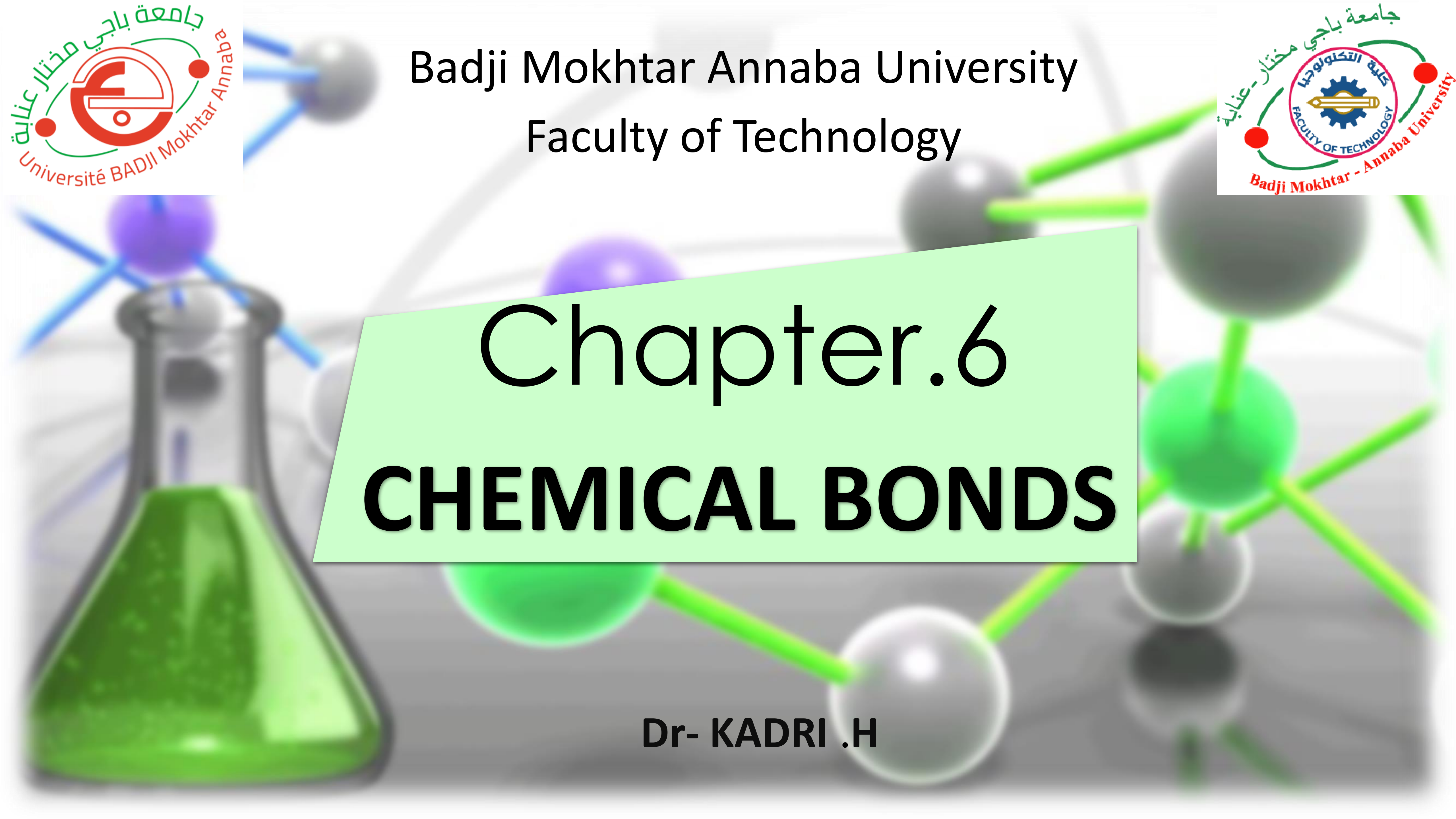
Badji Mokhtar Annaba University
Faculty of Technology



Chapter.6

CHEMICAL BONDS

Dr- KADRI .H

Table content:

1) The covalent bond in Lewis theory :
    a. Valence layer
    b. The different types of bond: covalent bond, dative bond, ionic bond and polarized bond
    c. Lewis diagram

2) Polarized covalent bond, dipole moment and partial ionic nature of the bond

3) Chemical bonding:
    3.1- Theory of molecular orbitals (LCAO method):
        a. Formation and nature of bonds : - axial overlap: σ bond.
                                            - Lateral overlap: π bond.
        b. Energy aspect

3.2- Generalization to homo-nuclear and hetero-nuclear diatomic molecules :

- a. Energy diagram of molecules
- b. Bond order
- c. Magnetic properties

3.3- Polyatomic molecules or atomic orbital hybridization theory :

- a. Hybridization sp
- b. Hybridization sp2
- c. Hybridization sp3

4) Molecular geometry: Gillespie or VSEPR theory

1) The covalent bond in Lewis theory :

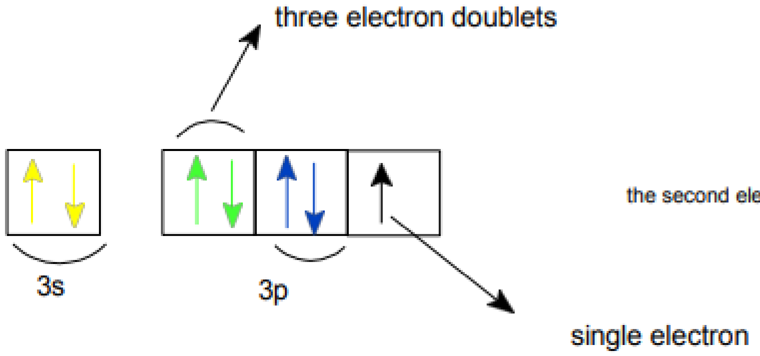
1) The covalent bond in Lewis theory :

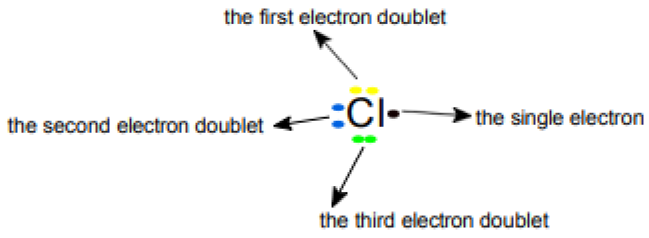
a. Valence shell

In the ground state, the electrons in the layer with the highest principal quantum number n play the main role in reactions, and in particular in the formation of bonds between atoms. This layer is known as the valence, outer shell. The existence of electron doublets, single electrons or empty atomic orbitals (empty squares or box) in this shell determines the chemical properties of a given element.

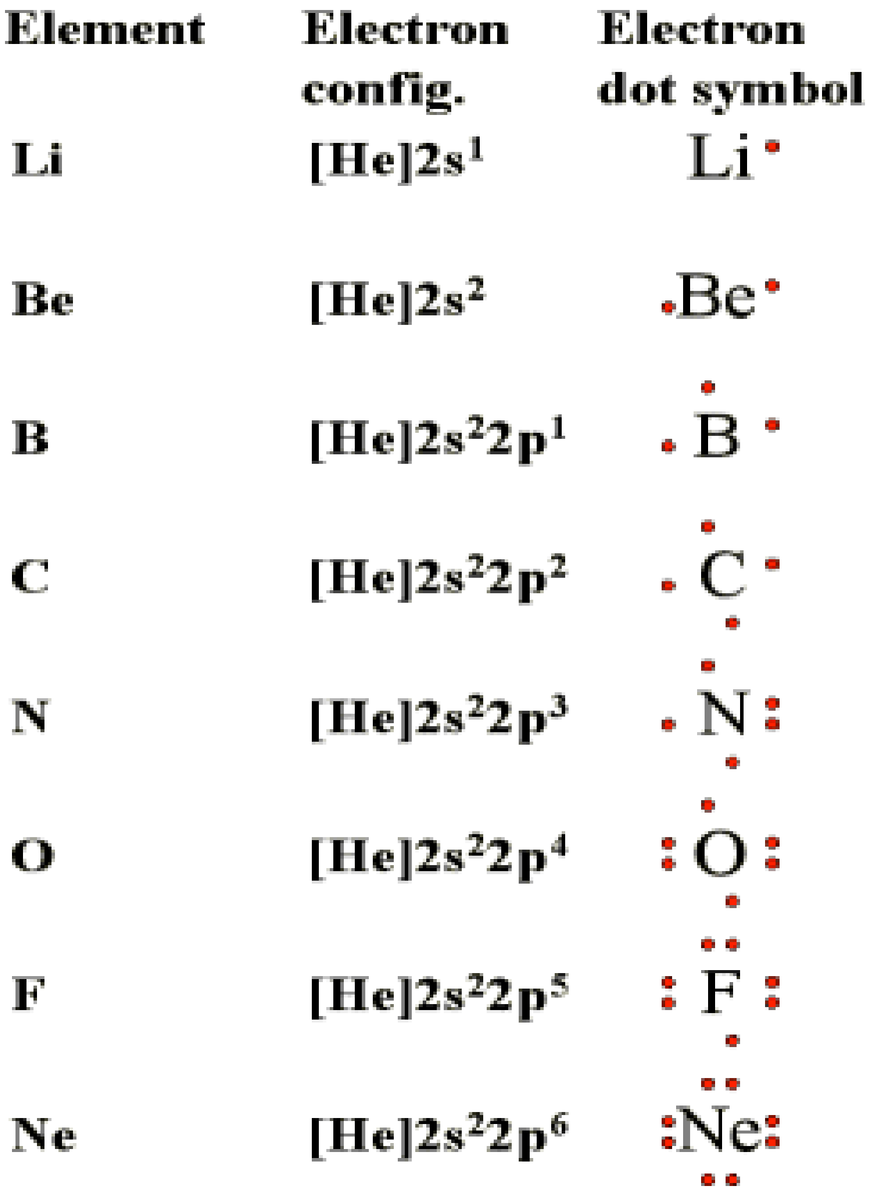
Example: ${}_{17}$Cl : 1s2 2s2 2p6 **3s2 3p5**

The principal quantum number in this case is n=3, and we can also see that the valence shell contains 3 electron doublets and a single electron.





Lewis symbol and the octet rule



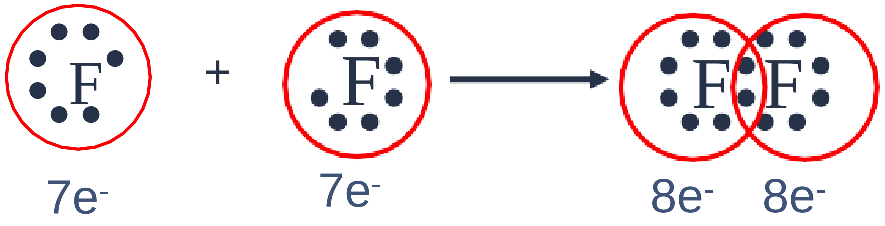
Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li·
Be	[He]$2s^2$	·Be·
B	[He]$2s^22p^1$	·Ḃ·
C	[He]$2s^22p^2$	·Ċ·
N	[He]$2s^22p^3$	·Ṅ:
O	[He]$2s^22p^4$	:Ȯ:
F	[He]$2s^22p^5$	:F̈:
Ne	[He]$2s^22p^6$	:N̈e:

b. The different types of bond: covalent bond, polar bond , dative bond and ionic bond

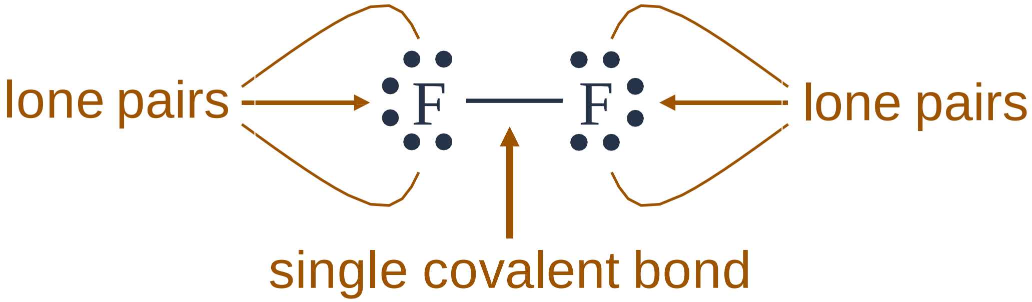
1- The Covalent Bond :

A covalent bond is a chemical bond in which two or more electrons are shared by two atoms.

Covalent bond occurs normally between nonmetal and nonmetal and the electron only shared between elements (not transfer from element to another element).



