Chapter I

Chemical Bonding

I/ ATOMIC ORBITALS

1. Quantum Number

An electron is described by a function called the **wave function**, denoted ψ (*psi*). This function ψ is characterized by four **quantum numbers** such as n, l, m and S.

n : Principal quantum number → $n \geq 1$

Letter	*K*	*L*	*M*	*N*	.	.	.
n	1	2	3	4			

l : Secondary quantum number → $0 \leq l \leq (n-1)$

Symbol of atomic orbital	*s*	*p*	*d*	*f*
l	0	1	2	3

m : Magnetic quantum number → $-l \leq m \leq +l$

S : Spin quantum number $S = +\frac{1}{2} \uparrow$ $S = -\frac{1}{2} \downarrow$

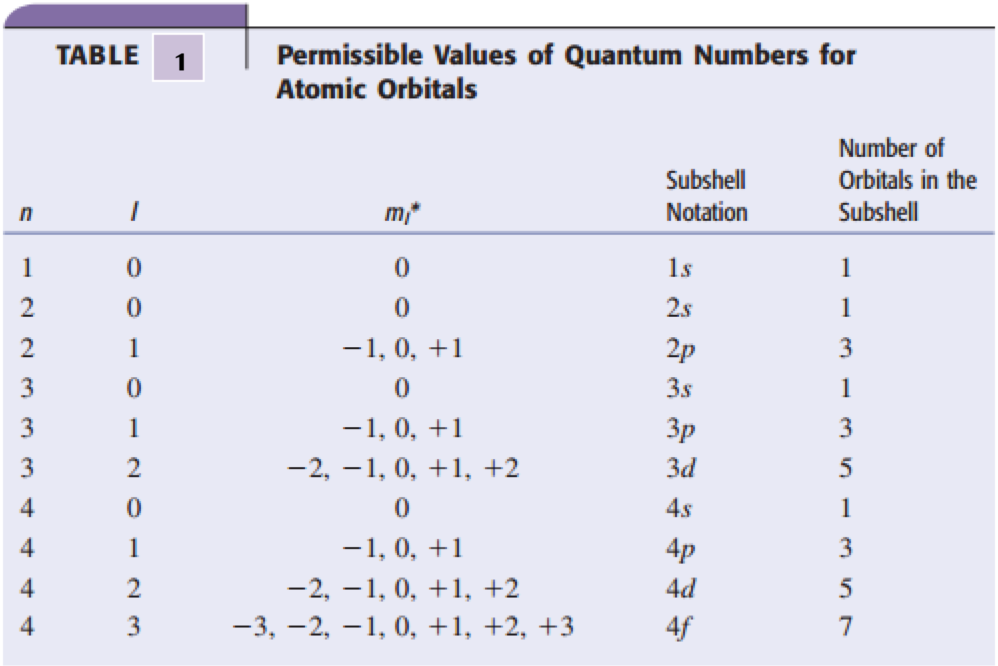


TABLE 1 Permissible Values of Quantum Numbers for Atomic Orbitals

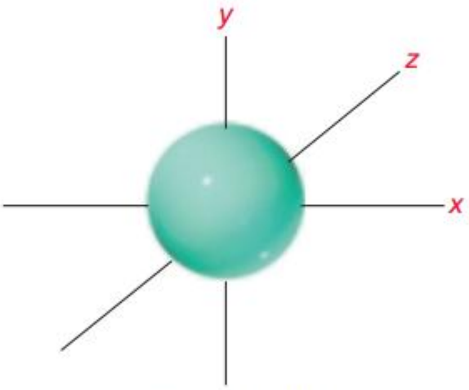
n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1s	1
2	0	0	2s	1
2	1	−1, 0, +1	2p	3
3	0	0	3s	1
3	1	−1, 0, +1	3p	3
3	2	−2, −1, 0, +1, +2	3d	5
4	0	0	4s	1
4	1	−1, 0, +1	4p	3
4	2	−2, −1, 0, +1, +2	4d	5
4	3	−3, −2, −1, 0, +1, +2, +3	4f	7

2. Quantum case

Subshell	Number of electrons	Quantum case
s	2	↑↓
p	6	↑↓ ↑↓ ↑↓
d	10	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
f	14	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓

