

Chemical bonding and the structure of molecules

I/ Formation of covalent bonds and Lewis structures

I.1/ Lewis notation

G. N. Lewis proposed a very practical method to describe atoms:

- ✓ Valence electrons are represented around the chemical symbol of the element
- ✓ Single electrons are represented by dots.
- ✓ Electron pairs are represented by a dash.

IA ns^1	IIA ns^2	IIIA ns^2np^1	IVA ns^2np^2	VA ns^2np^3	VIA ns^2np^4	VIIA ns^2np^5	VIIIA ns^2np^6
Li•	•Be•	•B•	•C•	•N•	•O•	•F•	•Ne•

I.2/ Formation of covalent bonds

A covalent bond is the sharing of two valence electrons.

A covalent bond results from the sharing of one or more pairs of electrons between two atoms.

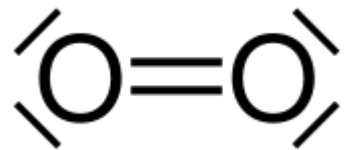
A covalent bond is shown by two dots or, more commonly, by a dash.



Such a representation is called a Lewis structure.

The pair of electrons located between the two atoms is a bonding pair (or bonding electron pair, BP).

The other pairs, located on the atoms and belonging to them, are lone pairs (or non-bonding electron pairs, LP).



A double bond



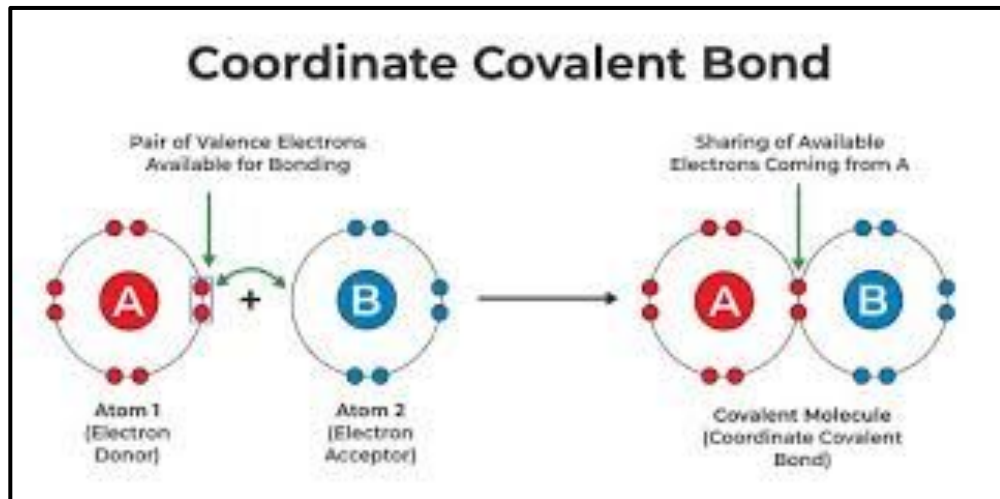
A triple bond

There are two possible cases for the sharing of two valence electrons.

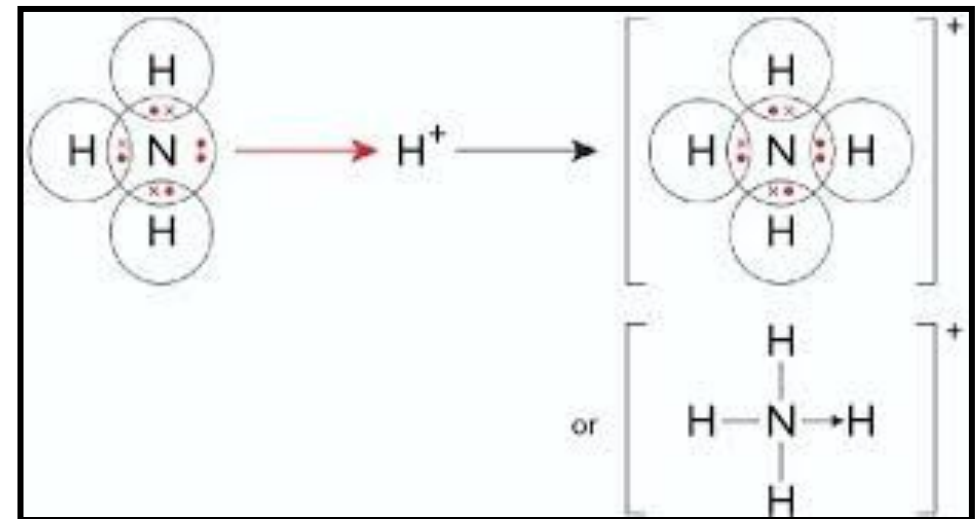
- ✓ Each atom provides one electron: a single covalent bond.



- ✓ Both electrons come from the same atom (dative bond). One atom donates the electron pair, and the other atom provides an empty orbital.



Example



The bonds formed can be single or multiple:

Single bond: 1 σ pair.



Double bond: 1 σ pair and 1 π pair.



Triple bond: 1 σ pair and 2 π pairs.