Lewis structure of F_2



The Covalent Bond

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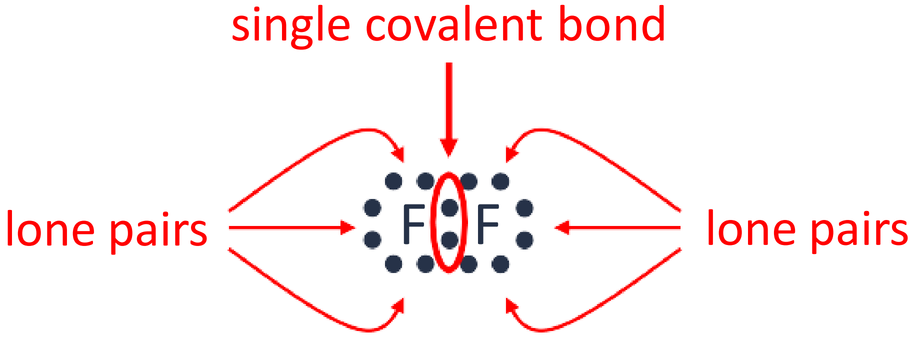
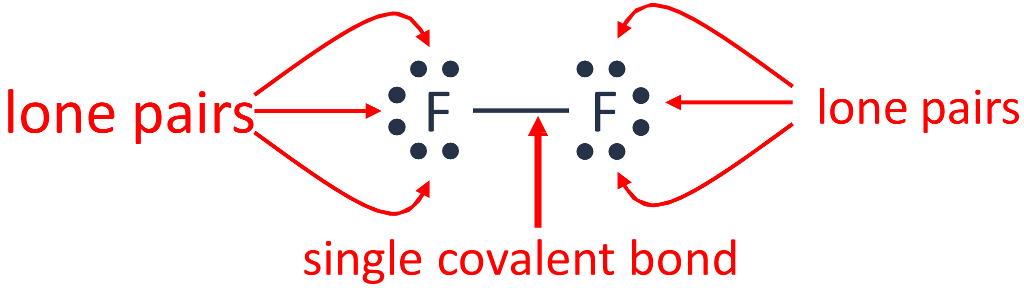
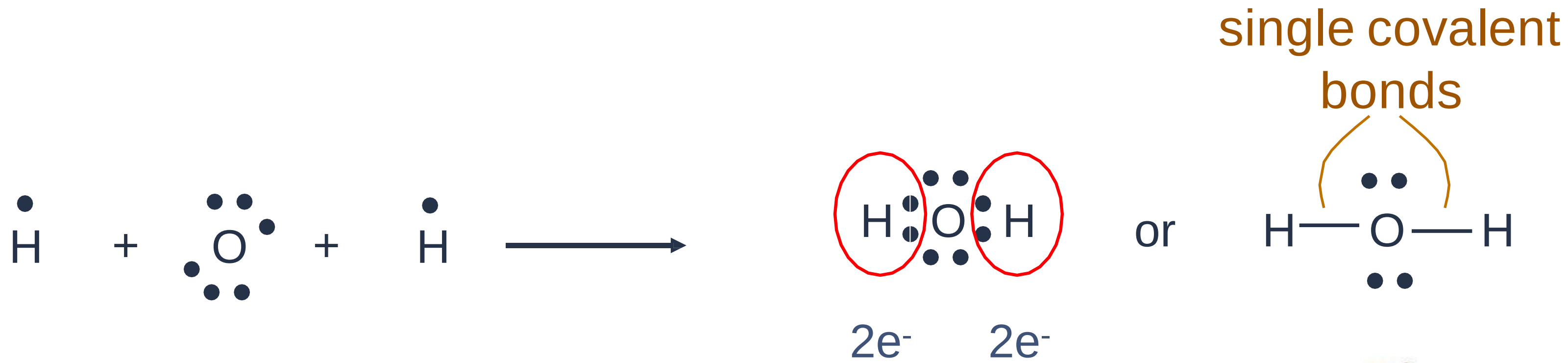


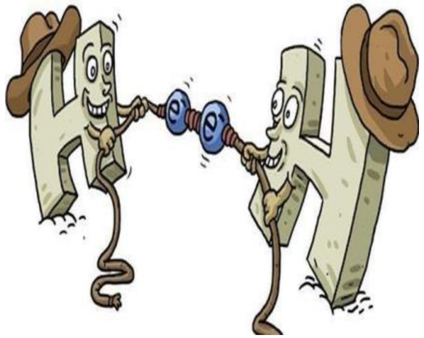


lone pairs: pairs of valence electrons that are not involved in covalent bond formation.

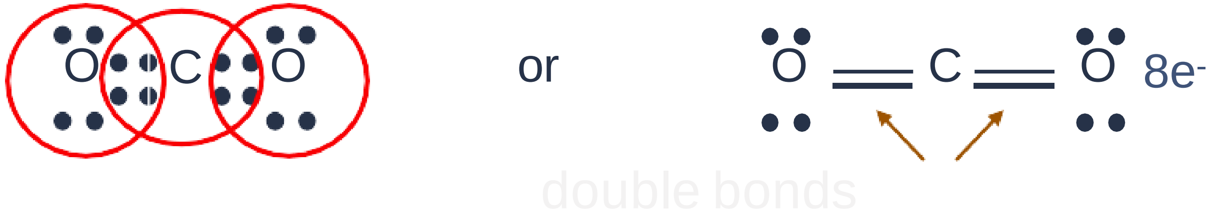
The Covalent Bond

Single bond – two atoms share **one pairs** of electrons





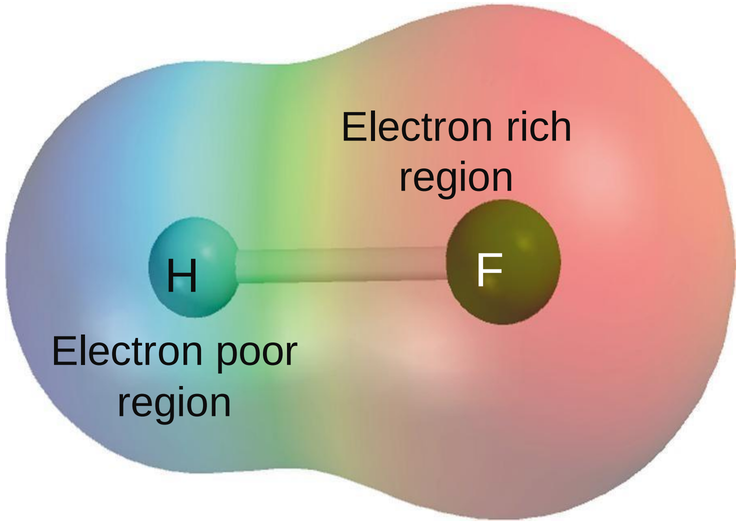
Double bond – two atoms share **two pairs** of electrons

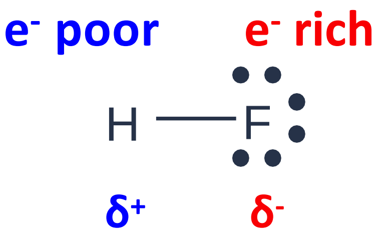


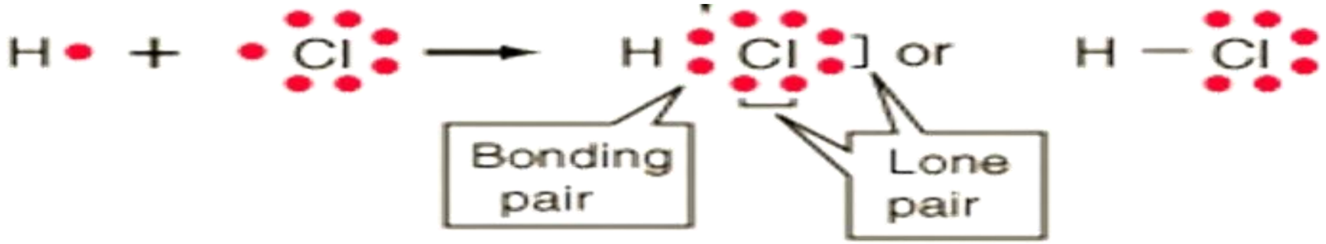
Triple bond – two atoms share **three pairs** of electrons

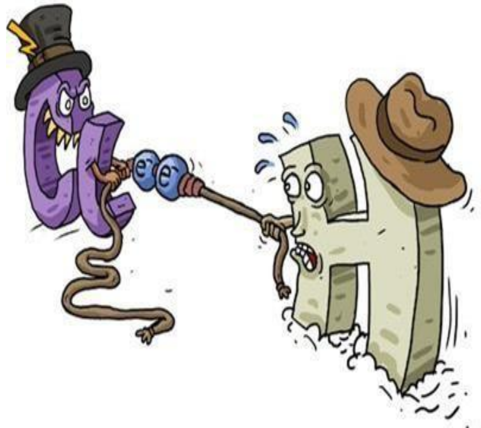
2- Polar covalent bond:

Polar covalent bond or **polar bond** is a covalent bond with greater electron density around one of the two atoms





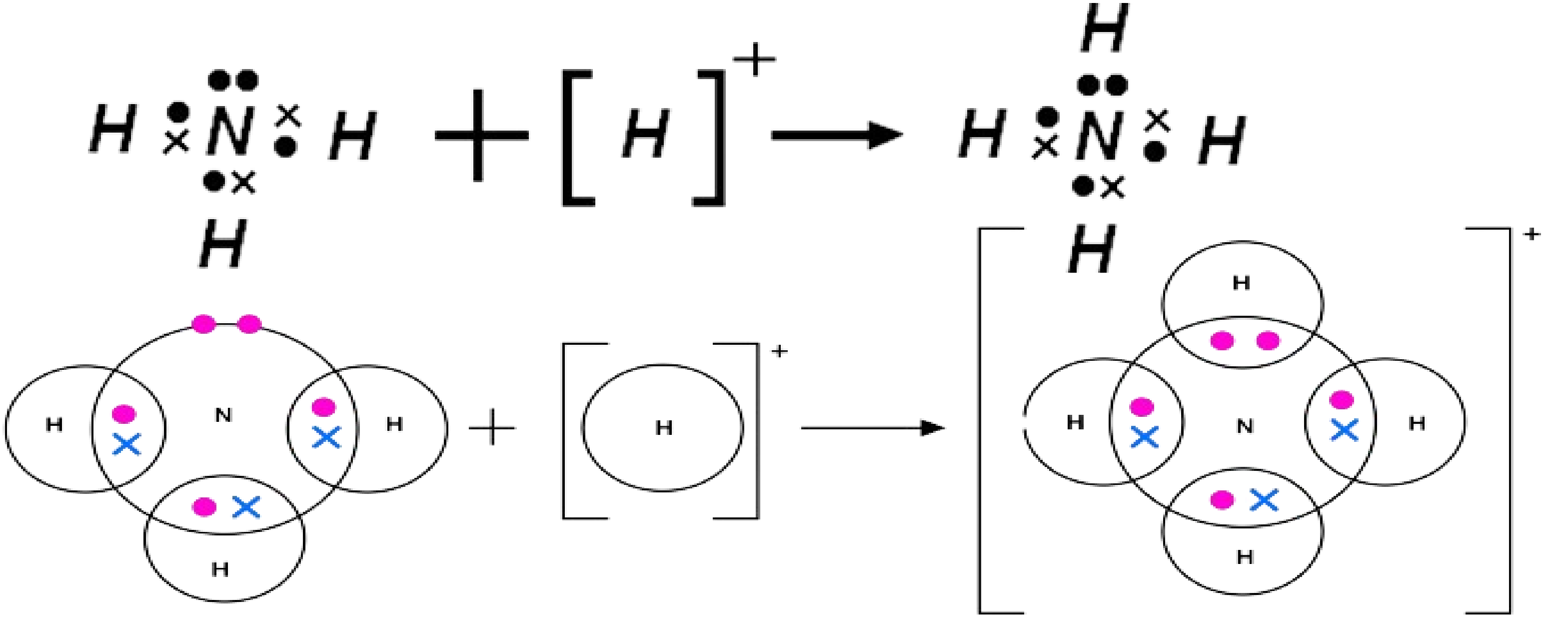




3- Dative covalent bonds:

It is a bond in which one of the atoms donates an electron pair, and the other participates with a free quantum state.

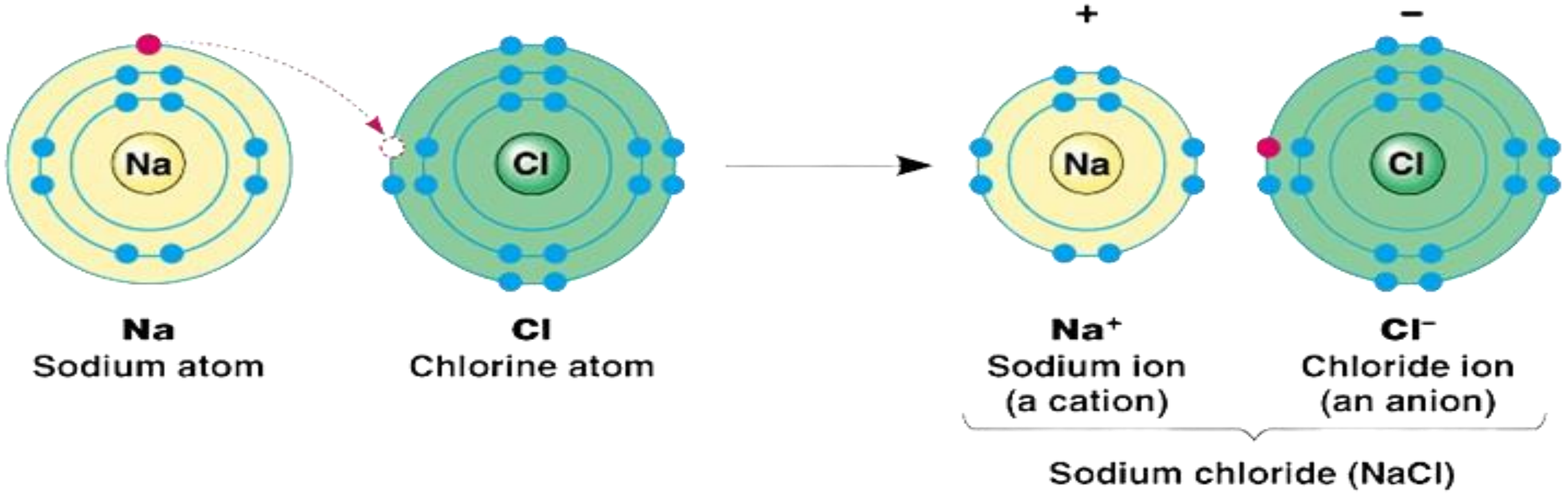
Example: in NH_4^+, the nitrogen from ammonia donate a pair of electrons when forming bonds with a H+ (a proton) Ammonium has 3 polar covalent bonds and 1 coordinate (dative) covalent bond.