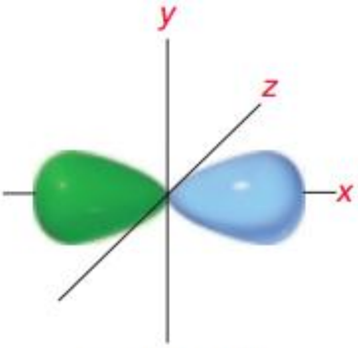
3. Atomic orbitals

S Orbital

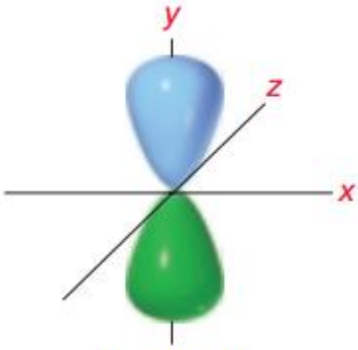


2*s* atomic orbital

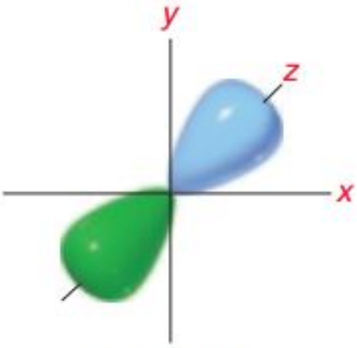
P Orbitals



2p_x orbital

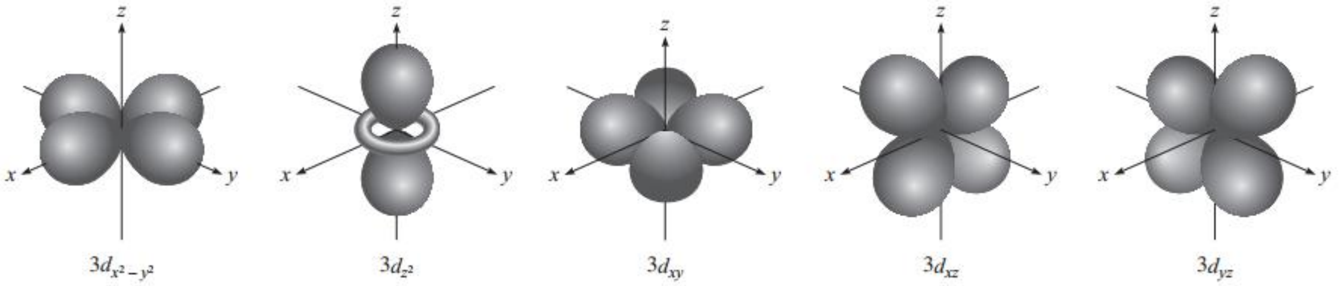


2p_y orbital



2p_z orbital

d Orbitals



4. Electron configuration

The electron configuration of an atom is the distribution of electrons in the orbitals. The filling of these orbitals by electrons follows three mains rules.

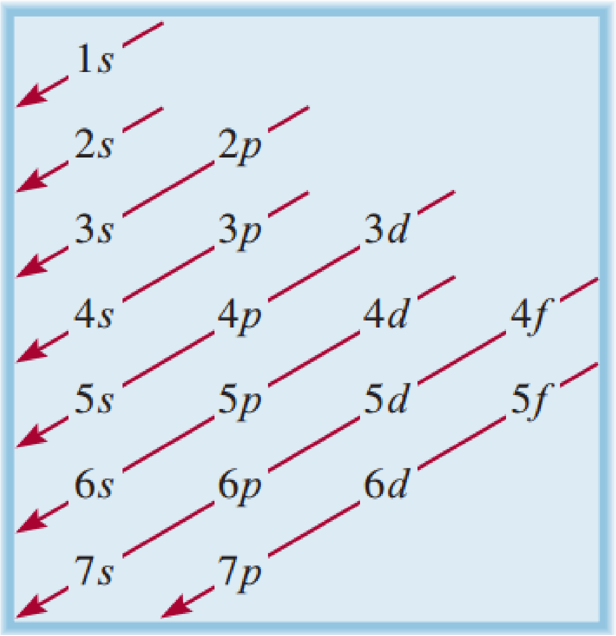


Figure 1: ***Klechkowski's rule*** *allows to establish the order of filling of the different orbitals.*

- **RULE 1**

The ***Aufbau principle*** dictates that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to the atomic orbitals.