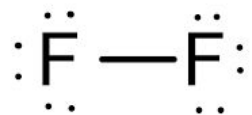


There may be a remaining single electron (a radical).

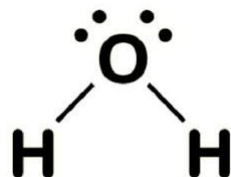


✓ Octet rule

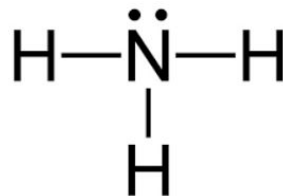
Maximum stability is reached when all atoms are surrounded by 4 electron pairs (bonding or non-bonding), because atoms tend to achieve the $s^2 p^6$ electron configuration.



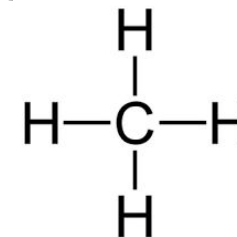
F is monovalent



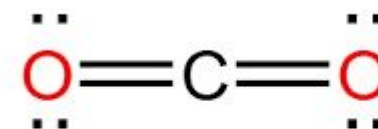
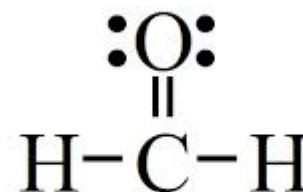
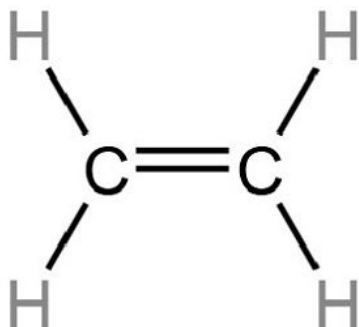
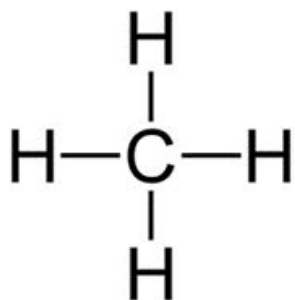
O is divalent



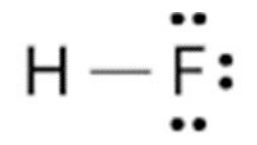
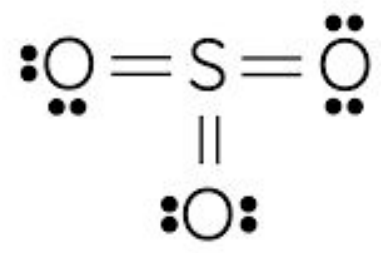
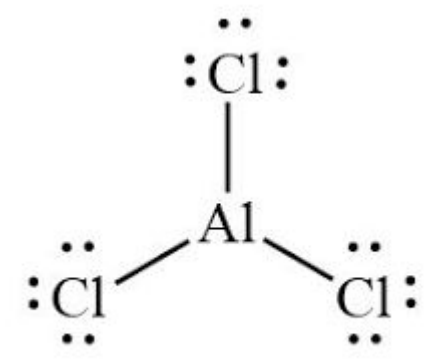
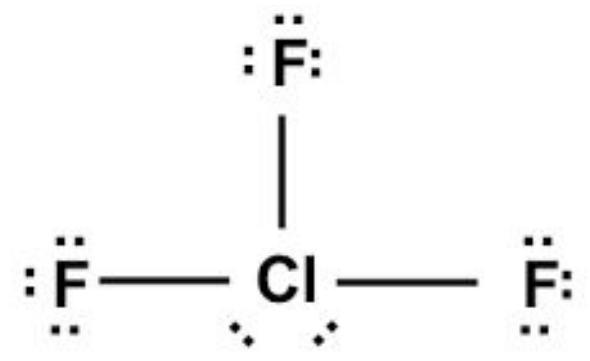
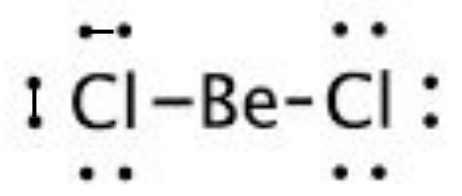
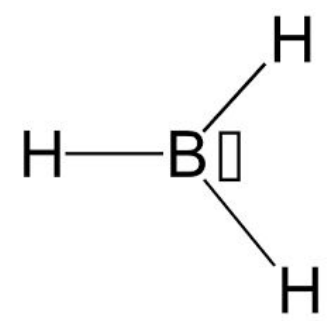
N is trivalent



C is tetravalent



✓ Limitations of the octet rule



I-3/ Characteristics of the covalent bond

✓ Energy of the covalent bond

Bond energy is the amount of energy that must be supplied to break the bond (BE).

Example : C–C: 345 kJ/mol

C–O: 356 kJ/mol

The length of a covalent bond is on the order of a few hundred picometers. The stronger a bond is, the shorter it becomes.

Example : C–C: 154 pm

C–O: 143 pm

For two given elements, multiple bonds are stronger and shorter than single bonds.

