5.1. Introduction

Atoms bond with each other to form molecules, molecular ions, or crystals. Depending on the type of these atomic associations, matter can exist in various physical states: solid, liquid, or gas.The electrons that participate in the formation of bonds are the valence electrons (outer shell electrons of the atom).

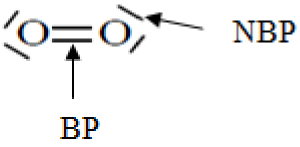
* Octet rule

It is based on the hypothesis that atoms that bond to form molecules must be surrounded by a maximum octet of electrons: 8 electrons (4 bonding electron pairs (BP) or non-bonding electron pairs (NBP)), to acquire the most stable electronic configuration, which is that of the nearest noble gas in the periodic table.

Example: The O_2 molecule

$_8O : 1s^2\ 2s^2\ 2p^4$

[↑↓] [↑↓ | ↑ | ↑]



Each oxygen atom has 4 pairs [2 bonding pairs (BP) and 2 non-bonding pairs (NBP)], so 8 electrons (the octet rule is satisfied).

Note:

- The electrons that participate in bond formation are bonding electrons (BP).
- The electrons that do not participate in bond formation are non-bonding electrons (NBP).

5.2. Lewis diagram

a/ Lewis diagram of atoms

The Lewis diagram concerns the valence structure. Unpaired electrons are represented by **dots** and paired electrons are represented by **dashes**.

Atom	electronic configuration	valence structure	Quantum boxes of valence structure	Lewis Diagramme
$_{12}Mg$	$1s^2 2s^2 2p^6 3s^2$	$3s^2$	[↑↓]	ǀ Mg
$_5B$	$1s^2 2s^2 2p^1$	$2s^2 2p^1$	[↑↓] [↑ | |]	ǀ B·
$_{14}Si$	$1s^2 2s^2 2p^6 3s^2 3p^2$	$3s^2 3p^2$	[↑↓] [↑ | ↑ |]	ǀ Si :

Note

Elements in the same group have the same valence structure, therefore, they have the same Lewis diagram.

Example: $_9F$ and $_{17}Cl$ are halogens (group VII_A).

$_9F : 1s^2 2s^2 2p^5$ [↑↓] [↑↓ | ↑↓ | ↑] ǀ $\overline{\underline{F}}$ ·

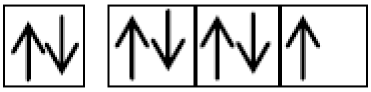
$_{17}Cl : 1s^2 2s^2 2p^6 3s^2 3p^5$ [↑↓] [↑↓ | ↑↓ | ↑] ǀ $\overline{\underline{Cl}}$ ·

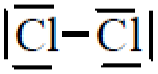
b/ Lewis diagram of molecules

To create the Lewis diagram of molecules, one must know the Lewis diagram of its atoms.

Example 1 : The Cl_2 molecule

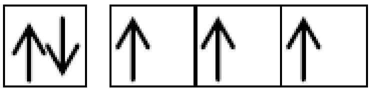
$_{17}Cl : 1s^2 2s^2 2p^6 \mathbf{3s^2 3p^5}$





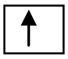
Example 2 : The N_2 molecule

$_{7}N : 1s^2\ \mathbf{2s^2\ 2p^3}$

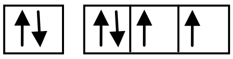


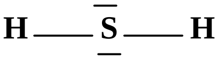
Example 3 : The H_2S molecule

$_{1}H : \mathbf{1s^1}$



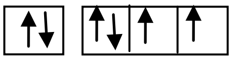
$_{16}S : 1s^2 2s^2\ 2p^6 \mathbf{2s^2\ 2p^4}$

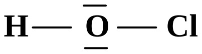




Example 4 : The HOCl molecule

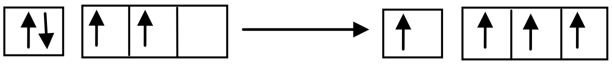
$_{8}O : 1s^2 \mathbf{2s^2\ 2p^4}$



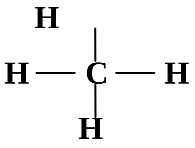


Example 5 : The CH_4 molecule

$_{6}C : 1s^2 \mathbf{2s^2\ 2p^2}$



Ground state Excited state



Choice of the central atom

1st condition: Choose the atom with **the smallest stoichiometric coefficient**. Otherwise, move on to the second condition.

2nd condition: We choose the atom with **the highest number of unpaired electrons**. Otherwise, move on to the third condition.

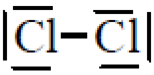
3rd condition: We choose the atom with **the highest atomic number Z**.