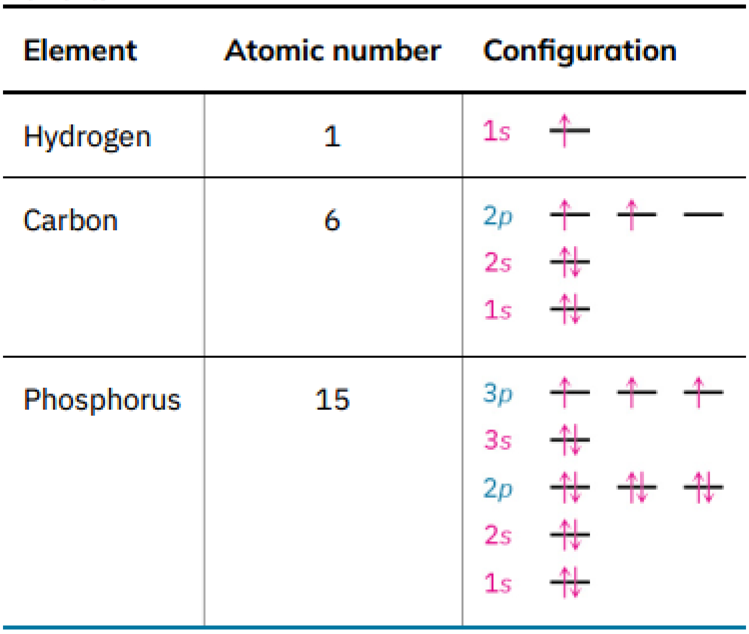
- **RULE 2**

Pauli exclusion principle: In an orbital, there can be only two electrons with opposite spins. (**+ ½, - ½**).

- **RULE 3**

Hund's: The most stable state is achieved when a maximum number of orbitals of the same energy are occupied by electrons with identical spin.

TABLE 2: Ground-State Electron Configurations of Some Elements



Element	Atomic number	Configuration
Hydrogen	1	1s ↑
Carbon	6	2p ↑ ↑ — 2s ↑↓ 1s ↑↓
Phosphorus	15	3p ↑ ↑ ↑ 3s ↑↓ 2p ↑↓ ↑↓ ↑↓ 2s ↑↓ 1s ↑↓

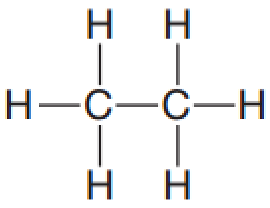
II/ CHEMICAL BONDS

1. Covalent Bonds

Any bond formed by the sharing of electrons is a covalent bond.

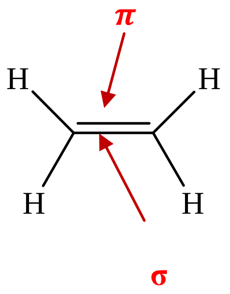
1.1. Single covalent bond and multiple bonds

Exemple : <u>Cl_2</u> $_{35}Cl : 3s^2\ 3p^5$

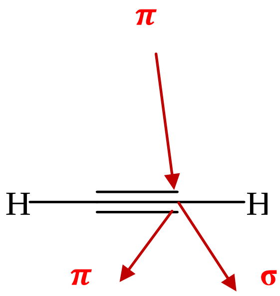


Ethane

Single bond



Double bond

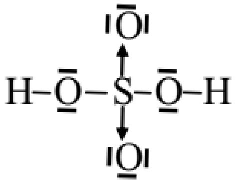


Triple bond

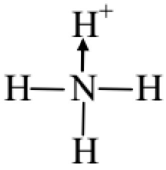
1.2. Dative bond

A dative bond is symbolized by an arrow pointing from the donor to the acceptor.

H_2SO_4

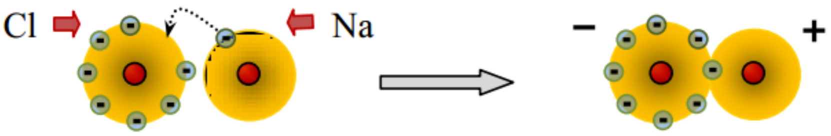


NH_4^+



2. Ionic Bonds

Ionic bonds are formed by the transfer of one or more electrons from one atom to another to create ions. Ionic bonding occurs in compounds of highly electropositive elements, such as alkali metals, bonded to highly electronegative elements, like halogens (for example, NaCl).