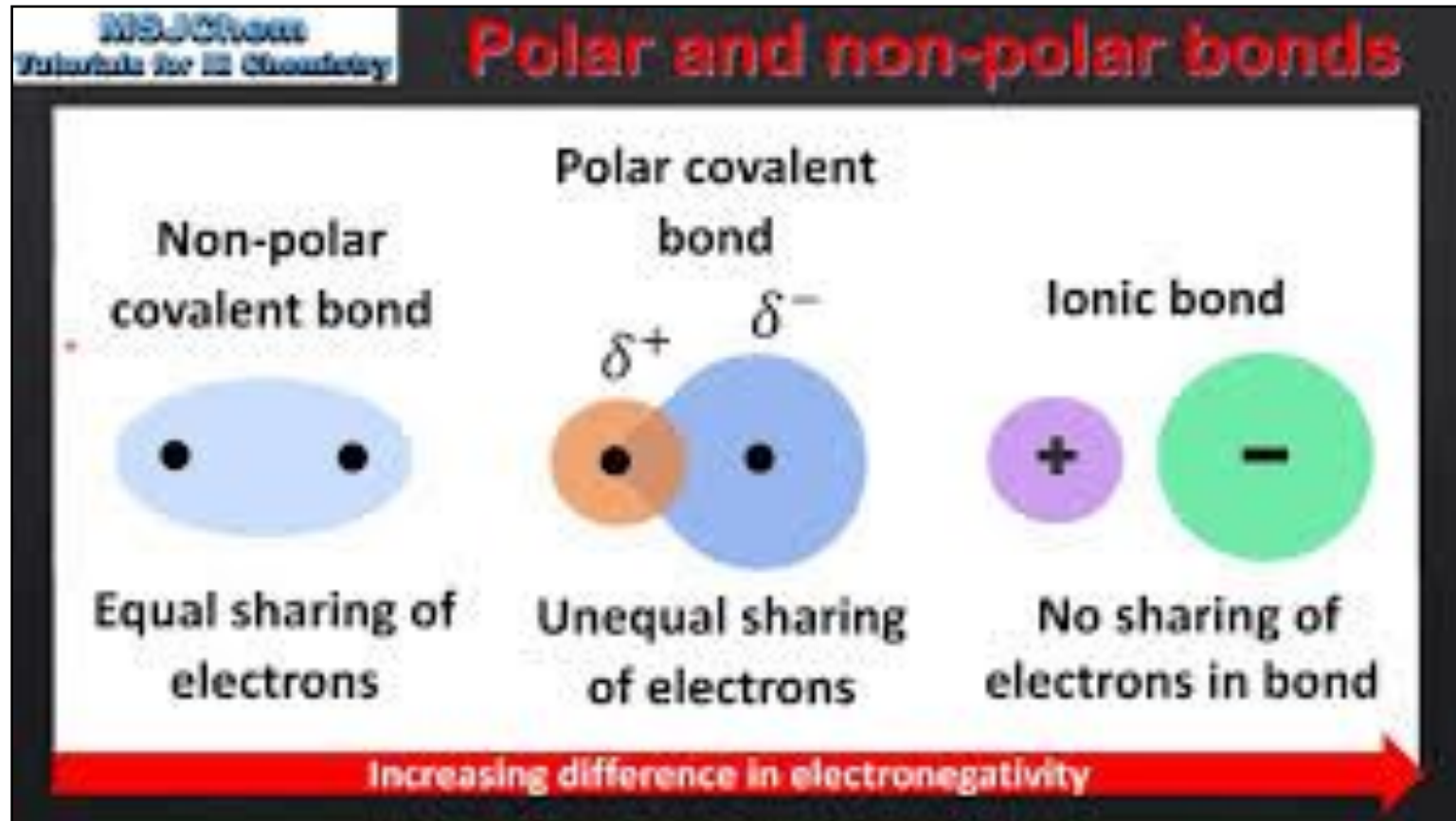
Example : C–C : 154 pm $E_L = 345 \text{ kJ/mol}$

C=C : L = 134 pm $E_L = 615 \text{ kJ/mol}$

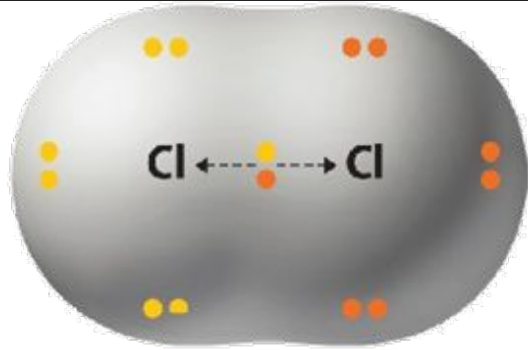
C≡C : L = 120 pm $E_L = 812 \text{ kJ/mol}$

✓ Polar property of the covalent bond

A polar bond is a covalent bond in which the electrons are unequally shared between the two atoms.

