Atomes et molécules

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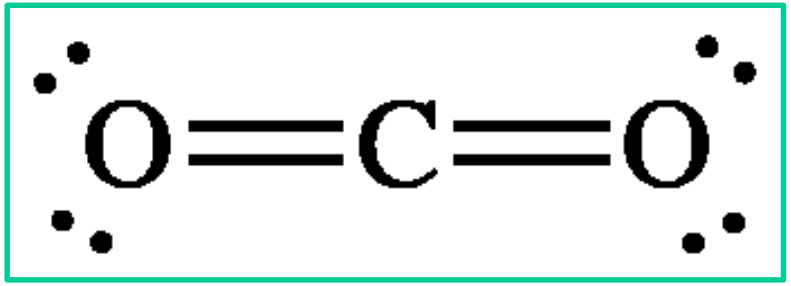
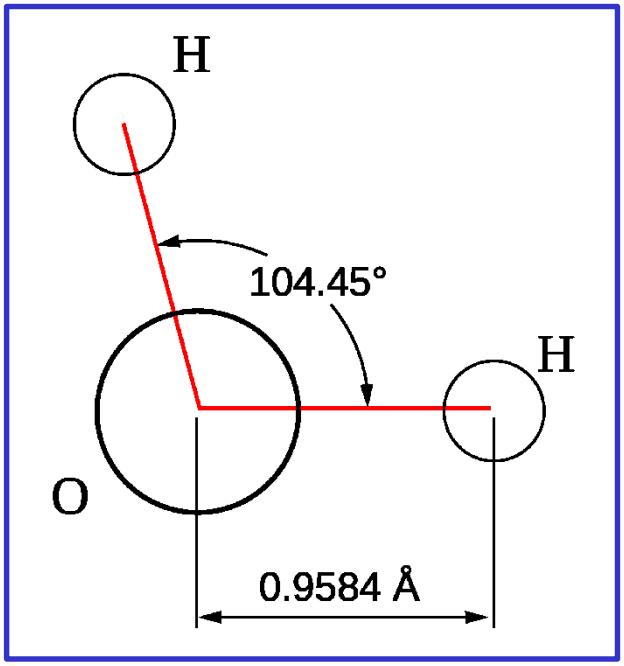
Chapter 8 : **Valence-Shell Electron-Pair Repulsion Theory (VSEPR)**

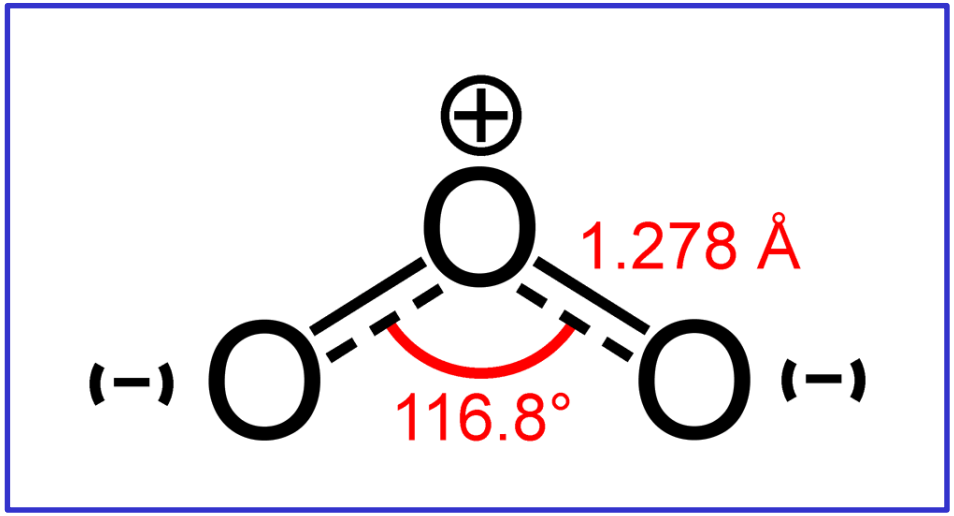
1 – The VSEPR method

2- Molecular geometry



3- Bond length





1-1. Introduction

- Lewis structures are only planar representations of molecular bonds. No information about the geometry.

- **The valence shell electron pair repulsion** (**VSEPR**) **theory** is a model used, in chemistry, to predict the geometry of individual molecules from their **Lewis structure**.

- This theory predicts the direction in space of all bonds around a central atom.

1-2) Theory

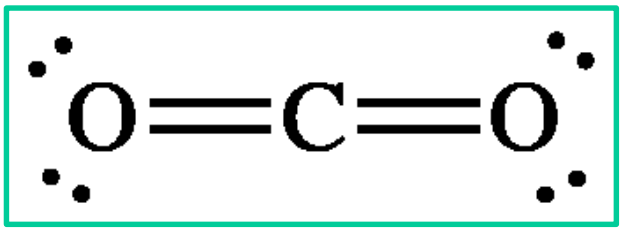
VSEPR theory proposes that the geometric arrangement of atoms about a central atom is determined solely by the repulsion between electron pairs present in the valence shell of the central atom.

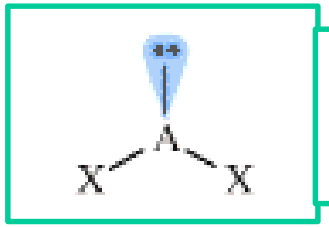
The geometry of the molecule depends on the number of bonding groups (pairs of electrons) and the number of non-bonding electrons around the central atom.

The most stable configuration is obtained for:

⟺ minimum electrostatic repulsion.

⟺ maximum distance between electron pairs





Non bonding pair on atom A changes the geometry

1-3) The method

- Establish the Lewis structure

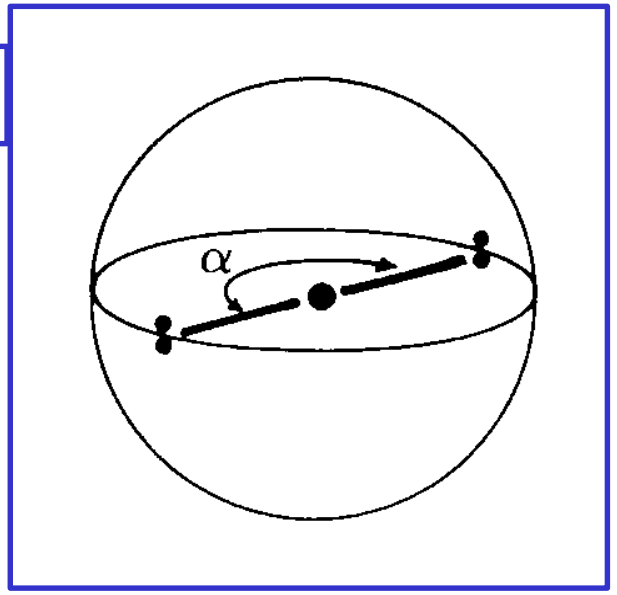
- Determine **the number N of bonding and lone pairs**.
- All electron pairs are situated at the same distance from the central atom (thus with a spheric geometry around the central atom).
- **Electron pairs are positioned in a way to minimize the electrostatic repulsion between the electron pairs**.

Multiple bonds are accounted as simple bonds.

