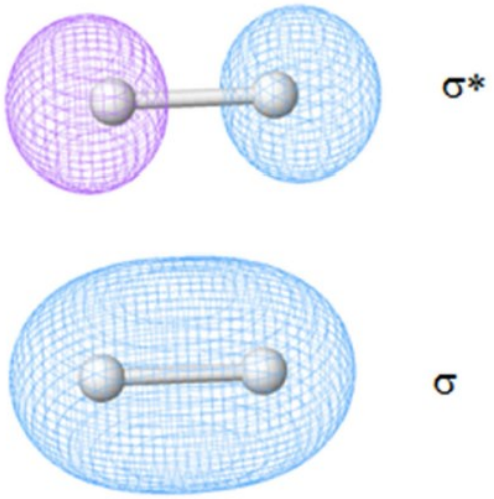


The energy associated to $\psi^*(d)$ is minimal for $d = \infty$,
No bonding is created by the electrons since they tend to move away from each other (E↓ when d↑)
The molecular orbital $\psi^*(d)$ is called **ANTI BONDING**.
and written **σ*.**

The energy associated to $\psi(d)$ is minimal for $d = d_0$,
Nuclei move spontaneously to the equilibrium distance d_0
The molecular orbital $\psi(d)$ is called **BONDING**..
and written **σ.**

From an energetic point of view:





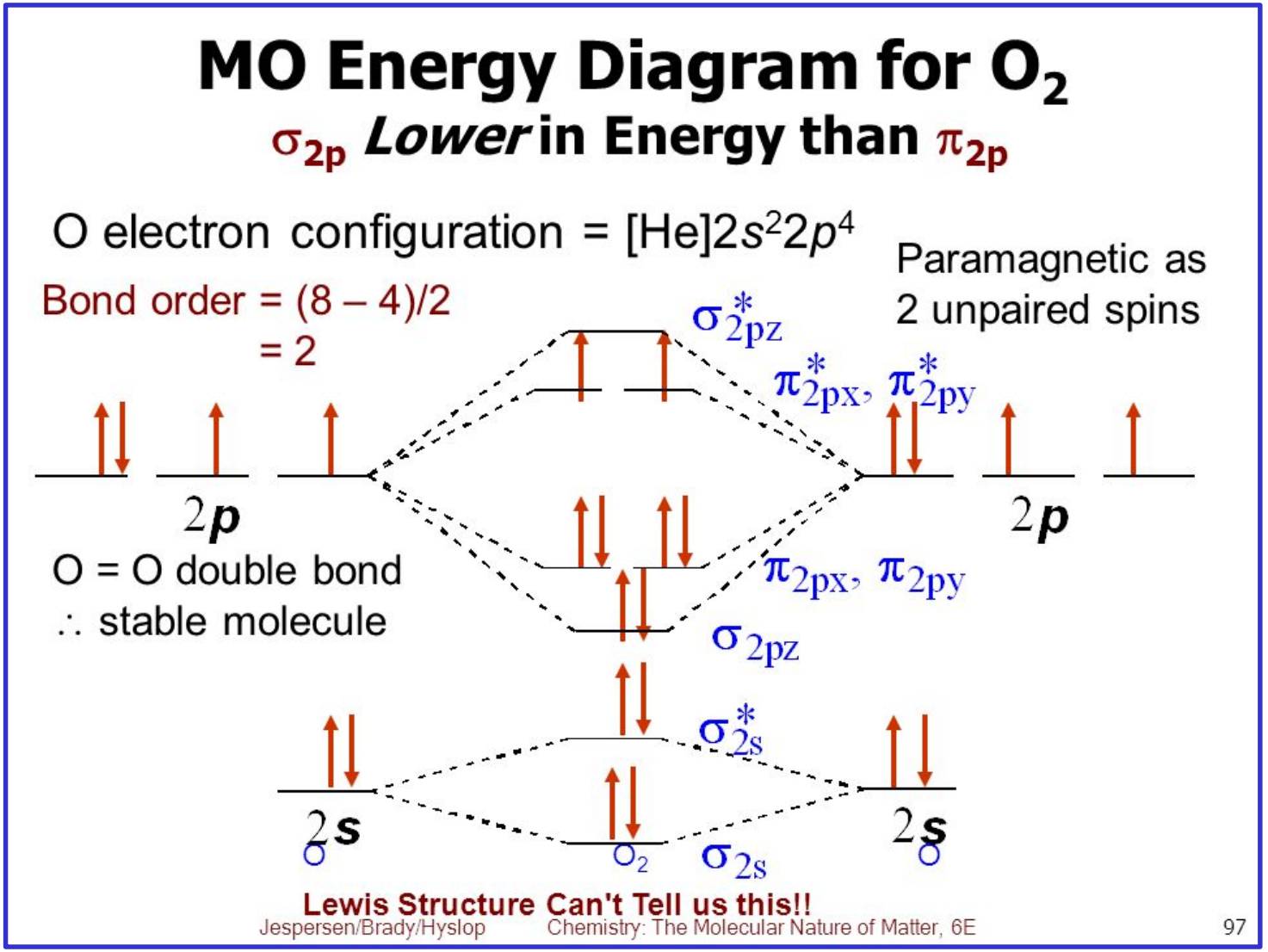
The energy level of the H-H OM(σ) is lower than the OA(1s) of the individual H atoms

The OM(σ) is occupied by 2 é- since it has a lower energy than σ*

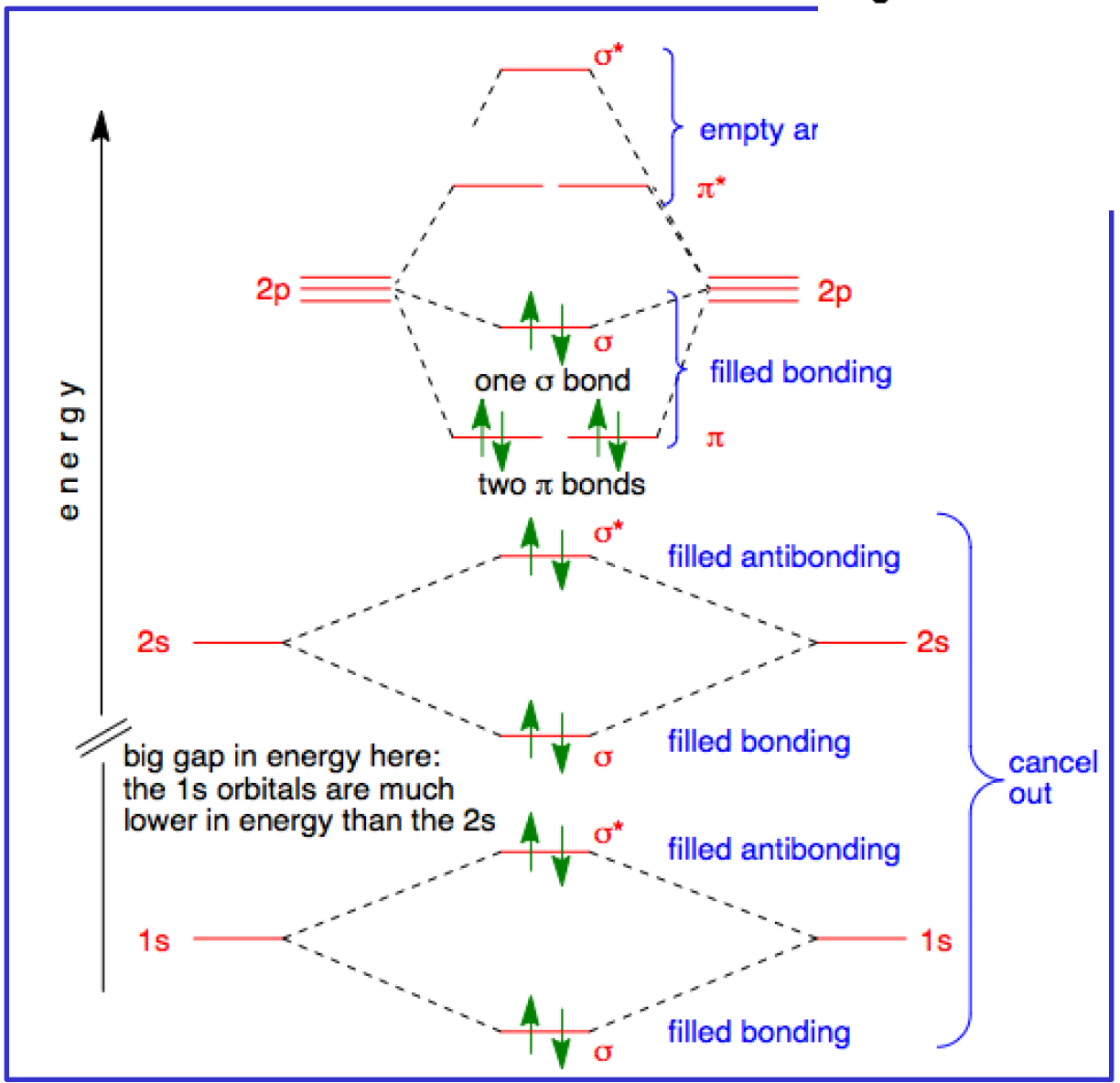
The system is stabilized by the formation of the molecule

The OM(σ*) has no é- : it is unoccupied

Molecular orbitals energy diagram for O_2



Molecular orbitals energy diagram for N_2



II) Generalisation

Formation of the A-B molecule :

n OA for atom A
and
m OA for atom B,

Each OA couple (one for each atom) rearrange itself in 2 OM
(1 bonding and 1 antibonding)

⬇

n+m OM

The number of electrons must be conserved (= $e^-_A + e^-_B$)
The electrons occupy the OM according to the same rules (Hund et Pauli) as for the atoms.
OM of lower energy are filled first

Molecular orbitals of type σ and π

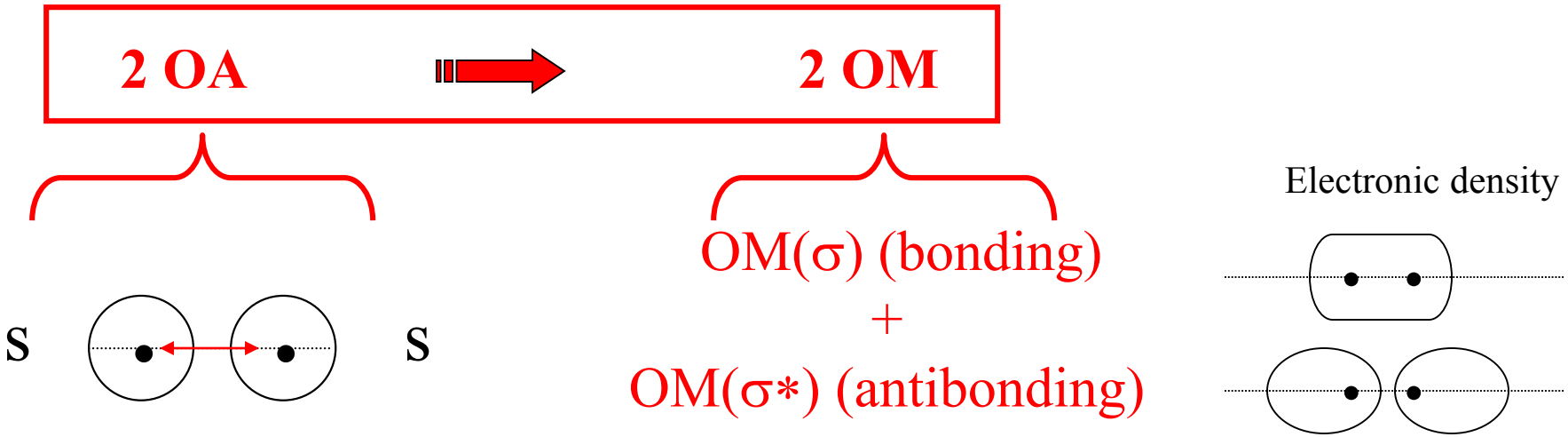
They are characterized by different geometrical overlap of the atomic orbitals

Molecular Orbitals of type σ

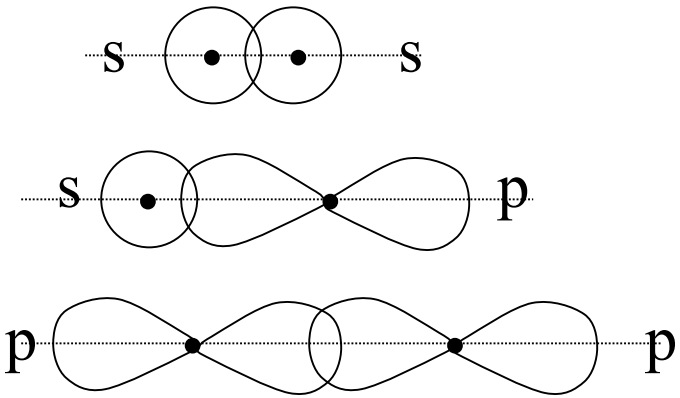
≡ OM formed by the overlap of two approaching OA

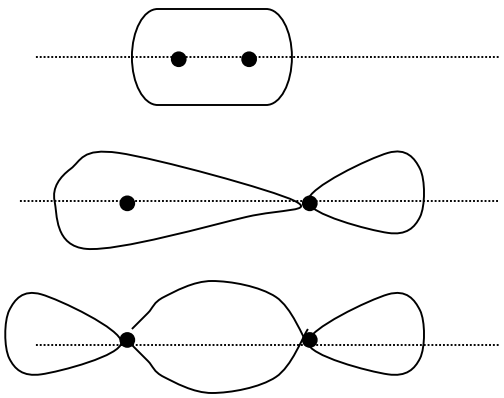
Along a common axis

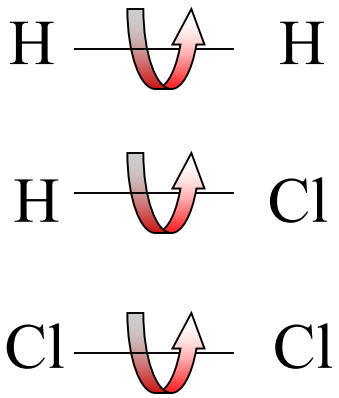
(AXIAL OVERLAP)



Molecular orbitals of type σ :







- Characterized by :
  An axial symmetry around the axis formed by both nuclei

- The rotation of the atoms around the bonding axis does not require any energy

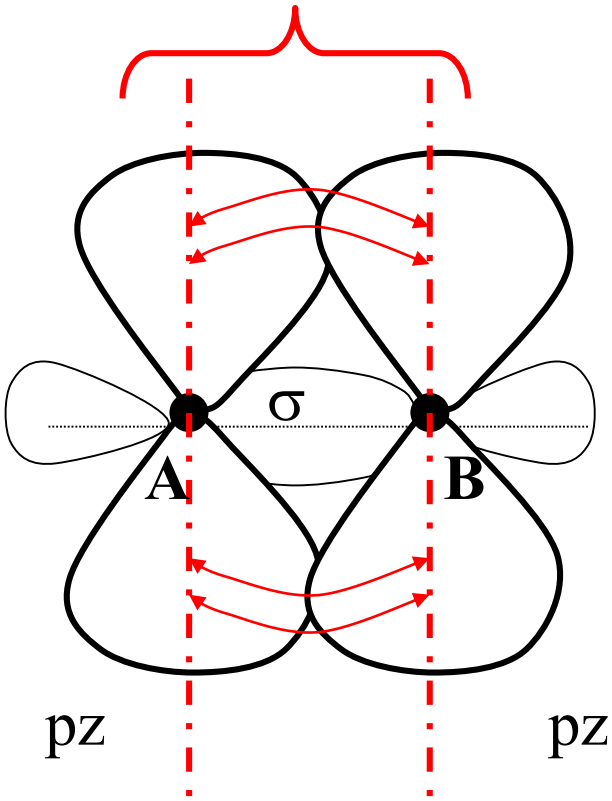
FREE ROTATION of the A – B $^{\sigma}$ bonding

