Institute of veterinary sciences Constantine 1- Frères Mentouri university

Part I : Atomistic / Chapter II

Chemical bonds

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Objectives :

- ✓ Represent the electronic structure (Lewis structure) of a covalent compound based on its molecular formula.
- ✓ Predict the type of bond between two chemical elements.
- ✓ Determine the geometry of a molecule.

Why do chemical bonds form ?

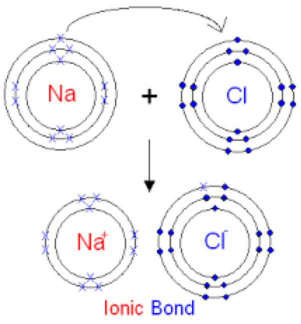
In the universe, all bodies tend to acquire a state of maximum stability. Atoms are no exception: they achieve this stability by forming chemical bonds with other atoms.

I.Types of chemical bonds :

I.1 Ionic bond (electrovalent) :

Within the octet rule and achieving a noble gas configuration, the ionic (electrovalent) bond is the easiest to describe. Group 1 elements (except H) have GR ns^1 structure; low ionization potential makes +1 ion formation easy. Group VII have GR ns^2np^5; high electron affinity favors -1 ions. Electron transfer restores noble gas configs, e.g., $Na + Cl \rightarrow Na^+ Cl^-$.

Occurs between alkali/alkaline earth and halogens/chalcogens with high electronegativity difference.



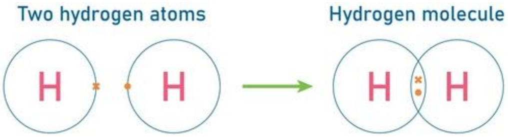
I.2 Covalent bond :

I.2.1 Pure covalent bond :

A covalent bond is formed by **sharing electron pairs**.

Example: Hydrogen molecule (H_2)

Each hydrogen atom contributes one electron. A shared electron pair (bonding pair) is formed.



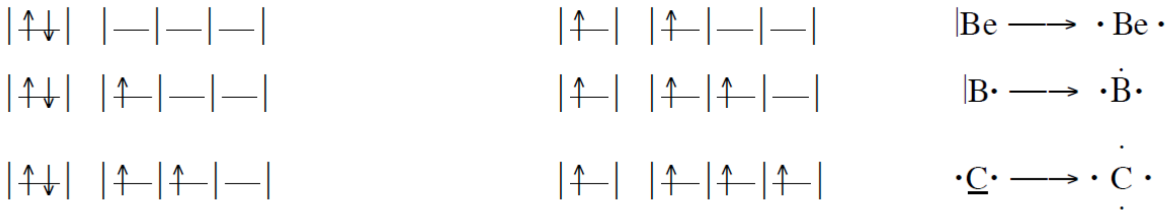
This type of bond occurs between **identical atoms** (e.g., F_2, Cl_2).

I.2.2 The Notion of Valence State:

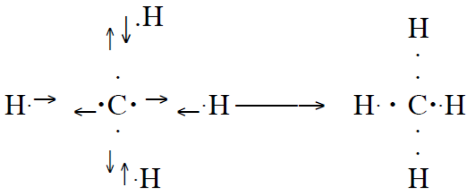
The previous description does not allow us to describe all encountered situations. For example, this presentation suggests the existence of a molecule such as CH_2. This molecule exists but is not very stable; however, a stable form, CH_4, exists, suggesting the availability of four unpaired electrons on the carbon atom, which lead to the formation of four bonds.

The description of the atom in molecules is different from that of the isolated atom. Within a molecule, the atom can pass into a different "**valence state**" (pass into an excited atomic state) provided that the overall energy balance is favorable, i.e., that the energy cost related to this "**promotion**" is compensated by the energy gain related to the formation of the new bond in the stable molecule.