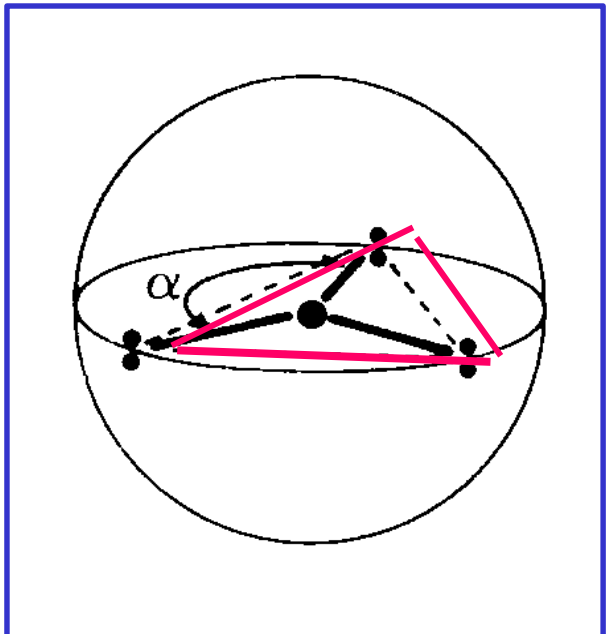
Depending on the value of N: total number of bonding and lone pairs, the electronic geometry is:

Linear $\alpha = 180°$

N = 2



Electrostatic repulsion between the electron pairs is minimized

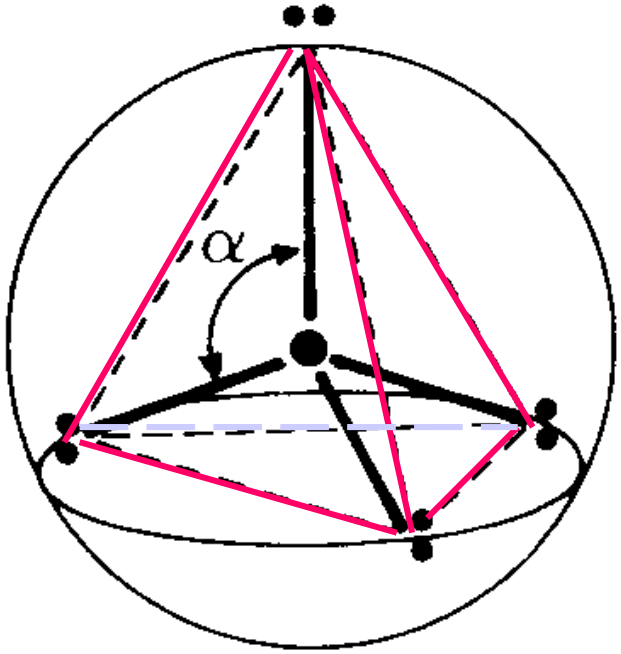


N = 3

Trigonal planar $\alpha = 120°$

Depending on the value of N: total number of bonding and lone pairs, the electronic geometry is:

N = 4



Tetrahedral $\alpha = 109,5°$

Electrostatic repulsion between the electron pairs is minimized

Depending on the value of N: total number of bonding and lone pairs, the electronic geometry is:

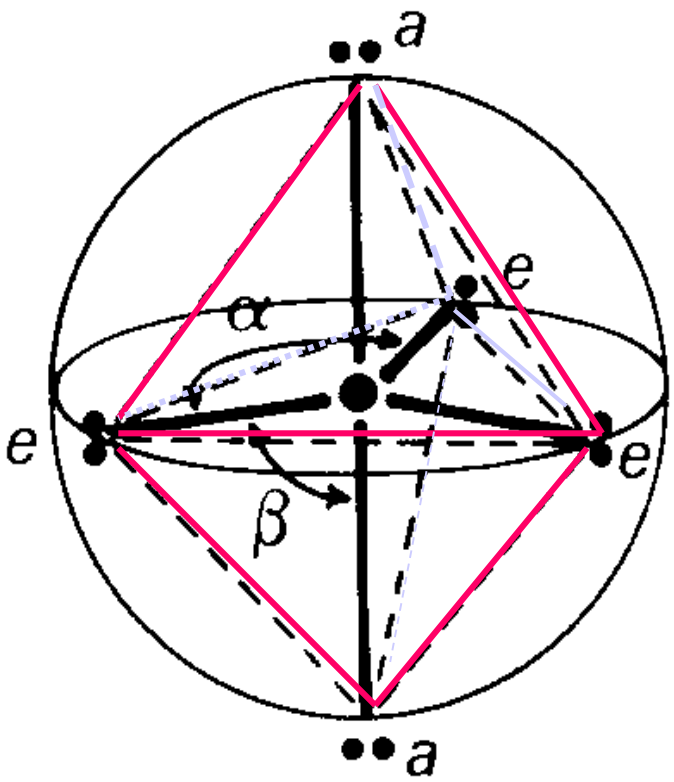
N = 5

Trigonal

Bipyramidal

α = 120°

β= 90°



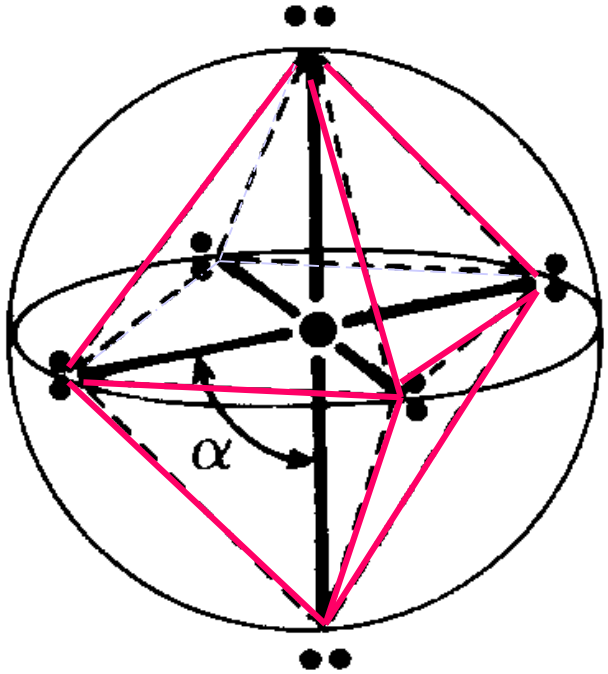
Electrostatic repulsion between the electron pairs is minimized

Depending on the value of N: total number of bonding and lone pairs, the electronic geometry is:

N = 6

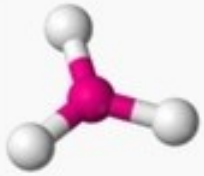
Octahedral

α = 90°



Electrostatic repulsion between the electron pairs is minimized

Possible electronic geometries

Molecule Type	Shape	Electron arrangement†	Geometry‡	Examples
AX_2E_0	Linear			$BeCl_2$, $HgCl_2$, CO_2
AX_3E_0	Trigonal planar			BF_3, CO_3^{2-}, NO_3^-, SO_3
AX_4E_0	Tetrahedral			CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^-, $TiCl_4$, XeO_4
AX_5E_0	Trigonal bipyramidal			PCl_5
AX_6E_0	Octahedral			SF_6, WCl_6

The geometrical molecular type is given by

$$\mathbf{A\,X_m\;E_p}$$

A: central atom

X: other atoms (m: number of other atoms)

E: number of lone pairs =p

with (m + p) = N

Let's distinguish two cases :

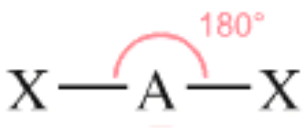
- p=0, no lone pairs are present
- p not 0, at least one lone pair is present.