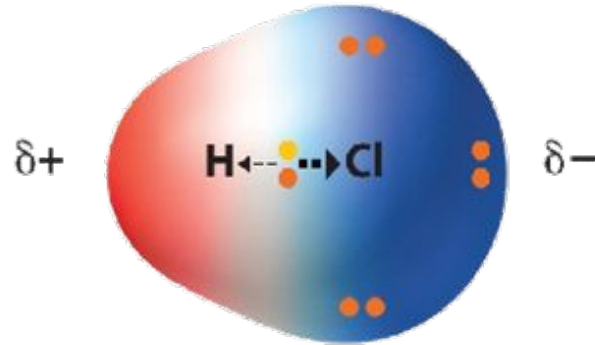


Example



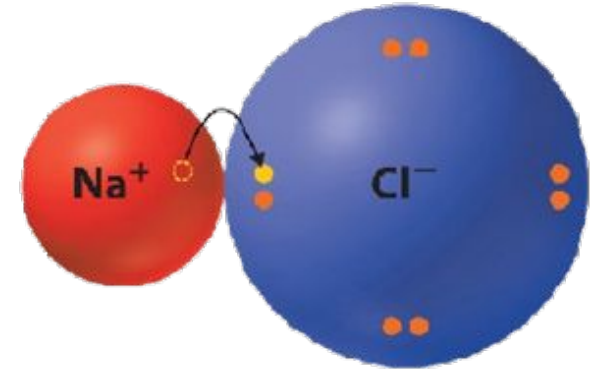
Non-Polar Covalent Bond

Bonding electrons *shared equally* between two atoms.
No charges on atoms.



Polar Covalent Bond

Bonding electrons *shared unequally* between two atoms.
Partial charges on atoms.



Ionic Bond

Complete *transfer* of one or more valence electrons.
Full charges on resulting ions.

II/ VSEPR Theory

The VSEPR theory (Valence Shell Electron Pair Repulsion), also known as Gillespie's theory, provides information about the spatial geometry of the species.

The geometry of a molecule around a given atom will be the one in which the repulsions between electron pairs are minimized.

AX_nE_m notation:






A: central atom

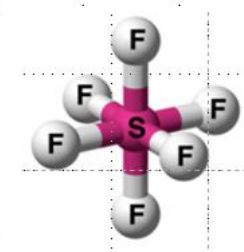
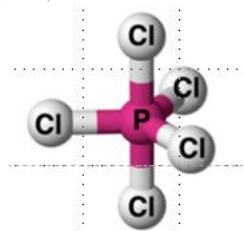
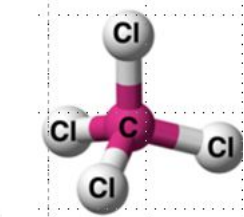
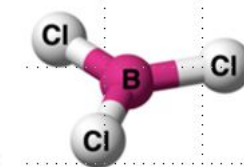
n: number of bonding directions (bonding electron pairs)


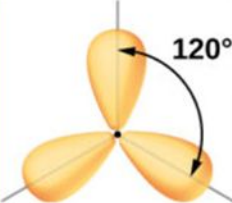
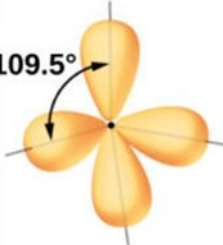
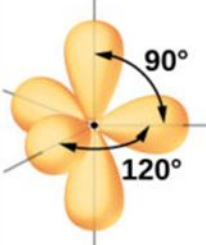
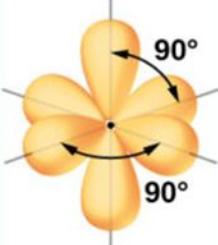
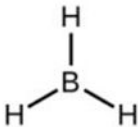
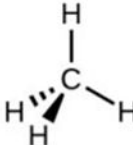
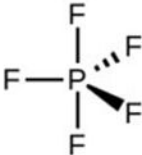

m: number of lone pairs on atom A

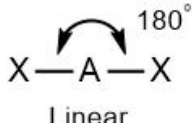
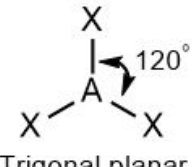

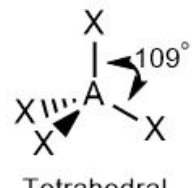

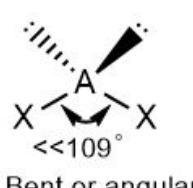
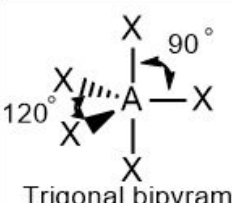
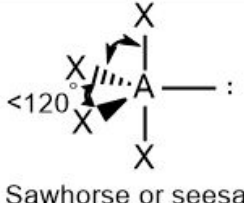
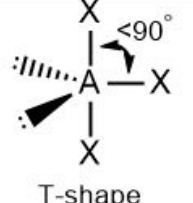
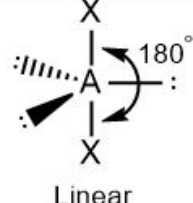
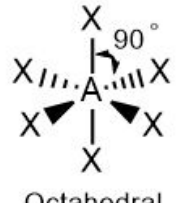
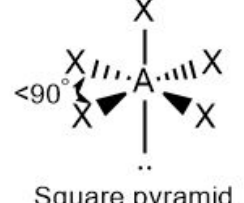
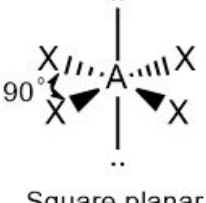
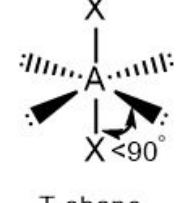
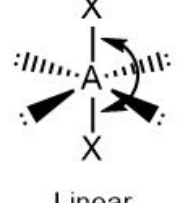
✓ AX_nE_m repulsion geometries