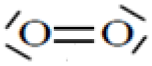
5.3. Different types of bonds

a. Covalent bond

A covalent bond is a pair of electrons shared between two identical atoms, each contributing one valence electron.

Examples

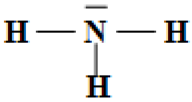




b. Polarized bond

A polarized bond is a pair of electrons shared between two different atoms, each contributing a valence electron, but this pair is shifted towards the more electronegative atom.

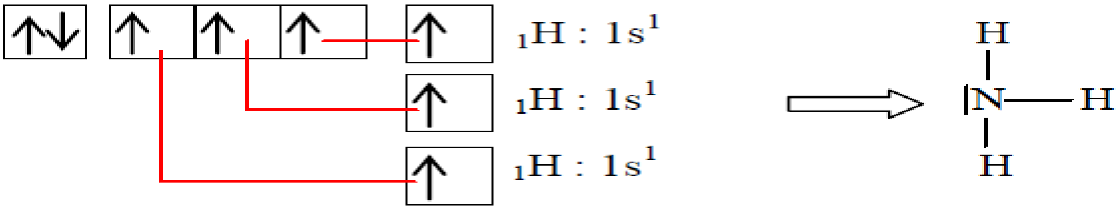
Examples



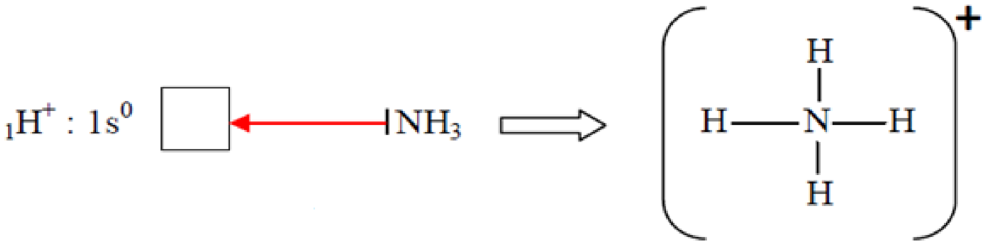
c. Dative bond (coordination)

It is a pair of electrons shared between two different atoms; it belongs only to one of the atoms (**donor**), and the other atom (**acceptor**) has an empty (free) quantum box to receive the pair.

Example 1: The ammonium ion NH_4^+ is the combination of NH_3 and H^+.

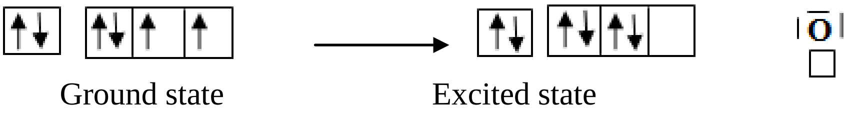


It is the non-bonding pair that will participate in the dative bond:

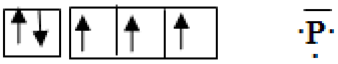


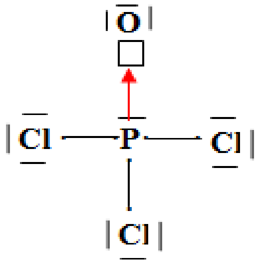
Example 2 : The PCl_3O molecule

$_8O : 1s^2\mathbf{2s^2\ 2p^4}$



$_{15}P : 1s^22s^2\ 2p^6\mathbf{3s^2\ 3p^3}$





d. Ionic bond

If the two atoms A and B of the molecule A-B have a significant difference in electronegativity, the more electronegative element takes an electron from the less electronegative element. The molecule is composed of two ions A^+ and B^-.

There is no sharing of electrons between the two atoms that form the bond, but rather a transfer of electrons from one atom to another.

Example: Sodium chloride NaCl

$_{11}$Na loses an electron → $Na^+ : 1s^2 2s^2 2p^6$

$_{17}$Cl wins an electron → $Cl^- : 1s^2 2s^2 2p^6\ 3s^2 3p^6$

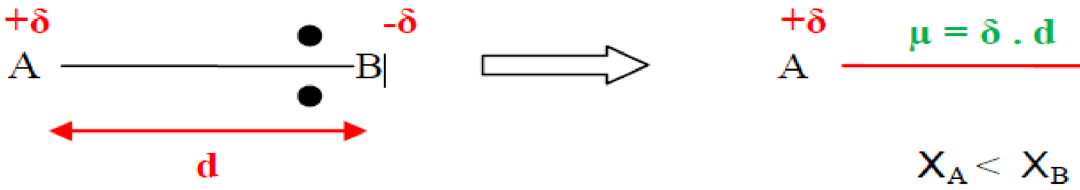
$$\left.\begin{cases} Na \rightarrow Na^+ + 1e^- \\ Cl + 1e^- \rightarrow Cl^- \end{cases}\right\} Cl + Na \rightarrow Cl^- + Na^+ \rightarrow Na^+\,Cl^-$$

Note: Ionic bonds are formed between elements with very low electronegativity that are electron **donors** (I_A, II_A), and elements with very high electronegativity that are electron **acceptors** (VI_A, VII_A).