2-1) Molecules without lone pairs (p=0)

A X_m

The geometry of the molecule is identical to the electronic geometry.

N = m = 2



Linear

AX_2

Cl—Be—Cl

$BeCl_2$

O=C=O

CO_2

H—C≡C—H

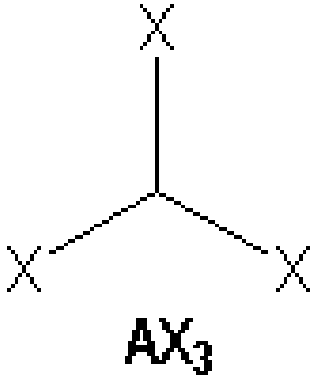
C_2H_2

H—C≡N

HCN

N = m = 3, (p=0)

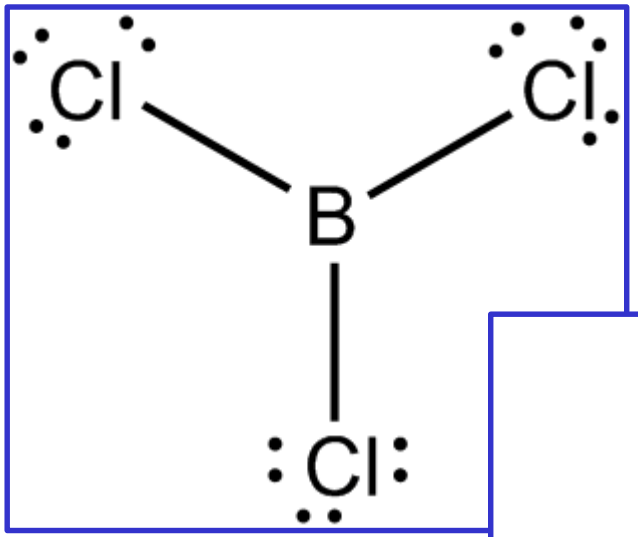
Trigonal planar molecule with angles = 120°



Examples :

B (Z =5)

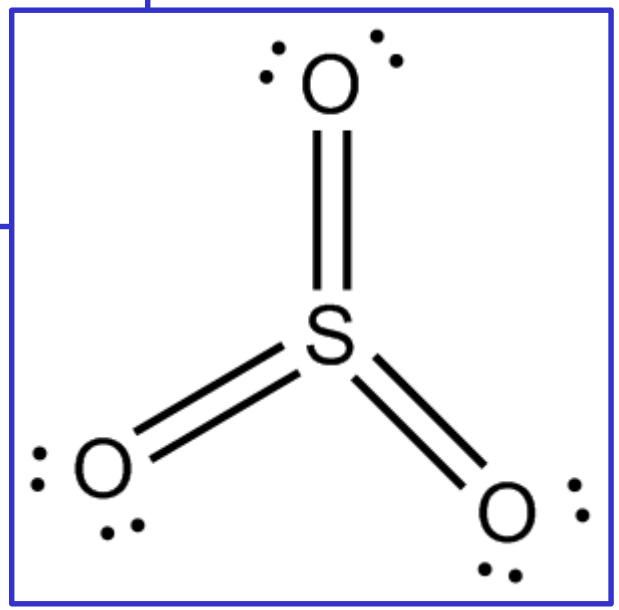
[He] $2s^2$ $2p^1$



Molecule with single bonds:

S (Z = 16)

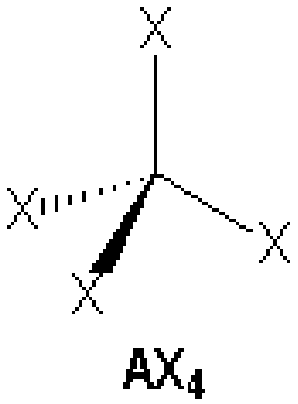
[Ne] $3s^2$ $3p^4$



Molecule with double bonds:

N = m = 4, (p=0) **AX_4**

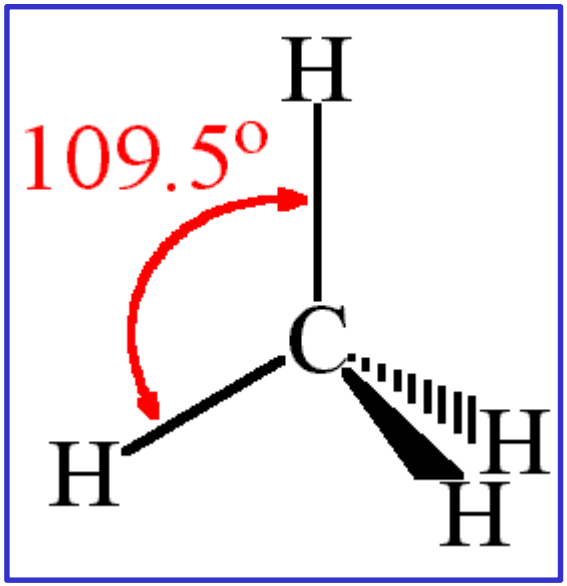
Tetrahedral molecule with angles α = 109,5°

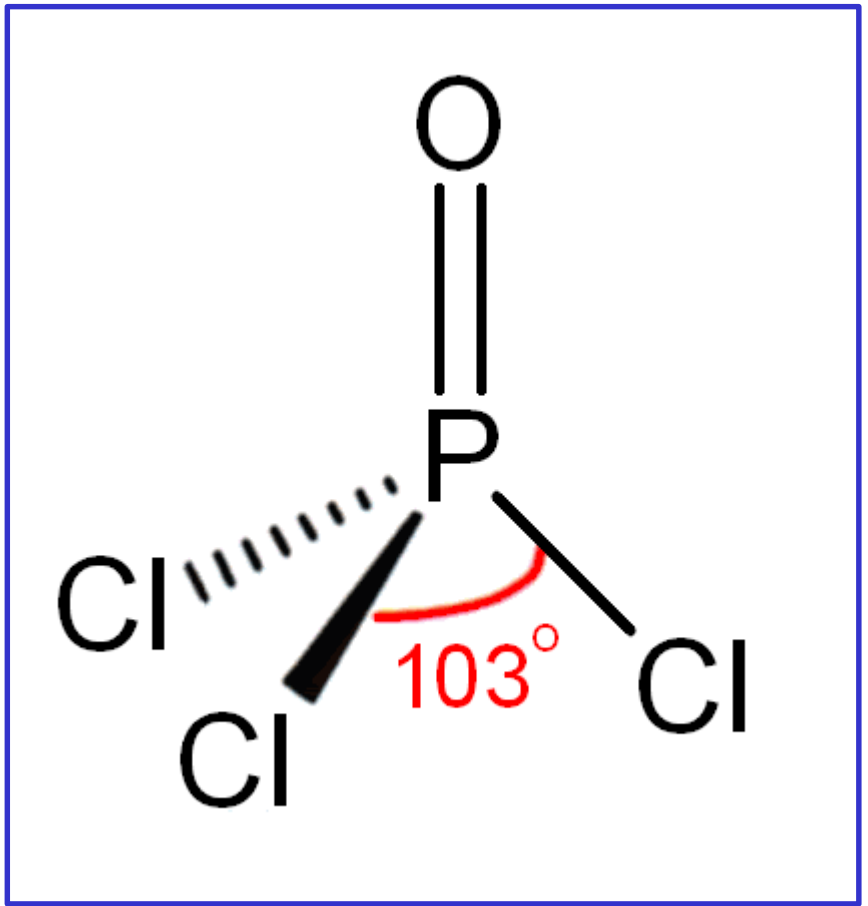


AX_4

Examples :

