*Chapter 10: Molecular Geometry and Chemical Bonding Theory

→Molecular Geometry: the general shape of a molecule, as determined by the relative positions of the atomic nuclei.

*10.1: The Valence-shell Electron-Pair Repulsion (VSEPR) Model.

→(VSEPR) Predicts the shapes of molecules and ions by assuming that the valence-shell electron pairs are arranged about each atom so that electron pairs are kept as far away from one another as possible, thus minimizing electron-pair repulsions.

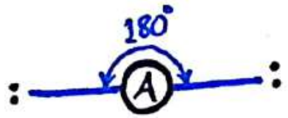
* The direction in space of the bonding pairs gives you the ~~geo~~ molecular geometry.

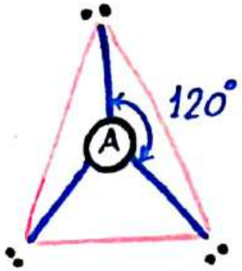
* Arrangement of electrons pairs about an atom.

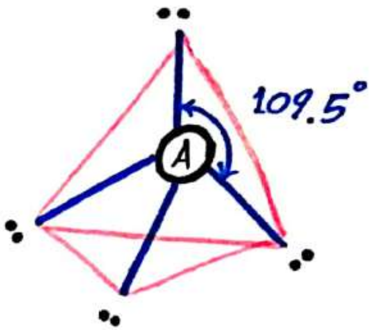
incompleted octate — octate

Number of pairs → 2 —— 3 —— 4

Arrangement of pairs → Linear —— Trigonal plannar —— Tetrahedral



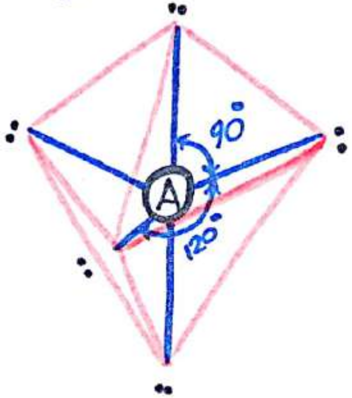


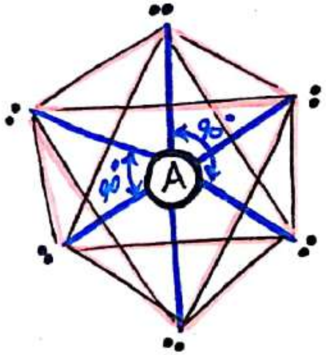


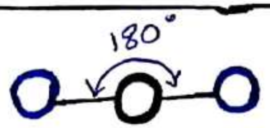
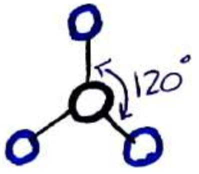
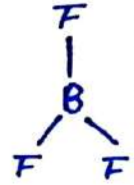
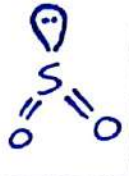
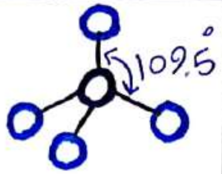
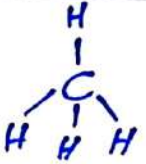
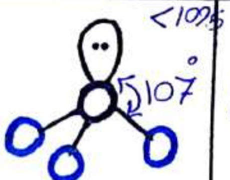
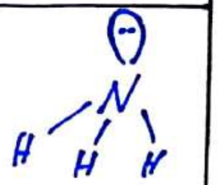
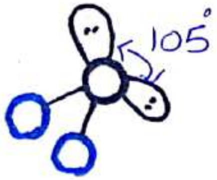
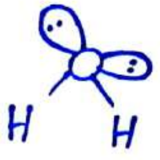
expanded octate