5.4. Dipole moment and partial ionic character of the bond

a. Dipole moment

The dipole moment (μ) of a molecule A–B (where atom B is more electronegative than A) is the tendency of the electron pair to move closer to the more electronegative atom (atom B). The charge (δ) is less than (e) because atom B attracts the electron from atom A towards itself but does not completely capture it. It is characterized by a vector and oriented, by convention, from the positive charge to the negative charge.



The dipole moment is given by: $\mu = \delta . d$

Where:

δ: the partial electric charge shared between the two atoms (δ<e).

d: the distance separating the two charges (bond length) (m).

In the SI unit system, μ is expressed in ***Coulomb-meter (C.m)***, or in ***Debye (D)***:

$1D = 3{,}33\ .10^{-30}$ C.m

1. Nonpolar molecules (A_2 molecules)

$\mu = 0$

Example : Cl_2

2. Polar molecules (AB molecules)

$\mu \neq 0$

Example : HCl

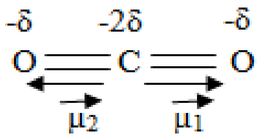
3. AX_2 molecules

The permanent dipole moment of a polyatomic molecule is the vector sum of the bond dipole moments.

3.1. Linear AX_2 molecules

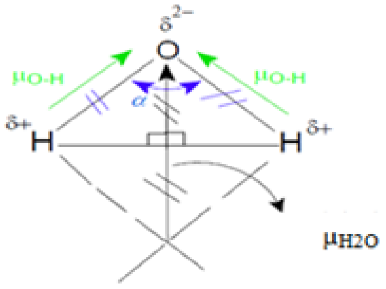
$\mu = 0$

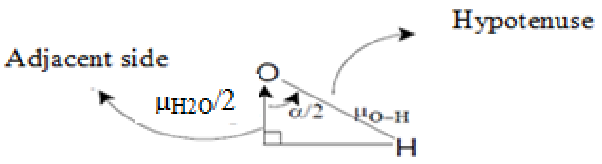
Example : CO_2



$$\vec{\mu}_{CO2} = \vec{\mu}_1 - \vec{\mu}_2 = 0 \Longrightarrow \|\vec{\mu}_1\| = \|\vec{\mu}_2\|$$

3.2. Angular AX_2 molecules





Since the bisector forms a right triangle, therefore:
$\cos(\alpha/2) = (\mu_{H2O}/2) / \mu_{O-H} \Leftrightarrow \boldsymbol{\mu_{H2O} = 2.\ \mu_{O-H}\ .\ \cos(\alpha/2)}$

b. Partial ionic character of the bond:

The determination of the ionic character of a bond requires knowledge of its dipole moment. It is given by the following relation:

I.C = $(\mu_{experimental}/\mu_{theoretical})$*100 = (δ.d/e.d)*100 = (δ /e)*100

If:
I.C = 50% (δ /e = 0.5): the bond is 50% ionic,
I.C = 100% (δ = e): the bond is purely ionic,
I.C = 0% (δ = 0): the bond is purely covalent.

Example: HCl molecule with d = 1.28 Å and μ_{exp} = 1.07 D
I.C = (μ_{exp}/μ_{theo})***100** = $(1{,}07 * 3{,}33.10^{-30})/(1{,}6.10^{-19} * 1{,}28.10^{-10})$ ***100** = 17%
The bond in the HCl molecule is 17% ionic and (100 – 17) = 83% covalent.

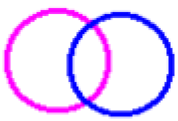
5.5. Chemical bonding in the quantum model

5.5.1. Molecular orbital theory (LCAO method)

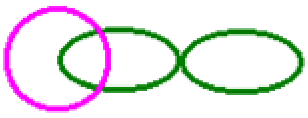
This theory is based on the Linear Combination of Atomic Orbitals. (CLOA). From two atomic orbitals (AO) originating from two atoms, two molecular orbitals (MO) are constructed (1 bonding MO (δ) and 1 anti-bonding MO (δ*)) that will form the molecule.

5.5.2. Formation and nature of bonds:

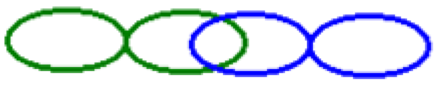
***Axial overlap:** This type of overlap concerns atomic orbitals of type s and p, and leads to the formation of **σ** bonds.