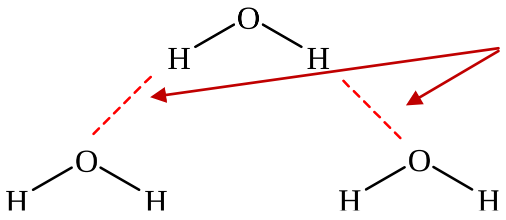


3. Hydrogen Bonds

It involves the bond between a hydrogen atom attached to an electronegative atom (N or O) and the lone pair of electrons on another electronegative atom (N or O).

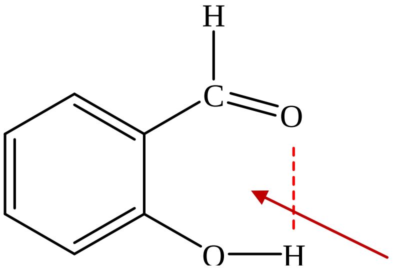
There are two types of hydrogen bonds:

Hydrogen bonds can be ***intramolecular*** (between two parts of the same molecule) or ***intermolecular*** (between two different molecules).



Intermolecular hydrogen bonding

(Hydrogen bridge)



Intramolecular hydrogen bond

The presence of hydrogen bonds explains the exceptionally high boiling point of water. The H_2O molecule is a small molecule (M = 18 g/mol). Its boiling point of 100 °C is nothing like that of methane (CH_4, M = 16 g/mol), which is -162 °C. Water forms a network through hydrogen bonds in which the oxygen atoms are bonded to four hydrogen atoms (two by covalent O–H bonds and two by hydrogen bonds).

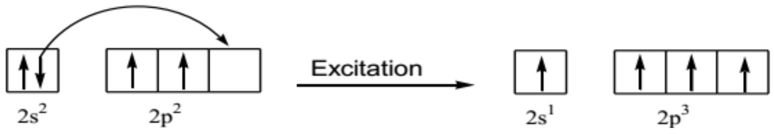
Thus, to transition from the liquid state to the gaseous state, where the molecules are far apart from each other, a significant amount of energy must be provided to break the hydrogen bonds; this explains the high boiling point of water.

III/HYBRIDIZATION OF THE CARBON ATOM

1. Hybridization SP^3 of carbon

The electronic configuration: $_1H : 1S^1$ $_6C : 1S^2\,2S^2\,2P^2$

Carbon must be in an excited state, meaning that one electron from the 2*S* subshell moves to the 2*P* subshell. Carbon is tetravalent.



Ground state **Excited state**

Example : **CH_4** (Tetrahedral geometry)

In its ground state, when carbon is placed in the presence of four hydrogen atoms, it undergoes a rearrangement of its 2*S* and 2*P* orbitals to form four SP^3 hybrid orbitals with an angle of 109° each containing 1 electron and oriented towards the vertices of a tetrahedron.

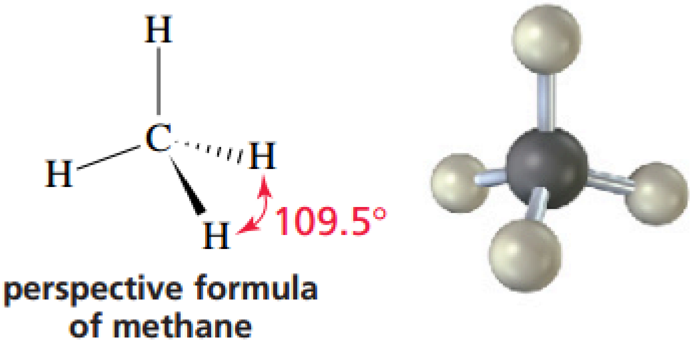


Figure 1; The structure of methane, showing its 109.5° bond angles.