What is this valence state? When the p subshell is vacant, one can conceive a promotion of one of the 2s electrons to the free 2p subshell. This will be the case for beryllium, boron, and carbon, which take the following configurations:



These configurations respectively possess two, three, and four unpaired electrons, a situation encountered in many molecules, including CH_4. In this case:



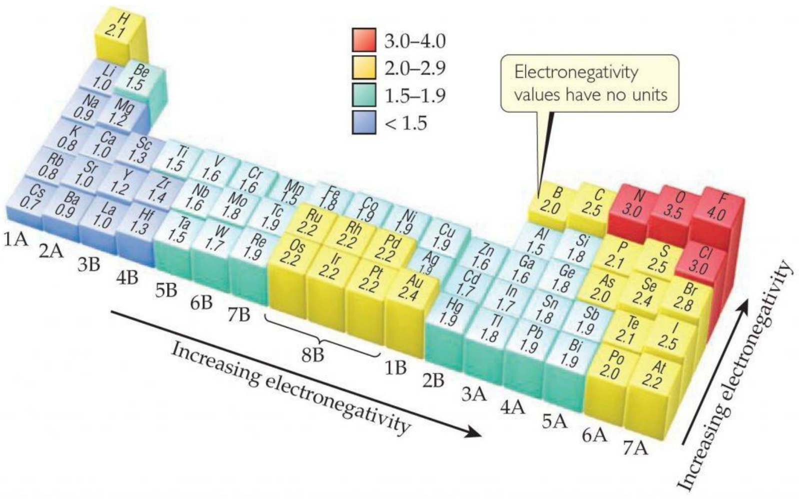
I.2.3 The Polar Covalent Bond:

The covalent bonds we have just described differ from the pure covalent bond in that they unite atoms of different natures. However, as we have seen, not all atoms have the same tendency to exchange electrons. Some lose an electron more easily, while others gain an electron more easily. Electronegativity measures this tendency. Consequently, the shared electrons in the covalent bond will be preferentially attracted towards one of the two atoms; the bond is said to be polarized. A way to estimate this polarization, due to the preferential displacement of the bonding electron pair towards one of the two bonded atoms, was discussed by Pauling.

"Pauling's electronegativity measures the tendency of an atom in a molecule to attract the electron cloud towards itself."

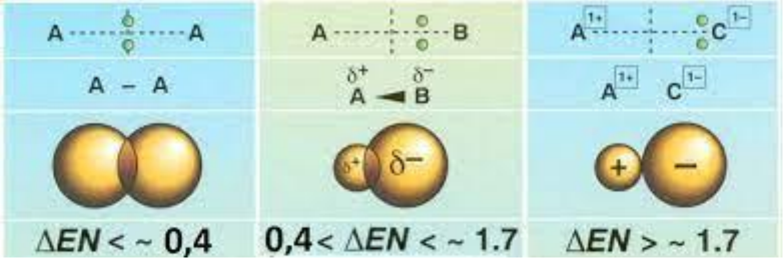
I.2.4 Bond Polarization:

In his 1939 work The Nature of the Chemical Bond, Pauling developed the concept of electronegativity, a dimensionless quantity that reflects the tendency of an atom to attract bonding electrons towards itself. The Pauling scale, below, remains the most commonly used today.



The difference in electronegativity between two atoms proves to be the most relevant quantity for predicting the **polarization** of a bond. Pauling focused on this.

- In the **[pure (nonpolar) covalent bond]{.underline}**, electrons are shared and equally distributed between the two atoms; case where the electronegativity difference **[$\Delta EN < 0.4$].**
- In the **[polar covalent bond]{.underline}**, the more electronegative atom in a polar bond attracts the covalent bond electrons towards itself. Case where the electronegativity difference **[$0.4 < \Delta EN < 1.7$].**
- In the **[ionic bond]{.underline}**, electrons are transferred from one atom to another; case where the electronegativity difference **[$\Delta EN > 1.7$]**



Pauling showed that between these two "limit" cases, most bonds are polar covalent (or polarized). In this case, the more electronegative atom attracts the bonding electrons towards itself and then bears a partial negative charge, denoted δ^-. Conversely, the other atom in the bond obviously bears a partial positive charge δ^+.

II. The Lewis formula:

II.1. Duet and octet rules :

Noble gases (rare gases) all have a full valence shell (the outer shell):

- The valence shell (K shell) of helium (He) atoms contains an **electron doublet**;
- The valence shell of all other noble gases (Ne, Ar, etc.) contains eight electrons. They are said to possess an **electron octet** on their valence shell.