Molecular orbitals of type π

During the formation of a (σ) type OM through the overlap of 2 OA of type (px) from 2 atoms A and B, the py and pz orbitals also get closer but they do not interact along a common axis

There is a **LATERAL OVERLAP**

2 OA → **2 OM**

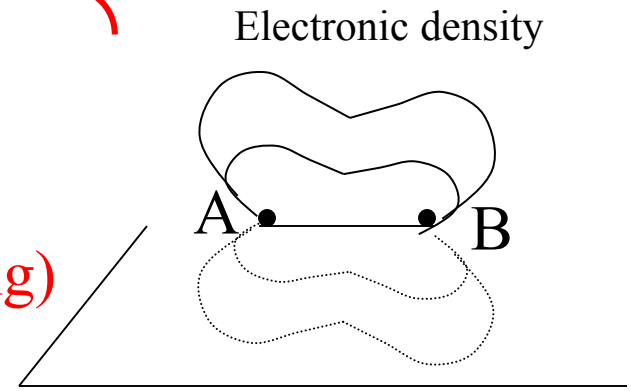


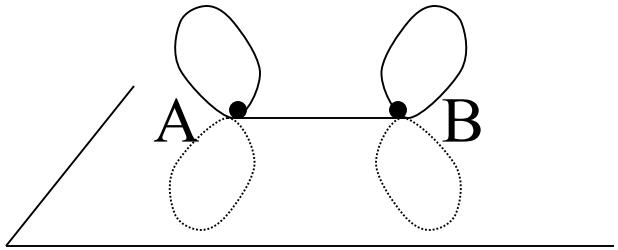
OM(π) (bonding)

+

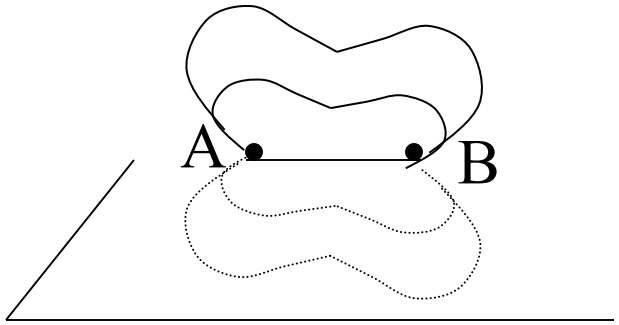
OM(π*)

(antibonding)





Molecular orbitales of type π :



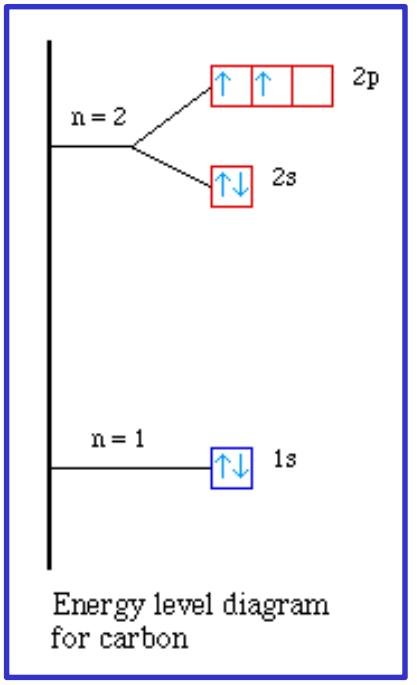
- A plane symmetry is formed: a strong electron density is present above and below the plane implying strong reactivity in those zones.

- Without any energy supply, both atoms are blocked in a particular geometry // (OA py ou pz axis)

RIGID BONDING A - B $^{\pi}$

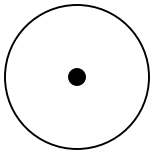
III) Hybridation of molecular orbitals

Formation of methan CH_4 (tetrahedral geometry) ≡ creation of 4 C-H bonding



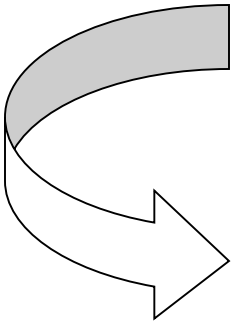
Hydrogen in the fondamental state: $1s^1$

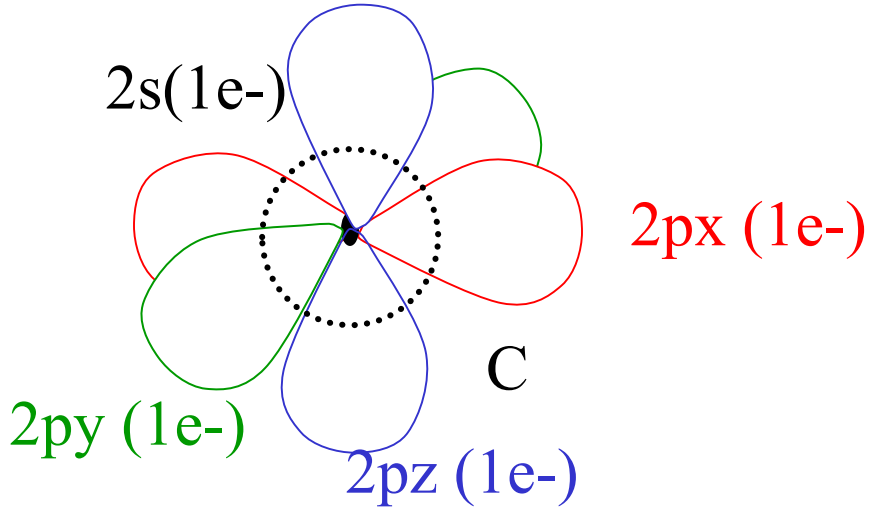
1 é- in s type **atomic orbitals** (OA)

4 x  1s (1e-)

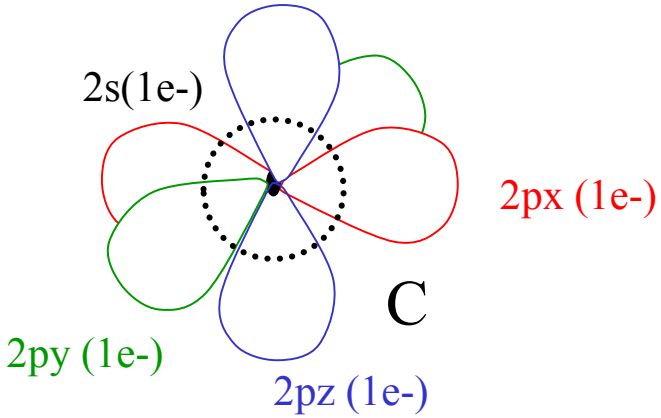
Carbon in fondamental state : $1s^2\ 2s^2\ 2p^2$

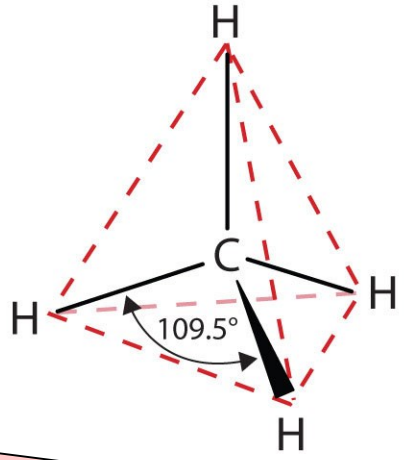
4 é- : { 2 in type s **atomic orbitals**; 2 in type p **atomic orbitals**





Carbon OA





HYBRIDATION
Energetic and spatial rearrangement

Hybrid Carbon OA

≡ 4 symetric **Molecular orbitals organised**
and directed towards the corners of a regular tetrahedron

Formation of the 4 C-H hybrid bonding of CH_4

Chapter 11 : Molecular bondings in the wave model

The hydridation of atomic orbitals concerns very often the s and p orbitals of 2nd period elements like:

C, N and O

mainly 3 types of hybridation exist

written

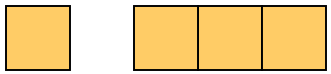
sp^3, sp^2 et sp

For molecules of following periods(n=3,4..) hybridations implying orbitals exist and are written

d^2sp^3, sp^3d, sp^3d^2, ...

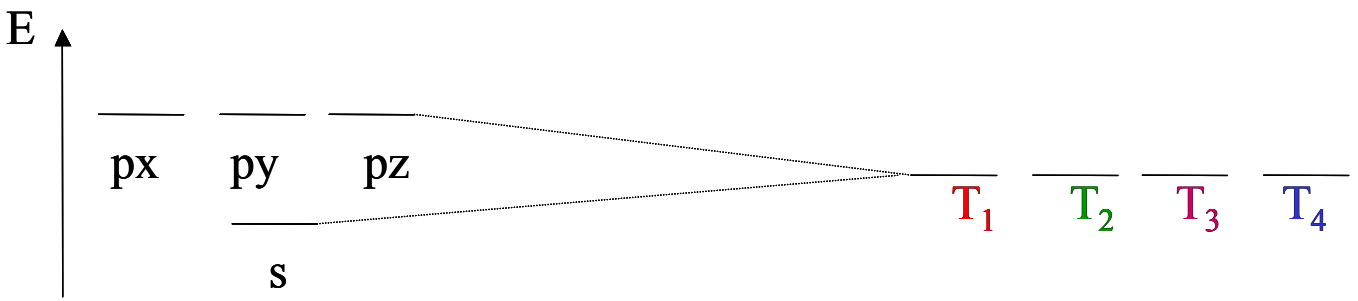
III-1) Hybridation sp^3

1 OA (s)
+
3 OA (p)



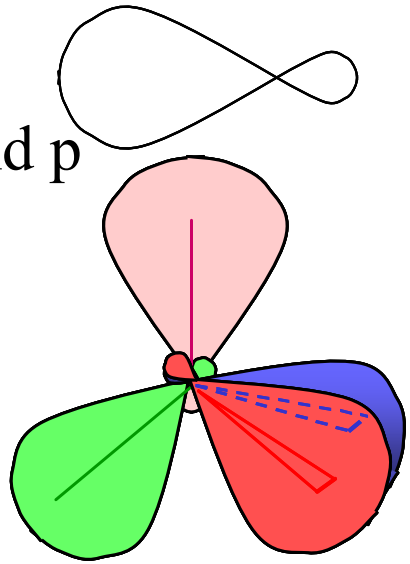
hybridation

4 new OA
≡
hybrid OA written sp^3

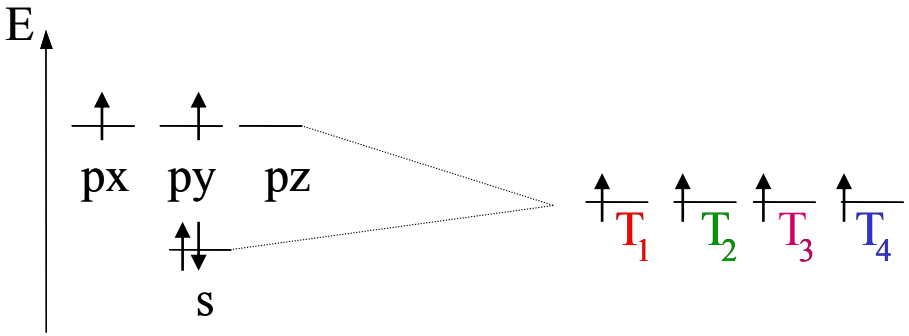


sp^3 orbitales are identical and have
the same energy intermediate between the s and p
energy level of the fundamental configuration

directed towards the cormer
of a regular tetrahedron.