Molecule with single bonds:

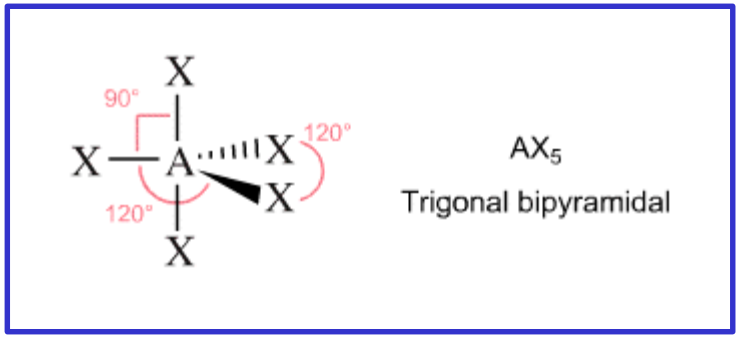




Molecule with double bonds:

N = m = 5, (p=0)

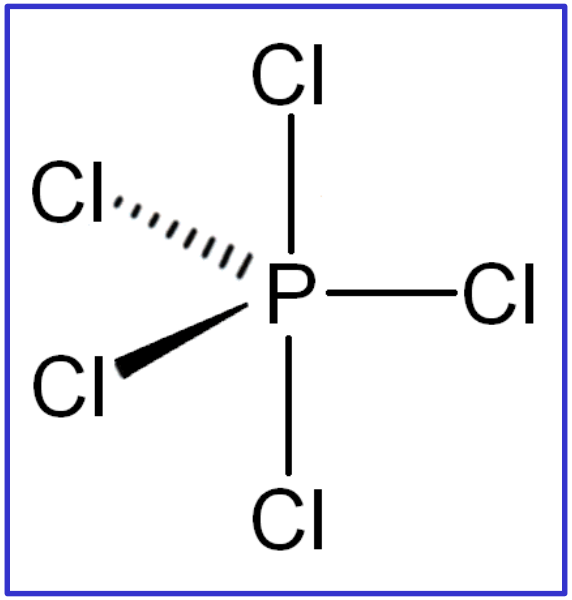
α = 120° β= 90°



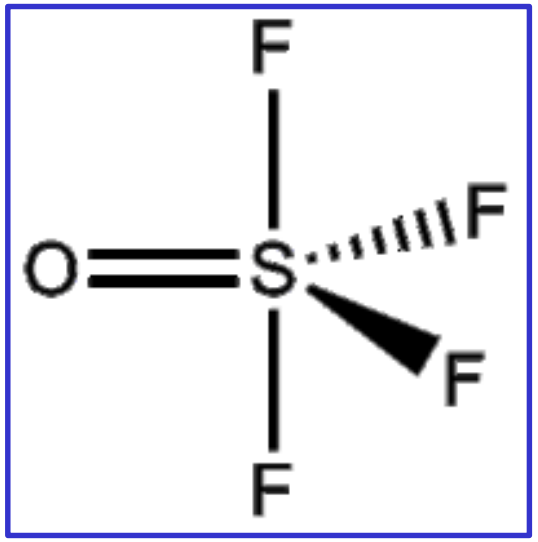
AX_5

Exemples :

Molecule with single bonds:



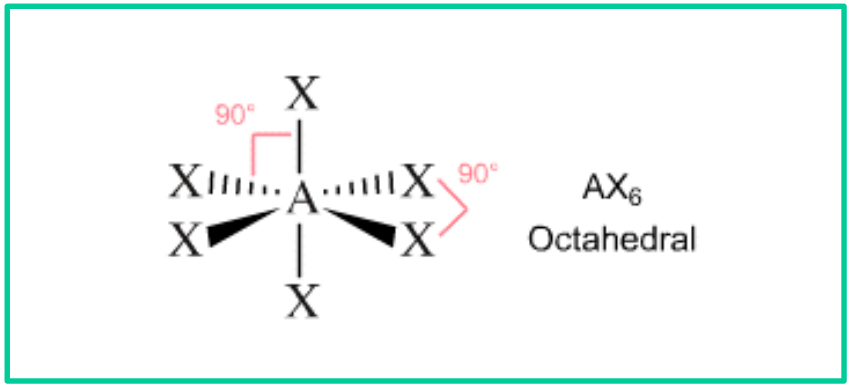
Molecule with double bonds:



N = m = 6, p= 0

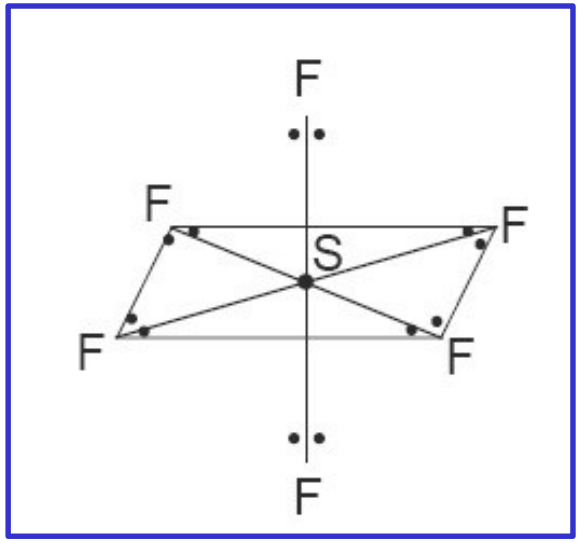
Octahedral, α = 90° β= 90°

AX_6

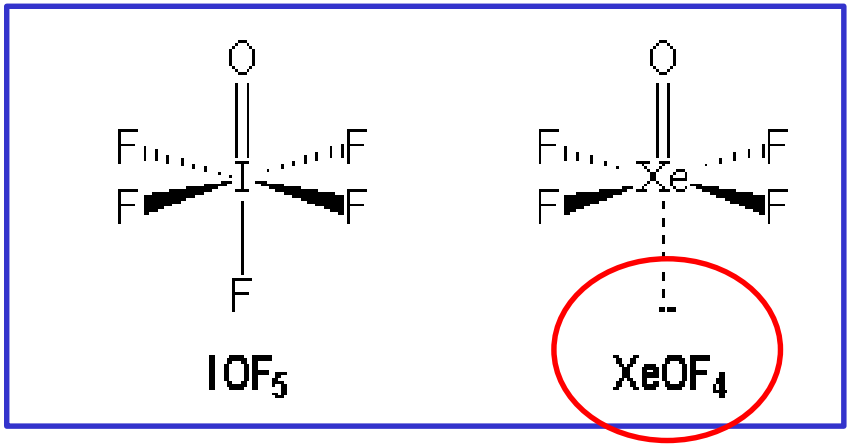


Examples :