4- The Ionic Bond:

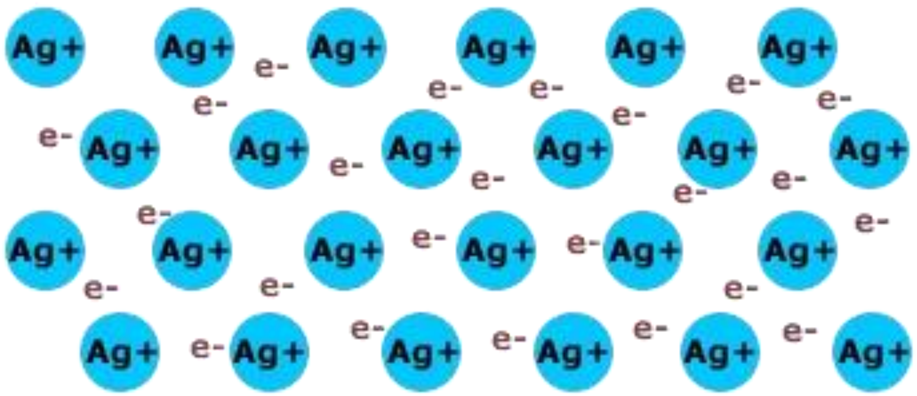
Ionic bond is the electrostatic force that holds ions together in an ionic compound.

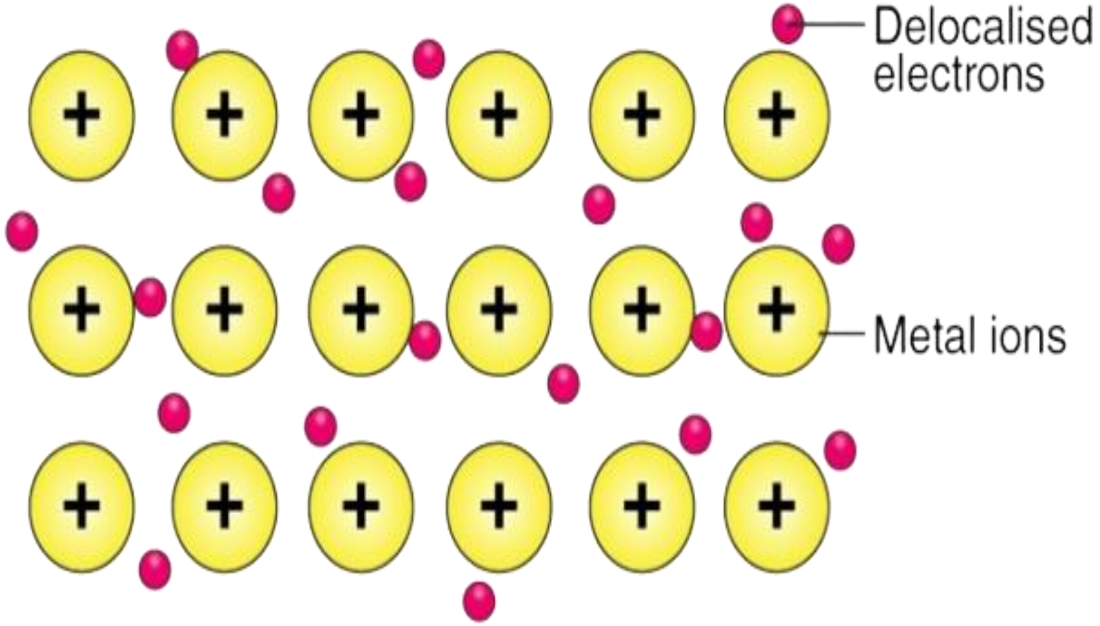
(metal-LOW EN- & non-metal-HIGH EN-)



Also , there is another type of chemical bond called **metallic bond**:

A **metallic bond** is the **electrostatic force** of attraction between the **positive metal ions** and the **delocalized electrons.**





C- Lewis model

- **octet rule**

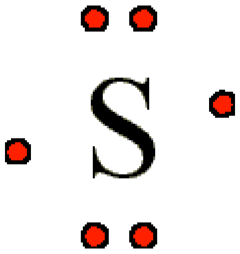
The simplest description of chemical bonding was proposed by **G.N. Lewis** in 1915. He separated core electrons from valence electrons, He discovered, while studying S and P block elements, that in chemical bonds, the outer electron shells "valence electron " (valence comes from the Latin valere, "to be strong") tend to saturate at 8 electrons. This is known as **the octet rule**, meaning that, to form a stable compound, atoms usually gain, lose or share electrons until they have 8 in the outer shell to reach the same electronic configuration of the noble gasses ($ns^2 np^6$).

Note: there are many exceptions to the octet rule (He and H, for example), but it provides a useful model for understanding the basis of chemical bonding.

➢ Electron-dot symbols (Lewis model):

convenient representation of valence electrons allows you to keep track of valence electrons during bond formation *consists of the chemical symbol for the element plus a dot for each valence electron*

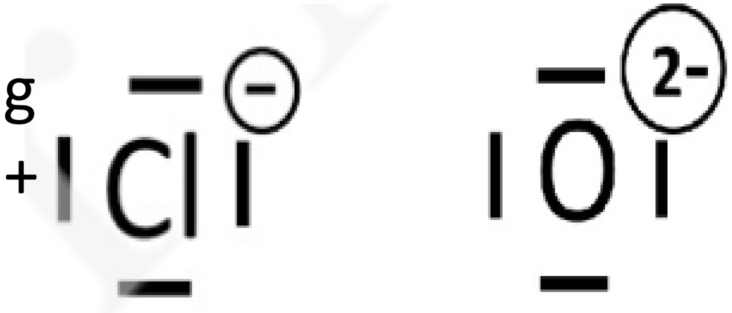
Sulfur: Electron configuration is [Ne]$3s^2 3p^4$, thus there are six valence electrons. Its Lewis symbol would therefore be:



According to Lewis, the bond is schematized by a line —
representing the electron pair, and lone pairs are represented by either a line or two dots ●

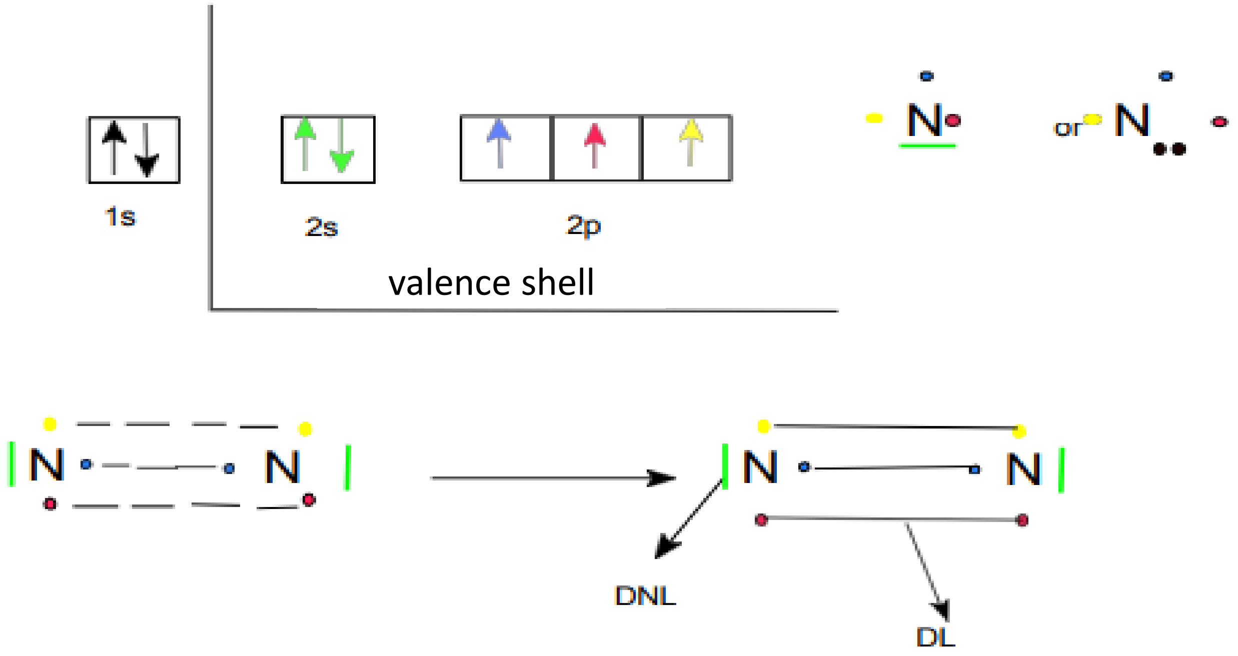
and the empty square is represented by a rectangle ▯

For ions, they are represented in the same way, by removing (or adding) dots (electrons), and also specifying the charge + or -.



Example: Formation of the covalent bond within the molecule N_2

Lewis is interested in the electrons of the valence shell



Rules for writing the Lewis diagram (Octet Rule)

Lewis provided some important rules for proper representation of S and P block elements.

1.Sum the valence electrons of all atoms.

2.Use a pair of electrons to form a bond between each pair of bonded atoms.

3.Distribute the remaining electrons in such a way that hydrogen follows the duet rule, while other elements follow the octet rule.

To write the Lewis diagram for molecules or polyatomic ions, it is crucial to know the number of free (non-bonding) electron pairs, the number of bonding electron pairs, and the number of unpaired electrons.

For this, the formula $S = N - A$ can be used.

Where:

- S: total number of bonding electrons in the molecule or ion.
- N: total number of electrons needed to achieve the noble gas structure for the atoms in the molecule.
- A: number of valence electrons for all atoms in the molecule or ion. (When calculating A, consider the charge in the case of ions).

The number of bonds formed is equal to S/2.

- If the number of bonds is greater than the number of atoms in the molecule, attempts are made to form double or triple bonds.
- The remaining number of electrons is A-S, and these electrons are distributed as pairs on the atoms following the octet rule.

Remarks: for a correct Lewis structure, it is necessary to:

- Know the molecular skeleton (usually, the first atom is the central atom); otherwise, an attempt is made to represent the molecule symmetrically.
- A molecule can have more than one Lewis structure; one structure is chosen.

Ex:

The difluoride F2

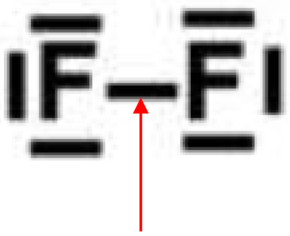
F : [He] 2s22p5

N=2*8(for two F atoms)=16é

A=27(for 2 F atoms)=14é

S=N-A=16-14=2é

2/2=1 1bond



Hydrogen fluoride, HF

F : [He] 2s22p5

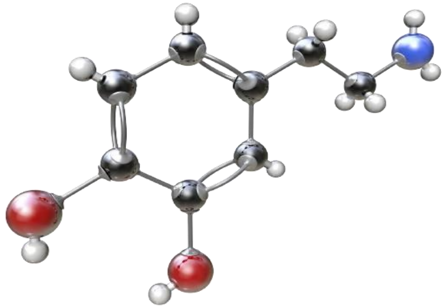
N=1*2(for one **H** atom)+1*8 (for one F atom)=10

A=1* 1(for one **H** atom)+1*7 (for one Fatom)=8

S=N-A=10-8=2é

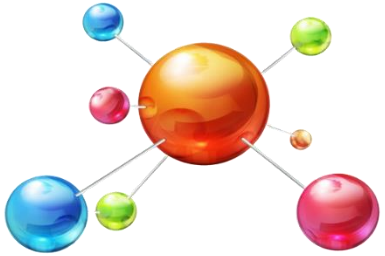
2/2=1 1bond

Exceptions to the Octet Rule

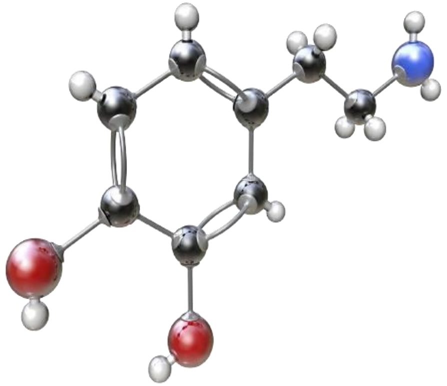


There are three general ways in which the octet rule breaks down:

1. **Molecules with an odd number of electrons**
2. **Molecules in which an atom has less than an octet**
3. **Molecules in which an atom has more than an octet**