Exemple 1 : CH_4 molecule

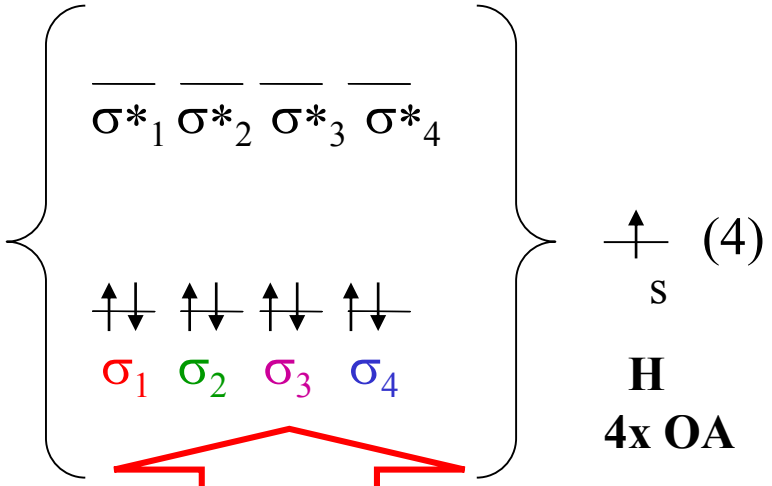


C in fondamental state

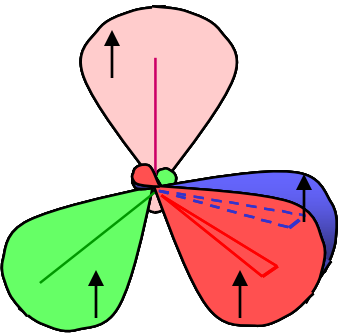
$_6C$: $1s^2$ **$2s^2$ $2p^2$**

C in hybrid sp^3

4 hybrid OA



Energy diagram for the 8 OM of CH_4

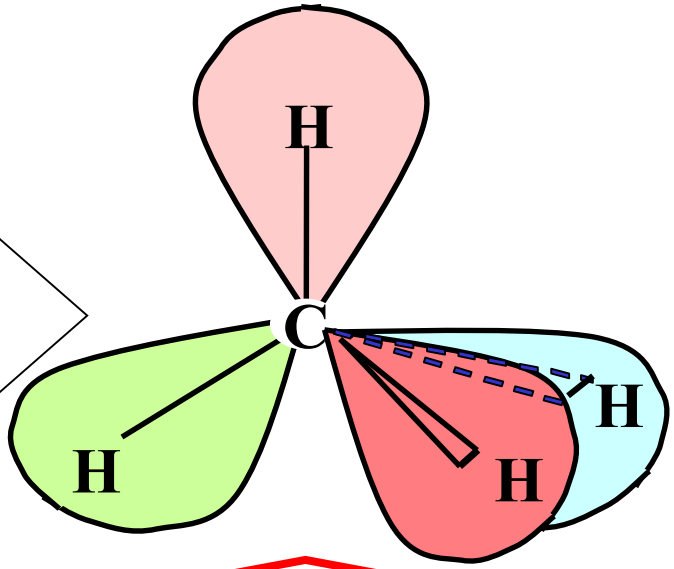


hybrid sp^3 OA of C

+ 4 times

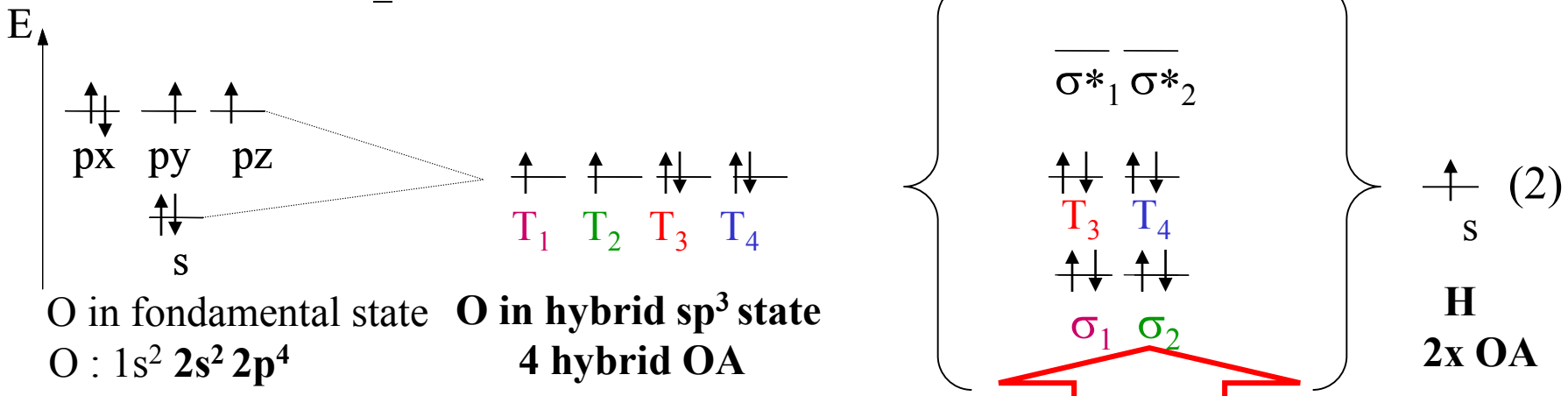
4 OA s of H

formation of type σ bonding

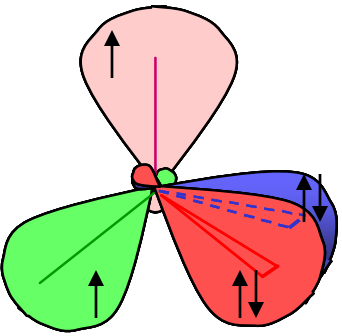


OM of CH_4

Exemple 2 : H_2O molecule



Energy diagram for the 6 OM of H_2O

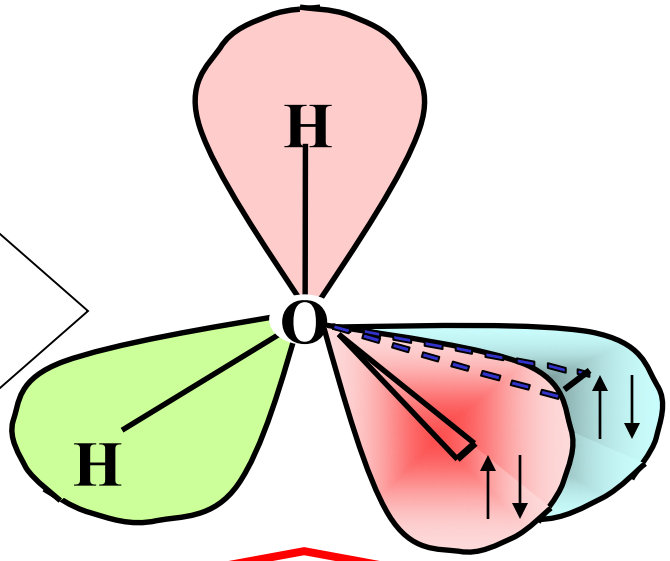


hybrid sp^3 OA of O

+ 2 times ↑

2 OA s of H

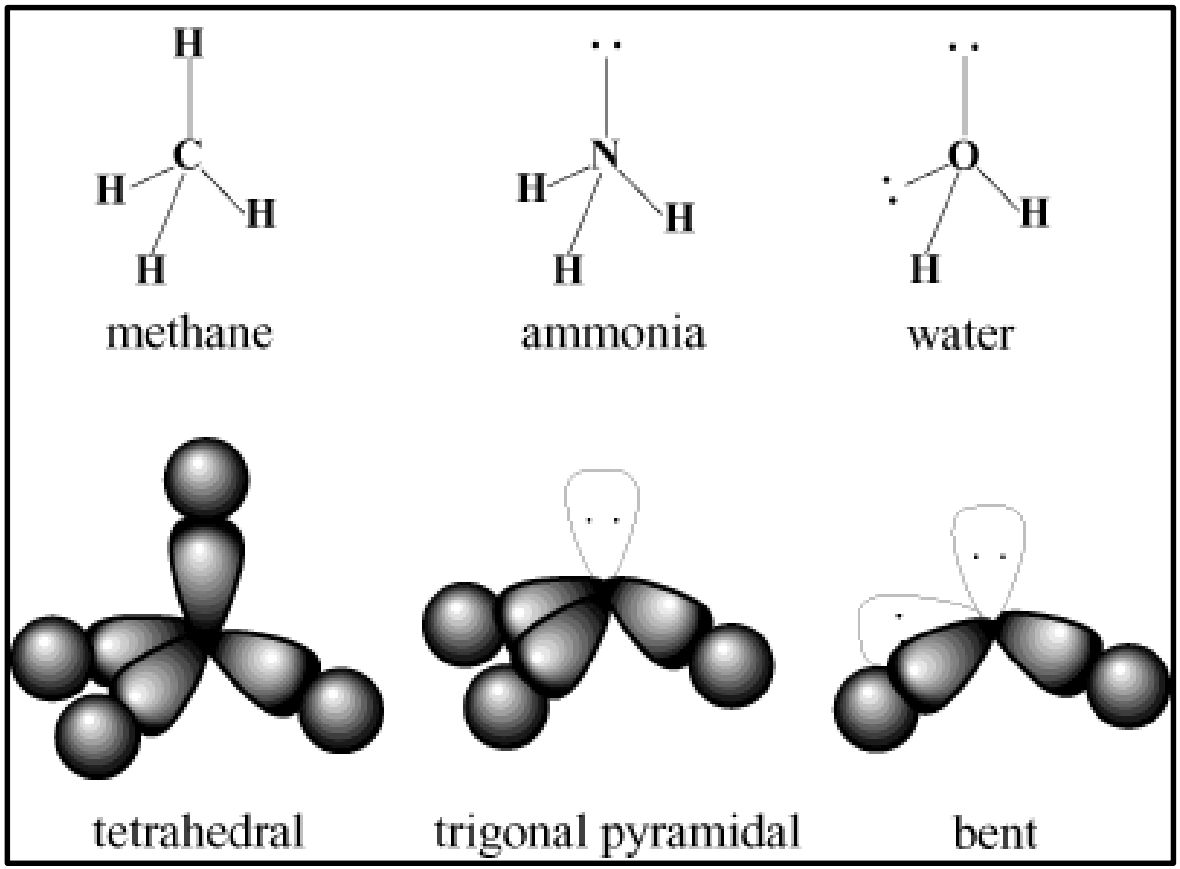
formation of type σ bonding



OM for H_2O

Hybridation sp^3 : Summary

- **SINGLE bonds**
- **TETRAHEDRAL** geometry
- bonding angles of **109°**

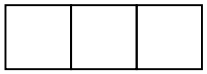


III-2) Hybridation sp^2

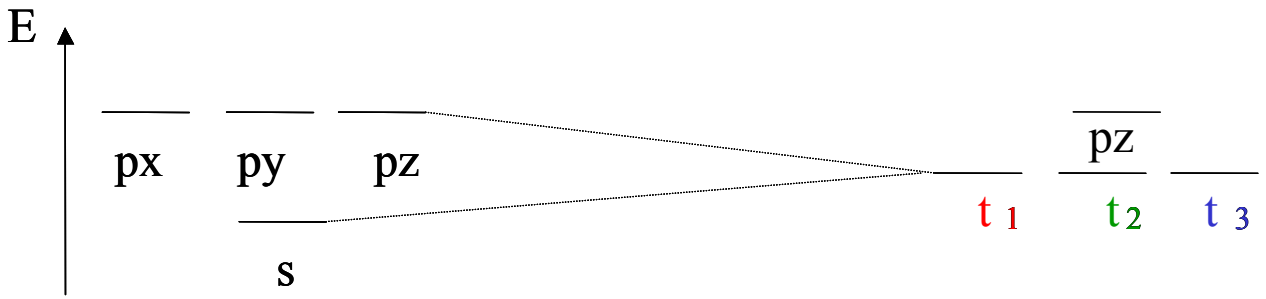
1 OA (s)
+
2 OA (p)

hybridation

3 new OA
≡
OA hybrids written sp^2



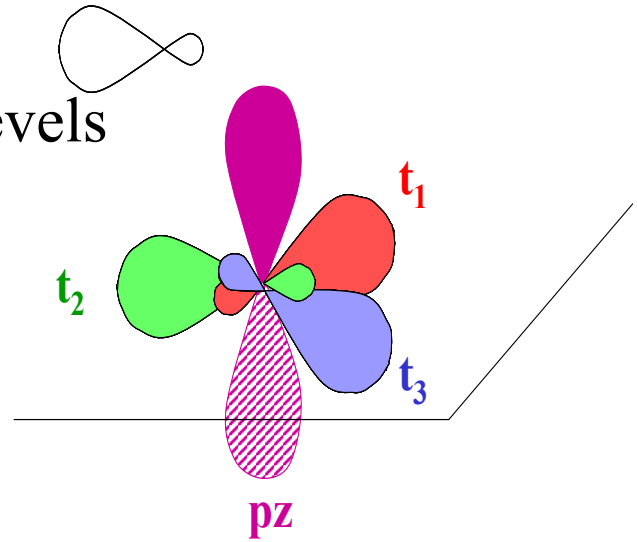
+ pz



Atom in fondamental state

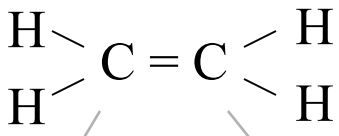
atom in hybrid sp^2 state

3 OA sp^2 (t_1, t_2 et t_3) have identical shape
the same energy intermediate between starting levels
They have 120° angles with each other
In the same plane
One pz OA subsists and is not modified
It is directed ⊥ to the plans of the sp^2 orbitals



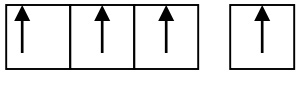
Example : molecule C_2H_4 (ethylene)

LEWIS diagram:



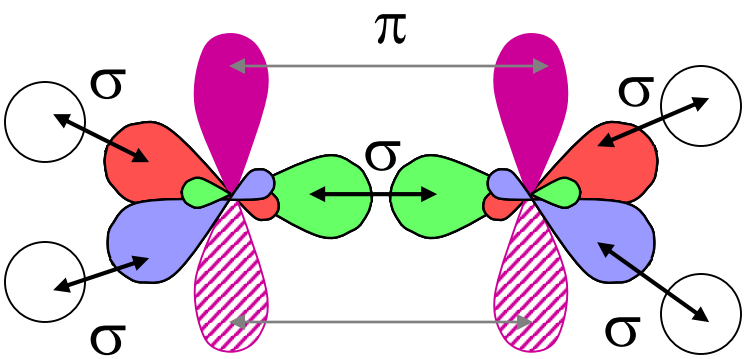
Geometry (VSEPR) : AX_3 AX_3 : triangular plan

Hybridation : sp^2 sp^2



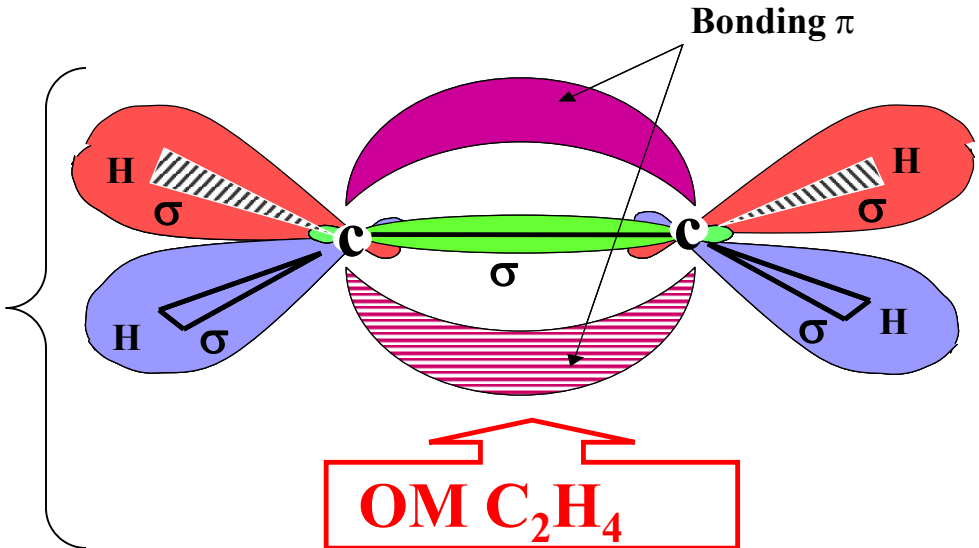
3 σ bonding

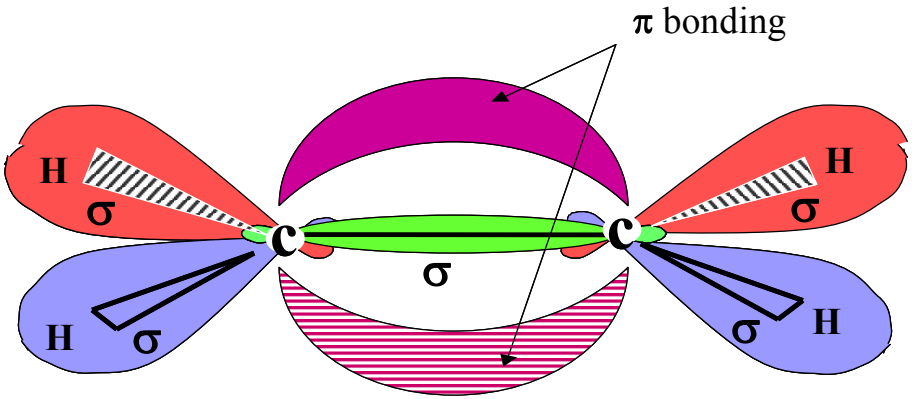
1 π bonding

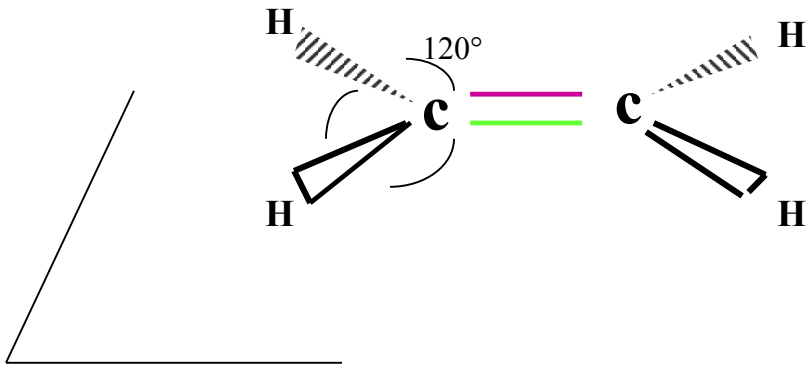


OA diagram

formation of type σ and π **bonding**







Axial overlap sp^2 C(1)- sp^2 (C2)

σ C-C bonding

4 axial overlaps sp^2 C- (1s) (H)

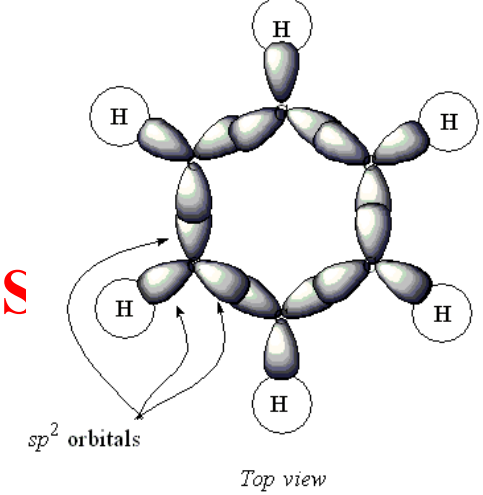
4 σ C-H bondings

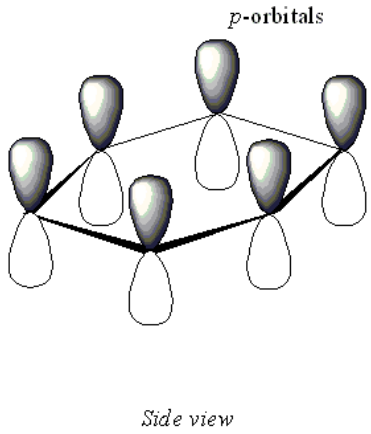
Lateral overlap p_z C(1)- p_z (C2)