Axial overlap s-s

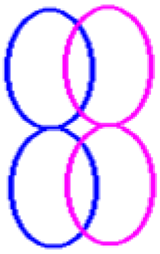


Axial overlap s-p



Axial overlap p-p

***Side overlap:** This type of overlap only concerns p orbitals and leads to the formation of π-type bonds.



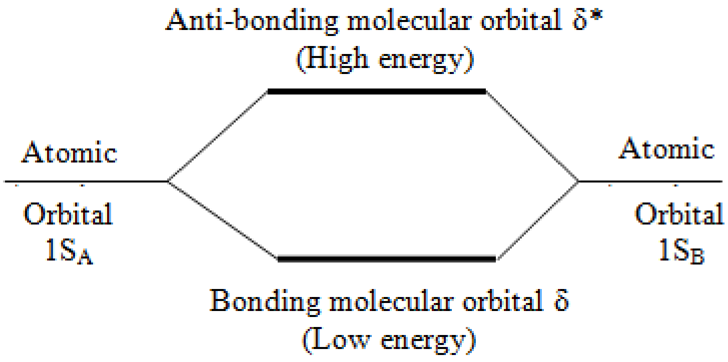
Side overlap p-p

The σ bond is stronger than the π bond because it corresponds to better overlap.

5.6. Generalization to homo-nuclear and hetero-nuclear diatomic molecules

a) Energy diagram of molecular orbitals

The energy diagram is represented as follows:



The Pauli principle, the stability principle, and Hund's rule are applicable to molecular orbitals.

It is then possible to write the electronic configuration of a homo-nuclear molecule A_2 or a hetero-nuclear molecule AB,

***For [$2Z_A$ or (Z_A+Z_B)] ≥ 16**, we will have:

$\sigma_{1s}\ \sigma^*_{1s}\ \sigma_{2s}\ \sigma^*_{2s}\ \sigma_{2pz}\ (\pi_{2px} = \pi_{2py})\ (\pi^*_{2px} = \pi^*_{2py})\ \sigma^*_{2pz}\ \sigma_{3s}\ \sigma^*_{3s}$..........

The energy of the σ_{2pz} MO is higher than that of the $\pi_{2px,y}$

***For (Z_A+Z_B) < 16, there will be an inversion of the MO: σ_{2pz} and ($\pi_{2px} = \pi_{2py}$)**, according to:

$\sigma_{1s}\ \sigma^*_{1s}\ \sigma_{2s}\ \sigma^*_{2s}\ (\pi_{2px} = \pi_{2py})\ \sigma_{2pz}\ (\pi^*_{2px} = \pi^*_{2py})\ \sigma^*_{2pz}\ \sigma_{3s}\ \sigma^*_{3s}$...........

The inversion of the molecular orbitals is due to the fact that the energy difference between the 2s and 2p atomic orbitals is quite small. It is also said that there is interaction between these orbitals, hence the inversion.

b) Bond order (BO) (number of bonds)

BO = 1/2 (n-n*)

n: number of bonding electrons.
n* : number of antibonding electrons.

Nature of the bond

The BO is general, it contains both the number of σ and π bonds.
In the case where BO = 1: a **single bond** is necessarily a σ bond.

In the case where BO = 2: a **double bond** formed by a σ bond and a π bond.
In the case where BO = 3: a **triple bond** consisting of one σ bond and two π bonds, π_x and π_y.
In the case where BO = 0: this hypothetical molecule cannot exist because the bond order is zero, so **no bond formation**.

- for σ bonds:

BO = 1/2 [n(σ)-n*(σ*)]

- for π bonds:

BO = 1/2 [n(π)-n*(π*)]

c) Stability of molecules

The higher the bond order (higher value), the more stable the molecule. A molecule with a bond order equal to 1 is less stable than a molecule with a bond order of 2.

Example:

For the following three molecules, we have:

- BO (O_2) = 1/2 [(8)-(4)] =2
- BO (O_2^+) = 1/2 [(8)-(3)] =2.5
- BO (O_2^-) = 1/2 [(8)-(5)] = 1.5

So, according to the BO values, we classify the stability of the molecule and the ions in the following increasing order:

$O_2^- < O_2 < O_2^+$

d) Magnetic properties

***Diamagnetic molecule**

The molecule has no unpaired electrons (even number of electrons).