Molecule with single bonds:



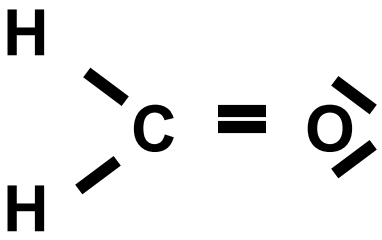
Molecule with double bonds:

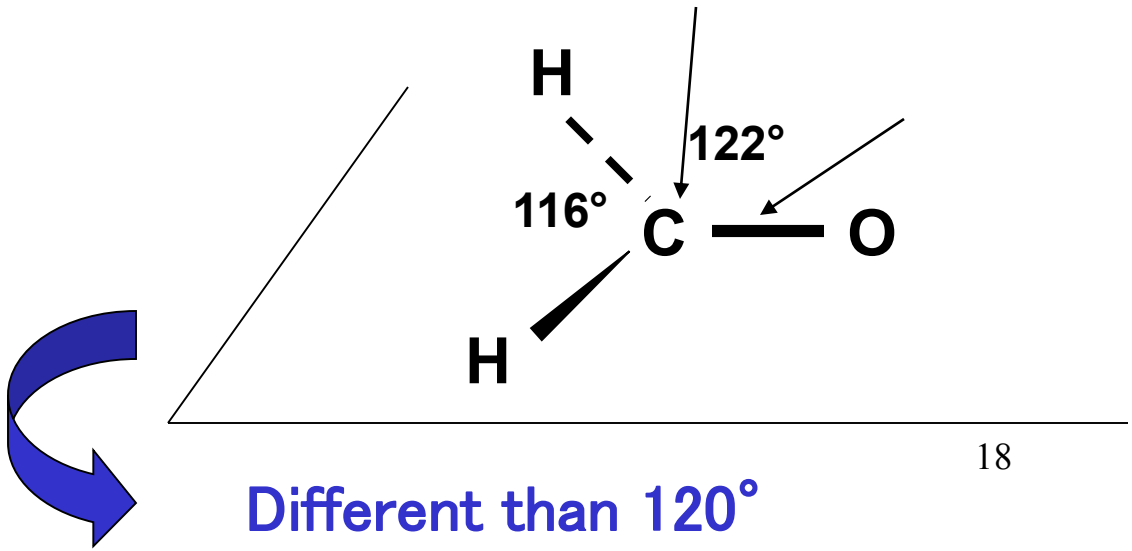


The repulsion of a multiple bond is stronger than for a single bond.

Therefore, the angles formed by the bonds in the case of a multiple bond is different than in the presence of only single bonds.

Example:

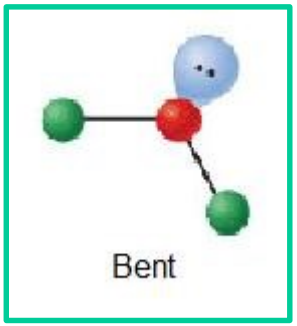




2-2) Molecules with lone pairs (p≠0)

$$A X_m E_p$$

$A X_2 E$

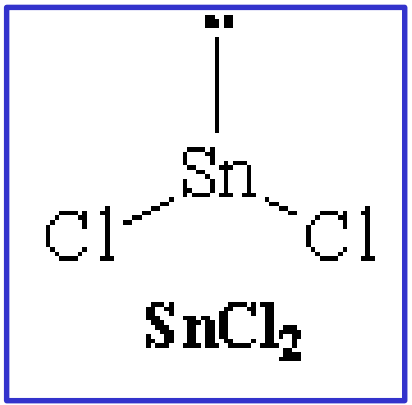


Example : **$Sn Cl_2$** (Sn; Z = 50)

N = 3 ➡ planar trigonal geometry

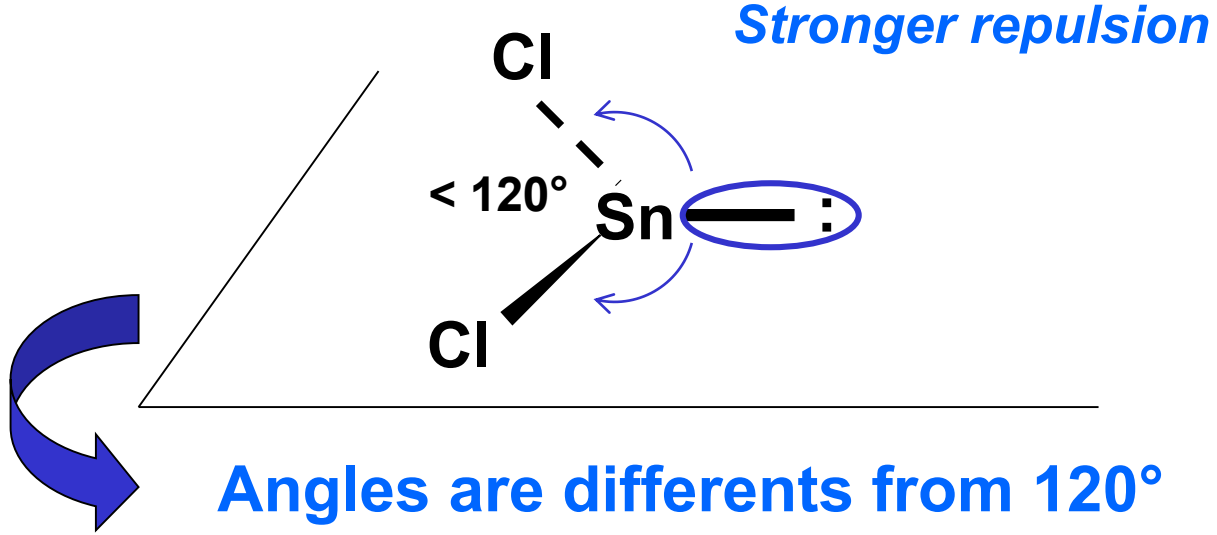
Presence of one lone pair

The molecule is bent.



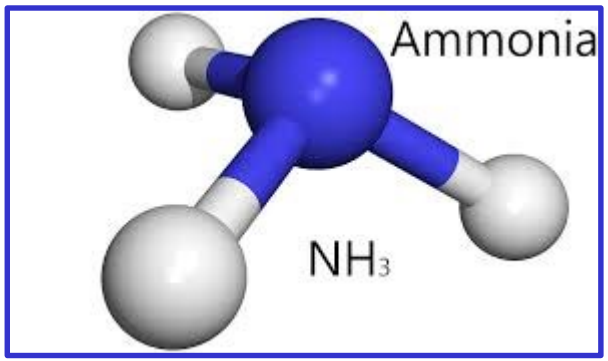
The repulsion of a lone pair is stronger than for a bonding pair.

Therefore, the angles formed by the bonds in the case of a lone pair is different than in the presence of only bonding pairs.