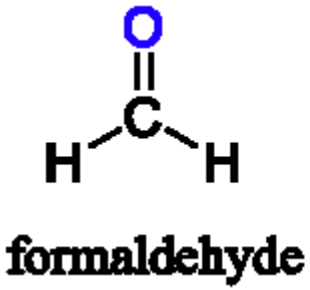
Π C-C bonding

Hybridation sp^2 : Summary

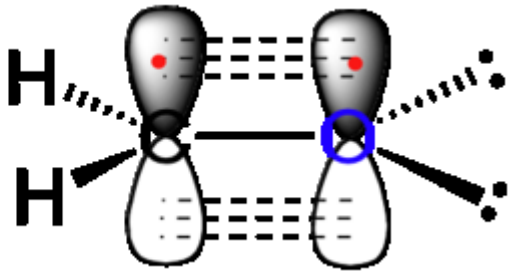
- Formation of **DOUBLE BONDS**
- **PLANAR MOLECULES**
- bonding angles of **120°**







formaldehyde

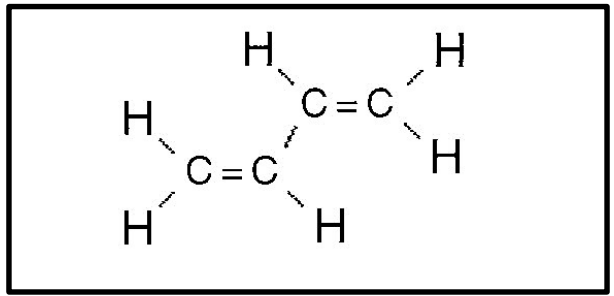


Le benzene

QCM 3

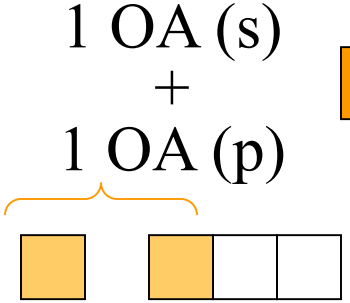
Dans la molécule de butadiène ($CH_2 = CH - CH = CH_2$), tous les atomes de carbone sont hybridés sp^2.

a. Vrai **b.** Faux



III-3) Hybridation sp

1 OA (s)
+
1 OA (p)

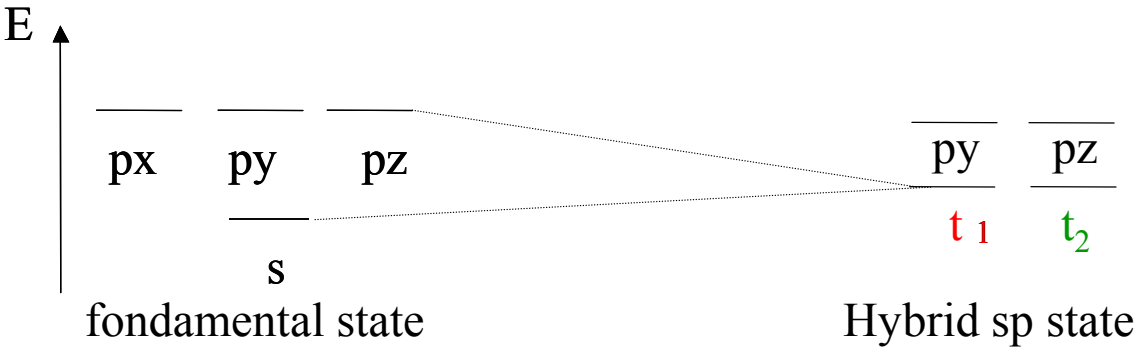


hybridation

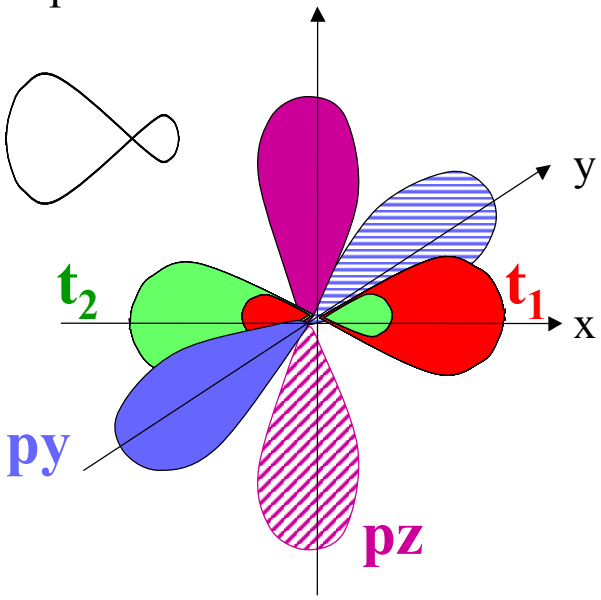
2 new OA
≡
hybride OA sp

+

py et pz
remain



2 OA sp (t_1 and t_2) are identical
With the same energy,
intermediate between two levels
Directed 180° from each other
Along a common axis (x for example)
2 OA remain unmodified (py et pz) along y and z axis

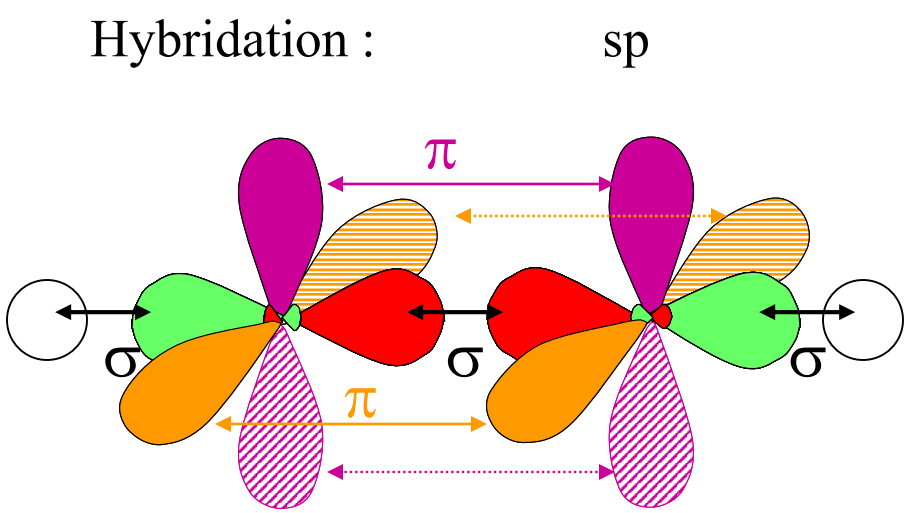


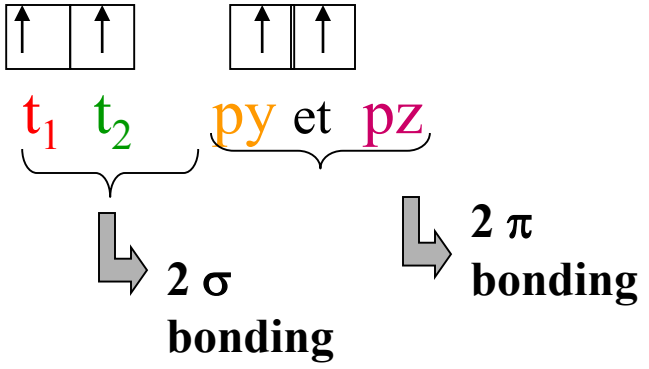
Example : molecule C_2H_2 (acetylene)

LEWIS Diagram : $H - C \equiv C - H$

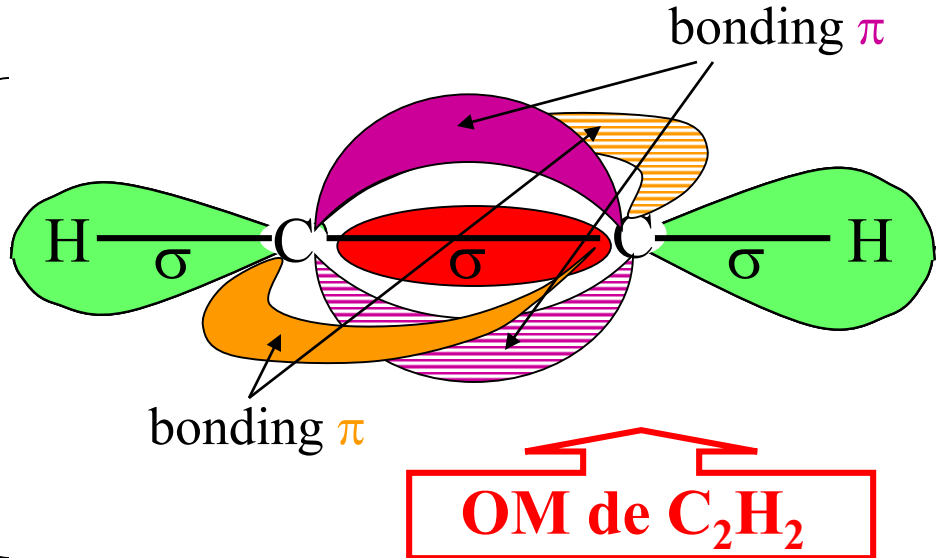
Geometry (VSEPR) : AX_2 AX_2 : linear

Hybridation : sp sp

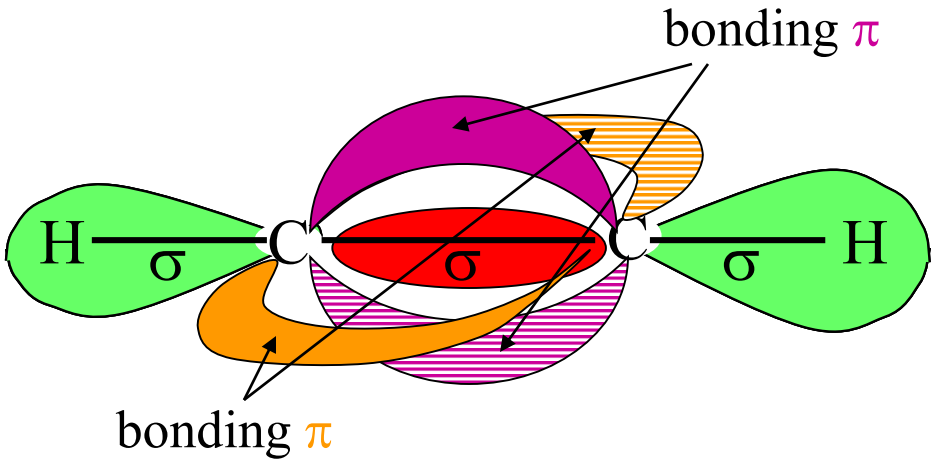




formation of type σ and π bonding



OM de C_2H_2



Axial overlap sp C(1)- sp (C2)

bonding **σ C-C**

2 axial overlap sp C- (1s) (H)

2 bonding **σ C-H**

Lateral overlap p_z C(1)- p_z (C2)

first bonding **Π C-C**

Lateral overlap p_y C(1)- p_y (C2)

2nd bonding **Π C-C**

Hybridation sp : Summary

- formation of **TRIPLE BONDS**
- formation of **LINEAR MOLECULES**
- bonding angles of **180°**

Hybridation sp : Summary

formation of **TRIPLE BONDS**
formation of **LINEAR MOLECULES**
bonding angles of **180°**

Hybridation sp^2 : Summary

Formation of **DOUBLE BONDS**
PLANAR MOLECULES
bonding angles of **120°**

Hybridation sp^3 : Summary

SINGLE bonds
TETRAHEDRAL geometry
bonding angles of **109°**

Chapter 11 : Molecular bondings in the wave model

Exercice 2

a. Préciser l'état d'hybridation de chaque atome de carbone et de l'atome d'azote dans la molécule d'acétonitrile CH_3CN. Représenter les OA des différents atomes avant formation des liaisons

b. Expliquer la formation des différentes liaisons intervenant dans cette molécule.

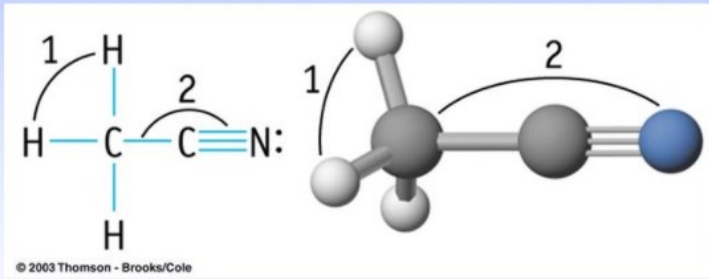
c. Les 6 atomes de cette molécule sont-ils coplanaires ? Pourquoi ?

Acetonitrile, CH_3CN

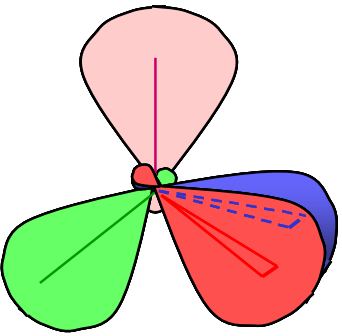
Define bond angles 1 and 2

Angle 1 = 109°

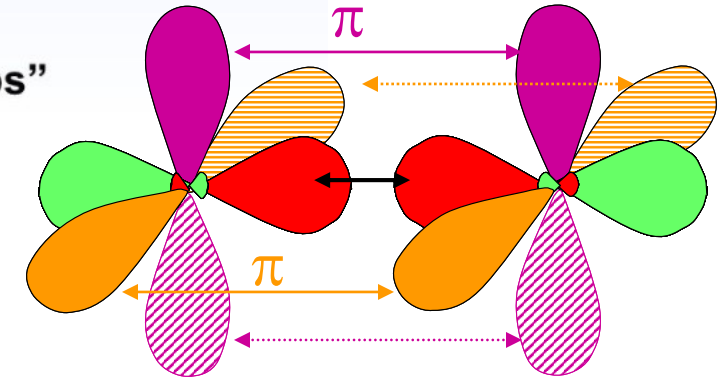
Angle 2 = 180°



One C is surrounded by 4 electron "lumps" and the other by 2 "lumps"



hybrid sp^3 OA of C



Chapter 11 : Molecular bondings in the wave model

Exercice 3

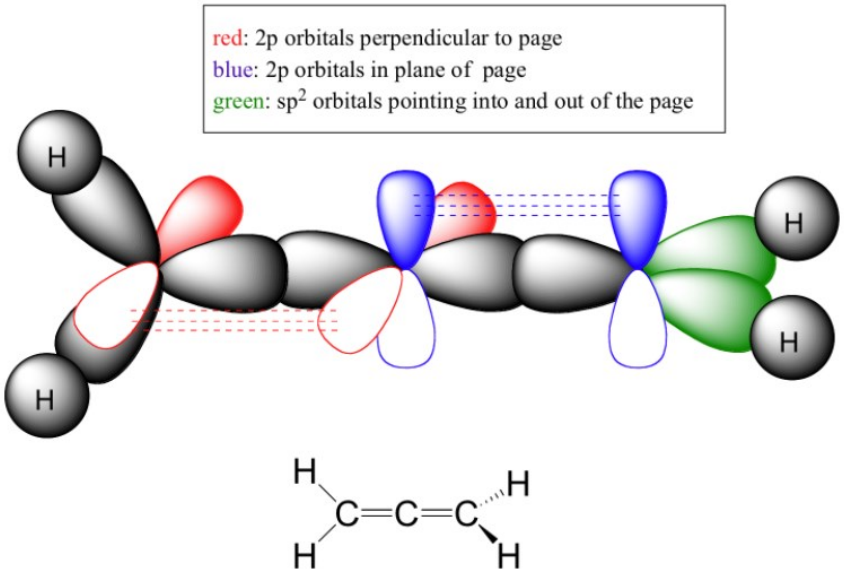
a. Dans la molécule $H_2C{=}C{=}CH_2$, donner l'état d'hybridation des atomes hybridés.

b. Dessiner les orbitales atomiques avant recouvrement des orbitales.

c. Expliquer comment se forment les liaisons (type de recouvrement et type de liaison formée).

d. Représenter les orbitales moléculaires (pour les liaisons Π, on pourra utiliser une représentation schématique).

e. Quelle géométrie peut-on prévoir autour de l'atome central de cette molécule ?