*** Paramagnetic molecule**

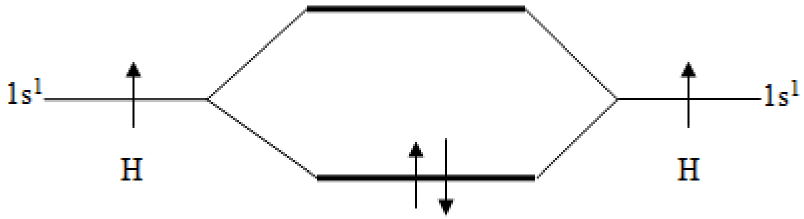
The molecule has unpaired electrons (odd number of electrons).

f) Energy diagram of homo-nuclear diatomic molecules (symmetric)

***H_2 molecule**

$_1H : 1s^1$ $2Z_A = 2 < 16$

The electronic configuration of the MO is: σ_{1s}^2

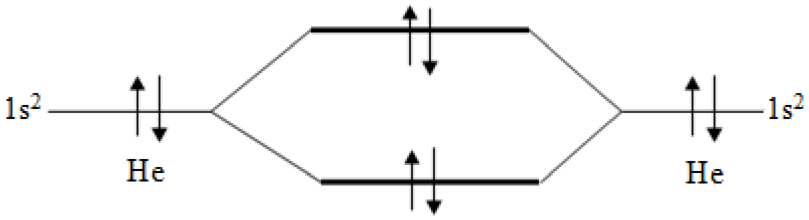


The bond order BO = ½ (2 – 0) = 1 bond for the hydrogen molecule (1 δ bond).
There are no unpaired electrons → the N_2 molecule is **diamagnetic**.

***He_2 molecule**

$_2He : 1s^2$ $2Z_A = 4 < 16$

The electronic configuration of the MO is : $\sigma_{1s}^2\ \sigma^*{}_{1s}^2$

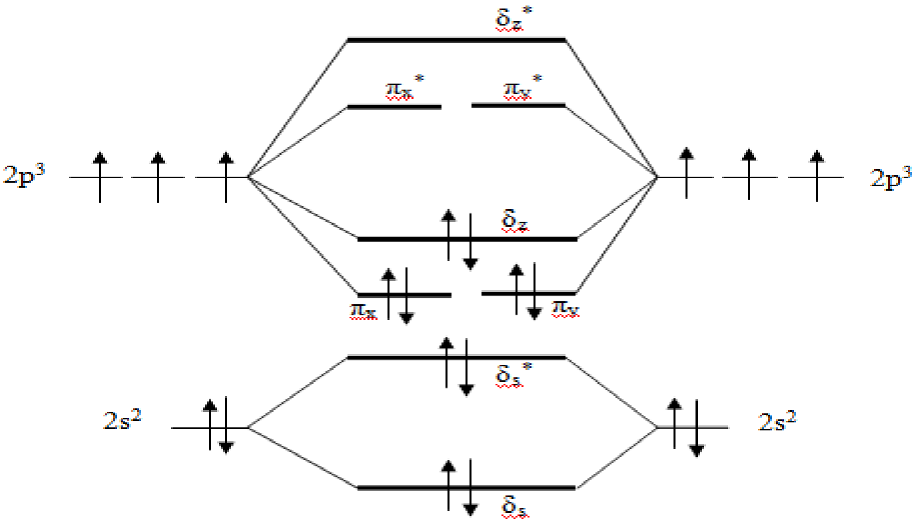


The bond order BO = ½ (2 – 2) = 0 bond for the helium molecule (He_2 cannot be obtained).

* N_2 molecule

${}_7N$: $1s^2\ 2s^2 2p^3$ $2Z_A = 14 < 16$ (inversion of MO)

The electronic configuration of the MO is: $\sigma_{1s}{}^2\ \sigma^*{}_{1s}{}^2\ \sigma_{2s}{}^2\ \sigma^*{}_{2s}{}^2\ \pi_{2px}{}^2\ \pi_{2py}{}^2\ \sigma_{2pz}{}^2$



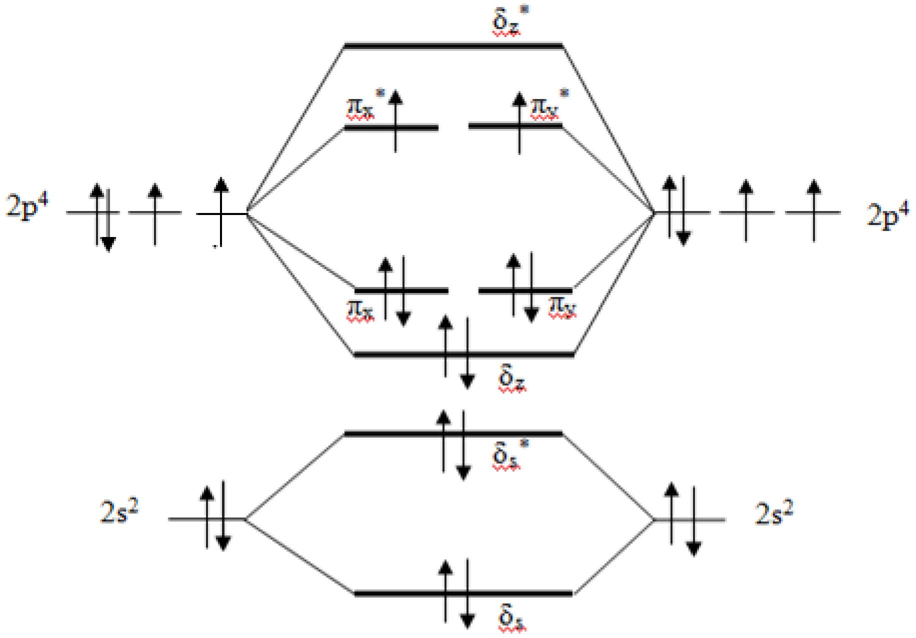
BO = ½ (8 – 2) = 3 bonds (1 σ bond and 2 π bonds).