A X_3 E

Example : NH_3



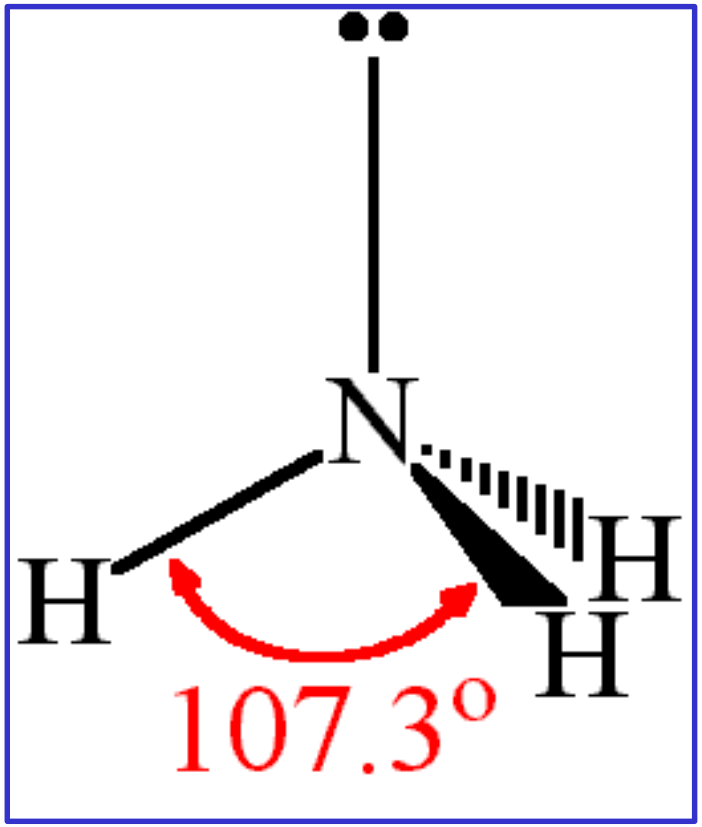
N = 4 ➡ tetrahedral geometry

but with ONE lone pair

the molecular geometry becomes a trigonal pyramid

Repulsive effect of the nitrogen lone pair:

- **angles < 109,5° (107.3°)**



$A X_2 E_2$

Exemple : H_2O

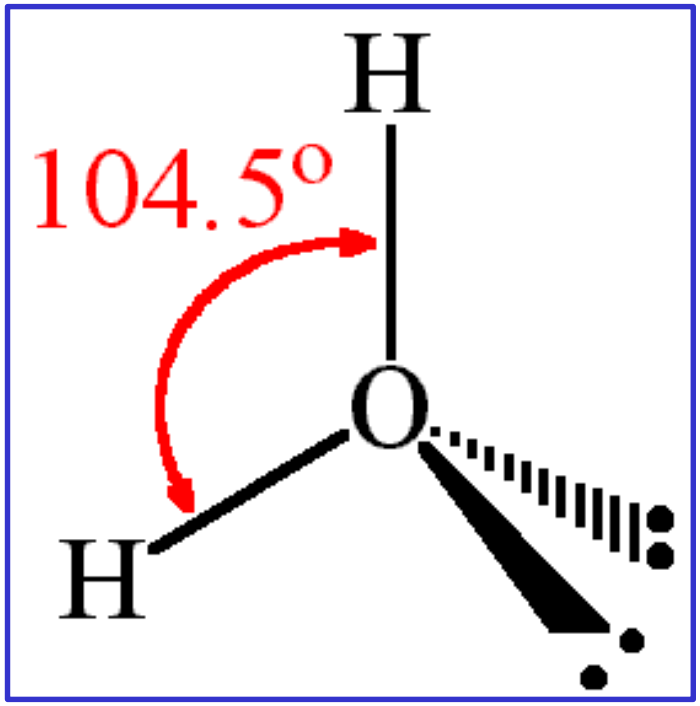
N = 4 ➡ tetrahedral geometry

but with TWO lone pairs

The molecular geometry is bent

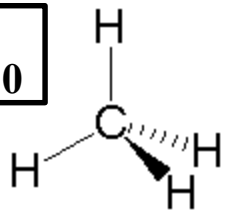
Repulsive effect of both oxygen lone pairs:

- **angles < 109,5° (104.5°)**



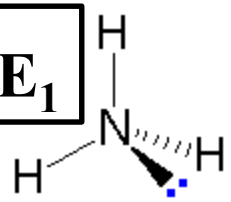
N = 4 : tetrahedral geometry

$A X_4 E_0$

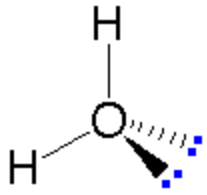


Methane

$A X_3 E_1$



Ammonia



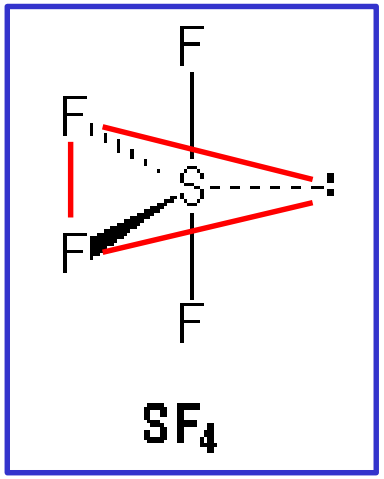
Water

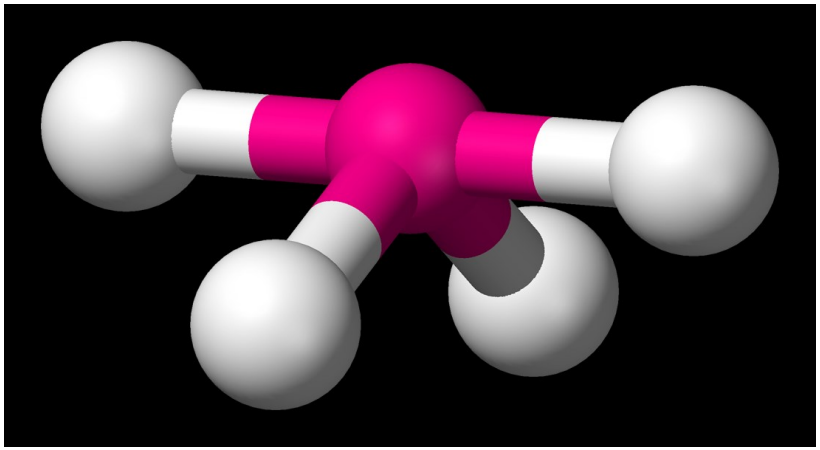
$A X_2 E_2$

AX_4E

Exemple : SF_4

N = 5 ➡





trigonal bipyramidal geometry

But one lone pair exists which

will take one position in the triangular

base of the pyramid.

the molecular geometry
is a seesaw (BASCULE)

$A X_3 E_2$

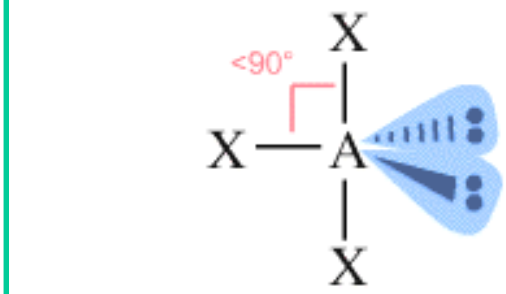
Example : ClF_3

N = 5 ➡

trigonal bipyramidal geometry

But two lone pairs exist which take positions in the triangular base of the pyramid.