To become stable, elements adopt the structure of the nearest noble gas either by losing or gaining one or more electrons.

- If the nearest noble gas is Helium, **[the duet rule]** is applied.

- If the nearest noble gases are Neon or Argon, **[the octet rule]**is applied.

Example :

Cl: Z = 17, 17 electrons, its electronic configuration is Cl: [$1s^2 2s^2 2p^6$] $3s^2 3p^5$; **therefore, 7 electrons on the outer shell.**

Cl^-: Z = 17 but there are 18 electrons, so the electronic configuration of this ion is [$1s^2 2s^2 2p^6$] $3s^2 3p^6$ and it has **8 electrons on the outer shell (full valence shell)**.

Chloride ions are found in nature, but not chlorine in atomic form. Chloride ions are therefore stable species, unlike chlorine.

How do atoms respect these rules?

- - Either by forming monoatomic or polyatomic ions;
- Or by forming molecules.

A molecule results from the association of at least two atoms. This association allows each atom to respect the duet or octet rule and thus be surrounded by two or eight electrons.

Consequently:

The maximum number of bonds an atom can form is x = 8 - Nv, (where Nv is the number of valence electrons).

This is valid for the second and third periods of the table.

- Exception for hydrogen: (x = 2 - 1 = 1 bond maximum)
- Exception for n greater than 4.

II.2. The General Method for Writing Lewis Structures:

Consider a molecule with a central atom (connected to all other atoms in the molecule). We will write the Lewis structure for the molecule COH_2 (formaldehyde).

Very generally, the central atom is the least electronegative. For this example, the carbon atom will be the central atom.

1) Step 1:

Count all available electrons: $N_e = \Sigma N_v - z$

Where Nv is the number of valence electrons for each atom, and z is the (algebraic) number of elementary charges carried by the molecule.

Example: A^(z±), with z > 0 for a cation, and z < 0 for an anion.

For the COH_2 molecule: Ne = 4 (C) + 6 (O) + (2×1)(H) - 0 = 12.

Number of possible doublets:

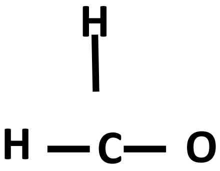
Nd = Ne / 2; if Ne is even.

Nd = (Ne - 1) / 2*; otherwise.

Here **Nd** = 6

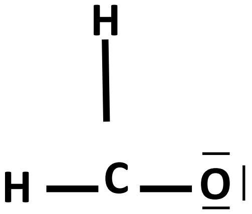
2) Step 2:

Create simple covalent bonds between the central atom and the peripheral atoms.



3) Step 3:

On réalise l'octet des atomes périphériques (en leur attribuant des doublets non liants)



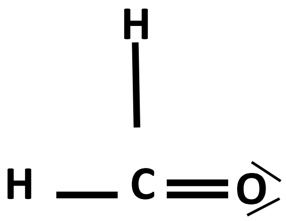
4) Step 4:

Assign all remaining doublets and electrons to the central atom and check if it satisfies the octet rule. If not, proceed to the fifth step.

Here, no change; C does not satisfy the octet.

5) Step 5 :

On recommence en envisagent des liaisons multiples entre l'atome central et l'atome périphériques.



6) Step 6 :

Assign a formal charge to each atom:

Count, for each atom, the number of electrons belonging to it.

$$N_a = \Sigma\, e^- \in DNL + \frac{1}{2}\Sigma\, e^- \in DL$$

1/2 because each electron in a bonding doublet belongs to two atoms.

Thus: $N_a = 2*Nbr_{DNL} + Nbr_{DL}$

Definition: CF: Formal charge $C_F = e * (N_v - N_a)$; (e est la charge élémentaire).