There are no unpaired electrons → the N_2 molecule is **diamagnetic**.

*O_2 molecule

${}_8O$: $1s^2\ 2s^2 2p^4$ $2Z_A = 16$ (no inversion of MO)

The electronic configuration of the MO is: $\sigma_{1s}{}^2\ \sigma^*{}_{1s}{}^2\ \sigma_{2s}{}^2\ \sigma^*{}_{2s}{}^2\ \sigma_{2pz}{}^2\ \pi_{2px}{}^2\ \pi_{2py}{}^2\ \pi^*{}_{2px}{}^1\ \pi^*{}_{2py}{}^1$

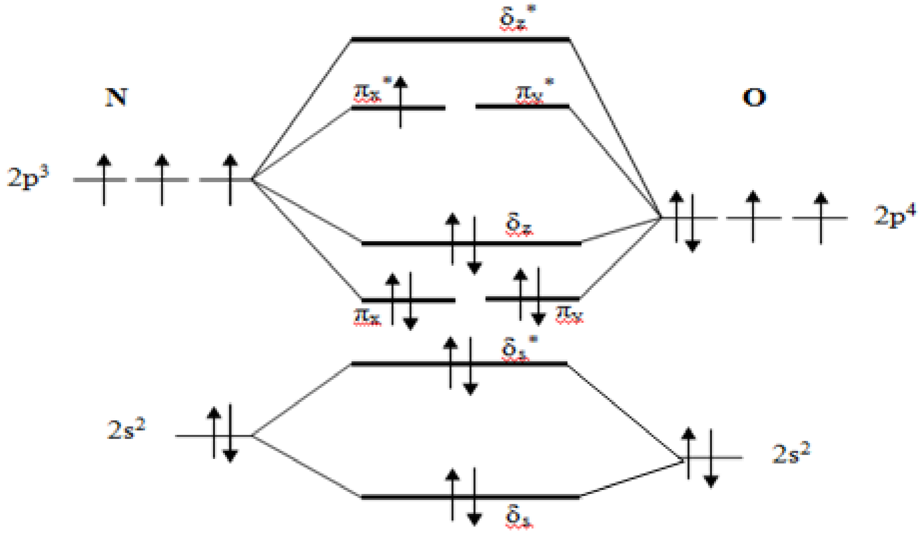


BO = ½ (8 – 4) = 2 bonds (1 σ bond and 1 π bond).
There are unpaired electrons → the N_2 molecule is **paramagnetic**.

g) Energy diagram of heteronuclear diatomic molecules (asymmetric)

The molecules are formed from different atoms. The "valence orbitals" are not at the same energy level, which results in an asymmetry in the energy diagram.

Example: NO molecule
$_7N : 1s^2 2s^2 2p^3$ $_8O : 1s^2 2s^2 2p^4$ $Z_N + Z_O = 15 < 16$ (inversion of MO)
The electronic configuration of the MO is : $\sigma_{1s}^2\ \sigma^*{}_{1s}^2\ \sigma_{2s}^2\ \sigma^*{}_{2s}^2\ \pi_{2px}^2\ \pi_{2py}^2\ \sigma_{2pz}^2\ \pi^*{}_{2px}^1$
The 2p orbital of O is at a lower energy level than that of 2p of N.



BO = ½ (8 – 3) = 5/2 bonds.
This value highlights a single electron → the NO molecule is **paramagnetic**.