The molecular geometry is a T-shape.

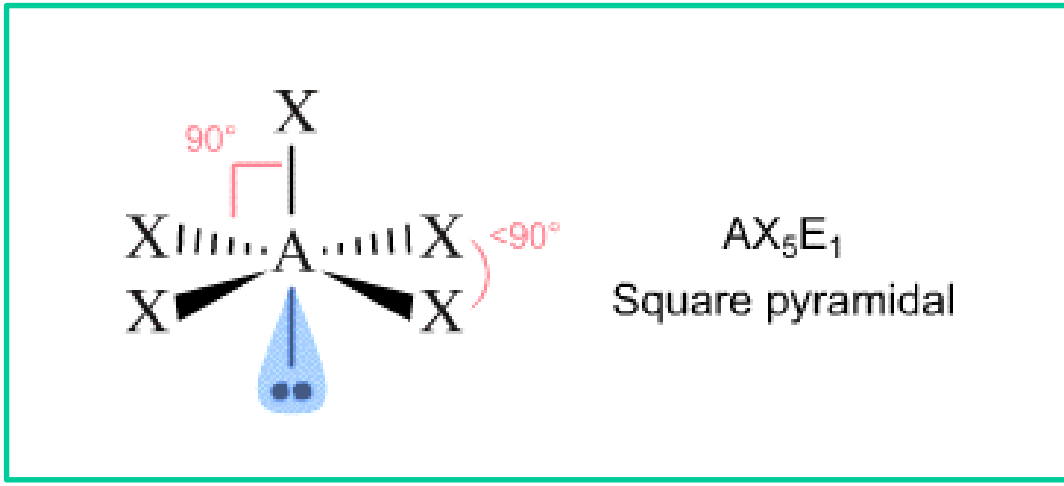


$A X_5 E$

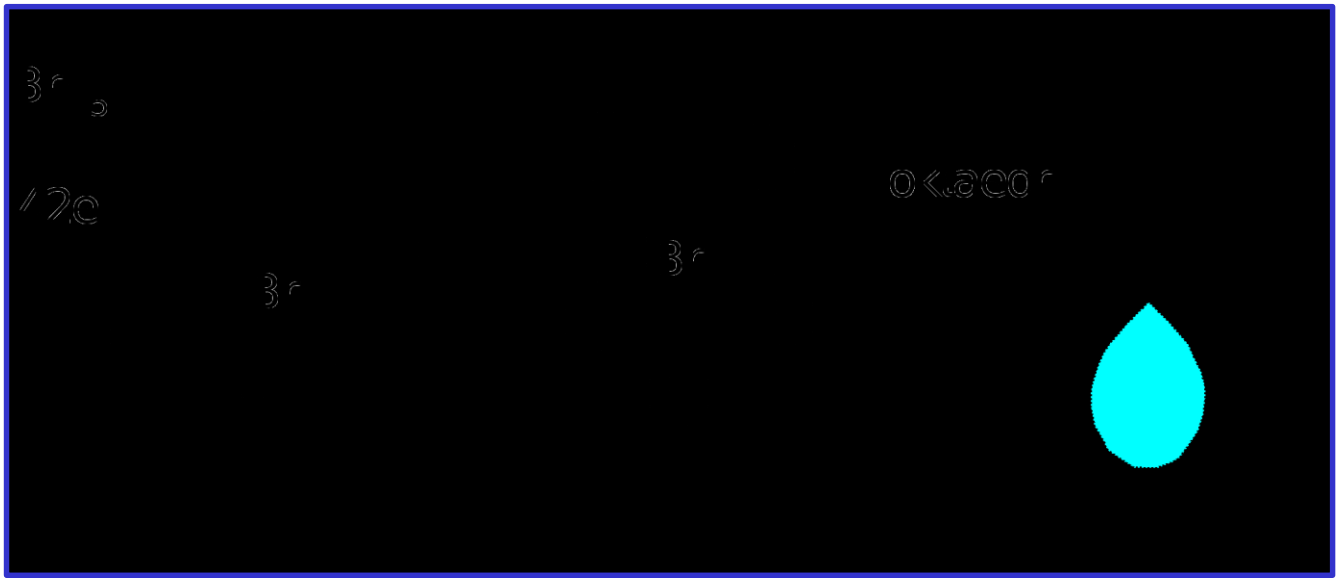
Example : BrF_5

N = 6 ➡ octahedric geometry

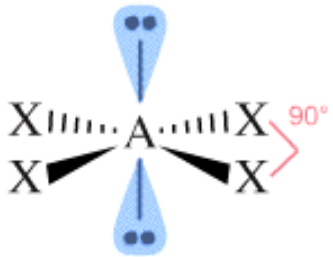
(square base bipyramide)



But one lone pair will take the place of a summit of the pyramid.



$A X_4 E_2$



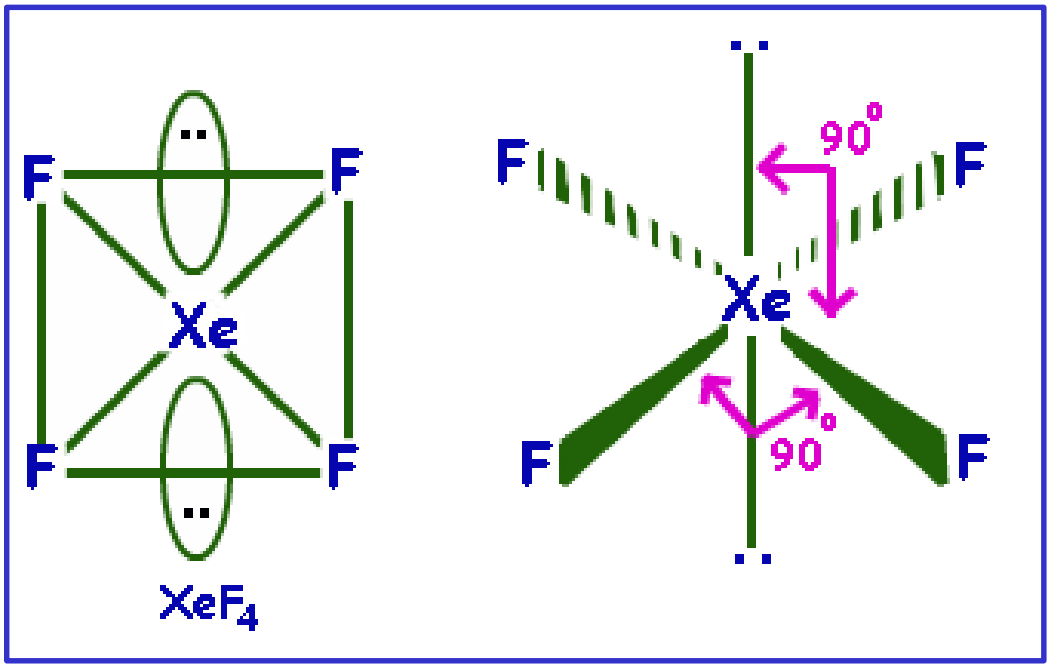
Exemple : XeF_4

N = 6 ➡ octahedric geometry

(square base bipyramide)

But two lone pairs will take the place of both summit of the pyramid.