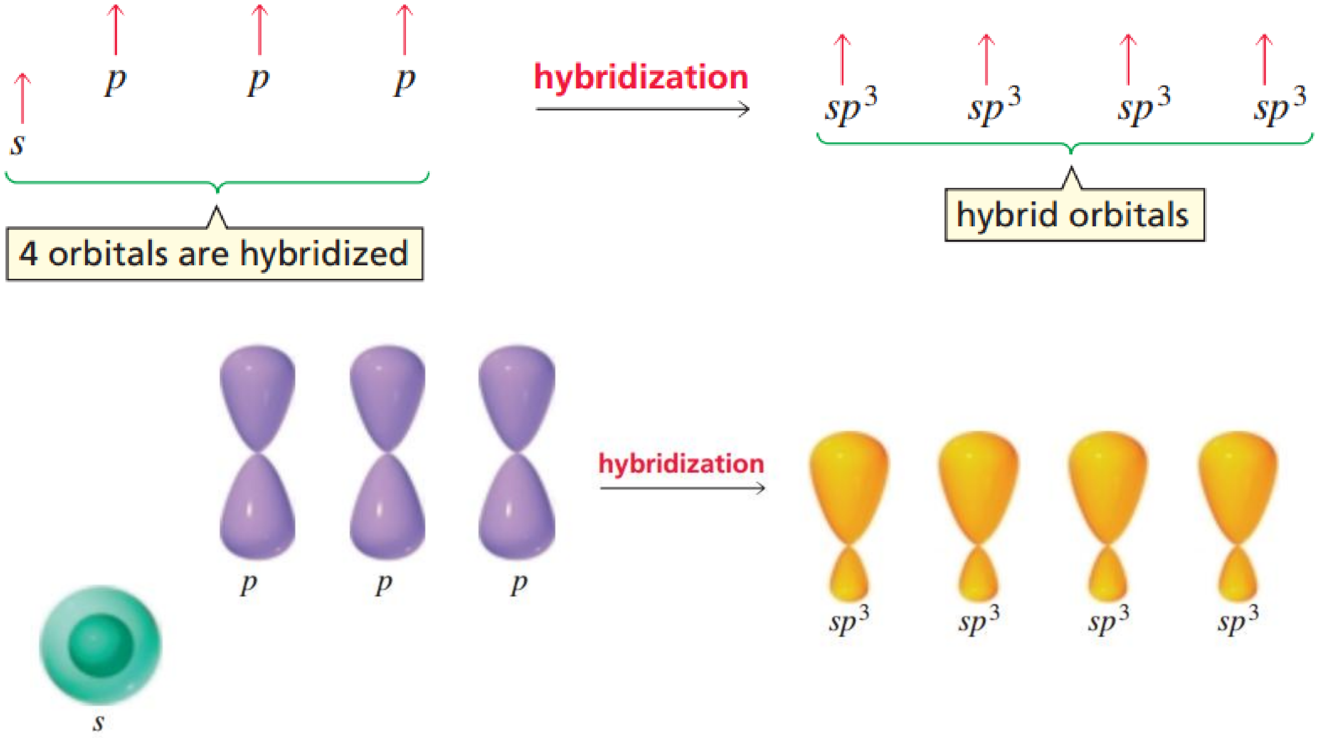


Figure 2; An *S* orbital and three *P* orbitals hybridize to form four SP^3 orbitals. An SP^3 orbital is more stable than a *P* orbital, but not as stable as an *S* orbital.

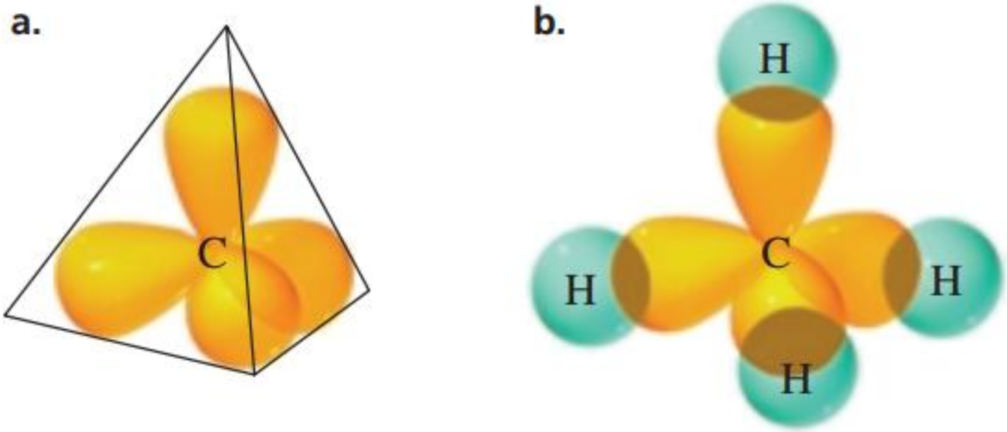
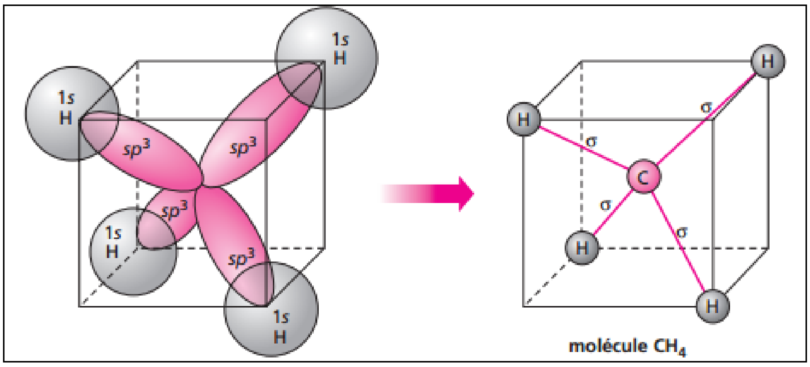