5.7. Polyatomic molecules - theory of hybridization of atomic orbitals

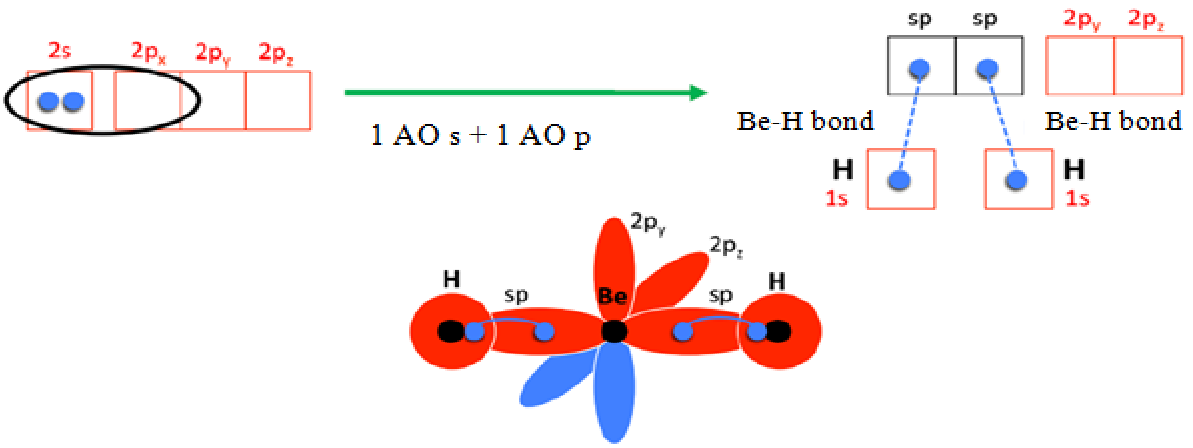
Hybridization is the combination of atomic orbitals (AO) of an atom to form a set of new atomic orbitals, either hybrid or mixed orbitals.

a. Different types of hybridization

a.1. "sp" hybridization

sp hybridization involves the mixing of an **s orbital** and a **p orbital**. The combination of these two atomic orbitals results in two equivalent **sp hybrid orbitals** oriented 180° from each other. The **sp** hybridization occurs in molecules of type AX_2 (or AXE) whose repulsion geometry is **linear**.

Example: BeH_2 molecule
$_4Be: 1s^2 2s^2$

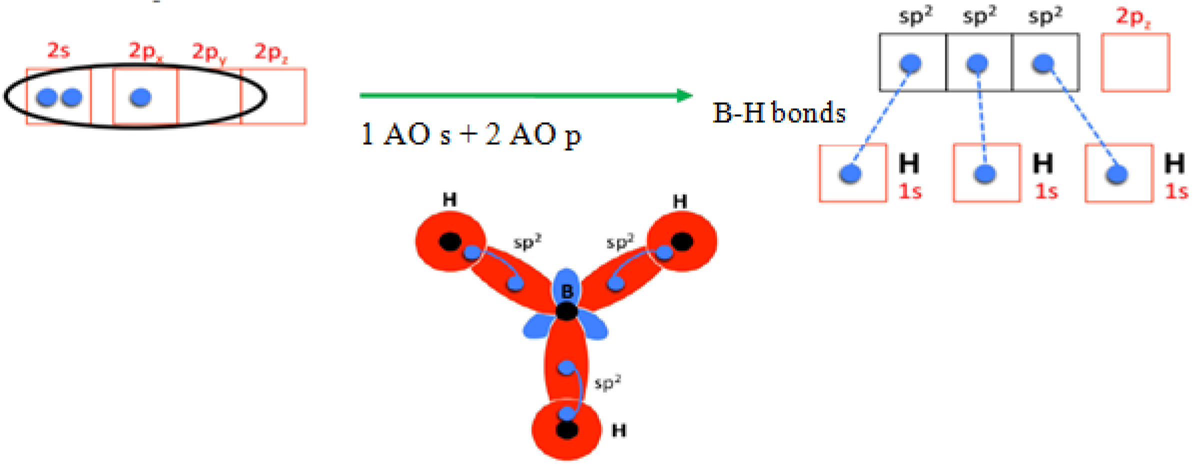


a.2. Hybridization "sp^2"

It results from the linear combination of **one s orbital** with **two p orbitals** from the same atom. There will be the formation of **3 sp^2 hybrid orbitals**. These are located in a plane and directed towards the vertices of an equilateral triangle (with an angle of 120° between each lobe). The **sp^2** hybridization occurs in molecules of type AX_3 (or AX_2E or AXE_2), whose repulsion figure is triangular.