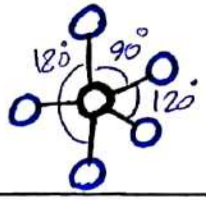
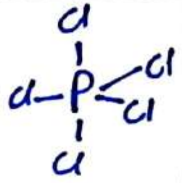
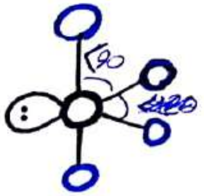
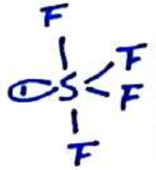
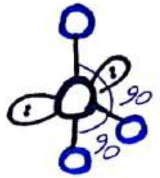
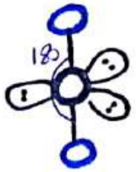
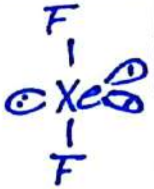
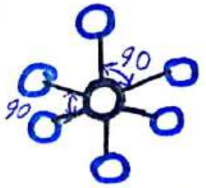
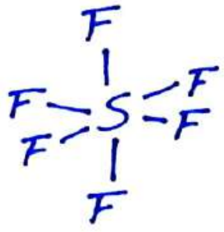
Number of pairs → 5 —— 6

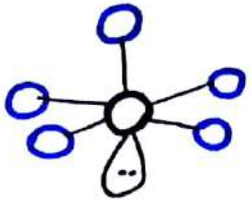
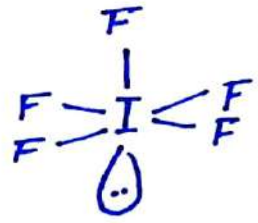
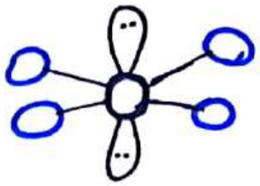
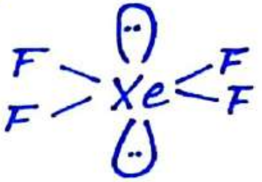
Arrangement of pairs → Trigonal bipyramidal —— Octahedral





Electron pairs			Arrangement of pairs	Molecular geometry	Example	Hyberdization
total	bonding	Lone				
2	2	0	Linear	linear AX_2 	F – Be – F BeF_2	sp
3	3	0	Trigonal Plannar	Trigonal Plannar AX_3 	BF_3 	sp^2
	2	1		Bent or angular AX_2E_1 	SO_2 	
4	4	0	Tetrahedral	Tetrahedral AX_4 	CH_4 	sp^3
	3	1		Tergonal Pyramidal AX_3E_1 	NH_3 	
	2	2		Bent or angular AX_2E_2  <109.5	H_2O 	

Electron pairs			Arrangement of pairs	Molecular geometry	Example	Hyberdiz-ation
total	bonding	Lone				
5	5	0	Trigonal Bipyramidal	Trigonal bipyramidal AX_5 	PCl_5 	sp^3d
	4	1		seesaw or distorted tetrahedron AX_4E_1 	SF_4 	
	3	2		T-shape AX_3E_2 	ClF_3 	
	2	3		Linear AX_2E_3 	XeF_2 	
6	6	0	octahedral	octahedral AX_6  all angles 90°	SF_6 	sp^3d^2

Electron pairs			Arrangment of pairs	Molecular geometry	Example	Hyberdization
total	bonding	lone				
6	5	1	octahedral	square pyramidal AX_5E_1 	IF_5 BrF_5 	sp^3d^2
	4	2		square plannar AX_4E_2 	XeF_4 	

*steps in the Prediction of Geometry by the VSEPR Model

step 1 write the electron dot formula from the molecular formula

step 2 determine from electron dot formula the no. of electron pairs around the central atom, including boding and nonbonding.

step 3 determine the arrangement of these electron pairs about the central atom

step 4 obtain the molecular geometry from the directions of the bonding pairs for this arrangement

***Example:** predict the geometry of the following using VSEPR method.

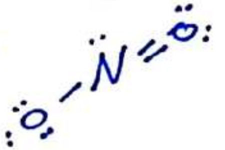
a. $BeCl_2$ 16 $:\ddot{Cl}-Be-\ddot{Cl}:$