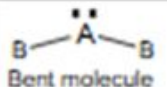
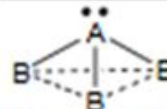
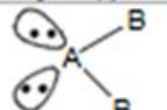
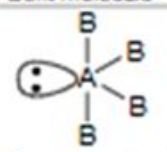
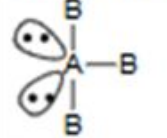
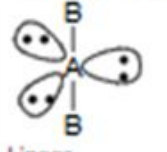
It is determined by the number of directions taken by the electron pairs around atom A.

# of Bonds	# of Lone Pairs	AXE Notation	e- Pair Geometry	Molecular Geometry	Visual Model	Bond Angle(s)
2	0	AX ₂ E ₀	Linear	Linear		180°
3	0	AX ₃ E ₀	Trigonal Planar	Trigonal Planar		120°
4	0	AX ₄ E ₀	Tetrahedral	Tetrahedral		109.5°
5	0	AX ₅ E ₀	Trigonal Bipyramidal	Trigonal Bipyramidal		120°, 90°
6	0	AX ₆ E ₀	Octahedral	Octahedral		90°



Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pair	3 lone pair	4 lone pair
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Class, AB _x E _y	Number of elec. pairs	Bonding pairs	Lone pairs	Overall geometry	Molecular Geometry
AB ₂ E SO ₂ , O ₃	3	2	1	Trigonal planar ∠ BAB ≤ 120°	 Bent molecule
AB ₃ E NH ₃	4	3	1	Tetrahedral ∠ BAB ≤ 109.5°	 Trigonal pyramid
AB ₂ E ₂ H ₂ O	4	2	2	Tetrahedral ∠ BAB ≤ 109.5°	 Bent molecule
AB ₅ E SF ₄ , IF ₄ ⁺ , XeO ₂ F ₂	5	4	1	Trigonal bipyramid Bond angles 120° and 180°	 See-saw molecule
AB ₃ E ₂ ClF ₃	5	3	2	Trigonal bipyramid ∠ BAB ≤ 90°	 T-shaped molecule
AB ₂ E ₃ XeF ₂ , I ₃ ⁻	5	2	3	Trigonal bipyramid ∠ BAB ≤ 180°	 Linear

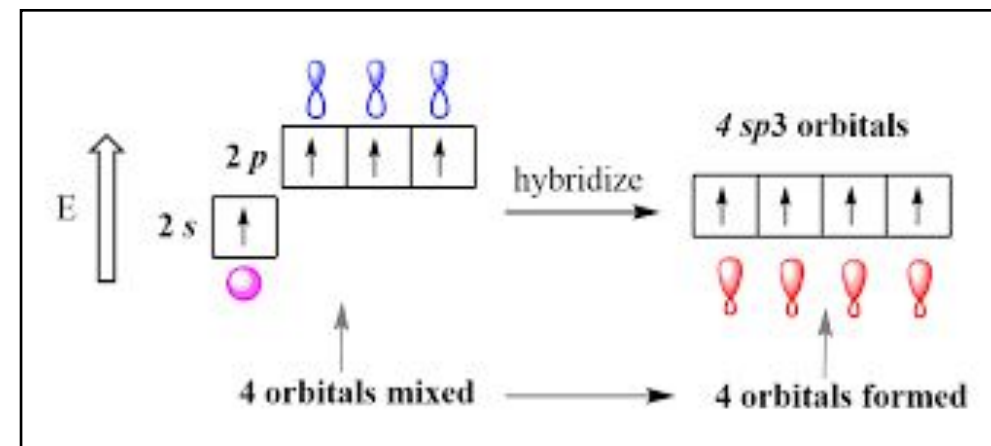
III/ Theory of hybrid atomic orbitals

We are going to study three types of hybrid orbitals: sp^3 , sp^2 and sp .