Notice that the central carbon is sp-hybridized, while the two end carbons are sp^2-hybridized: the left one with the three sp^2 hybrid orbitals in the plane of the page, the right one with two if the three orbitals pointing into or out of the plane of the page.

Chapter 11 : Molecular bondings in the wave model

Soit la molécule suivante, de formule semi-développée : $N \equiv C - CH_2 - CH = CH - CHCl - CH = O$.

IV.1. Numéroter les atomes de carbone à partir du groupement nitrile et donner l'état d'hybridation des six atomes de carbone dans cette molécule. Les justifier.

QCM 26 On considère la molécule d'éthylène (éthène) C_2H_4, quelle(s) est (sont) la (les) proposition(s) exacte(s) :

- **a.** Toutes les orbitales moléculaires de la molécule sont situées dans un même plan
- **b.** La molécule est plane
- **c.** Du recouvrement latéral des orbitales atomiques résiduelles P_z des 2 atomes de carbone de la molécule résulte la formation d'une liaison de type π
- **d.** Du recouvrement axial des orbitales atomiques hybridées sp^2 des 2 carbones de la molécule résulte la formation d'une liaison de type σ
- **e.** Les angles de liaison sont tous égaux à 120 °

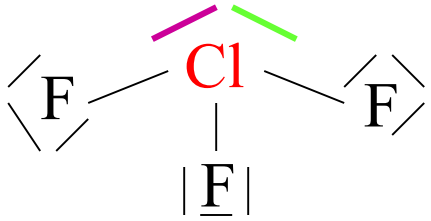
III-4) Other hybridation types

III-4-a) sp^3d

Example : ClF_3 (trifluorure de chlore)

Cl linked 3 F

Lewis :

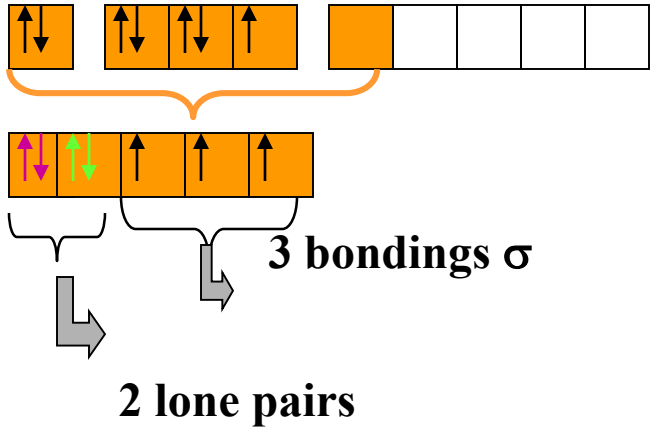


octet rule is not followed

For the formation of 3 type σ bondings: 3 single electrons forming bonds with single electrons from each of the 3 atomes of F

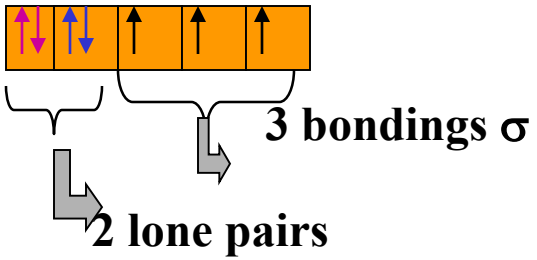
Fondamental state $_{17}Cl$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5\ 3d^0$

Hybrid state of Chlore :
5 OA type sp^3d



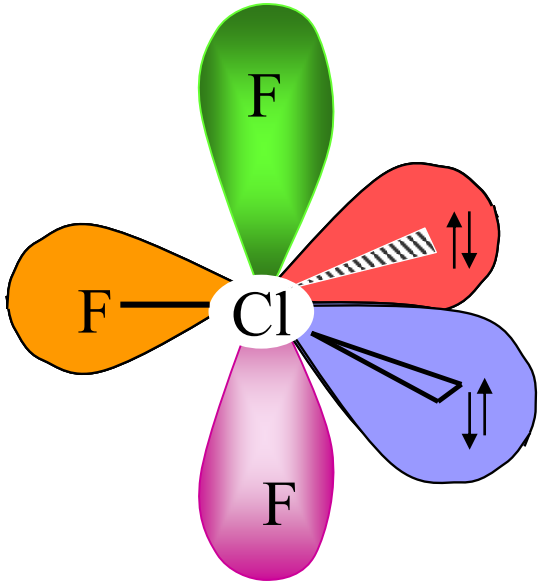
sp^3d

Hybrid state of Chlore :
5 OA of type sp^3d



Same shape
same energy
organised in space in the most symmetrical way

The molecule ClF_3 has a T shape

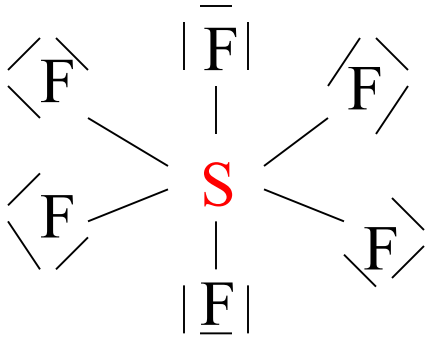


III-4-b) sp^3d^2

Example : SF_6 (hexafluorure de soufre)

S linked to 6 F

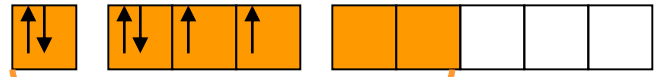
Lewis :



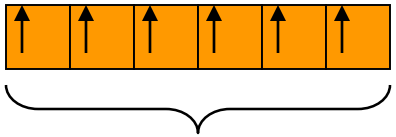
octet rule is not followed

For the formation of 6 σ bonds: 6 single electrons forming bonds with single electrons from each of the 6 atomes of F

Fondamental state $_{16}S$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$



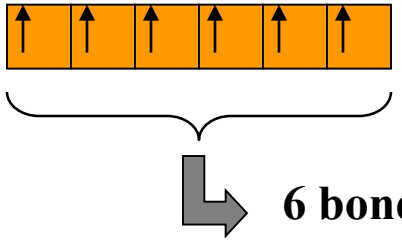
Hybrid state of sulfur :
6 OA type sp^3d^2



6 bondings σ

sp^3d^2

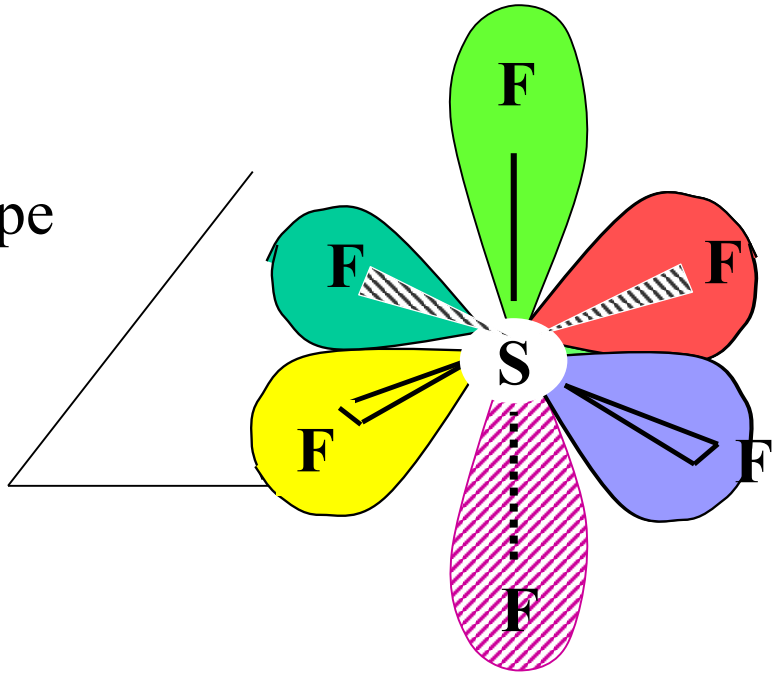
Hybrid state of sulfur :
6 OA type sp^3d^2



6 bondings σ

Same shape
same energy
organised in space in the most symmetrical way

The molecule SF_6 has a pyramidal shape with a square basis
(see theory VSEPR ≡ AX_6)

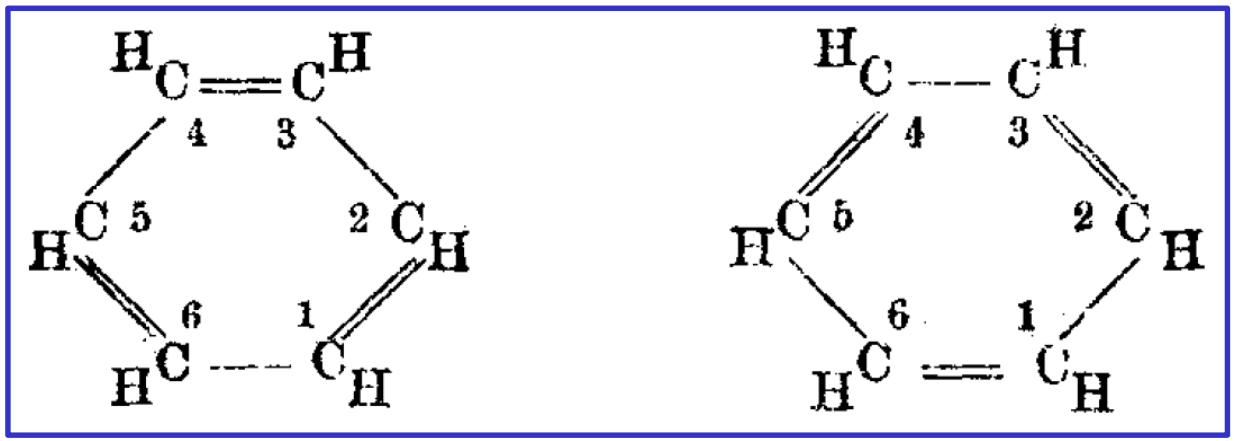


IV) Intermediate bondings :

delocalized electrons

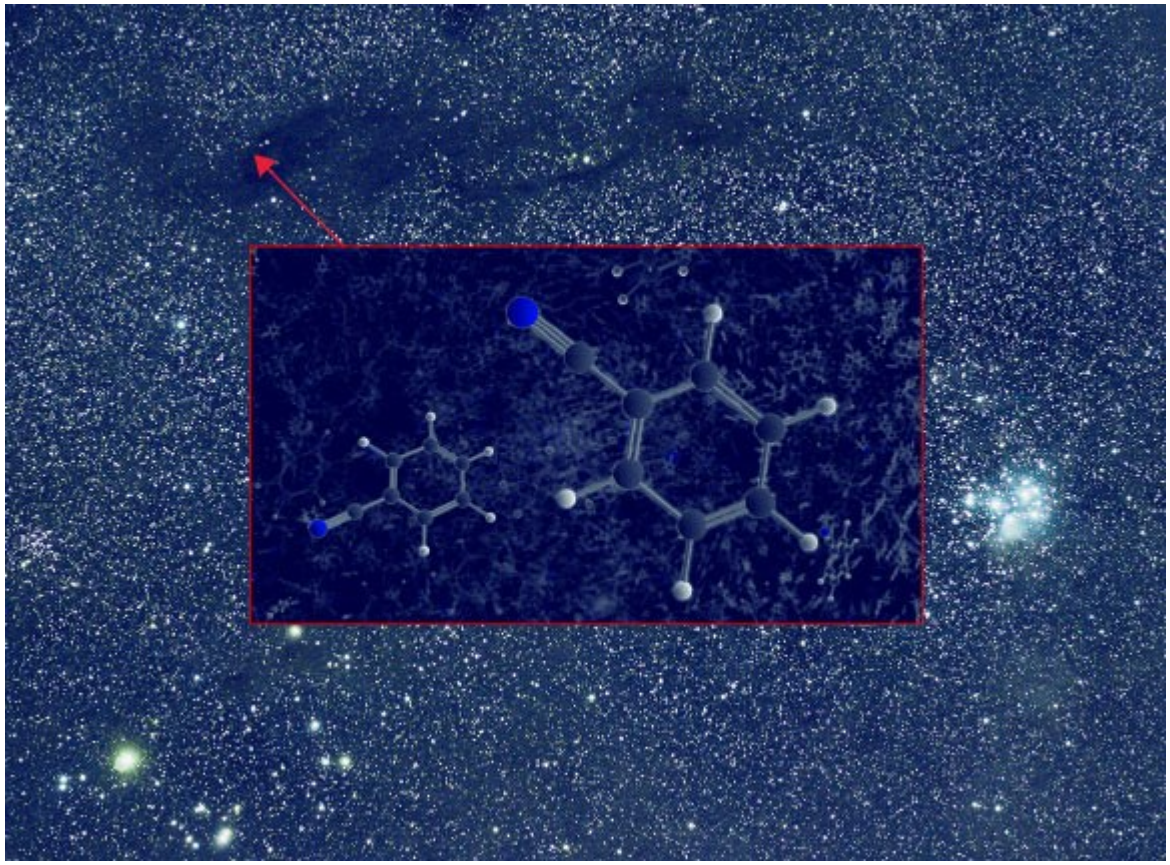
Resonance (or mesomerism)

En **1865**, Kékulé is searching for the structure of benzene, molecule with formula C_6H_6. Linear or ramified strcuture do not satisfy the monovalence of hydrogen (H) and mostly the tetravalence of carbone (C) !!

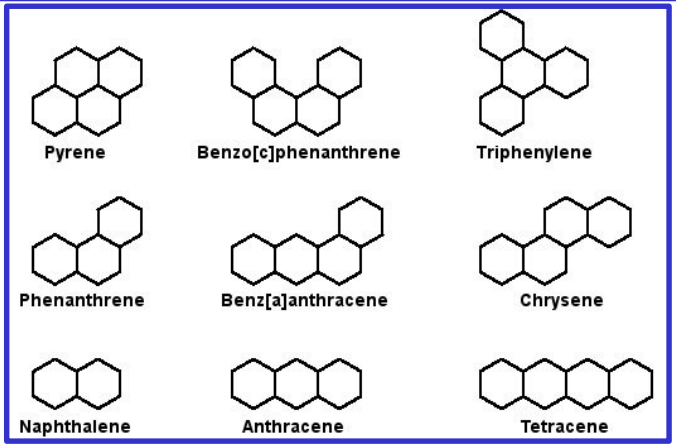


Chapter 11 : Molecular bondings in the wave model

Astronomers studying a well-known nearby cloud of interstellar gas with radio telescopes have detected the presence of benzonitrile (c-C_6H_5CN), an intriguing organic molecule that helps to chemically link simple carbon-based molecules and truly massive ones known as polycyclic aromatic hydrocarbons (PAHs). The finding marks the first time a specific aromatic molecule has been identified in space using radio spectroscopy.



polycyclic aromatic hydrocarbons (PAHs)



Chapter 11 : Molecular bondings in the wave model

In the LEWIS model, electrons are perfectly localized.