2 bonding pairs

linear

$:\ddot{Cl}-Be-\ddot{Cl}:$

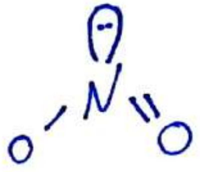
b. NO_2^- 18ē



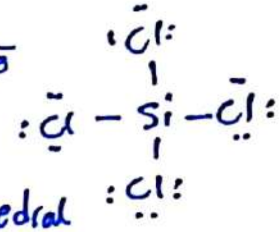
1 lone

2 bonding

trigonal plannar, bent

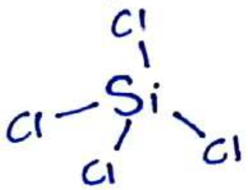


c. $SiCl_4$ 32ē ✓

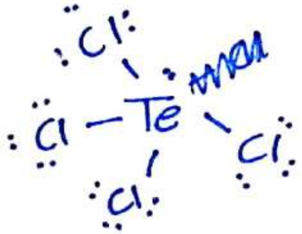


4 bonding

tetrahedral, tetrahedral



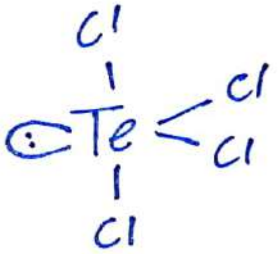
d. $TeCl_4$ 34ē



1 lone

4 bonding

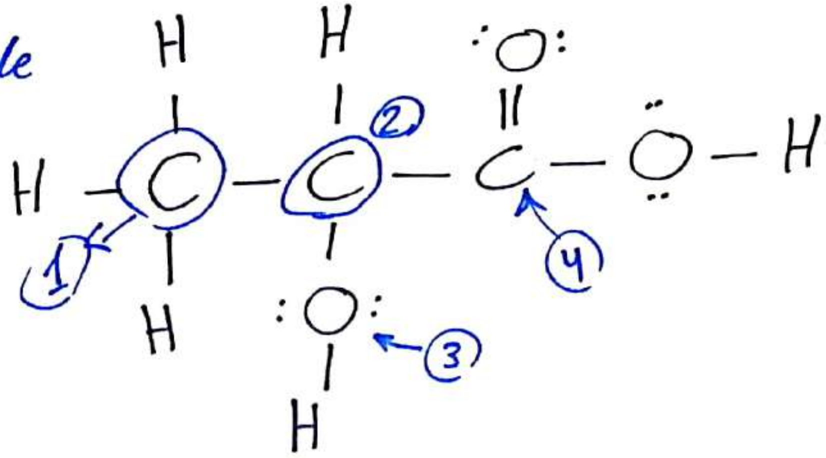
Trigonal biPyramidal, seesaw



㊀ Lone pairs require more space than a bonding pair.

*Applying the VSEPR Model to larger Molecules

→ broke the large molecule into small one we can apply VSEPR on.



→ ① Tetrahedral, Tetrahedral

② 〃 , 〃

③ Tetrahedral, bent

④ Trigonal plannar, Trigonal plannar

*10.2: Dipole Moment and Molecular Geometry

* Dipole Moment: a quantitative measure of the degree of charge separation in a molecule and is therefore an indicator of the polarity of the molecule.

$\mu = q \times d$ → in general, a positive charge q and a negative charge $-q$, separated by distance d has a dipole moment μ.