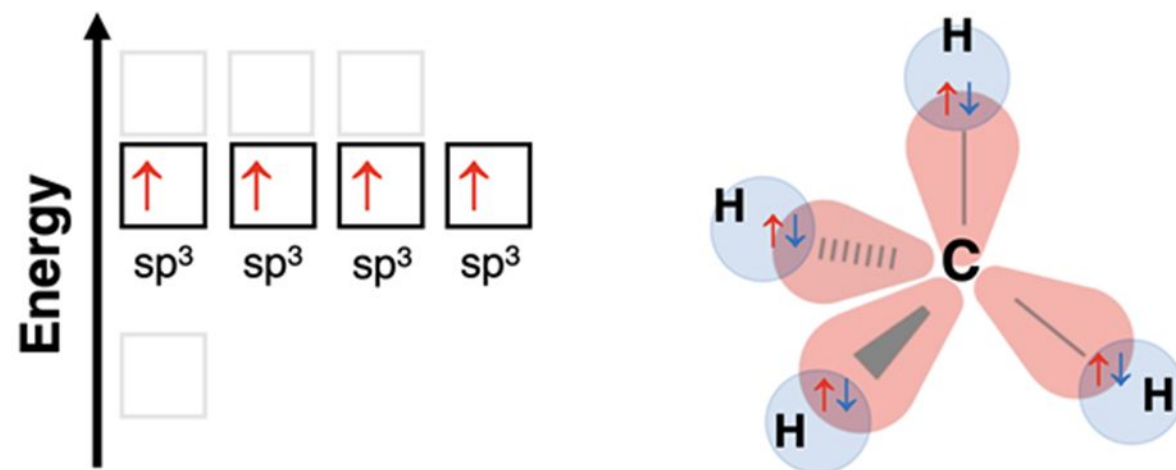
III.1/ SP^3 Hybridization

SP^3 hybridization is the mixing of one s orbital and three p orbitals to form four identical hybrid orbitals arranged in a tetrahedral shape

A common example of sp^3 hybridization is the carbon atom in methane (CH_4). Carbon forms four equivalent C–H bonds arranged in a tetrahedral shape



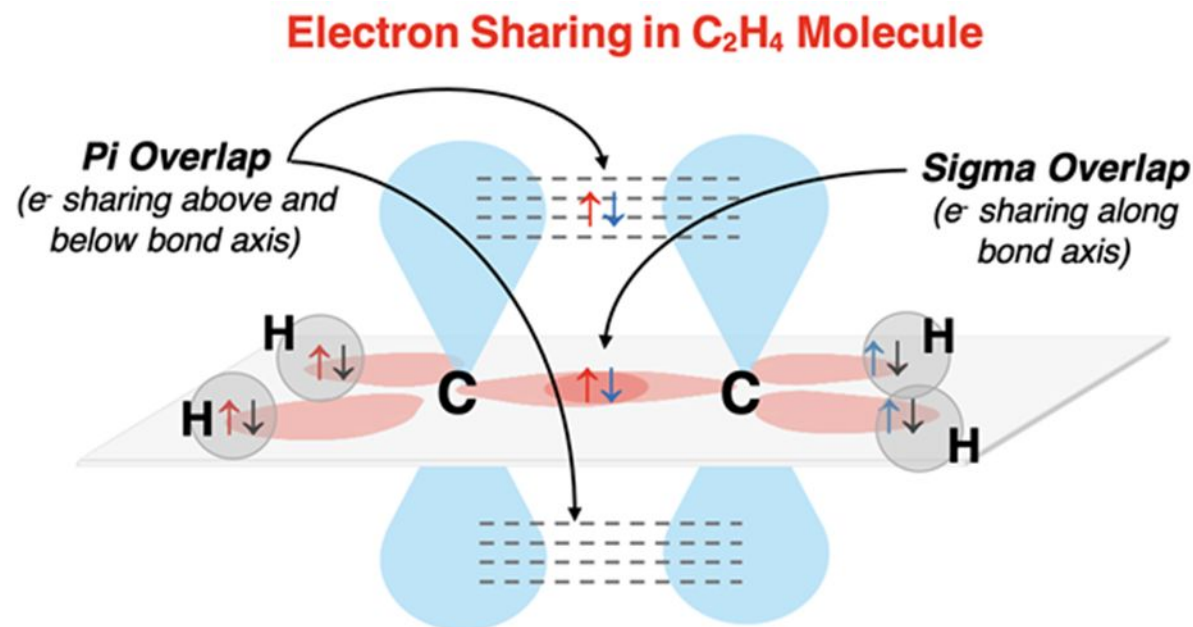
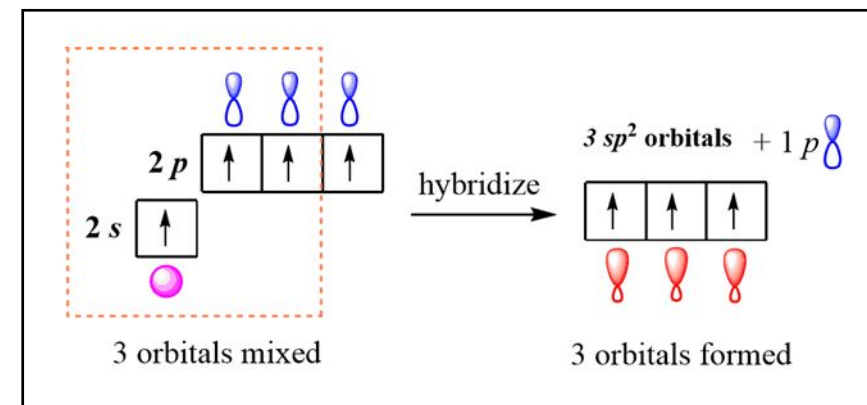
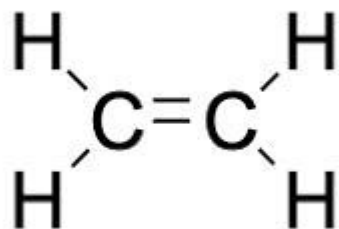
Electron Sharing in CH_4 Molecule



III.2/ sp^2 Hybridization

sp^2 hybridization is the mixing of one s orbital and two p orbitals to form three identical hybrid orbitals arranged in a trigonal planar shape.