Thus: $C_F = N_v - N_a$

Therefore: $C_F = N_v - (2*Nbr_{DNL} + Nbr_{DL})$

Returning to the example :

C : $C_F = 4 - (2*0 + 4) \rightarrow C_F = 0$

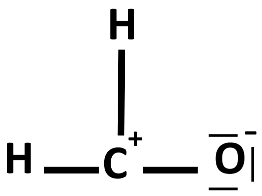
O : $C_F = 6 - (2*2 + 2) \rightarrow C_F = 0$

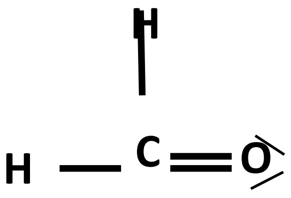
H : $C_F = 1 - (2*0 + 1) \rightarrow C_F = 0$

Mehod for determining the correct lewis formula :

Calculate $\Sigma|C_F|$. The correct strucure is the one where $\Sigma|C_F|$ is minimal.

Example :





$\Sigma|C_F| = 2$

$\Sigma|C_F| = 0$

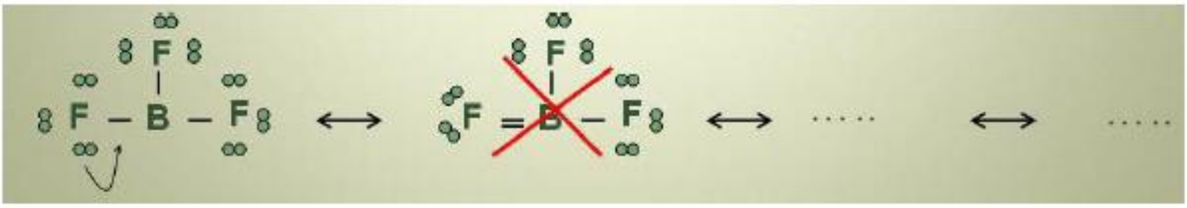
In the first formula, the positive charge will tend to attract the negative charge, which will neutralize C; the second is therefore better.

Remarks :

1. ***Molecule with an odd number of electrons:*** The octet rule cannot be satisfied; there is one unpaired electron. These species, notably free radicals, have a short lifespan and are very reactive.

2. ***Incomplete Octet*** :

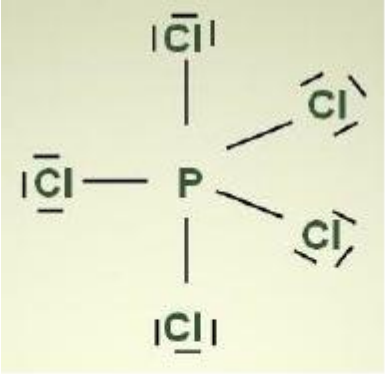
There are compounds in which certain atoms, especially elements on the left side of the p-block, have an incomplete octet.



Note that it is the first structure, where boron has an incomplete octet, that is the most stable

3. ***Expanded octet*** **:** The most common elements in the table only have 2s and 2p orbitals to form bonds. Their valence shells need 8 electrons.

Elements of the third period have unoccupied 3d orbitals; these orbitals can accommodate additional electrons.



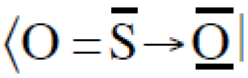
The molecule is surrounded by 10 electrons and occupies the 3s and 3d orbitals. It exhibits an expanded octet.

The size of the central atom plays an important role; the central atom must be sufficiently large to be surrounded by 5 chlorine atoms.

II.3. Limitations of the Lewis model :

The Lewis model is interesting for its simplicity; it allows for a satisfactory interpretation of the fundamental mechanisms of bond formation and breaking, which is the basis of any analysis of chemical reactivity. On the downside:

- In some cases, it does not allow for a single unique formula. For example, in the case of SO_2 we are led to propose the formula:



$$\langle O = \overline{S} \rightarrow \underline{\overline{O}}|$$

which unjustifiably distinguishes one oxygen from the other.