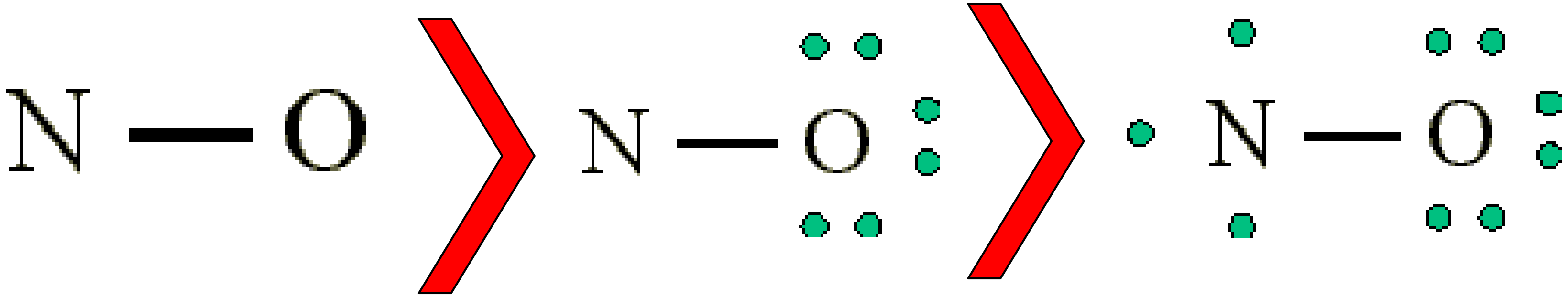


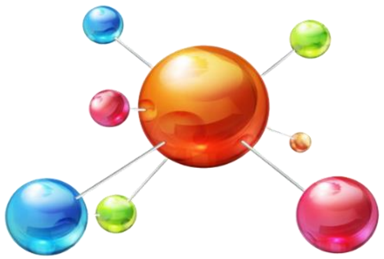
Exceptions to the Octet Rule



- Odd number of electrons -

NO : Total electrons: 6+5=**11**

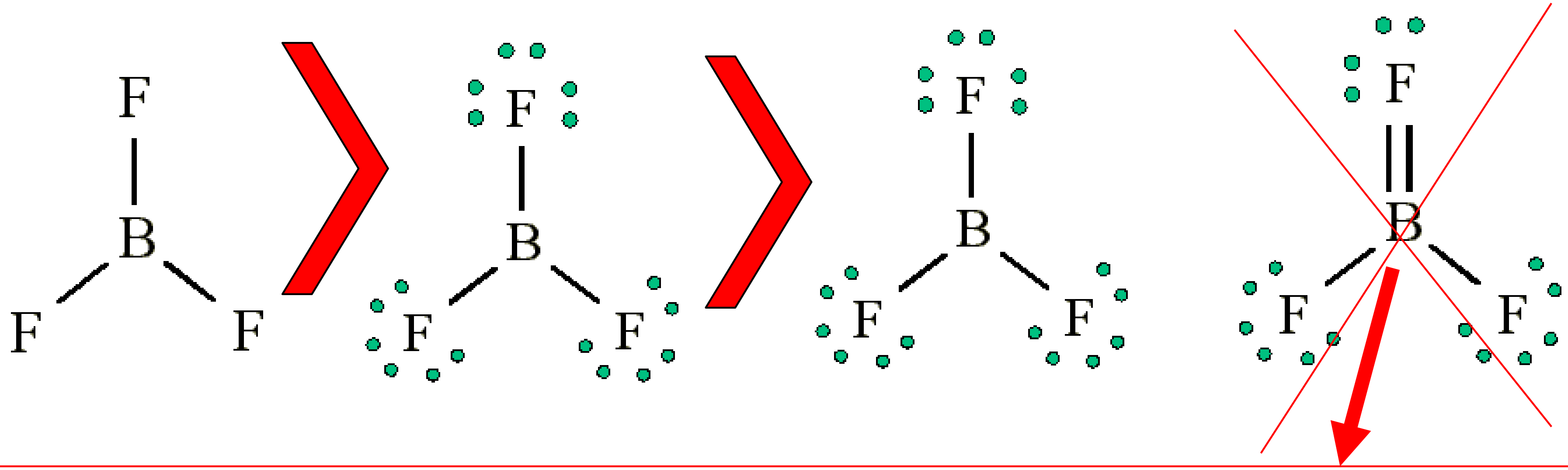




Exceptions to the Octet Rule

- Less than an octet -

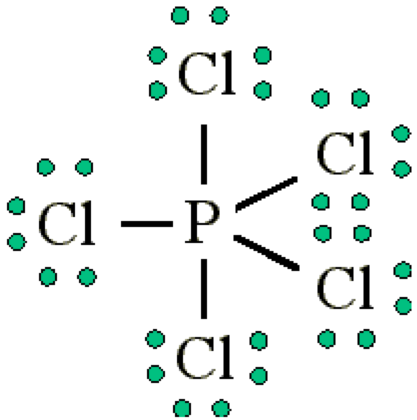
BF3 : Add electrons (3*7) + 3 = **24**



- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, ***the structure of BF3, with single bonds, and 6 valence electrons around the central boron is the most likely structure***

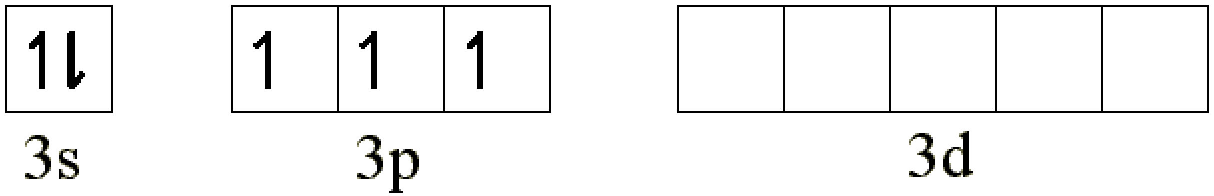
Exceptions to the Octet Rule

- More than an octet -



Third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons

- The 'octet' rule is based upon available ns and np orbitals for valence electrons (2 electrons in the s orbitals, and 6 in the p orbitals)
- Beginning with the n=3 principle quantum number, the d orbitals become available (l=2)



2) Polarized covalent bond, dipole moment and partial ionic nature of the bond:

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a) dipole moment :

Consider an A-B diatomic molecule, where A is more electronegative than B. The delocalization of the σ bonding pair towards A polarizes the A-B bond:

A dipole is characterized by its dipole moment μ : $\mu = q.d$

δ: the partial charge: this measures the partial ionic nature of the bond. δ ranges from 0 apolar bonds to 1 ionized atoms A- B+
μ : is a vector quantity which depends on the direction it is the dipole moment The effective partial charges are :

$+q = +\delta.e$ and $-q = -\delta.e$, hence $\mu = |\delta|.e.d$

with e: the elementary charge of the electron, equal to **$1.602.\ 10^{-19}$ C**

d : The bond length or distance between the two atoms A and B.

The unit of dipole moment in the International System (SI) is: (the coulomb. metre) (C.m), the commonly used nit is the Debye (D)

$$1D = 3.336\ .10^{-30}\ C.m$$

b) The partial ionic nature of the bond:

The covalent bond of a molecule has a partially ionic character due to its polarization. Experimental determination of the dipole moment μ A-B makes it possible to estimate this partial ionic character, since the ionic character (δ) is equal to : $\delta = \frac{\mu}{d}$ or δ.100% as a ionic percentage.

Application:

Let's take the following example:

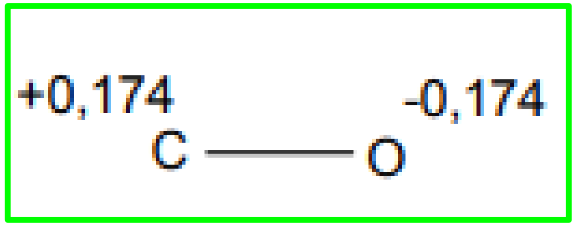
The dipole moment of the C-O bond is μ = 1.2 D, $d_{C\text{-}O}$ =143 pm = 143 pico meter = $143.\,10^{-12}$ m

Solution:

$$\mu_{C\text{-}O} = q.d = \delta.e.d \longrightarrow \delta = \mu \;\; e.d$$

So :
$$\delta = \frac{1{,}2\times 3{,}336 \;\times 10^{-30}}{1{,}6\times 10^{-19} \;\times 143 \times 10^{-12}} = 0{,}174$$

equivalent to 17,4 % ionic percentage



3) Chemical bonding in the quantum model :

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3.1- Theory of molecular orbitals (LCAO method):

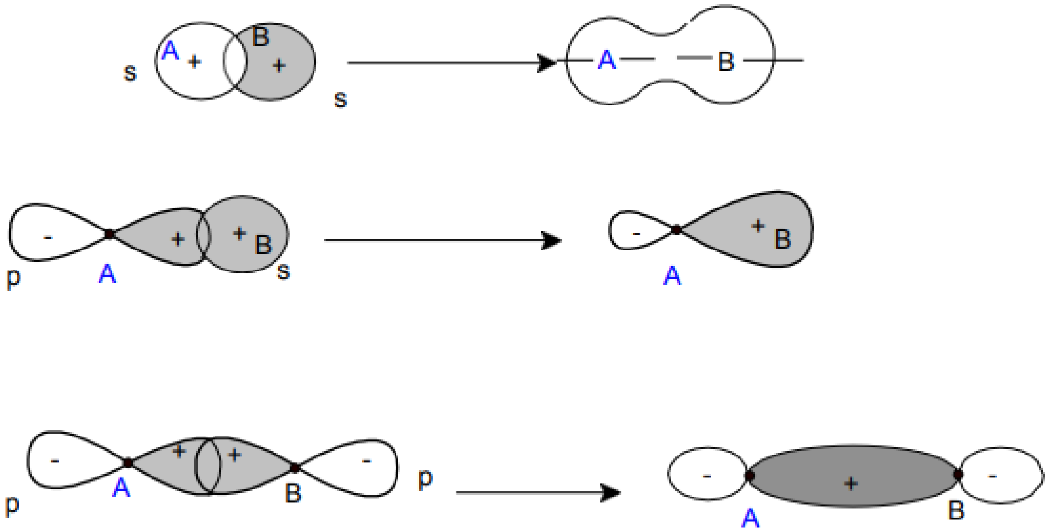
a. Formation and nature of bonds :

Linear Combination of Atomic Orbitals : Proposed by Mulliken in 1932, consists of assuming for a diatomic molecule that the molecular orbital M.O is formed between A and B atoms by **overlaping**.

- **Axial overlap: σ bond**
- **Lateral overlap: π bond**

- Axial overlap: σ bond

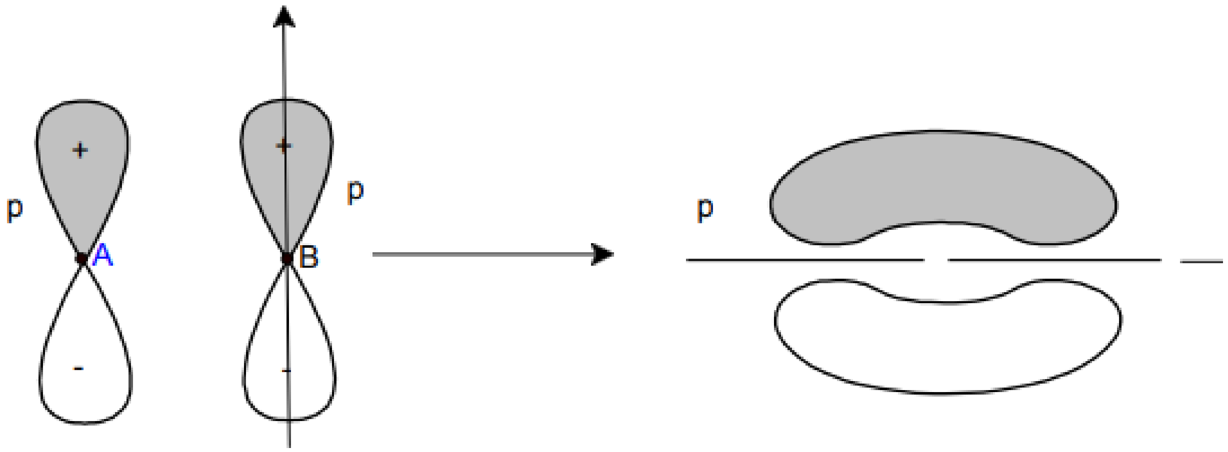
It is an overlap of two s orbitals, or of an s orbital and a p orbital, or of two coaxial p orbitals, the M.Os thus formed are called *σ* orbitals, the axial overlap gives rise to two sigma M.Os (σ, σ*) there is free rotation about the bond σ.



Axial overlap σ- bond formation

– Lateral overlap: π bond

It concerns p orbitals whose axes are parallel, this overlap leading to a π orbital. The corresponding bonds are weaker than σ bonds, in the absence of axial symmetry of the M.O., π bonds do not allow rotation around the π bond.



Lateral overlap formation of the π- bond

b. Energy aspect

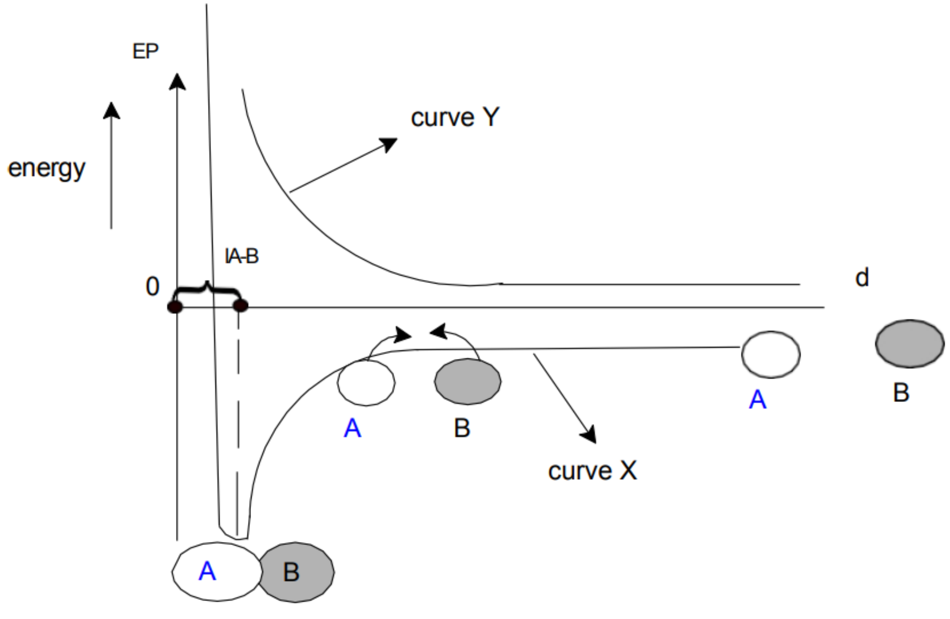
When atoms A and B are close together they enter into interaction, and the interaction energy at that moment will be equal to the sum of :

- the energy of attraction: nucleus of A (or B) with the electrons of atom A (or B)
- the energy of repulsions: nucleus A-or B and electrons A-electron B

The curves showing the variation in the energy of the orbitals of a system formed by two atoms as a function of their distance confirm the binding or antibonding (non – bonding) nature of the two M.O.s.