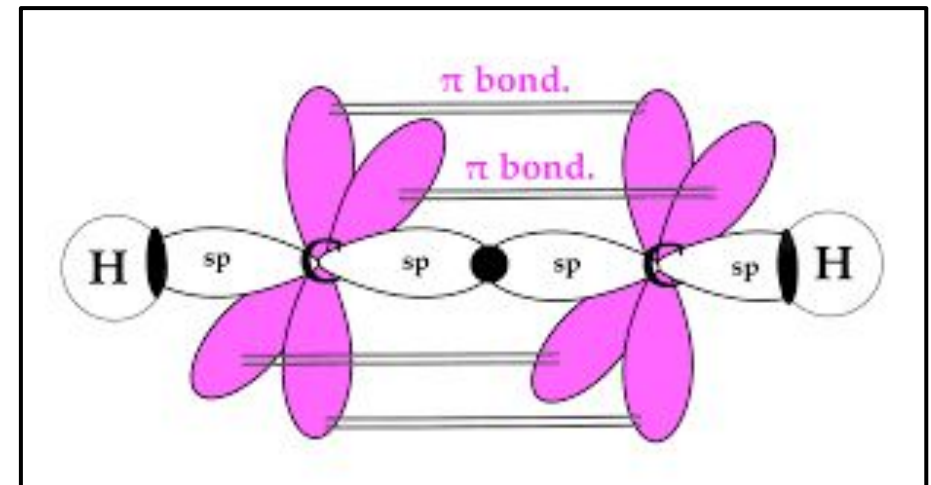
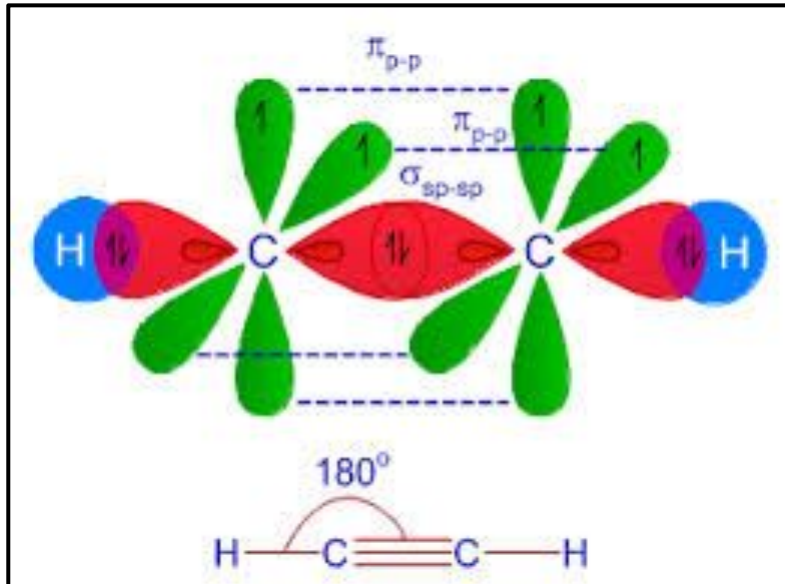
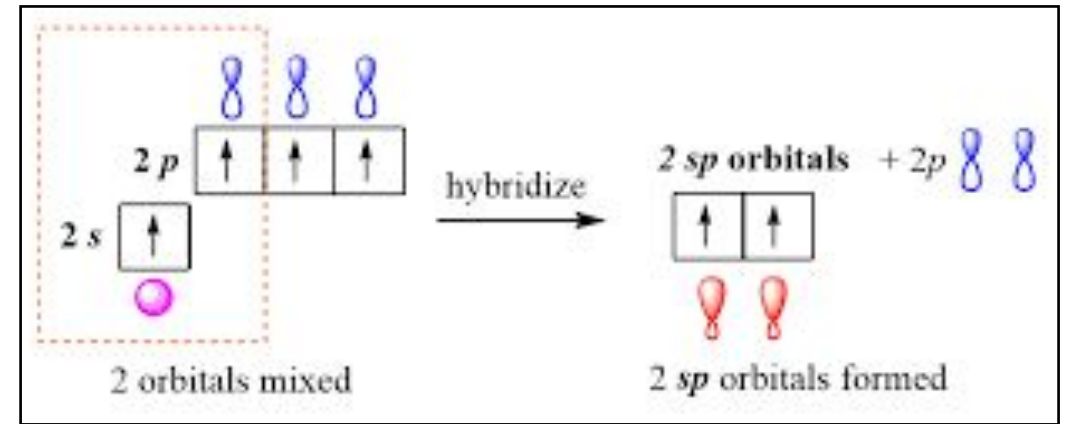
A common example of sp^2 hybridization is the carbon atom in ethene (C_2H_4). Each carbon forms three sigma bonds, and the remaining p orbital forms a π bond