Figure 3: **(a)** The four orbitals are directed toward the corners of a tetrahedron, causing each bond angle to be 109.5°. **(b)** An orbital picture of methane, showing the overlap of each orbital of carbon with the *S* orbital of hydrogen.

A carbon atom surrounded by four σ bonds is hybridized in *SP^3*. The four C-H bonds are identical and directed toward the four vertices of a tetrahedron.



***Example* :** The ethane molecule CH_3CH_3

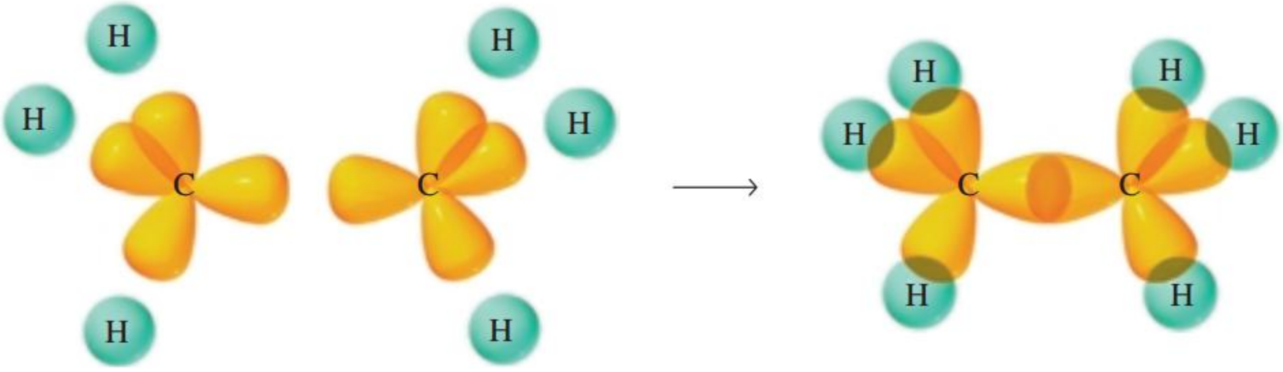


Figure 4: An orbital picture of ethane. The C-C bond is formed by *SP^3*-*SP^3* overlap, and each C-H bond is formed by*SP^3*-*S* overlap.

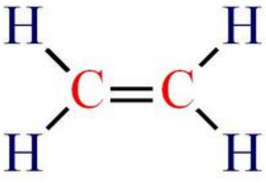
Each carbon is surrounded by 3 σ (C-H) bonds and one **σ** (C-C) bond.

2. Hybridization SP^2 of carbon

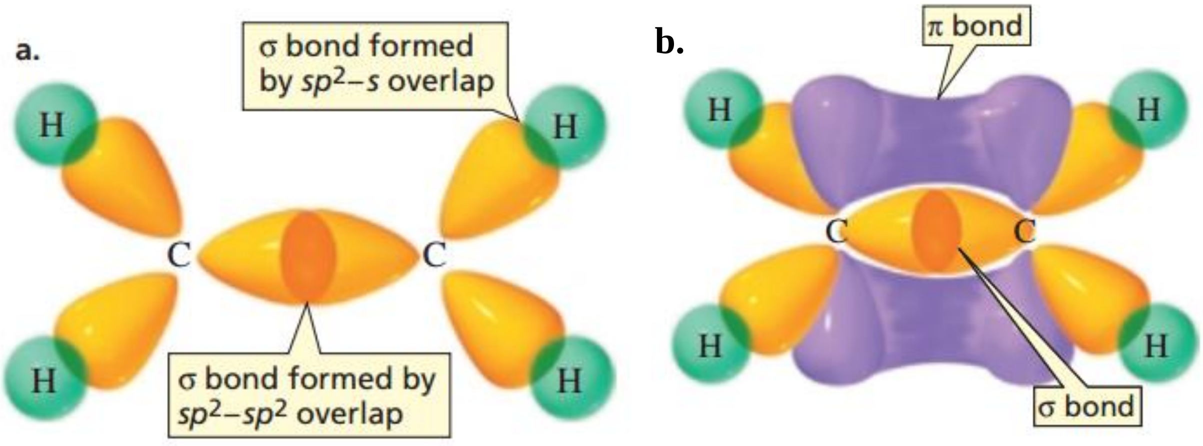
The SP^2 hybridization of one *S* atomic orbital and two *P* atomic orbitals leads to three “SP^2” hybrid atomic orbitals with an angle of 120°.