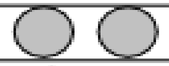
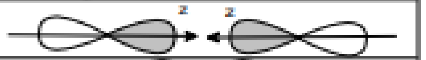
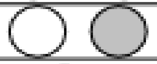
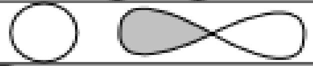
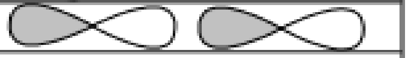
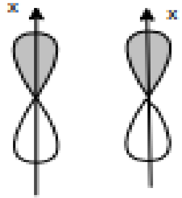
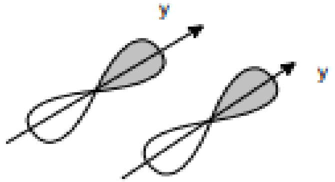
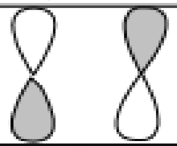
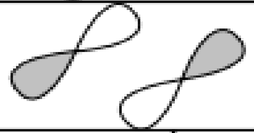
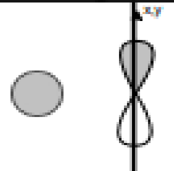
If the e-doublet shared by the two atoms A and B in the A-B bond occupies the bonding **molecular orbital** or **M.O.**: **σ**, the molecule is more stable - this is the case for curve (X) - whereas curve Y corresponds to the energy of the molecular orbital **σ***.

The closer the two atoms are, the greater the energy, but there is no stable equilibrium position, as the molecule would be less stable than two separate atoms.



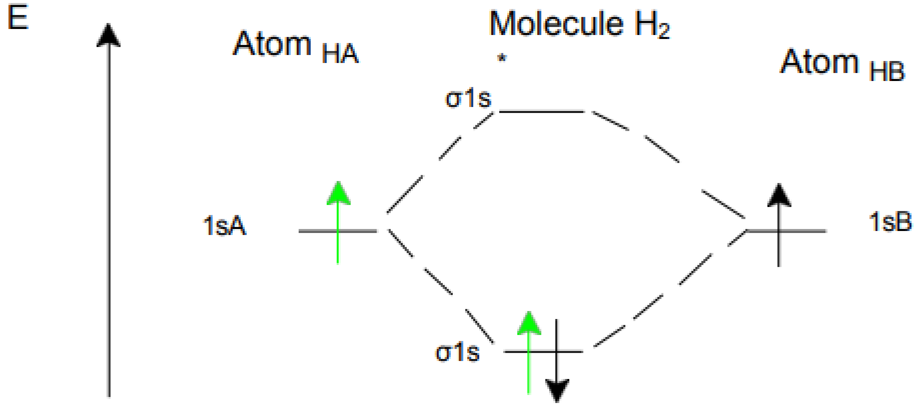
Energy of the system consisting of two atoms A and B as a function of the internuclear distance d

Table 1 : The different types of molecular orbital

Type of molecular orbital	**Symbol**	**Atomic orbitals**	**Molecular orbital diagram**
Bonding Sigma	**σ**	**ns+ns**	
		ns+npz	
		np +np$_{zz}$	
Anti-bonding Sigma	**σ***	**ns+ns**	
		ns-npz	
		np$_z$ -np$_z$	
Bonding Pi	**π_x**	**np$_x$ + np$_x$**	
	π_y	**np$_y$ + np$_y$**	
Anti-bonding Pi	**$\pi^*{}_x$**	**np$_x$ - np$_x$**	
	$\pi^*{}_y$	**np$_y$ - np$_y$**	
Non-bonding	**NL**	**ns+np$_{x,y}$**	

The relative energy levels of the two A.O.s and the two M.O.s to which they give rise are represented on an energy diagram by a linear combination of their wave functions. The diagram is called a molecular diagram.

Example: Molecule of H_2



3.2- Generalization to homo-nuclear and hetero-nuclear diatomic molecules :

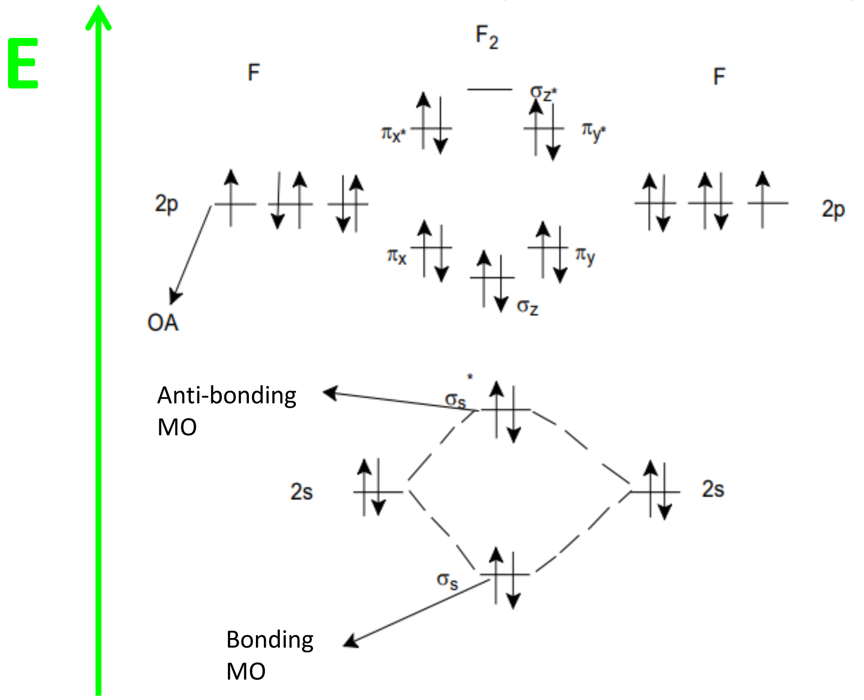
3.2- Generalization to homo-nuclear and hetero-nuclear diatomic molecules :

a. Energy diagram of molecules

- Energy diagram of homo-nuclear diatomic molecules :

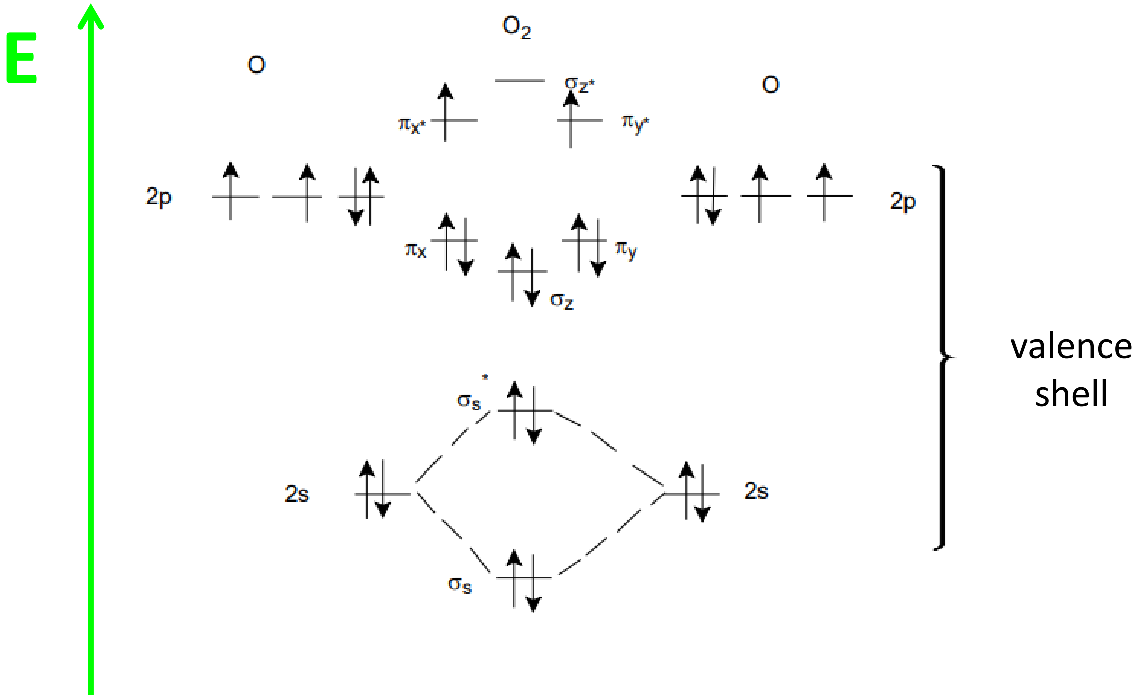
These are molecules made up of two identical atoms A_2, Let's take the case of $\mathbf{F_2}$, $\mathbf{O_2}$, note that we are only interested in valence electrons because internal electrons are not involved in the formation of bonds between atoms. And the **molecular electronic configuration** for the F_2 and O_2 molecules are respectively :

$\sigma^2 s, \sigma^2{}_z, \pi^2{}_x, \pi^2{}_y, \sigma^{2*}{}_s, \pi^{*2}{}_x, \pi^{*2}{}_y$



Molecular energy diagram

$\sigma^2 s, \sigma^2{}_z, \pi^2{}_x, \pi^2{}_y, \sigma^{2*}{}_s, \pi^{*1}{}_x, \pi^{*1}{}_y$



Molecular energy diagram

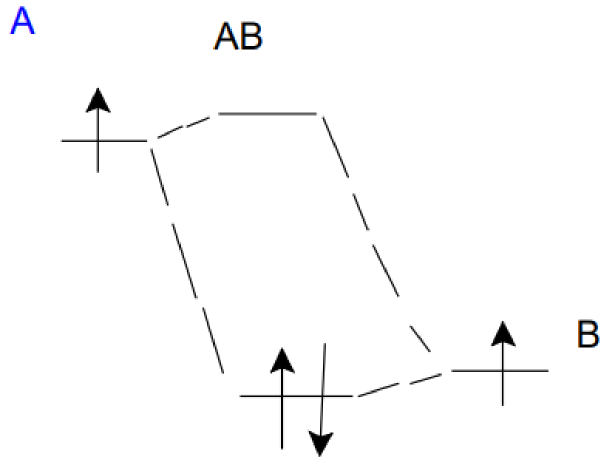
Note:

In the case of homo-nuclear diatomic molecules A_2 , the order of the energy levels is as follows:

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_x < \pi 2p_y = \pi 2p_z < \pi^* 2p_y = \pi^* 2p_z < \sigma^* 2p_x$

- Energy diagram of hetero-nuclear diatomic molecules :

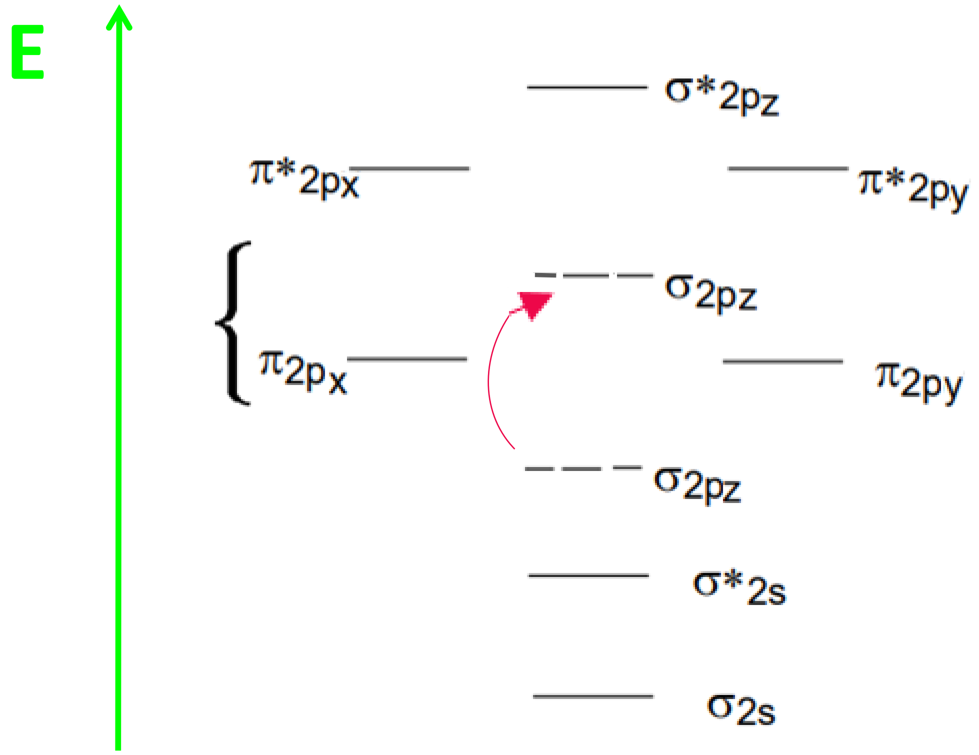
We are dealing with two different atoms A and B, so the two atoms do not give the same types of AO, and the energy levels of the AO are not the same. In general, the more electronegative an element is, the lower its atomic energy levels.