Example: BH_3 molecule

$_5B : 1s^2\ 2s^2\ 2p^1$

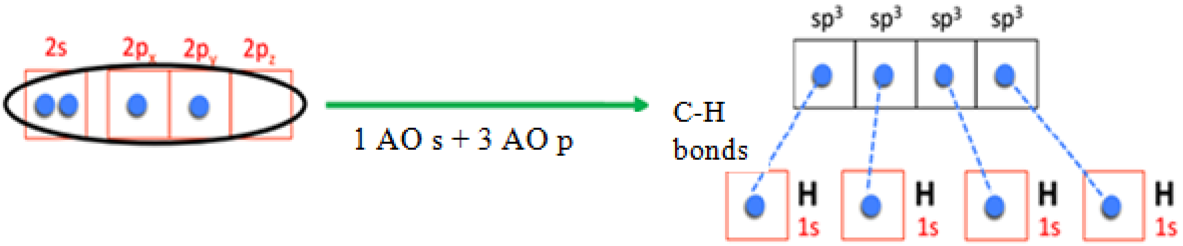


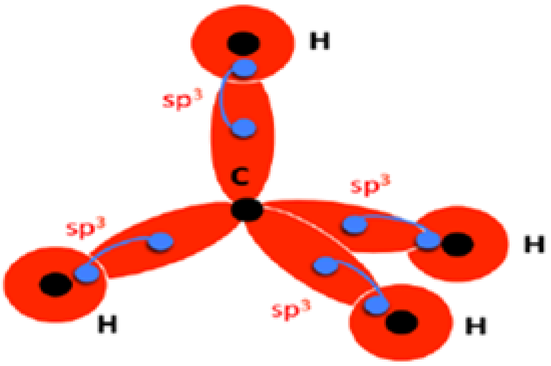
a.3. Hybridization "sp^3"

sp^3 hybridization involves the mixing of **one s orbital** and **three p orbitals**. The combination of these four atomic orbitals results in four **sp^3** hybrid orbitals oriented at 109.5° to each other. The sp^3 hybridization occurs in molecules of the AX_4 type (or AX_3E, AX_2E_2, etc.), whose repulsion figure is **tetrahedral**.

Example: CH_4 molecule

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





b. Molecular geometry: Gillespie theory or VSEPR

It is possible to predict the geometry of a molecule by applying **Gillespie's rules** based on the **V.S.E.P.R** method (Valence Shell Electron Pair Repulsion).

*Use of the V.S.E.P.R method

*Rule 1

We are interested in all the electron pairs in the valence shell of the **central atom "A"**. We write: $\mathbf{AX_nE_m}$
Where:
A: Central atom
X: Pairs participating in a bond with the central atom A (bonding pairs (BP))
n: Number of bonds (Number of BP)
E: Pairs not participating in a bond with the central atom A (non-bonding pairs (NBP))
m: Number of non-bonding pairs (NBP).
The sum **(n+m)** is called the **total number of pairs**. It provides information on the **state of hybridization**.

Example of the molecule CH_4: The central atom is C ⇒ A. The bonded atom is H, with **n = 4** bonding pairs ⇒ $\mathbf{X_4}$. The C atom in this molecule does not have any non-bonding pairs (**m = 0**) ⇒ $\mathbf{E_m = 0}$.

CH_4, sp^3 hybridized, will have the geometric shape $\mathbf{AX_4}$.

*Rule 2:

If the molecule has multiple bonds (double π bond or triple δ, π bonds) each bond will be considered as a single bond (δ bond):
C=C ⇒ 2 single bonds ⇒ 1 bonding pair.
C≡C ⇒ 3 single bonds ⇒ 1 bonding pair.

Example of the molecule C_2H_4

$H_2C=CH_2$: each carbon atom will have an sp^2 hybridization.

The central atom is C $\Rightarrow$**A**

The C atom is bonded to 2 H and 1 C, with **n = 3** bonding pairs $\Rightarrow$ $\mathbf{X_3}$.

m = 0 (no non-bonding pairs) $\Rightarrow$ $\mathbf{E_m = 0}$.

C_2H_4, sp^2 hybridized, will have the geometric shape $\mathbf{AX_3}$ for each carbon atom.

*<u>**Rule 3**</u>

In the molecule, electron pairs do not have the same equivalence:
1. A non-bonding pair is more disruptive than a bonding pair.
2. A multiple bond (double, triple) is more troublesome than a bonding pair.
3. An electronegative atom is more troublesome than an electropositive atom.

Example :

$$\left.\begin{array}{l} CH_4 \Rightarrow 109° \\ NH_3 \Rightarrow 107° \\ H_2O \Rightarrow 104° \end{array}\right\} \text{ Hybridization } sp^3$$

This decrease in the angle is due to the repulsive effect of the non-bonding pair in NH_3 and the two non-bonding pairs in H_2O.

To determine the hybridization of a molecule based on its $\mathbf{AX_nE_m}$ geometry, the procedure is as follows:

-If **m + n = 2** $\Rightarrow$ Hybridization of **1 AO s** and **1 AO p** $\Rightarrow$ **sp** hybridization.
-If **m + n = 3** $\Rightarrow$ Hybridization of **1 AO s** and **2 AO p** $\Rightarrow$ $\mathbf{sp^2}$ hybridization.
-If **m + n = 4** $\Rightarrow$ Hybridization of **1 AO s** and **3 AO p** $\Rightarrow$ $\mathbf{sp^3}$ hybridization.