Example : Ethylene $CH_2{=}CH_2$

On the same principle, for double bonds, the hybridization is of the SP^2 type, resulting in three identical SP^2 bonds and one unhybridized 2*P* orbital. This orbital form what is called a **π** bond; thus, in this case, there are three **σ** bonds and one **π** bond.



Ethene (ethylene)

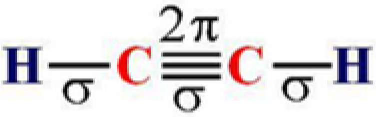


Three **σ** molecular orbitals are formed on each carbon atom through ***axial overlap***, and one π molecular orbital is formed through ***lateral overlap***.

3. Hybridization *SP* of carbon

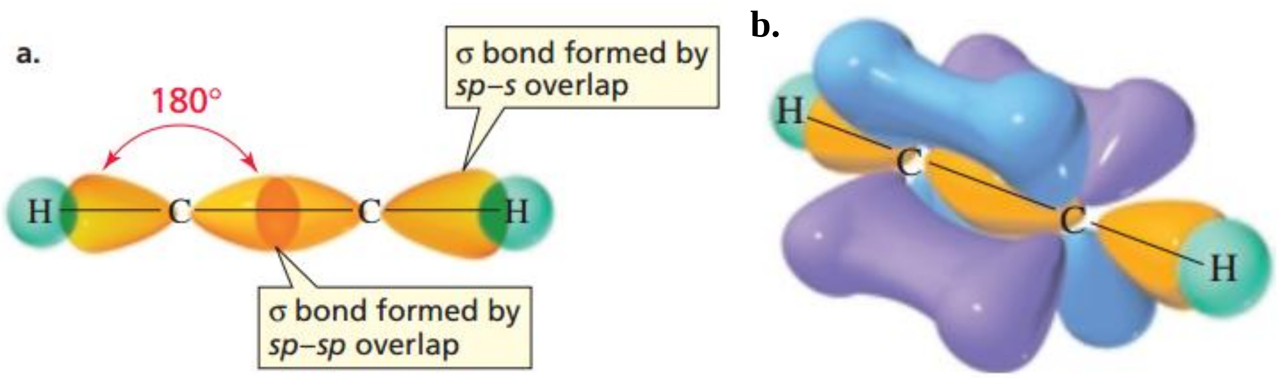
The *SP* hybridization of one *S* atomic orbital and one *P* atomic orbital leads to two *SP* hybridized atomic orbitals with an angle of 180°.

Exmaple : Acetylene : C_2H_2



$$H\underset{\sigma}{-}C\overset{2\pi}{\underset{\sigma}{\equiv}}C\underset{\sigma}{-}H$$

Ethyne (Acetylene)

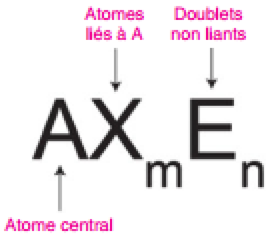


- ✓ The axial overlap results in a **σ** bond.
- ✓ The lateral overlap results in a ***π*** bond.

IV/ GEOMETRY OF MOLECULES

1. Method of Gillespie (V.S.E.P.R)

The Gillespie method or the **V.S.E.P.R** method (***V**alence **S**hell **E**lectron **P**air **R**epulsion*) (***répulsion des paires d'électrons de la couche de valence***), is designed to predict the geometry of molecules or simple ions based on the theory of electron repulsion in the valence shell. It applies to small molecules or ions of the type.



A : Central atom.