Note: In the case of :

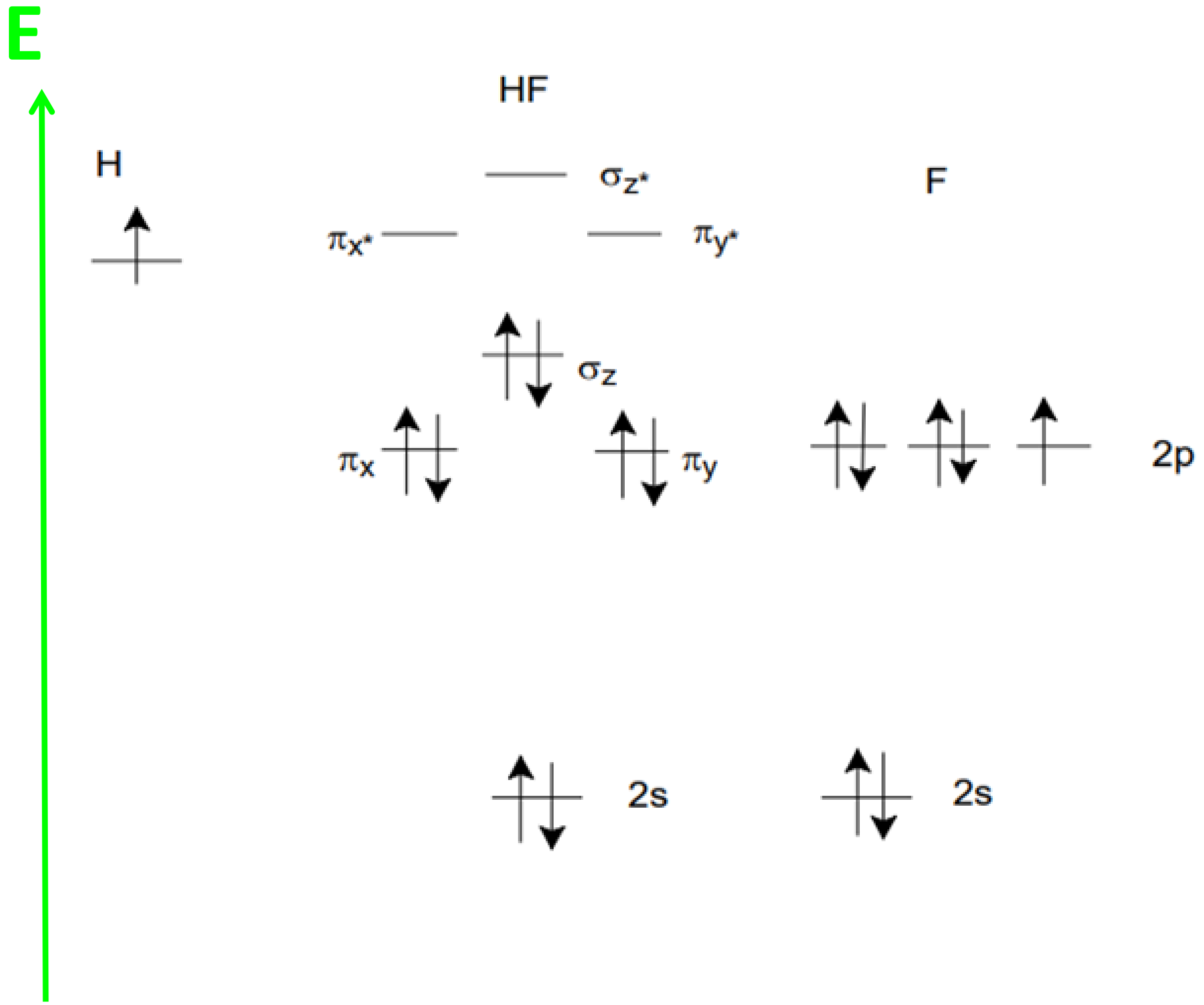
$Z\ (A_2)$ or $(AB) \leq 14 \rightarrow \sigma pz > \pi px = \pi py$

$Z\ (A_2)$ or $(AB) > 14 \rightarrow \sigma pz < \pi px = \pi py$



Example : **HF molecule**

In this molecule, only the 1s level of H and the 2p level of F, whose energies are close, participate in the formation of the bond. The atomic orbital of H can only co-axially overlap a single 2p orbital of the fluorine atom F, which is 2p.z



Molecular energy diagram

b. Bond order

The bonding order is the difference between the number of bonding electrons (n) and the number of non-bonding electrons (n*) divided by 2.

$$\textbf{Bond order} = \frac{1}{2}\,(n - n^*)$$

Example: of F_2 and O_2

F_2 : $\textbf{Bond order} = \frac{1}{2}\,(n - n^*) = \frac{1}{2}\,(8 - 6) = 1$

O_2 : $\textbf{Bond order} = \frac{1}{2}\,(n - n^*) = \frac{1}{2}\,(8 - 4) = 2$

Nature of bond:

This order is general, it contains both the number of bonds σ and π :

In the case where O.L = 1: a **single bond** is necessarily a σ-bond.

In the case where O.L = 2 a **double bond** is formed by a σ bond and a π bond

in the case where O.L = 3 a **triple bond** is made up of one σ bond and two π bonds: π x , πy .

In the case where O.L = 0: this hypothetical molecule cannot exist because the bond order is zero, so no bond is formed.

- **For σ-Bond: Bond order** $= \frac{1}{2}$ **[n(σ) – n* (σ*)]**
- **For π-Bond: Bond order** $= \frac{1}{2}$ **[n(π) – n* (π*)]**

Stability of bonds and molecules :

The greater the bonding order (higher value), the more stable the molecule. A molecule with an O.L equal to 1 is less stable than a molecule with an B.O = 2.

Example : For the following three molecules we have :

O_2^- : **Bond order** $= \frac{1}{2}(n - n^*) = \frac{1}{2}(8 - 5) = 1{,}5$

O_2 : **Bond order** $= \frac{1}{2}(n - n^*) = \frac{1}{2}(8 - 4) = 2$

O_2^+ : **Bond order** $= \frac{1}{2}(n - n^*) = \frac{1}{2}(8 - 3) = 2{,}5$

So, according to the B.O values, the stability of the molecules is in this ascending order:

$$O_2^- < O_2 < O_2^+$$

c. Magnetic properties

The existence of interactions between a given molecule and a magnetic field is related to the movement of electrons in atoms. These moving electrons are like a magnet interacting with the existing magnetic field.

Diamagnetism :

When a molecule has a number of electrons paired in doublets, associating two electrons with opposite spin numbers (no single electron), resulting in a zero global (total) magnetic moment, for example: H_2 , Cl_2 , F_2 , H_2O...etc. ($Ms = \sum ms$) < 0 with Ms the total spin number.

Paramagnetism :

On the other hand, a molecule has a number of electrons (single electrons), the total magnetic moment of the molecule is not zero, so the material is paramagnetic ($Ms = \sum ms$)> 0.

3.3- Polyatomic molecules or atomic orbital hybridization theory :

3.3- Polyatomic molecules or atomic orbital hybridization theory :

The geometry of molecules is described by the theory of hybridization, which emerged when Lewis theory proved inadequate to describe the structure of certain molecules, such as in the case of methane (CH_4).

In the ground state: 6C: $1s^2 2s^2 2P^2$ This structure does not allow the formation of the CH_4 molecule.
The change in the ground-state structure is called hybridization, where atomic orbitals combine to form new orbitals called hybrid orbitals with specific shapes.

The theory of hybridization is based on quantum mechanics. From a mathematical perspective, hybrid orbitals result from the combination of atomic wave functions to create new wave functions, each representing a hybrid atomic orbital

Hybridization

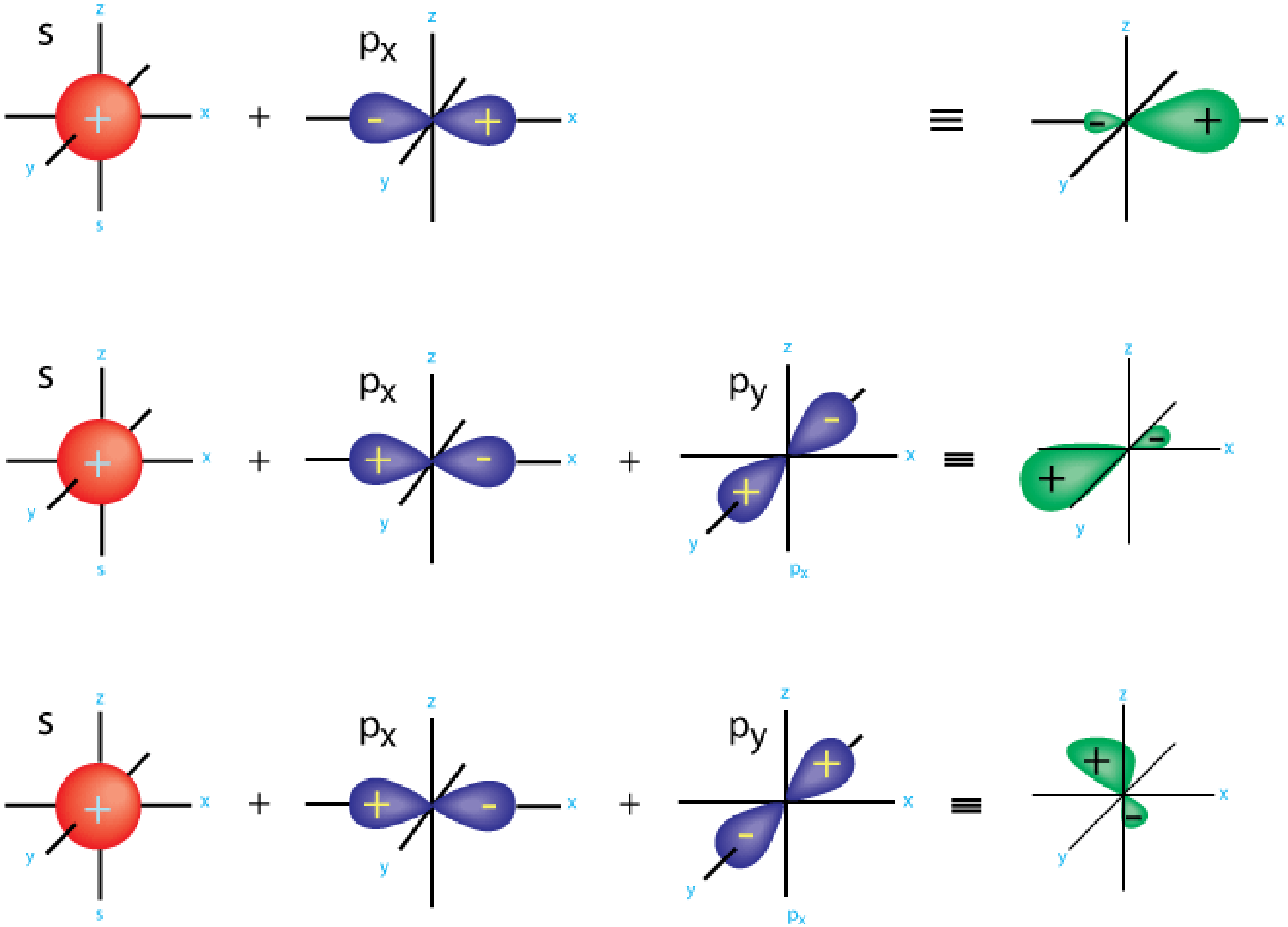
- Atomic orbitals can be combined together to form hybrid orbitals, and bonds involving such orbitals are called hybrid orbitals

- The electrons rearrange themselves again in a process called hybridisation.

- 3 main types of hybridisation, sp, sp^2 and sp^3. (Others such as sp^3d, sp^3d^2)

- In hybridisation, the no. of hybrid orbitals produced equals the total no. of atomic orbitals that are combined.

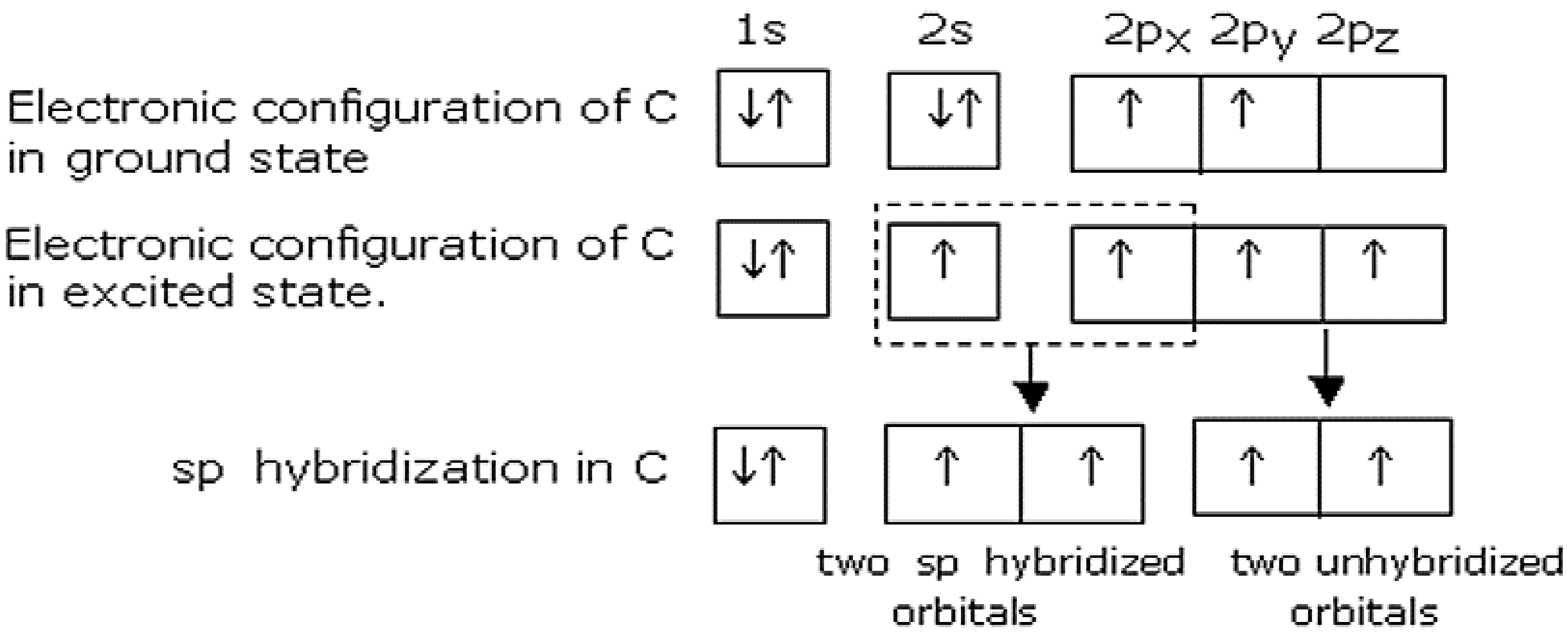
- For eg: sp^3 hybridisation produces (1+3) orbitals.