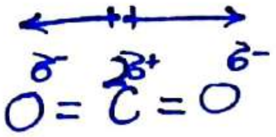
H-Cl : Cl atom is more electronegative than H atom, the electrons of the bond are pulled toward it, giving this atom a partial negative charge (δ-), The H atom then has an equal positive charge (δ+)

$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \qquad \mu = \delta d$$

*the unit for dipole is debyes (D): $1D = 3.34 \times 10^{-30}$ C.m

→ example: carbon dioxide:

it has two C-O bond, and each one has its polarity:



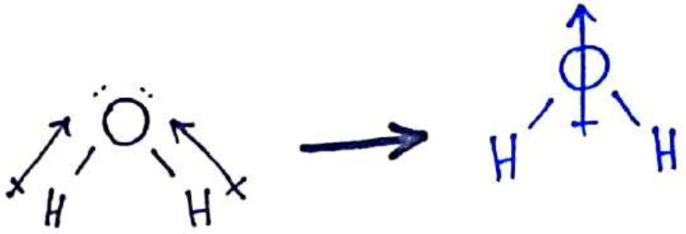
O has the higher electronegativity

* we will denote the dipole-moment contribution from each bond by an arrow from positive to negative +⟶

* dipole bonds like a force, is a vector quantity (has both magnitude and direction).

→ so the net dipole in CO_2 is Zero.

→ example: H_2O



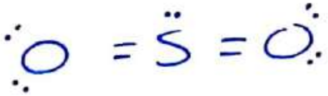
* Linear, Trigonal Planar (trigonal planar), Tetrahedral (Tetrahedral (AX_4)), Trigonal bipyramidal (trigonal bipyramidal (AX_5)), and Octahedral (octahedral (AX_6)) **have zero dipole moment.**

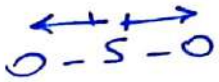
*** Example:** Each of the following molecules has a nonzero dipole moment. select the molecular geometry that is consistent with this information Explain your reasoning:

a. SO_2 Linear, [✓ bent]

b. PH_3 trigonal plannar, [✓ trigonal pyramidal]

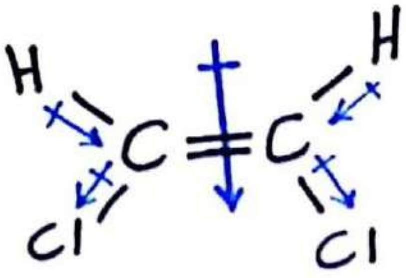
a. 2 (S-O)



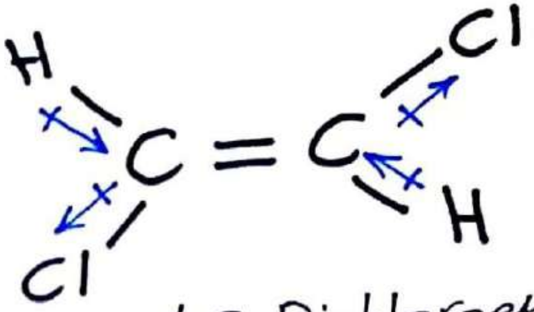


b.

* Effect of polarity on Molecular Properties:



Cis-1,2- Dichloroethene



trans-1,2-Dichloroethene

	Cis-1,2- Dichloroethene	trans-1,2-Dichloroethene
Dipole moment	1.9 D	0D
B.P (°C)	60.2	48.5

*10.3: Valence Bond Theory

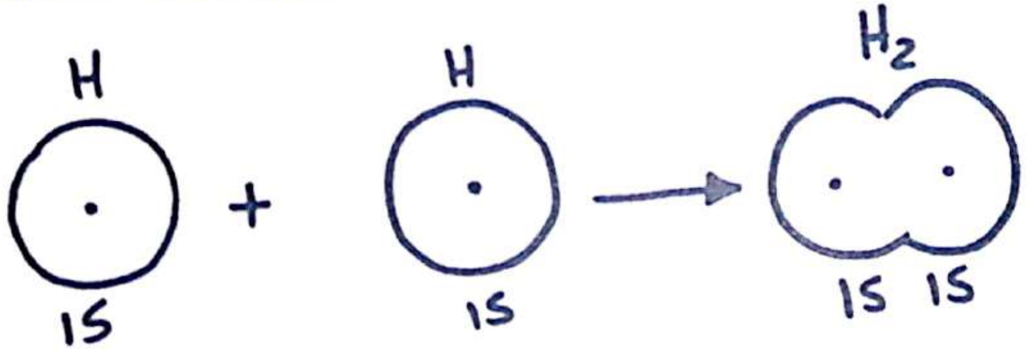
→ an approximate theory to explain the electron pair or covalent bond by quantum mechanics.