But the real distribution of the electrons is not always well represented by the Lewis model.

Molecules exist, where the electrons are not localized on a single bond or a single atom but shared by different bonds:

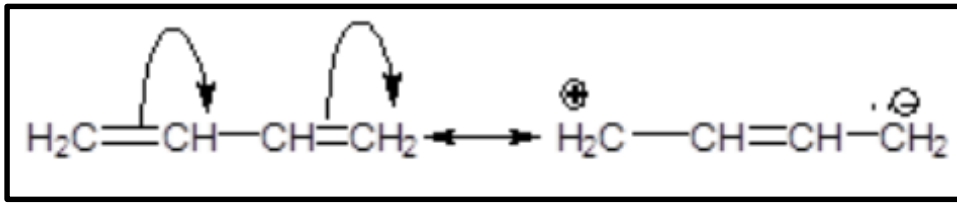
They are not localized on a single bond : delocalization

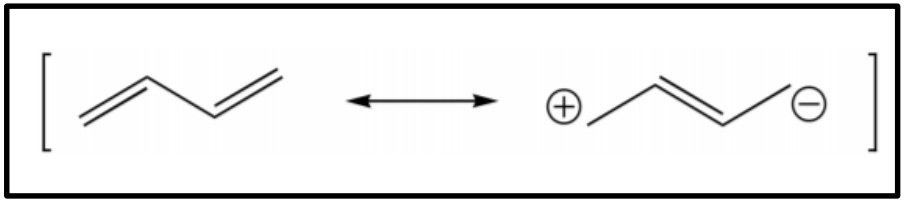
Those structures are described by an intermediate case between two Lewis description: a resonance hybrid or a conjugated system (mesomeric effect)

Different types of conjugated systems :

Alternance Π - σ - Π

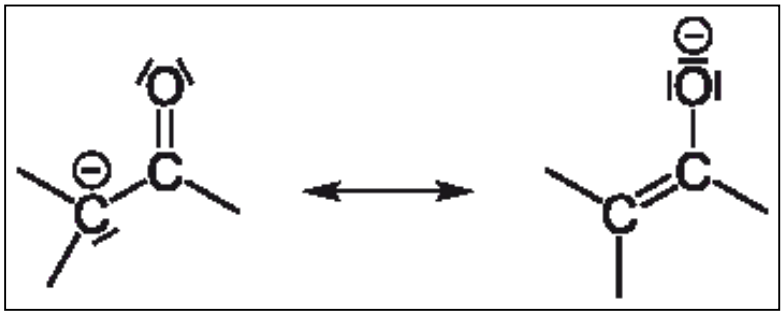
Ex: $C \overset{\Pi}{=} C \overset{\sigma}{-} C \overset{\Pi}{=} C$





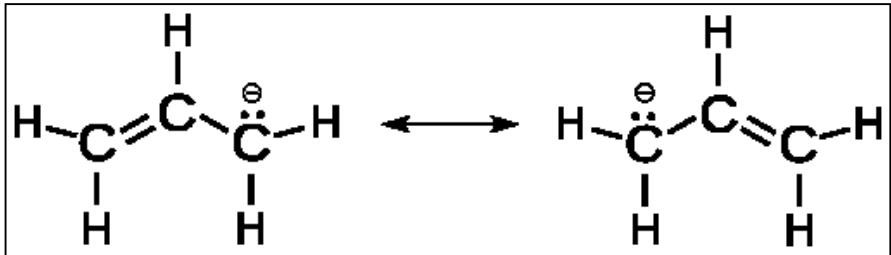
Alternance Π - σ - doublet non liant

Ex: $\underline{N} \equiv N^{+} - \underline{O}^{-}$

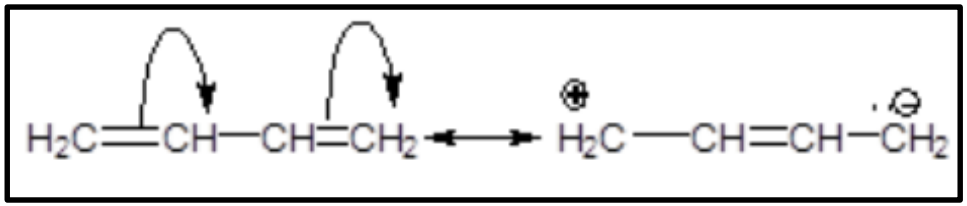


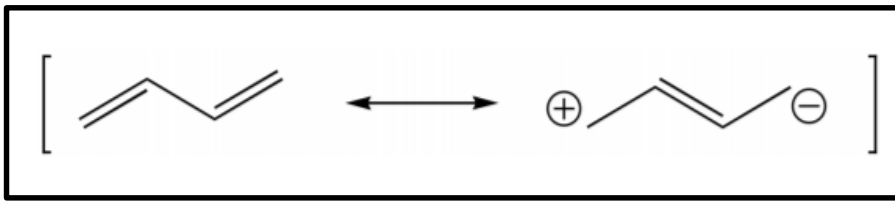
Alternance Π - σ - orbitale vide

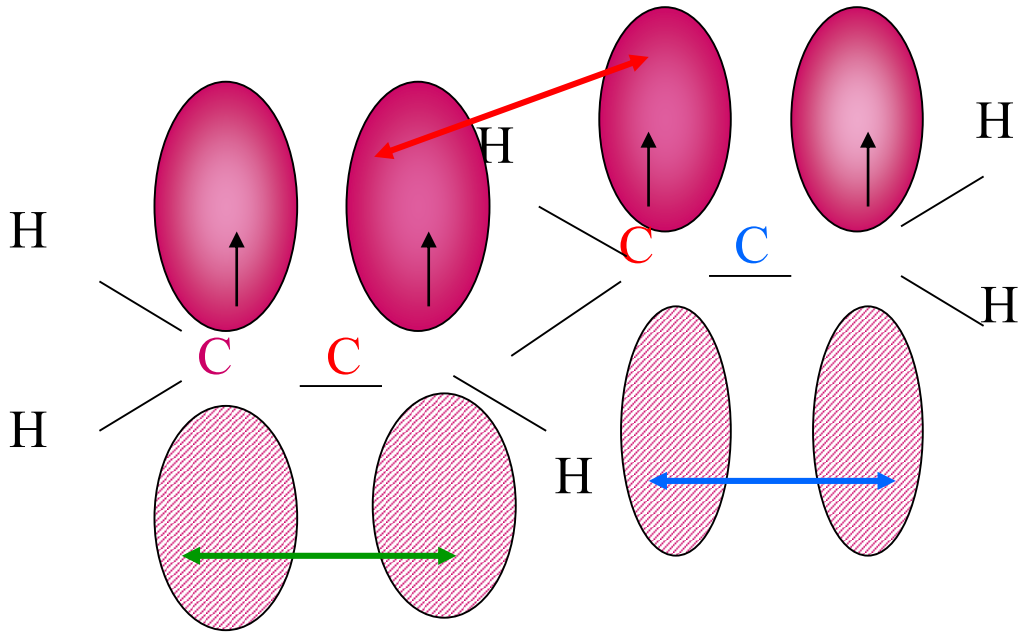
Ex: $A = B - C$



Conjugated systems :

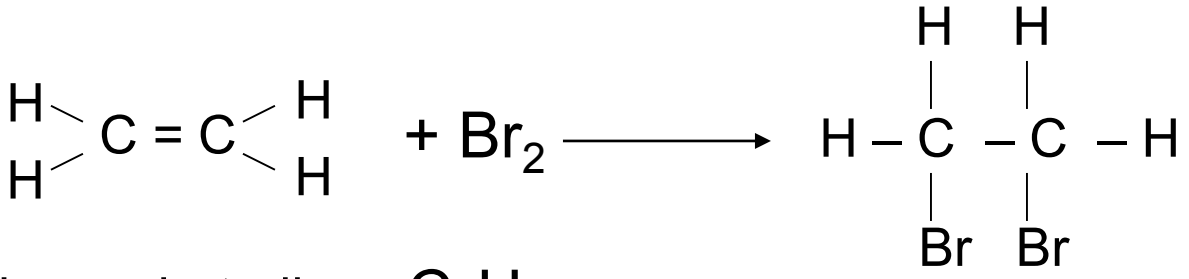




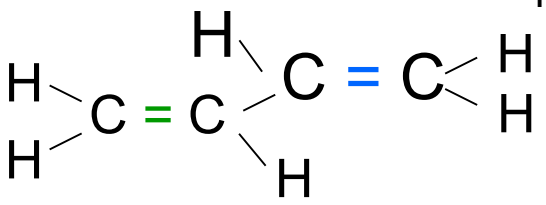


IV-1) Delocalization of electrons

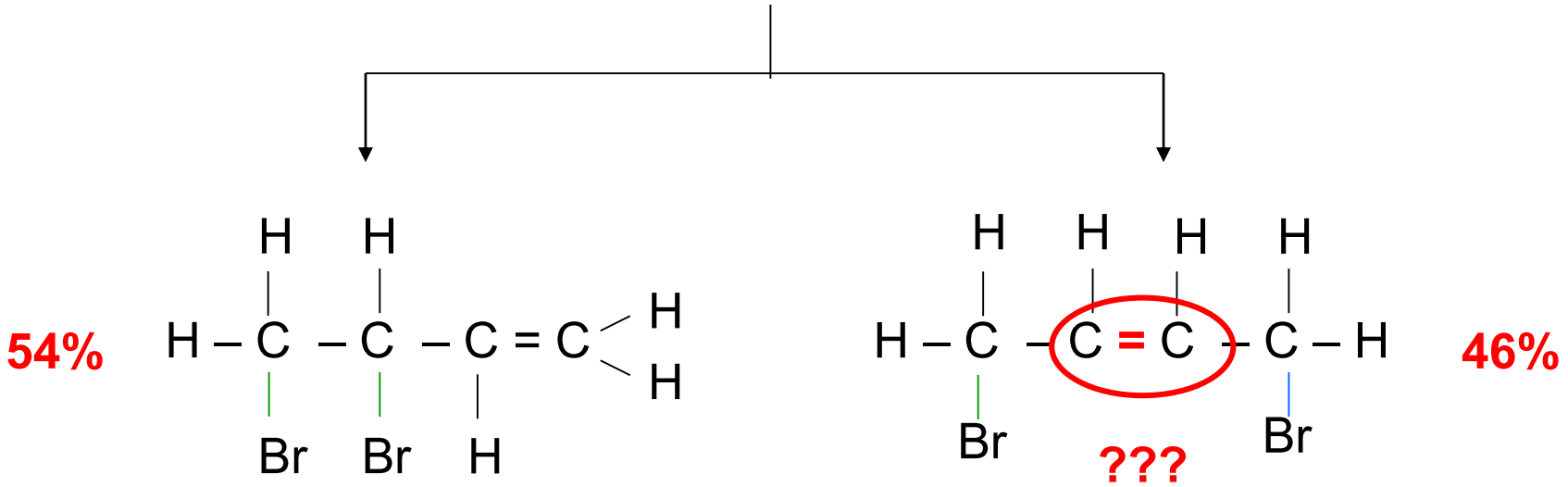
Addition of Bromine on the double bond of ethylene C_2H_4 :

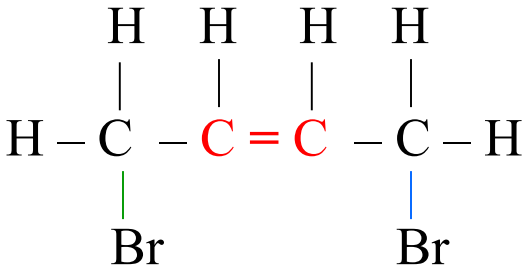


Addition of Bromine on butadiene C_4H_6 :



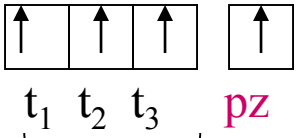
+ Br_2 (1 mole/mole)





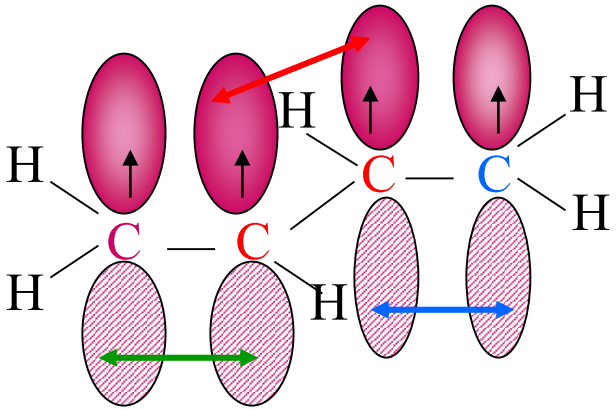
The formation of this molecule can only be understood in the case of an interaction between pz orbitals of the two carbons situated at the center of the molecule

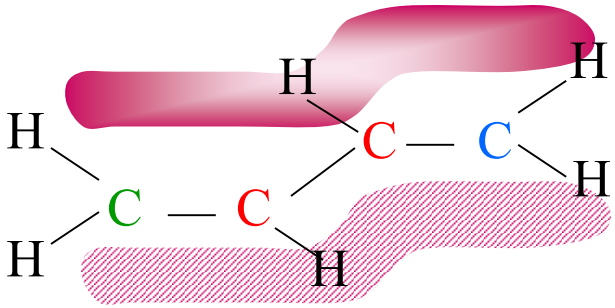
hybrid C sp^2



3 bonding σ

1 bonding π



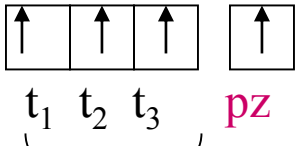


All π electrons belong collectively to the 4 C

The molecule becomes plane and rigid

Case of benzene: C_6H_6

6 hybrid C sp^2



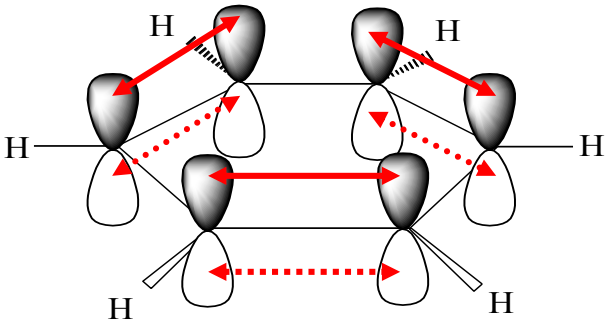
3 bonding σ

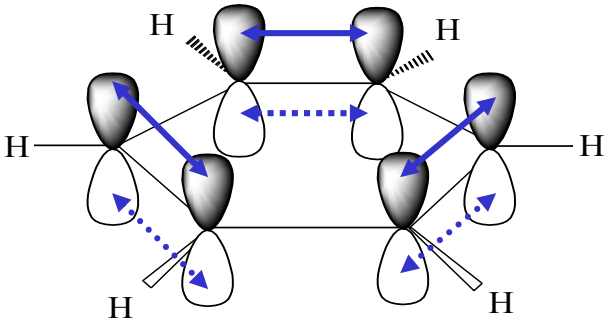
1 bonding π

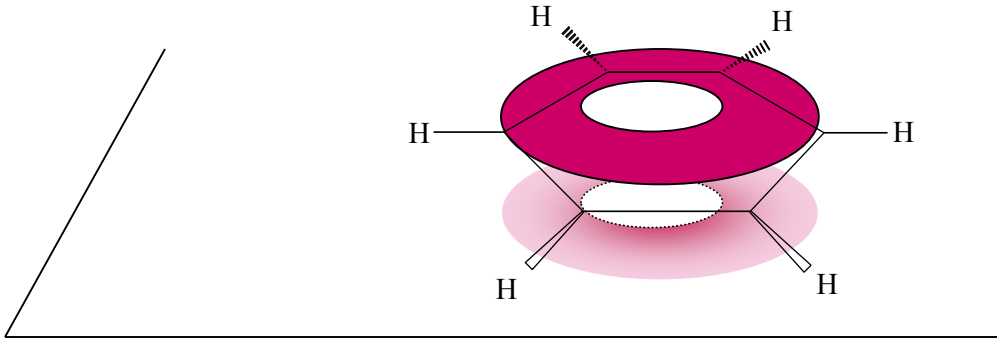
Geométry (VSEPR) :

AX_3 triangular plan

angle 120°







σ bonds

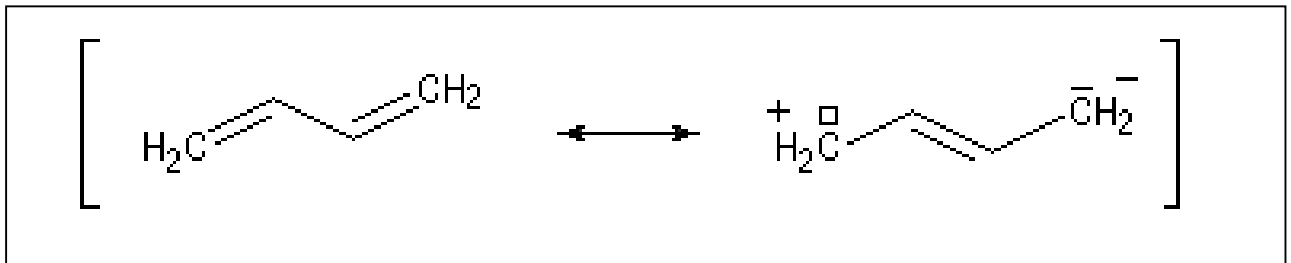
plane molecule

IV-2) Mesomerism (≡ resonance)

- It is a way of describing the delocalization of the electrons and keeping the rules of the Lewis representation.