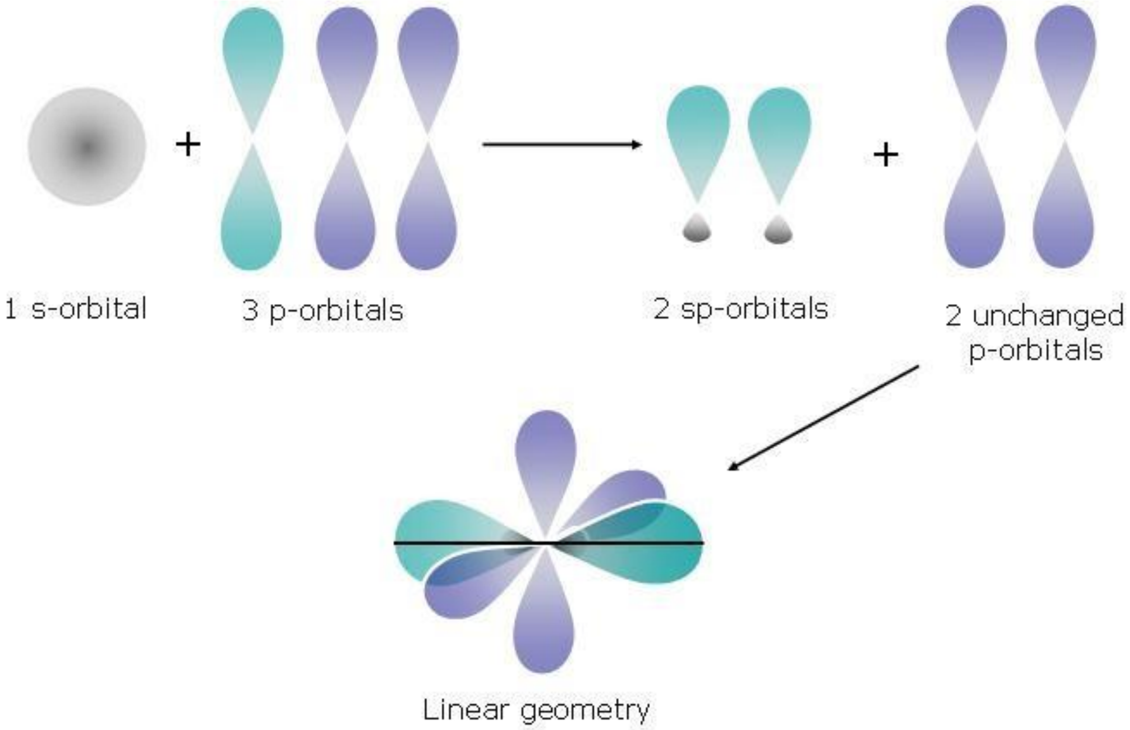

s
z
x
y
s
+
p_x
p_y
p_x
−
≡

sp Hybridization

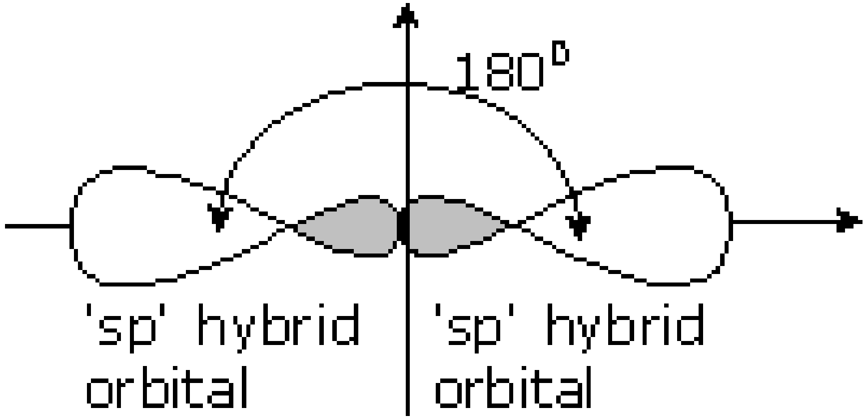
The sp orbital is the hybridization of an atomic s orbital with an atomic p orbital

Example: **$BeCl_2$, BeH_2 , C_2H_2**





Example : Ethyne C_2H_2

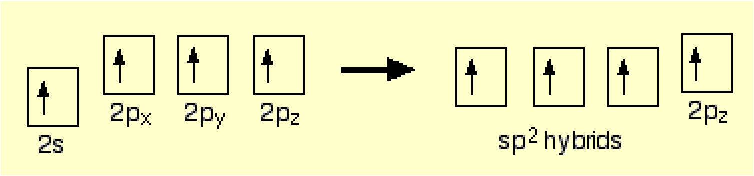


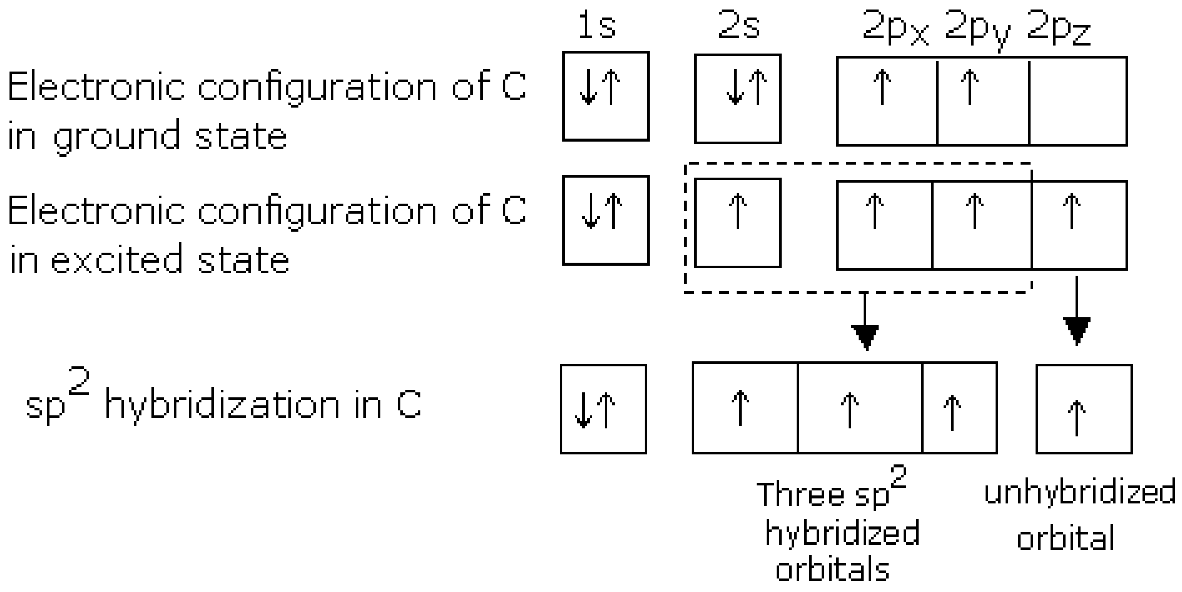
2 C-H σ bonds, 1 C-C σ bond, 2 C-C π bond

sp^2 Hybridization

- The 2s orbital combines with 2 of the 2p orbitals to form 3 sp2 hybrid orbitals. One 2p orbital remains unhybridized
- Hybrid orbitals are shorter and fatter

- The three sp^2 hybrid orbitals arrange themselves as far apart as possible - which is at 120° to each other in a plane.





1s 2s $2p_x$ $2p_y$ $2p_z$

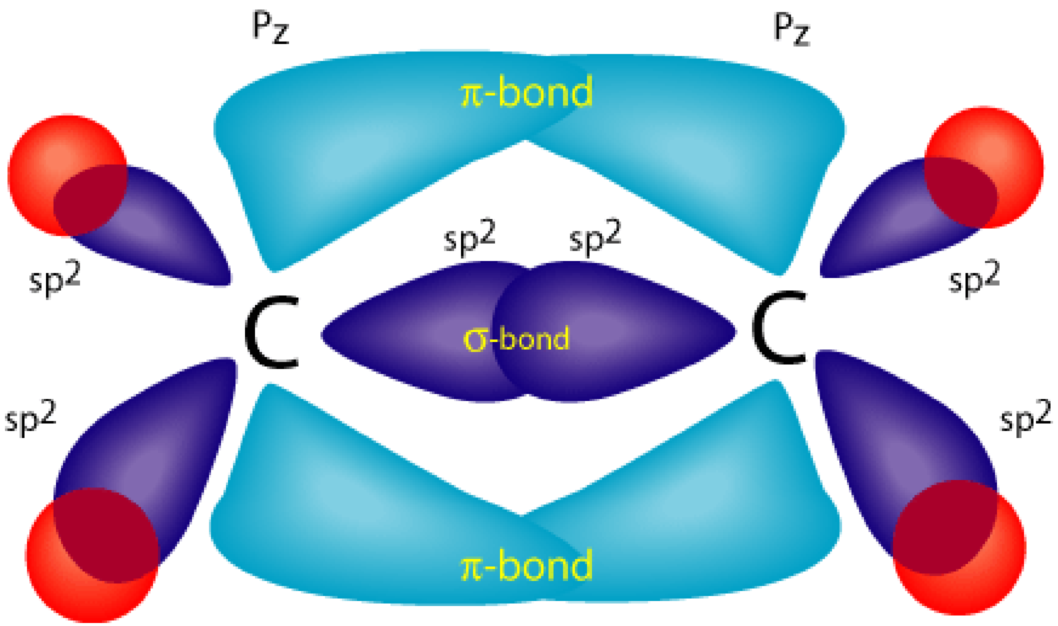
Electronic configuration of C in ground state

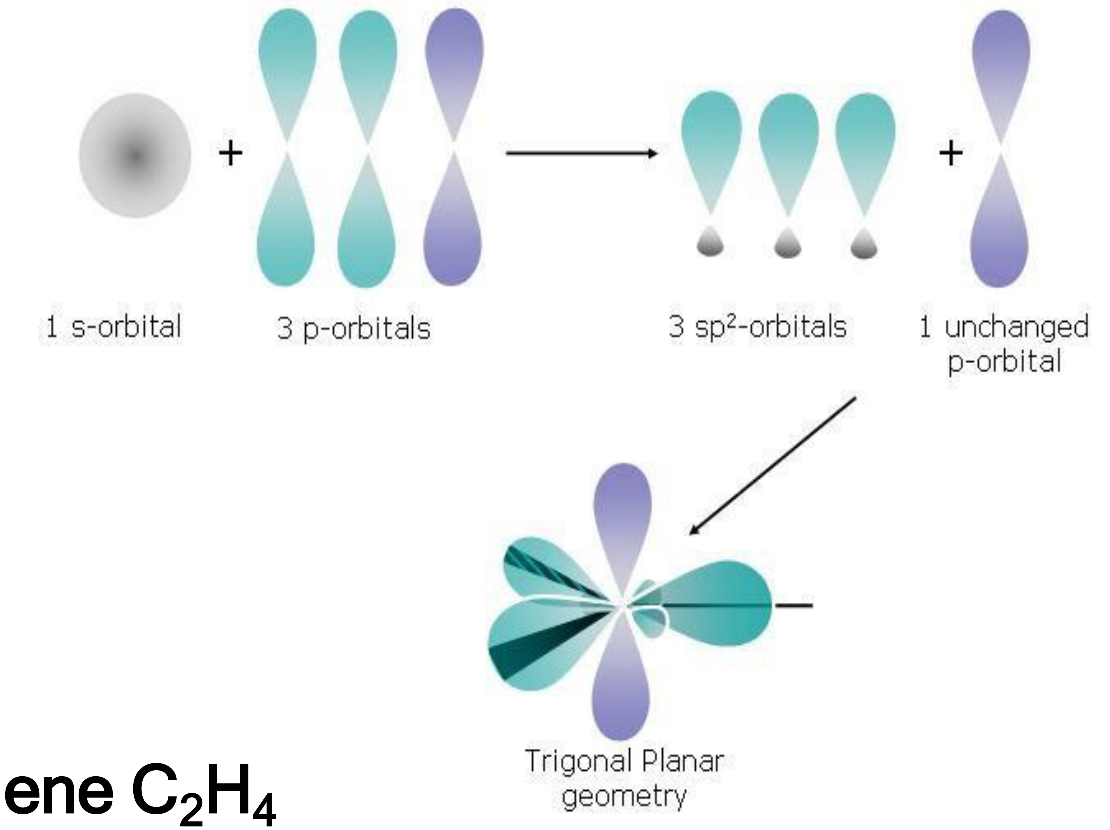
Electronic configuration of C in excited state