II.3.1 The notion of resonance (mesomerism) :

While for a large number of molecules, the structure formula that can be proposed based on the Lewis model very satisfactorily accounts for the properties of the compound, for a certain number of molecules, it is not possible to propose a single unique structure. Thus, for example, in the case of SO_2 mentioned in the previous paragraph, we are forced to propose two different, Although symmetrical, formulas:

$$\langle O = \overline{S} \rightarrow \overline{\underline{O}}| \qquad \leftrightarrow \qquad |\overline{\underline{O}} \leftarrow \overline{S} = O\rangle$$

Wave mechanics interprets this by stating that the molecule is not adequately represented by any of the proposed Lewis formulas. These structures are limiting formulas. The real structure is intermediate between all the structures that can be proposed; we say that the real structure is a weighted superposition of all these structures, that the molecule resonates between all its structures. Thus, the concept of resonance is defined. The main limiting structures, or resonance formulas, are reproduced and linked by the double arrow ↔, which means they are several representations of the same molecule.

One can attempt to represent this weighted superposition in a single formula which would be:

$$\langle O = \overline{S} = O\rangle$$

In this case, the Lewis structure is not respected, but since sulfur is part of the third period, one can invoke a promotion comparable to that presented for phosphorus above.

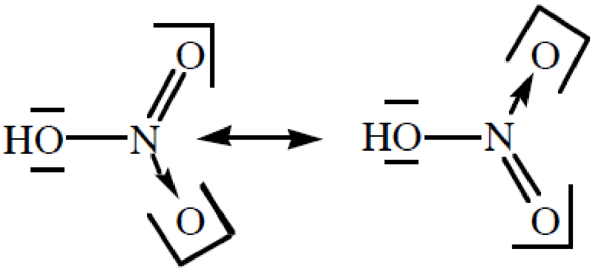
This can lead to a tetravalent, or even hexavalent, configuration for sulfur.

$$3s\,|\uparrow\downarrow|\quad 3p\,|\uparrow\downarrow|\uparrow|\uparrow| \longrightarrow 3s\,|\uparrow\downarrow|\quad 3p\,|\uparrow|\uparrow|\uparrow|\quad 3d\,|\uparrow|-|-|-|-|$$

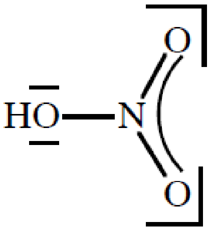
$$3s\,|\uparrow\downarrow|\quad 3p\,|\uparrow\downarrow|\uparrow|\uparrow| \longrightarrow 3s\,|\uparrow|\quad 3p\,|\uparrow|\uparrow|\uparrow|\quad 3d\,|\uparrow|\uparrow|-|-|-|$$

Resonance formulas are used to describe the structure of many compounds, such as:

- HNO_3 :acid



which is often written in a single form combining these two representations:



III. VSEPR Theory (Valence Shell Electron Pair Repulsion):

III.1 Principle :

- - Valence electron pairs (or doublets) (bonding and non-bonding) of an atom undergo electrostatic repulsions.
- ***Gillespie*** assumes they are arranged on the surface of a sphere.
- The center is occupied by the atom.
- The repulsion energy must be as low as possible.

This principle dictates the geometry of the molecule. Some rules allow for the qualitative estimation of bond angles.

III.2 GILLESPIE’s rule :

The shape of the repulsion figure describing an atom in a molecule depends on the number of atoms it bonds to and the number of its lone pairs.

Atoms in a molecule are thus classified according to their **VSEPR** type, using the general nomenclature:

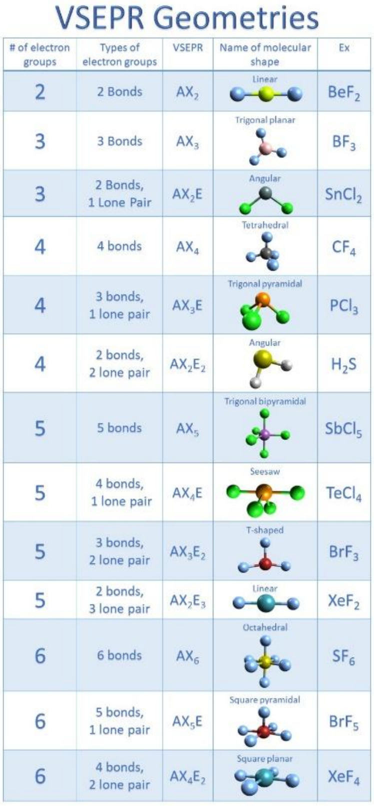
$$\mathbf{AX_mE_n}$$

A : Central atom.