→ A bond forms between two atoms when the following conditions are met:

1. An orbital on one atom comes to occupy a portion of the same region of space as an orbital on the other atom. The two orbitals are said to overlap.
2. The sum of the electrons in both orbitals is no more than two.

$$\left.\begin{array}{l} H + H \rightarrow H_2 \\ 1s^1 + 1s^1 \rightarrow \text{Total } 2e \text{ in both orbitals.} \end{array}\right\} \text{occur}$$

$$\left.\begin{array}{l} He + He \rightarrow He_2 \\ 1s^2 + 1s^2 \rightarrow \text{Total } 4e \text{ in both orbitals (more than } 2e) \end{array}\right\} \text{does not occur}$$



* Because the strength of bonding depends on orbitals overlap, orbitals other than S orbital bond only in given directions. Orbitals bond in the directions in which they protrude or point to obtain maximum overlap.

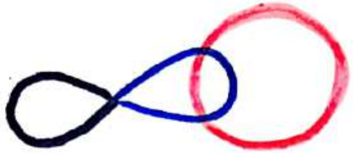
→ consider HCl molecule

H: $1s^1$ $\underline{\uparrow}$

Cl: $[Ne]3s^2 3p^5$

$\underset{3s}{\underline{\uparrow\downarrow}}$ $\underset{3p}{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}}$

the bonding of hydrogen atom has to occur with the singly occupied 3p orbital of chlorine.

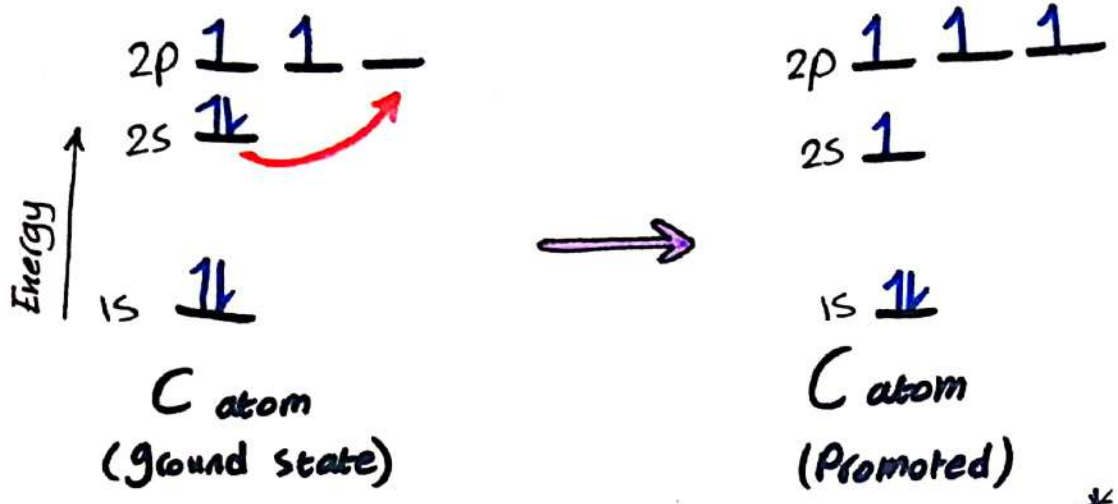


* Hybrid Orbitals: are orbitals used to describe bonding that are obtained by taking combinations of atomic orbitals of the isolated atoms