III.3/ SP Hybridization

SP hybridization is the mixing of one s orbital and one p orbital to form two identical hybrid orbitals arranged in a linear shape

A common example of sp hybridization is the carbon atom in acetylene (C_2H_2). Each carbon forms two sigma bonds and keeps two p orbitals to form two π bonds



IV/ Link between VSEPR theory and hybridization theory

# of e- Groups	Atomic Orbitals	Hybrid Orbitals	e- Pair Geometry	AXE Notation(s)	Examples
2	s, p	Two sp	Linear	AX ₂	BeF ₂ , CO ₂
3	s, two p	Three sp ²	Trigonal Planar	AX ₃ , AX ₂ E ₁	BH ₃ , SO ₃ , CO ₃ ²⁻
4	s, three p	Four sp ³	Tetra-hedral	AX ₄ , AX ₃ E ₁ , AX ₂ E ₂	CH ₄ , NH ₃ , H ₂ O, OCl ₂
5	s, three p, one d	Five sp ³ d	Trigonal Bipyramidal	AX ₅ , AX ₄ E ₁ , AX ₃ E ₂ , AX ₂ E ₃	PCl ₅ , SF ₄ , I ₃ ⁻
6	s, three p, two d	Six sp ³ d ²	Octa-hedral	AX ₆ , AX ₅ E ₁ , AX ₄ E ₂ , AX ₃ E ₃	SF ₆ , ClF ₅ , XeF ₄

IV/ Molecular Polarity and Dipole Moment

IV.1/ Permanent dipole moment of a molecule

The difference in electronegativity between atoms causes a non-uniform distribution of electrons in the bonding orbitals.

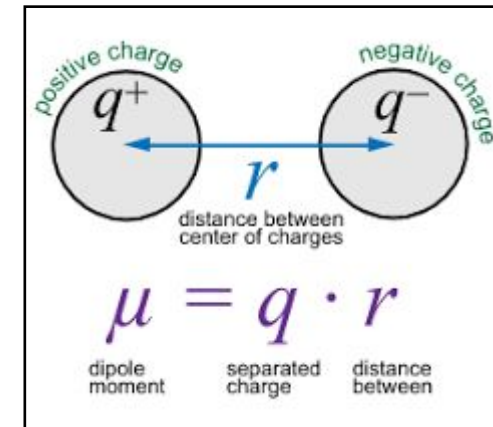
This leads to the formation of a bond dipole, and therefore a bond dipole moment.

q : separated charge (in C)

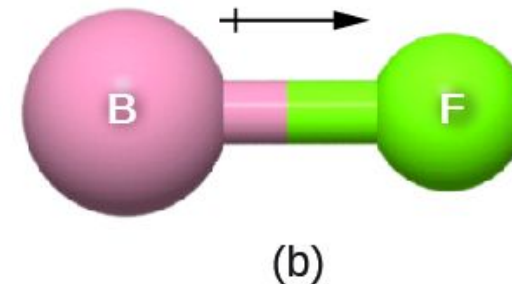
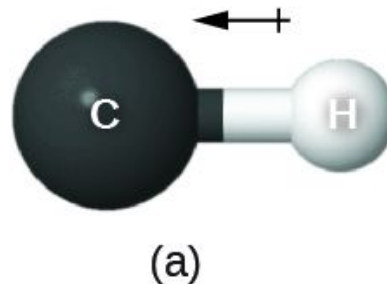
d : interatomic distance or bond length (in m)

μ : dipole moment (in C·m)

Dipole moment has a magnitude and a direction



Example



IV.2/ Theoretical dipole moment

The theoretical dipole moment is the value of the dipole moment calculated assuming a complete separation of charges, with one atom carrying a full positive charge and the other a full negative charge

$$\mu_{\text{theoretical}} = e \cdot d \quad \text{with } e = 1.6 \times 10^{-19} \text{ C}$$

IV.3/ Partial ionic

character

Partial ionic character is the percentage of ionic behavior in a bond, showing how much the electrons are shifted toward one atom due to the difference in electronegativity.

$$\delta = \frac{\mu}{\mu_{\text{theoretical}}}$$

$$\delta = \frac{\mu}{\mu_{\text{theoretical}}} = \frac{q \times d}{e \times d} = \frac{q}{e}$$

IV.4/ Percent ionic character

Percent ionic character is the percentage that shows how much a bond behaves like an ionic bond, based on the difference in electronegativity between the two atoms.

$$PI = \delta \times 100$$

Note: Debye unit is used to measure the dipole moment.

$$1 \text{ D} = 3.33 \times 10^{-30} \text{ C}\cdot\text{m}$$

IV.5/ The dipole moment of a molecule

It is equal to the vector sum of the dipole moments of each bond.

When the dipole moment of a molecule is zero, the molecule is said to be non-polar

Example