X : Atoms or molecules bonded to atom A by covalent bonds, and **m** is their number.

E : Lone pairs or unpaired electrons, and **n** is their number on the valence shell of atom A..

The shape of the repulsion figure around an atom is obtained by considering that ***bonds and lone pairs position themselves as far apart as possible*** from each other to minimize their mutual repulsion. Typical arrangements are obtained depending on the value of n+m.



VSEPR Geometries

# of electron groups	Types of electron groups	VSEPR	Name of molecular shape	Ex
2	2 Bonds	AX_2	Linear	BeF_2
3	3 Bonds	AX_3	Trigonal planar	BF_3
3	2 Bonds, 1 Lone Pair	AX_2E	Angular	$SnCl_2$
4	4 bonds	AX_4	Tetrahedral	CF_4
4	3 bonds, 1 lone pair	AX_3E	Trigonal pyramidal	PCl_3
4	2 bonds, 2 lone pair	AX_2E_2	Angular	H_2S
5	5 bonds	AX_5	Trigonal bipyramidal	$SbCl_5$
5	4 bonds, 1 lone pair	AX_4E	Seesaw	$TeCl_4$
5	3 bonds, 2 lone pair	AX_3E_2	T-shaped	BrF_3
5	2 bonds, 3 lone pair	AX_2E_3	Linear	XeF_2
6	6 bonds	AX_6	Octahedral	SF_6
6	5 bonds, 1 lone pair	AX_5E	Square pyramidal	BrF_5
6	4 bonds, 2 lone pair	AX_4E_2	Square planar	XeF_4

IV.Hybridization :

The theory of hybridization explains the geometry of certain molecules. It also gives the values of the angles between the bond directions in a polyatomic molecule.

There are three types of hybridization: sp^3, sp^2, and sp.

IV.1 sp Hybridization^3 :

In the CH_4 molecule, the four C-H bonds are identical. They form an angle of 109°28'.

A regular tetrahedral structure is adopted with carbon at the center of the polyhedron and hydrogen atoms at the vertices.

To explain this tetrahedral shape of CH_4, we proceed step by step.

1st step:

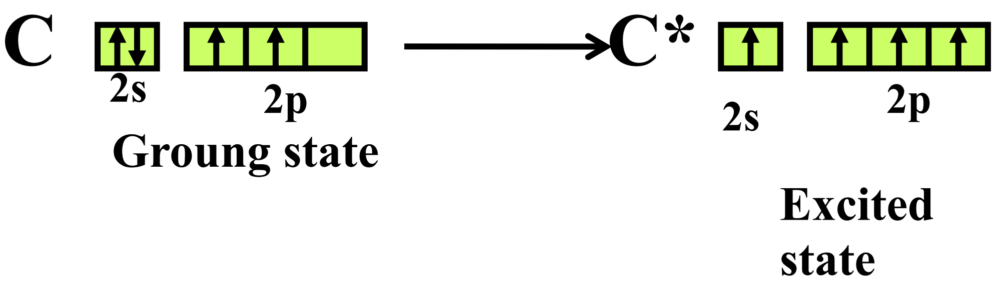
Configuration of carbon in the ***ground state***: $1s^2\ 2s^2\ 2p^2$

Considering only the valence electrons. Carbon has 2 unpaired electrons, so it can only form two bonds.

2nd step:

The electronic configuration of carbon in the ***excited state***: $1s^2\ 2s^1\ 2p^3$

According to the excited state: Carbon has four unpaired electrons. Therefore, four bonds can be explained.