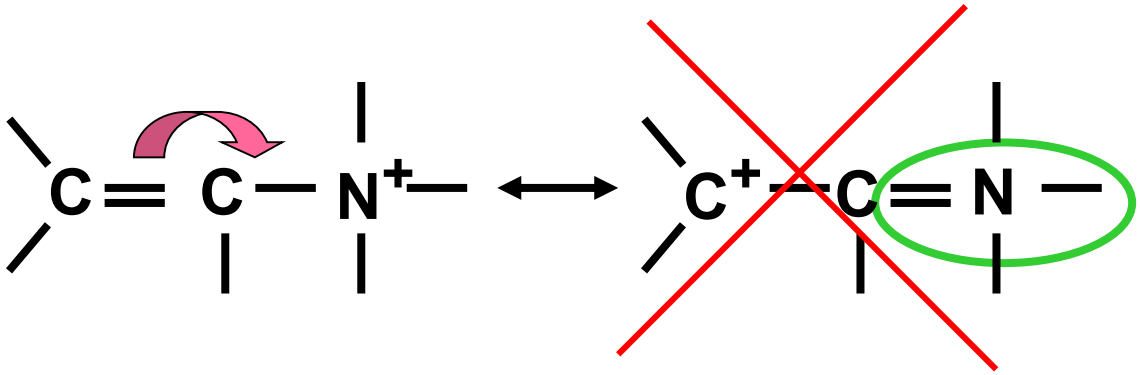
- Between the complexity of the molecular structure and the simplicity of the Lewis representation (OK in 90% of the cases), resonance cases are represented as resonance structure (« **formules limites** » ou encore « **formes mésomères** »)

- The real molecule is a **resonance hybrid** between those Lewis limit representation : the structure of the molecule is intermediate between those limit cases
- The symbol representing the resonance is: ↔



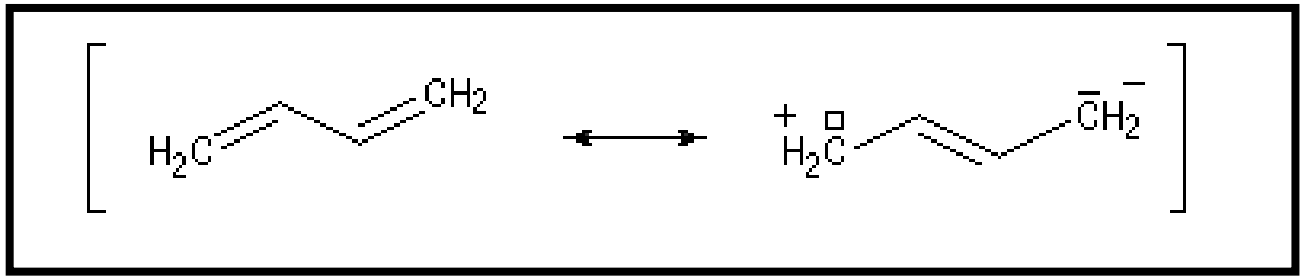
Mesomeric rules

- The Lewis limit representation must obey the octet rule for all elements of the second period (C, O, N).



octet rule is not followed

- The global charge must be preserved in all limit cases.



All limit forms are not equally probable.

Different limit forms have different weight :
Some forms are **more probable** and have a stronger weight because they are **more stable**.

Limit forms that have a stronger weight:

Those who include the highest number of bondings

(2 double bonds)

Example: butadiene

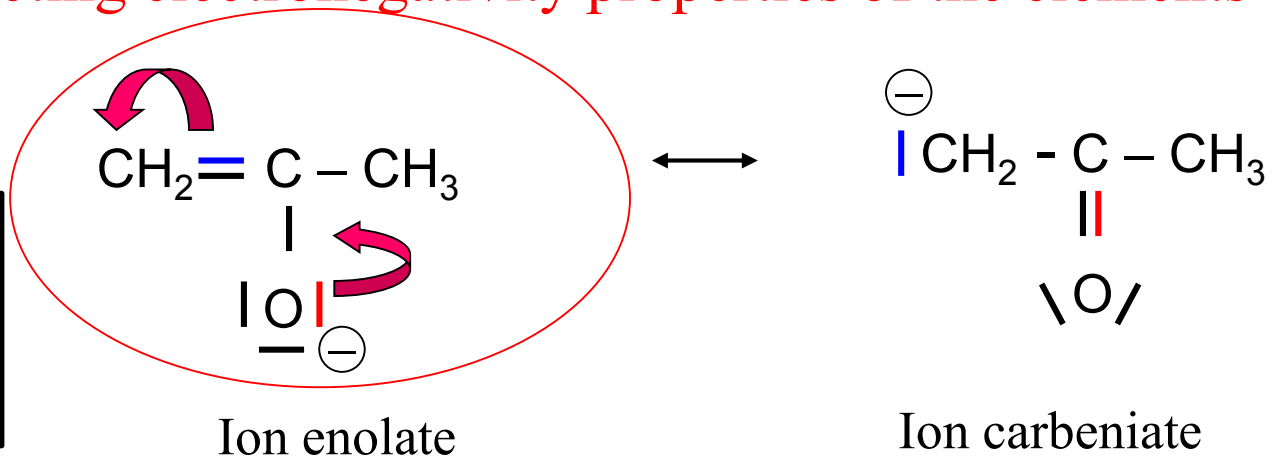
$\overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$ ⟷ $CH_2 = CH - CH = CH_2$ ⟷ $\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2$

(only one double bond)

Those respecting electronegativity properties of the elements

Exemple:

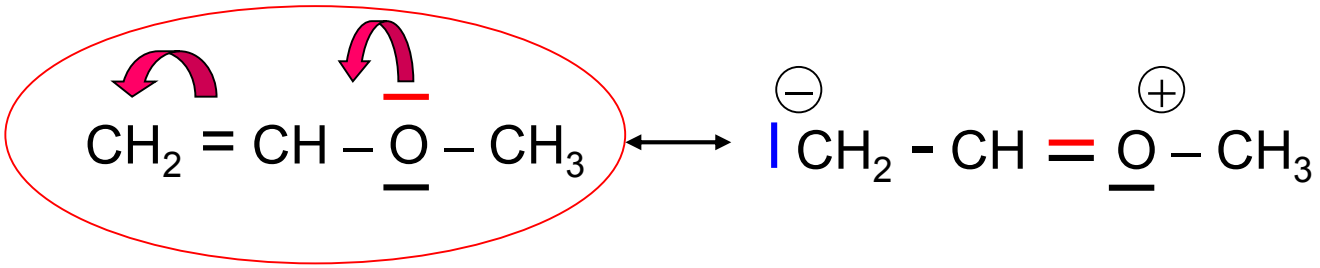
O more electronegative then C



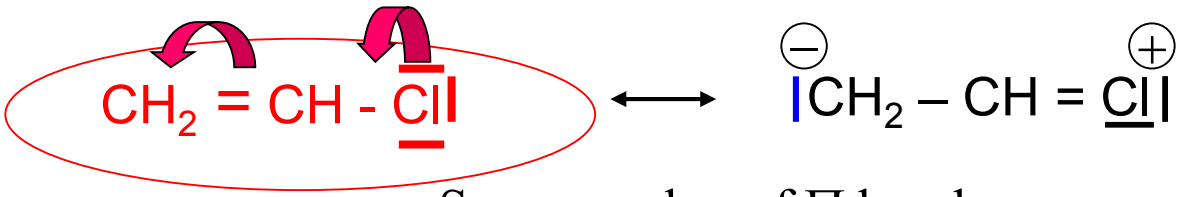
Ion enolate

Ion carbeniate

Those who do not show any charge separation



Same number of Π bonds

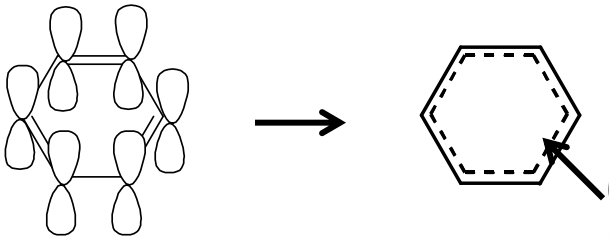


Same number of Π bonds

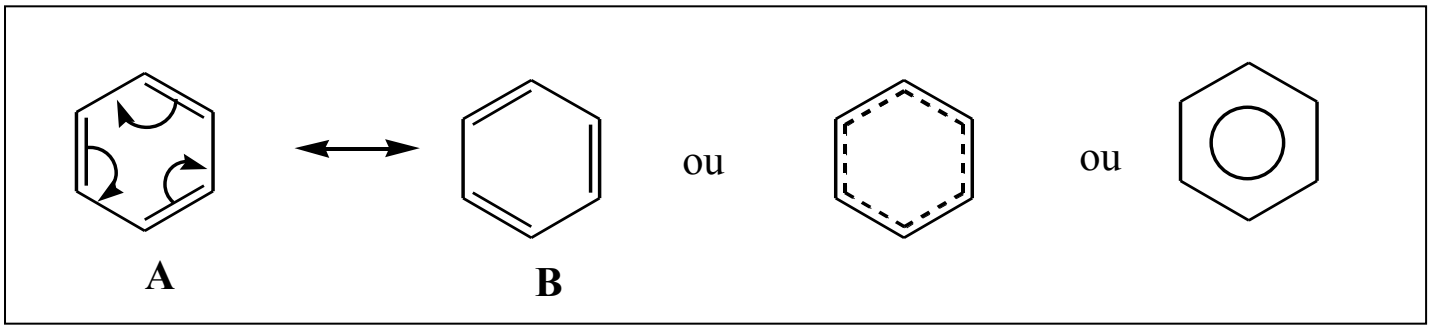
Cl more electronegative than C

IV-2) Mesomerism (≡ resonance)

Benzene C_6H_6



6 electrons π delocalized
= conjugated



Mesomeric form = limit forms

Hybrid

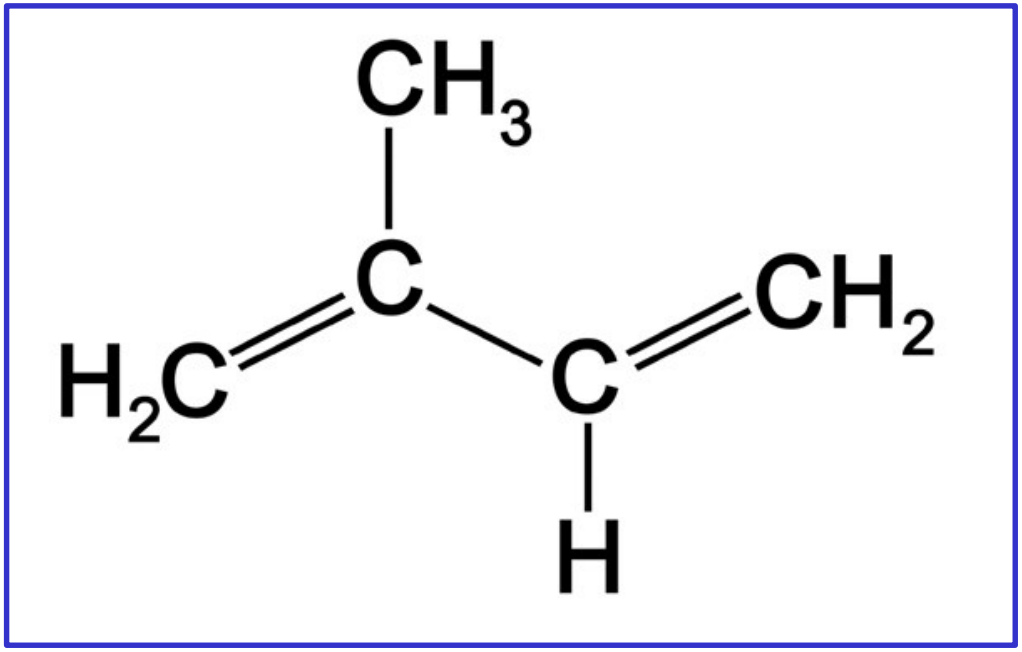
Exercice 2

L'isoprène est un hydrocarbure dont la formule brute est C_5H_8.

a. Sachant que l'isoprène comporte 2 doubles liaisons conjuguées et qu'il possède un atome de carbone qui n'est lié à aucun atome d'hydrogène, donnez la formule développée de l'isoprène.

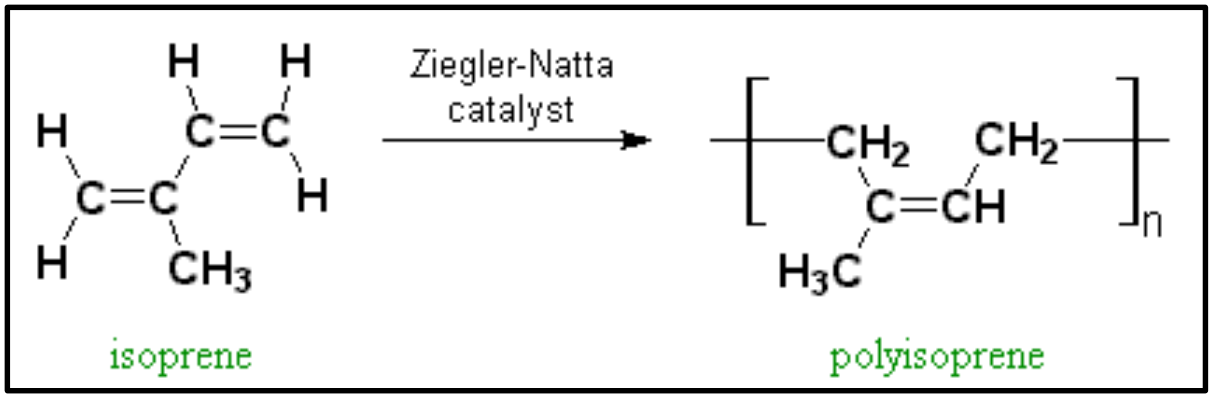
b. Représentez la molécule d'isoprène dans l'espace. Quels sont les atomes qui sont dans un même plan ? Vous expliquerez cette géométrie par l'état d'hybridation des atomes de carbone et par la nature des liaisons.