sp^2 hybridization in C

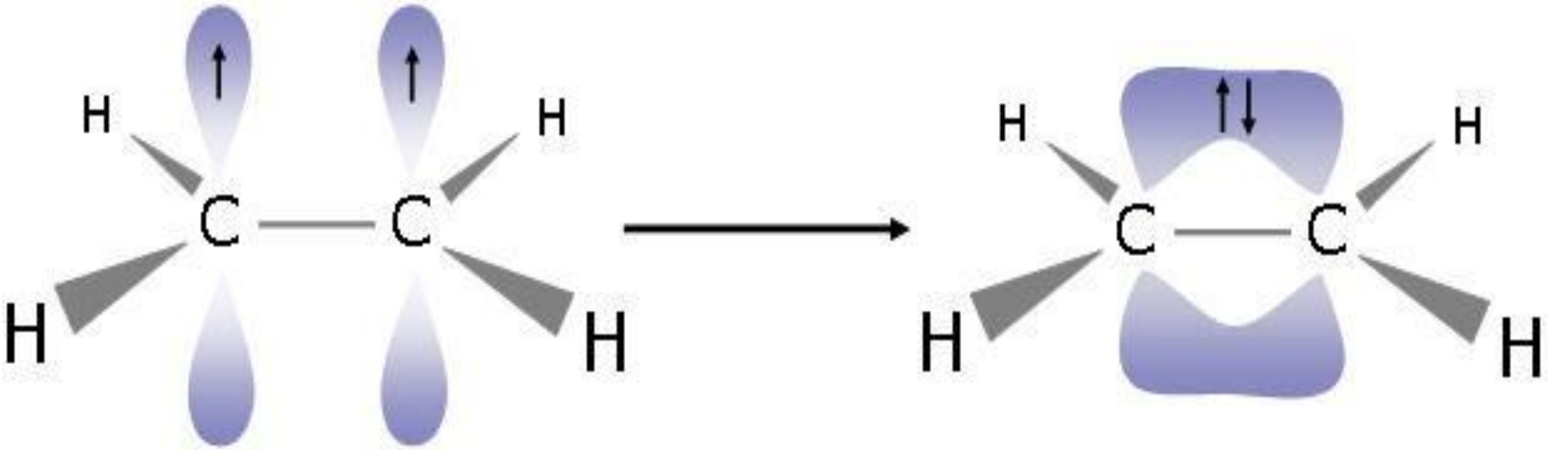
Three sp^2 hybridized orbitals

unhybridized orbital



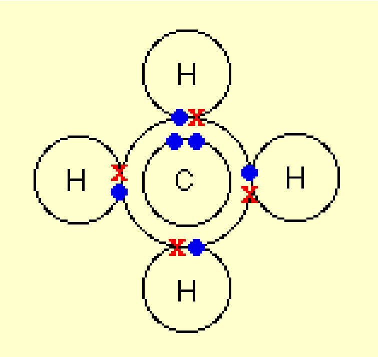


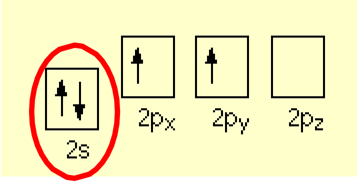
Example : Ethene C_2H_4



4 C-H σ bonds, 1 C-C σ bond, 1 C-C π bond

sp^3 Hybridization





What is this called?

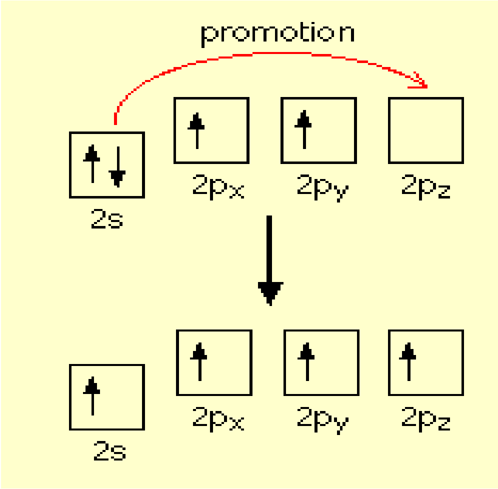
- There is a serious mis-match between this structure and the modern electronic structure of carbon, $1s^2 2s^2 2p_x\, 2p_y$.
  1 1

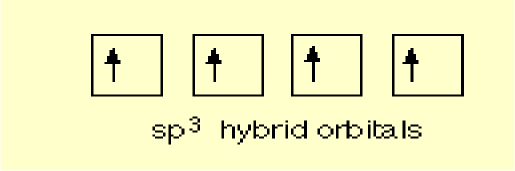
- When bonds are formed, energy is released and the system becomes more stable. If carbon forms 4 bonds rather than 2, twice as much energy is released and so the resulting molecule becomes even more stable.

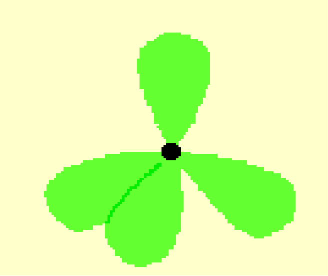
- There is only a small energy gap between the 2s and 2p orbitals, and so it pays the carbon to provide a small amount of energy to promote an electron from the 2s to the empty 2p to give 4 unpaired electrons.

- The extra energy released when the bonds form more than compensates for the initial input.

- The carbon atom is now said to be in an ***excited state***.

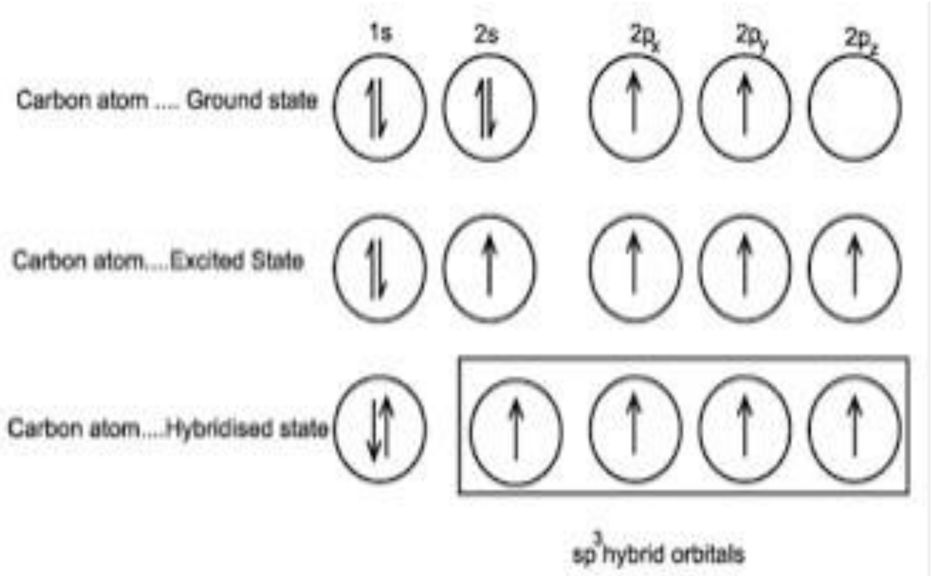




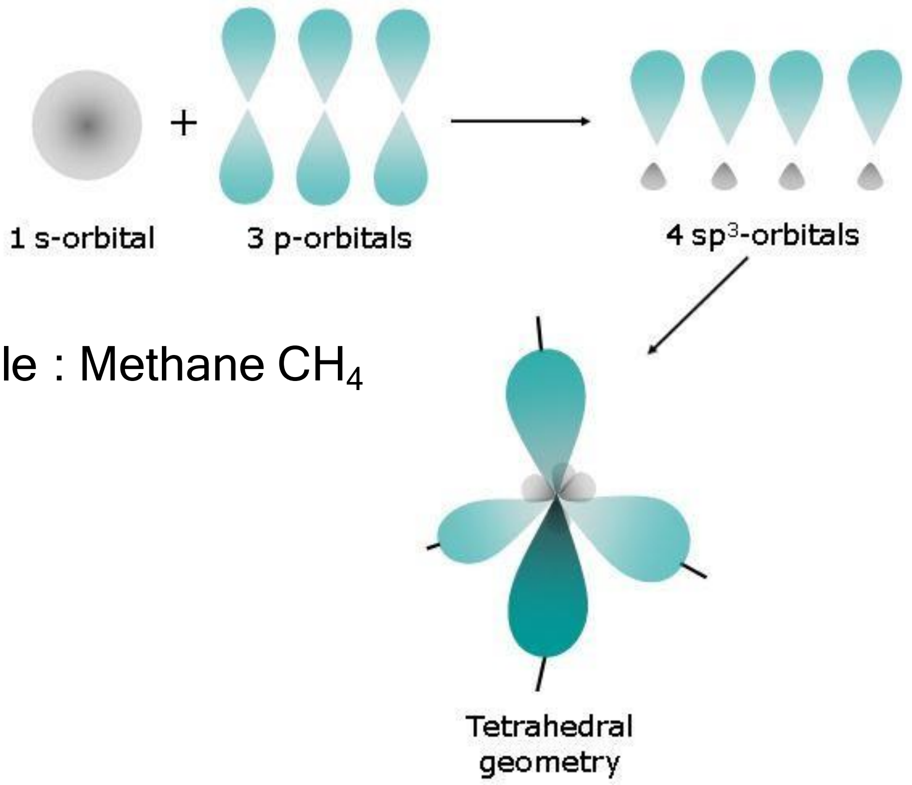


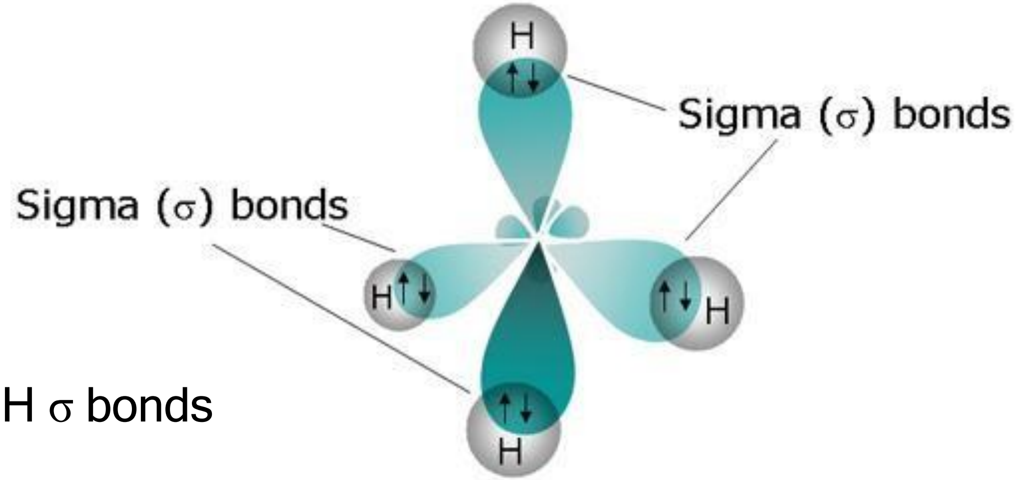
tetrahedron (a triangularly based pyramid)

- Other sp^3 examples : CCl_4, PCl_3



Example : Methane CH_4





4 C-H σ bonds

4) Molecular geometry: Gillespie or VSEPR theory

VSEPR

- Lewis structures tell us how the atoms are connected to each other.
- They don’t tell us anything about shape.
- The shape of a molecule can greatly affect its properties.
- Valence Shell Electron Pair Repulsion Theory allows us to predict geometry

VSEPR

- Molecules take a shape that puts electron pairs as far away from each other as possible.
- Have to draw the Lewis structure to determine electron pairs.
- bonding
- nonbonding lone pair
- Lone pair take more space.
- Multiple bonds count as one pair.

VSEPR

- The number of pairs determines
  - bond angles
  - underlying structure
- The number of atoms determines
  - actual shape

we generally represent the molecule as follows: AX_nE_p

A: central atom

X: atom bonded to A

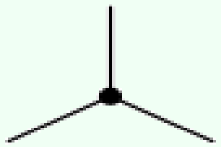
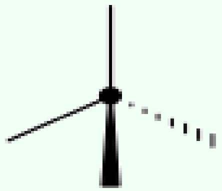
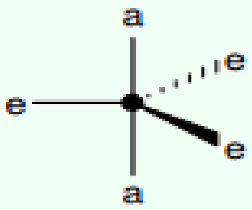
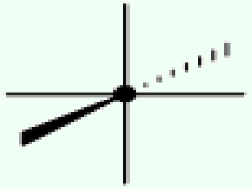
n: number of X atoms

E: lone pair on the A atom

p: number of lone pairs

VSEPR

Electron pairs	Bond Angles	Underlying Shape
2	180°	Linear
3	120°	Trigonal Planar
4	109.5°	Tetrahedral
5	90° & 120°	Trigonal Bipyramidal
6	90°	Octagonal

n+p	Electron Pair Arrangement		Molecular Shape		Examples
2		linear 180°	AX_2	linear	$BeCl_2$, CO_2
3		trigonal planar 120°	AX_3 AEX_2	trigonal planar bent	BCl_3, CH_3^+ $SnCl_2$, NO_2^-
4		tetrahedral 109.5°	AX_4 AEX_3 AE_2X_2	tetrahedral pyramidal bent	CH_4, PO_4^{3-} NH_3, ClO_3^- H_2O, SeF_2
5		trigonal bipyramidal 120° & 90°	AX_5 AEX_4 AE_2X_3 AE_3X_2	trig bipyramid "see saw" T-shaped linear	PF_5, $SeCl_5^+$ SF_4, BrF_4^+ ClF_3, XeO_3^{2-} XeF_2, ICl_2^-
6		octahedral 90°	AX_6 AEX_5 AE_2X_4	octahedral square pyramid square planar	SF_6, PCl_6^- BrF_5, SF_5^- XeF_4, IF_4^-

(A = central atom, X = terminal atom, E = lone pair)