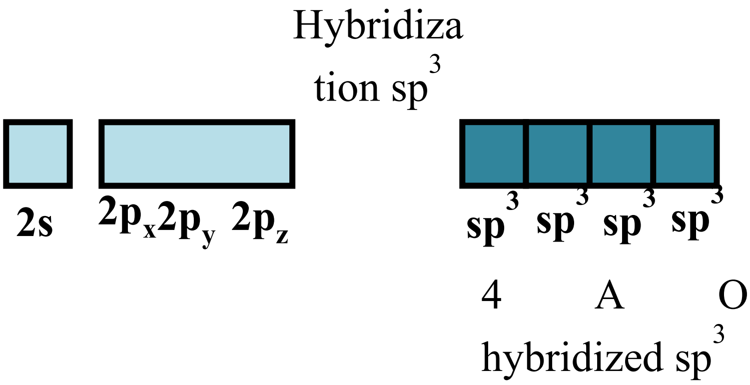
3rd step:

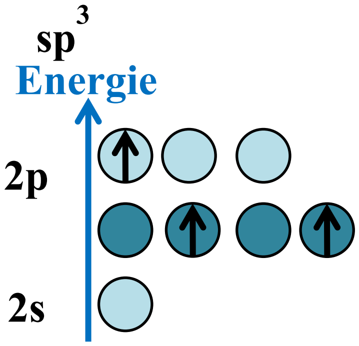
sp^3 hybrid orbitals.

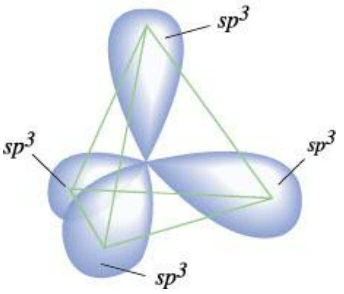
We consider that carbon in its reactive state has four equivalent hybrid orbitals obtained by mixing the basic atomic orbitals 2s, 2px, 2py, and 2pz.

Each **sp^3** hybridized AO has 25% **s** character and 75% **p** character.

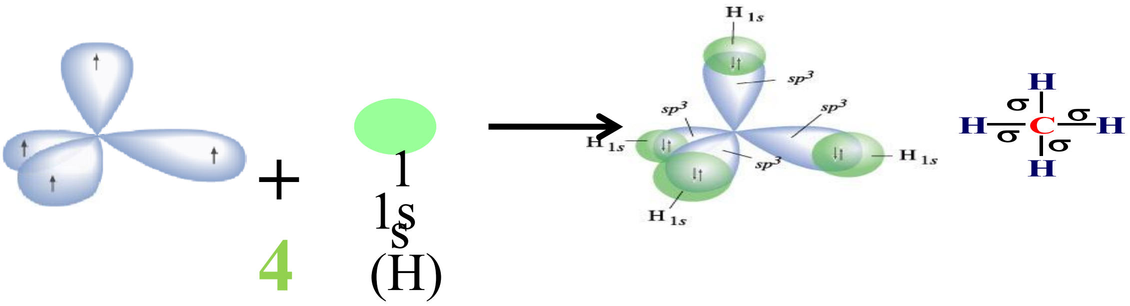
The 4 **sp^3** hybridized AOs are equivalent and are directed from the center to the vertices of a ***regular tetrahedron***; they are equivalent.