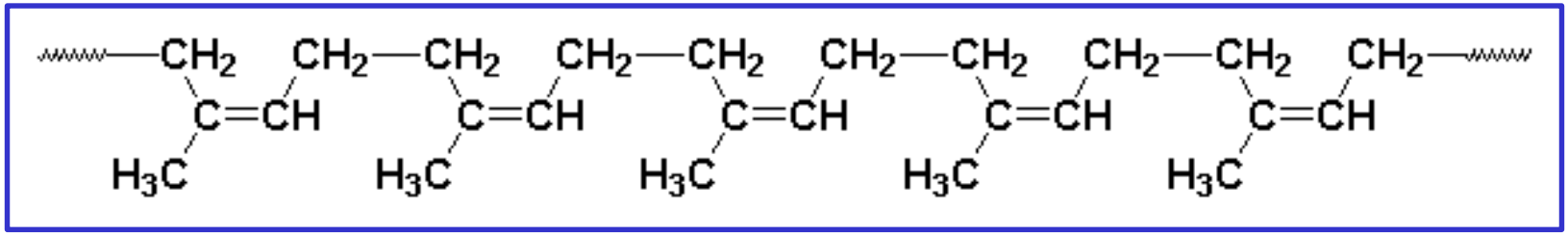
c. Expliquez, en vous aidant du schéma ci-dessus, l'origine de la conjugaison dans cette molécule. Représentez deux formes limites possibles.



Natural rubber is a polymer called *polyisoprene*

The major commercial source of **natural rubber** latex is the Pará **rubber** tree (Hevea brasiliensis)





In natural rubber the chain has thousands of repeat units, not just five like you see in the picture above.

QCM 30 Parmi les molécules suivantes, quelle(s) est (sont) celle(s) qui est(sont) un(des) système(s) conjugué(s) :

a. $H_2C = CH - CH = CH_2$

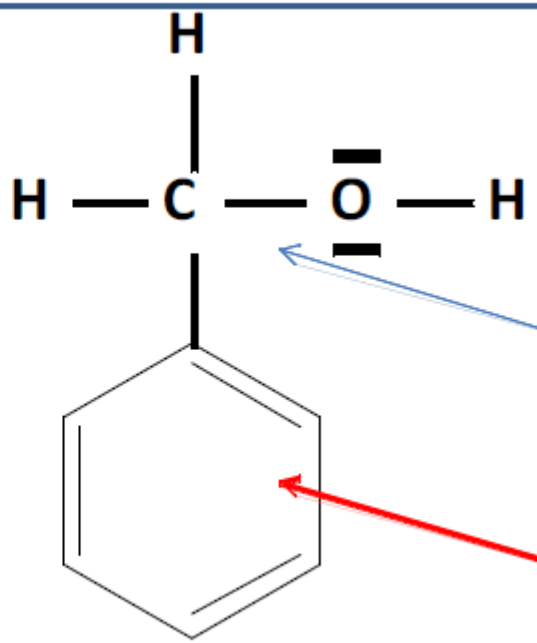
b. $H_2C = CHCl$

c. $H_2C = C = CH_2$

d. $H_2C = CH - O - CH_3$

e. $H_2C = CH - CH_2 - CH = CH_2$.

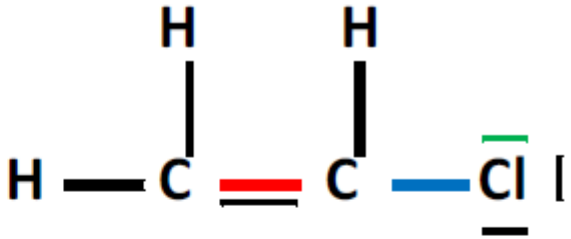
$C_6H_5CH_2OH$



Pas de conjugaison car 2 liaisons σ séparent le doublet non liant des doublets π du cycle

Conjugaison au niveau du cycle : alternance π-σ-π

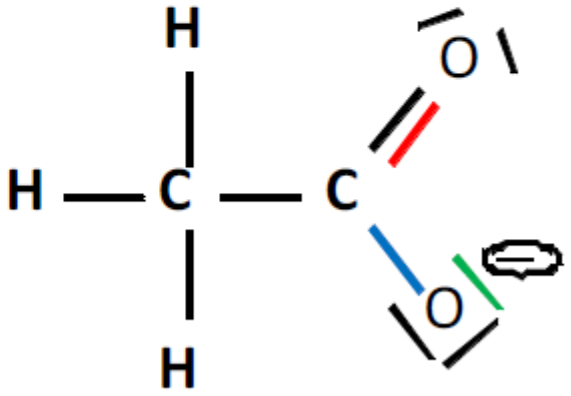
$CH_2=CHCl$

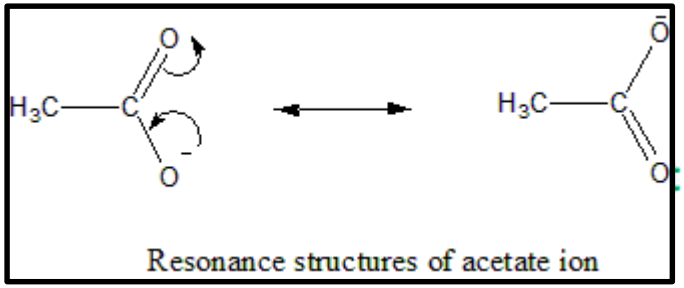


OUI :

alternance π-σ- doublet non liant

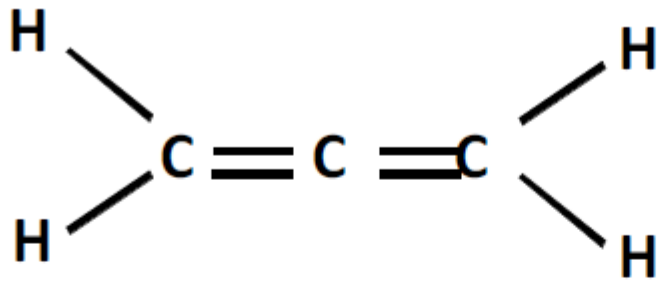
CH_3COO^-





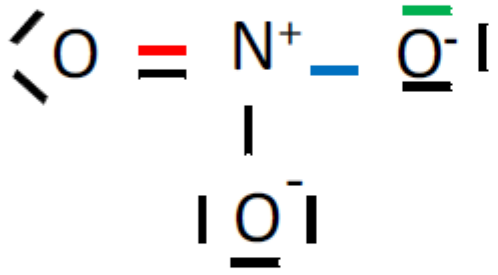
Resonance structures of acetate ion

$CH_2=C=CH_2$



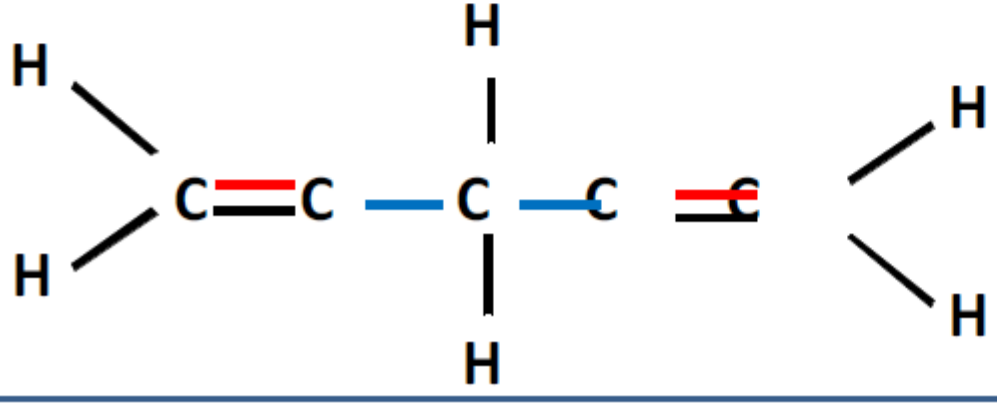
NON :
Pas de liaison σ entre
les 2 liaisons π

NO_3^-



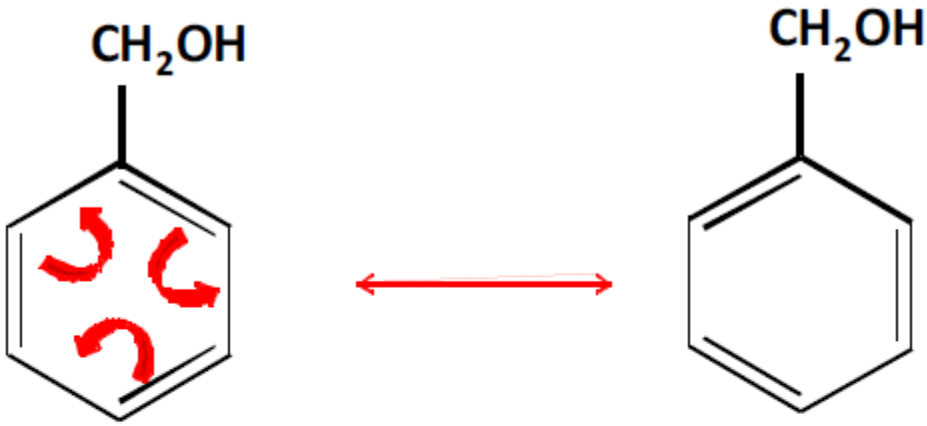
OUI :
alternance π-σ- doublet non liant

$CH_2=CH-CH_2-CH=CH_2$



NON :
2 liaisons σ entre
les 2 liaisons π

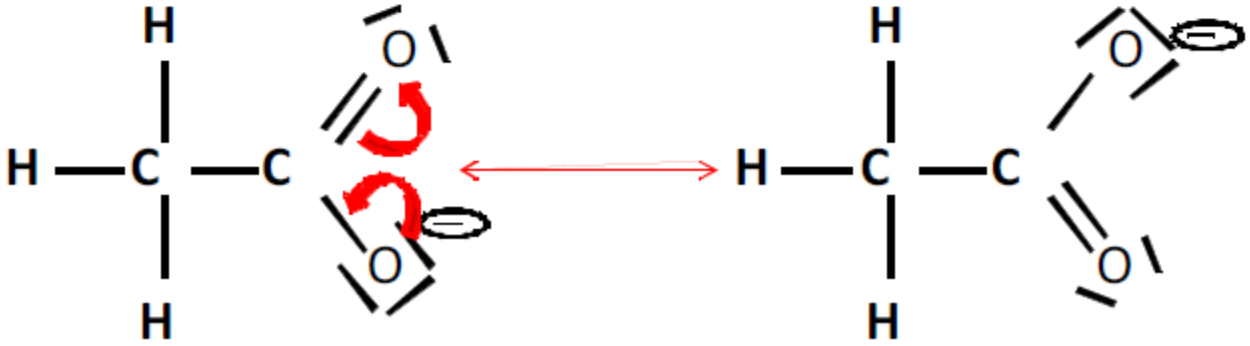
$C_6H_5CH_2OH$



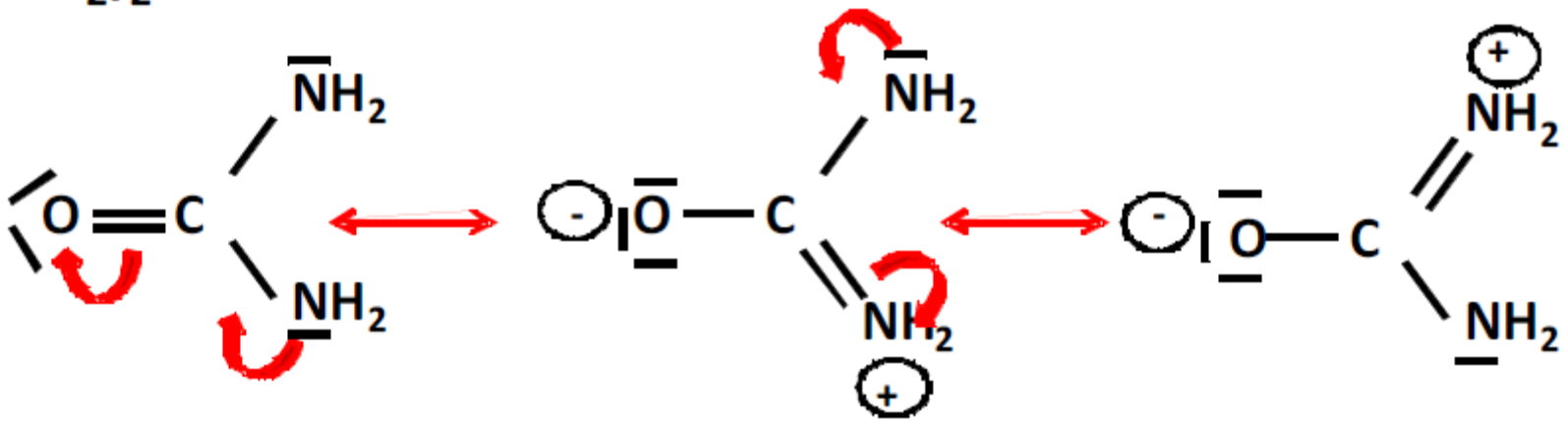
$CH_2=CHCl$

Prépondérante séparation de charge ! CF = -1 CF = +1

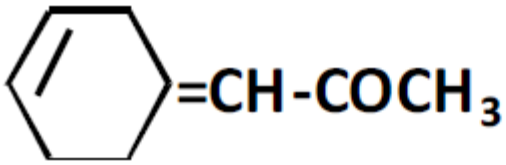
CH_3COO^-

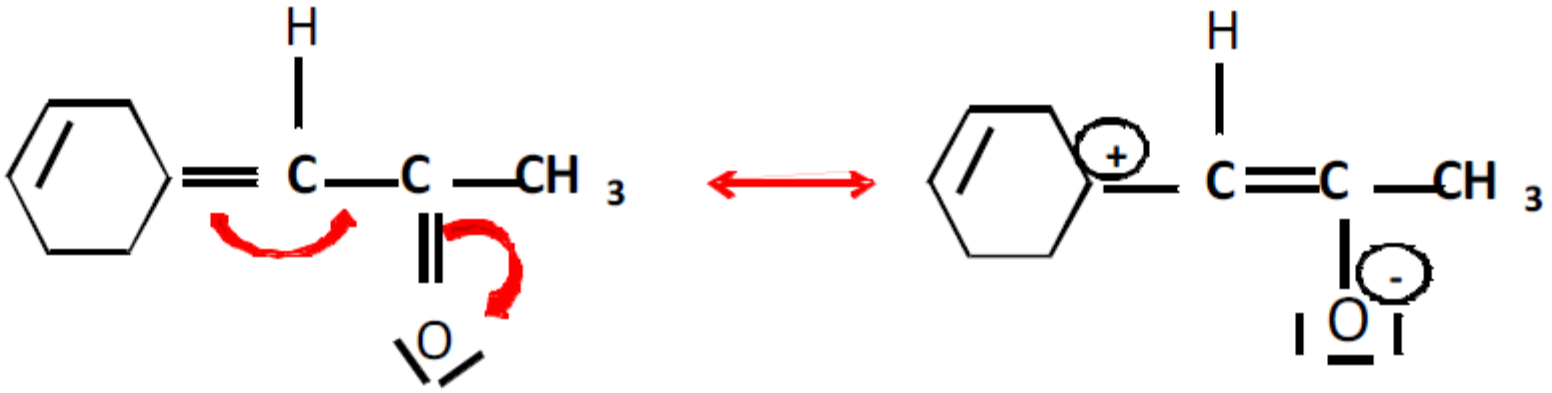


$CO(NH_2)_2$



prépondérante





prépondérante