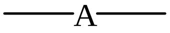
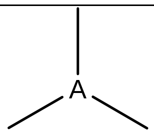
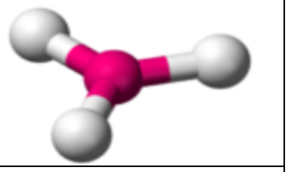
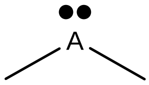
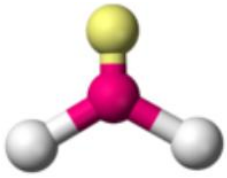
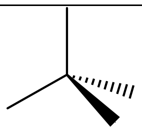
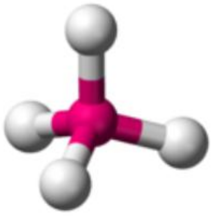
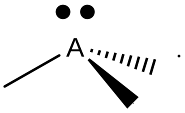
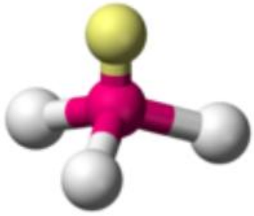
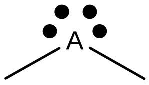
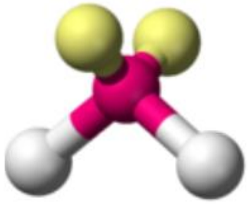
X : Represents the atoms bonded to atom A.

m : Number of atoms X bonded to A.

E : The non-bonding pairs (lone pair) around atom A.

n : Number of lone pairs around atom A.

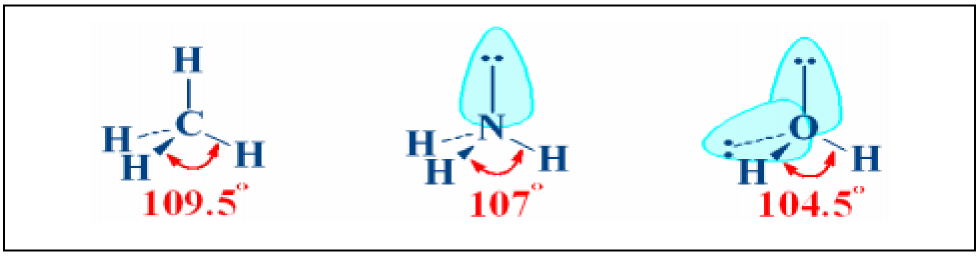
Table 1: Geometry around atom A according to the type of atom in V.S.E.P.R theory.

Number of pairs (m + n)			***Kind***	***Hybridization of the central atom***		***Geometry of the molecule (angle)***	***Example***
Total	***Binding***	**Non-binding**					
2	2	0	AX_2	**SP**		**Linear** (180°)	**BeH_2** 
3	3	0	AX_3	**SP^2**		**Trigonal plane (Triangular)** (120°)	**BF_3** 
	2	1	AX_2E	**SP^2**		**V-shape**	**$SnCl_2$** 
4	4	0	AX_4	**SP^3**		**Tetrahedral** (109°)	**CH_4** 
	3	1	AX_3E	**SP^3**		**Pyramidal**	**NH_3** 
	2	2	AX_2E_2	**SP^3**		**V-shape**	**H_2O** 

2. Factors that influence molecular geometry

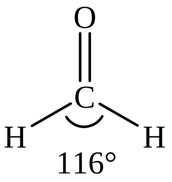
a) Influence of lone pairs

The presence of a lone pair causes a distortion of the angles. A lone pair E leads to the widening of the angles E-A-X and the reduction of the bond angles X-A-X.



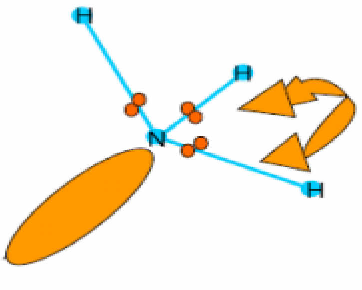
b) Influence of double bonds

Double bonds correspond to two lone pairs, or 4 electrons. Since the charge is greater, the repulsion will be higher, which will modify the angles.

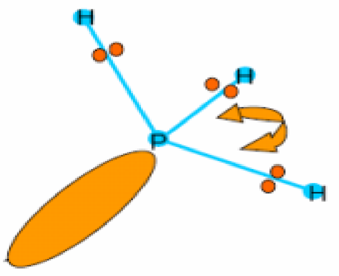


c) Influence of the central atom

For molecules that differ only by the nature of the central atom, variations in angles are also observed. These variations are due to the difference in electronegativity between the central atom and the surrounding atoms. The more electronegative an atom is, the more it tends to attract the bonding pairs it shares towards itself.



α = 107°



α' = 93°