➡ the molecular geometry is **planar square.**



Chapter 8 – 3. **Bond length**

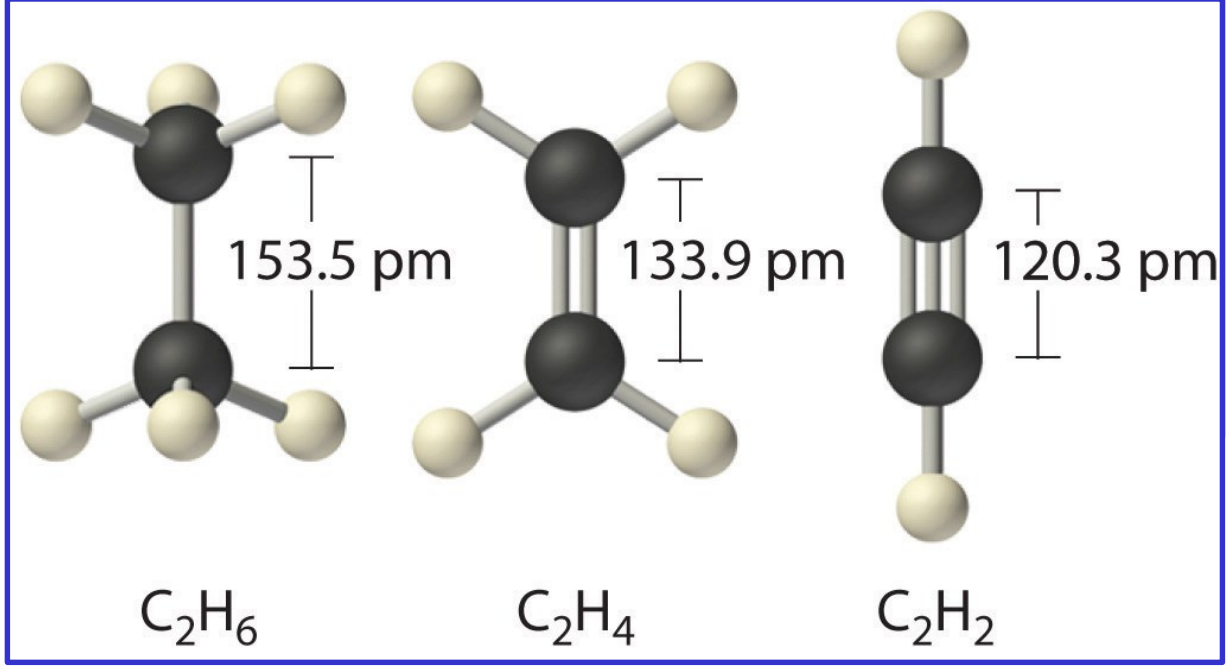
The bond length depends :

- on the species
- on the bond type

(simple, double …)

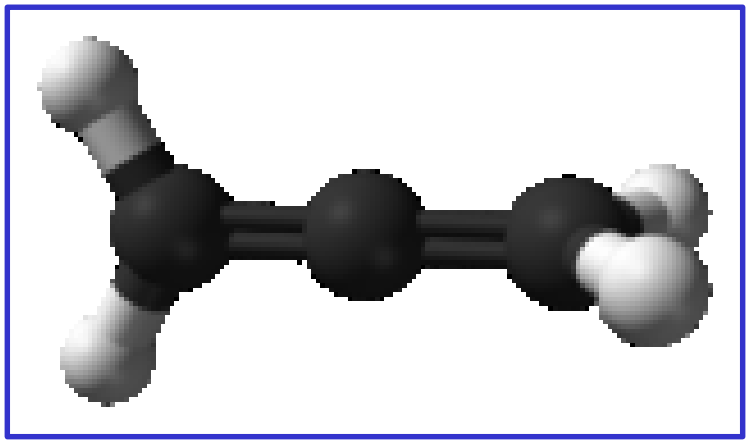
Average Single Bond Lengths (Picometers)

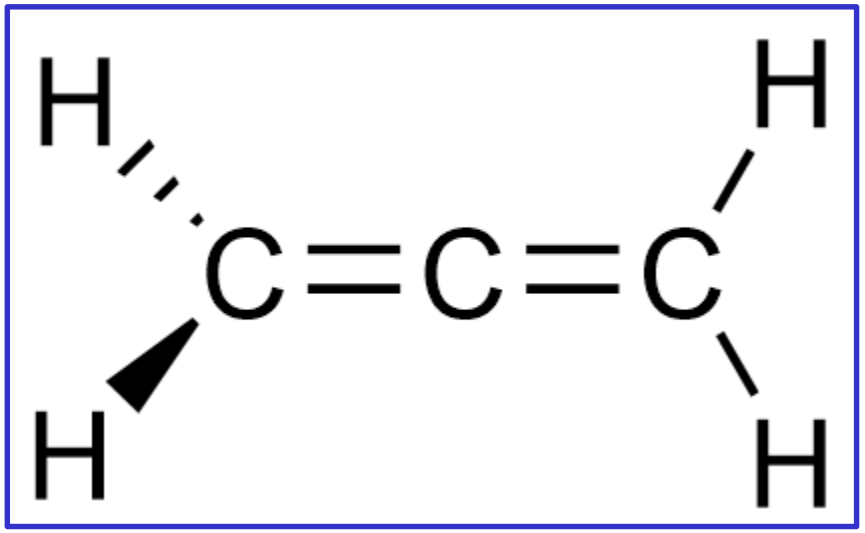
	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											266



Limits to the repulsion VSEPR method

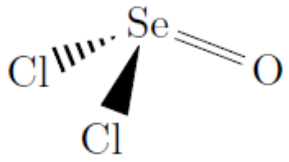
- The VSEPR method is very efficient to predict the geometry of a molecule when the central atom can be chosen without any doubts.
- The VSEPR method is less efficient to predict the global geometry of complex molecules.
- In particular, it is not possible to explain why the CH2 termination in the allene molecule are perpendicular to each other.





It can be explained by the quantum model.

QCM 14 Soit la molécule :



Dans le formalisme VSEPR cette molécule $\underline{Se}OCl_2$ ($Z_O = 8$, $Z_{Cl} = 17$ et $Z_{Se} = 34$) est du type :

a. AX_3
b. AX_3E
c. AX_3E_2
d. AX_4
e. AX_4E

$Z_I = 53$, même famille que Br, Cl, F

QCM 16 On considère la molécule $\underline{I}Cl_3$ ($Z_{Cl} = 17$ et $Z_{Br} = 35$). Quelle(s) est (sont) la (les) proposition(s) exacte(s) :

a. La formule VSEPR de la molécule $\underline{I}Cl_3$ est AX_3
b. La formule VSEPR de la molécule $\underline{I}Cl_3$ est AX_3E_2
c. La figure de répulsion de la molécule $\underline{I}Cl_3$ est une bipyramide à base triangulaire
d. La géométrie de $\underline{I}Cl_3$ est un triangle équilatéral plan
e. La géométrie de $\underline{I}Cl_3$ est en forme de T.