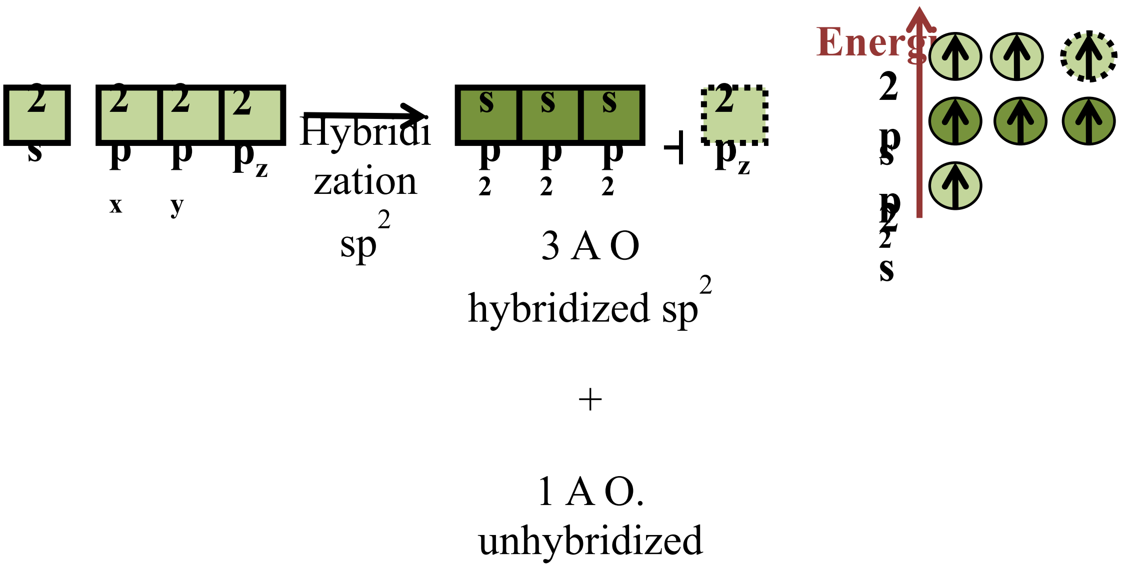


An sp^3 hybrid orbital can combine with another orbital (axial overlap) to give a **σ bond**.

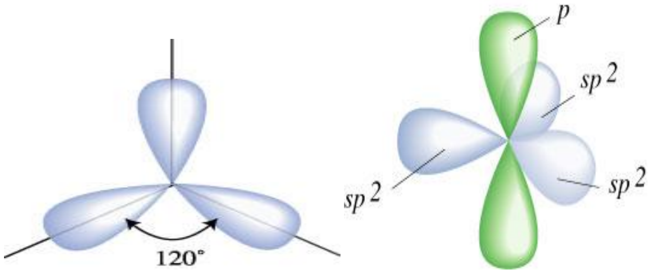


IV.2 sp² Hybridization :

This hybridization is an overlap between one **s** AO and two **p** AOs, giving rise to three identical sp² hybridized orbitals; the 3rd **p** AO remains unhybridized. Each sp² hybridized AO has 1/3 **s** character and 2/3 **p** character.

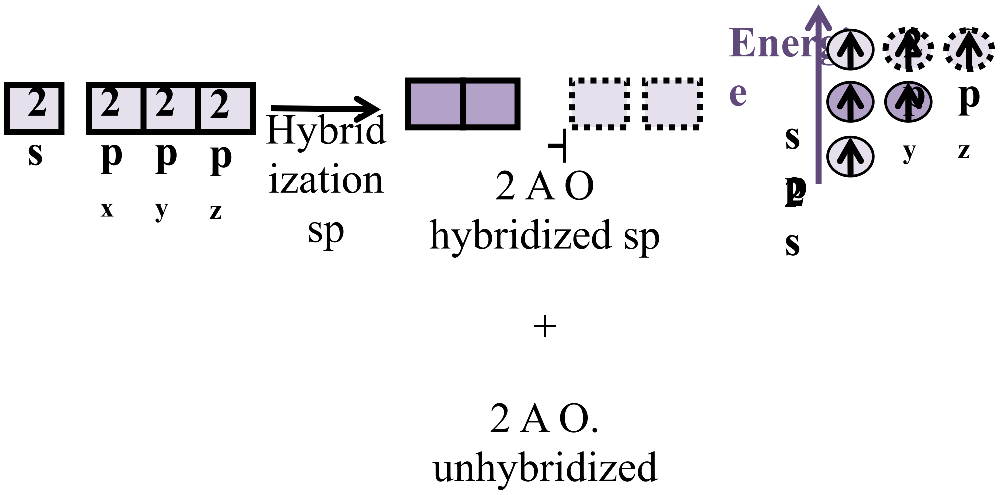


The three sp² hybridized AOs, also called trigonal AOs, have a planar configuration forming an angle of 120°.



IV.3 sp^1Hybridization :

This hybridization is an overlap between an ***s AO*** and a ***p AO***, giving rise to two identical ***sp hybridized*** orbitals.



The sp hybridized AOs are also called diagonal AOs. Each **sp** hybridized AO has 50% **s** character and 50% **p** character, and the angle between the hybrid orbitals is 180°.