① Cl atom $\underset{1s}{\underline{\uparrow\downarrow}}$ $\underset{2s}{\underline{\uparrow\downarrow}}$ $\underset{2p}{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}$ $\underset{3s}{\underline{\uparrow\downarrow}}$ $\underset{3p}{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}}$ has one unpaired ē, forms one bond

② O atom $\underset{1s}{\underline{\uparrow\downarrow}}$ $\underset{2s}{\underline{\uparrow\downarrow}}$ $\underset{2p}{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}$ has two unpaired ē, forms two bonds like H_2O

③ C atom $\underset{1s}{\underline{\uparrow\downarrow}}$ $\underset{2s}{\underline{\uparrow\downarrow}}$ $\underset{2p}{\underline{\uparrow}\ \underline{\uparrow}\ \underline{\quad}}$ has two unpaired ē and one empty orbital.



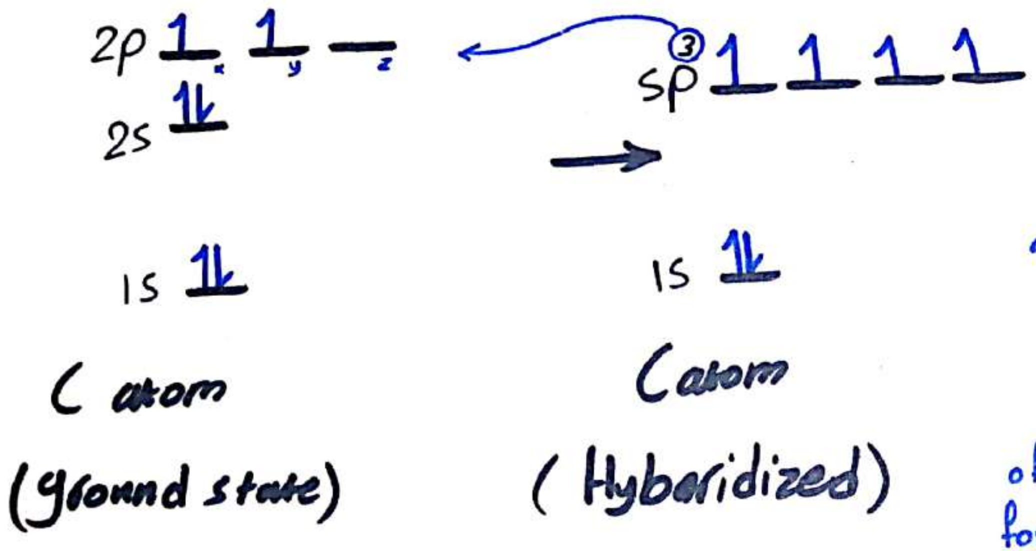
* The number of hybrid orbitals formed always equals the number of atomic orbitals used.

*steps to obtain the bonding description about <u>any</u> atom in a molecule:

1] write the Lewis electron-dot formula of the molecule.

2] Form the Lewis formula, use the VSEPR model to obtain the arrangement of electron pairs about this atom.

3] From the geometric arrangement of the electron pairs, deduce the type of <u>hybrid</u> orbitals on this atom required for the bonding description.



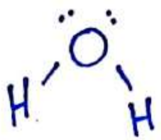
→ cont. of steps:

4] Assign valence electrons to the hybrid orbitals of this atom one at a time, pairing them only when nesscessary.

5] Form bonds to this atom by overlaping singly occupied orbitals of other atoms with singly occupied hybrid orbitals of this atom.

*** Example:** Describe the bonding in H_2O according to valence bond theory. Assume that the molecular geometry is the same as given by the VSEPR ?

Bent



sp^3

2p ↑↓ ↑ ↑

2s ↑↓

1s ↑↓

O atom
(ground state)

↑↓ ↑↓ ↑ ↑
sp^3

$1s^2$ ↑↓

O atom
Hybridized

⇒

↑↓ ↑↓ ↑↓ ↑↓
sp^3

$1s^2$ ↑↓

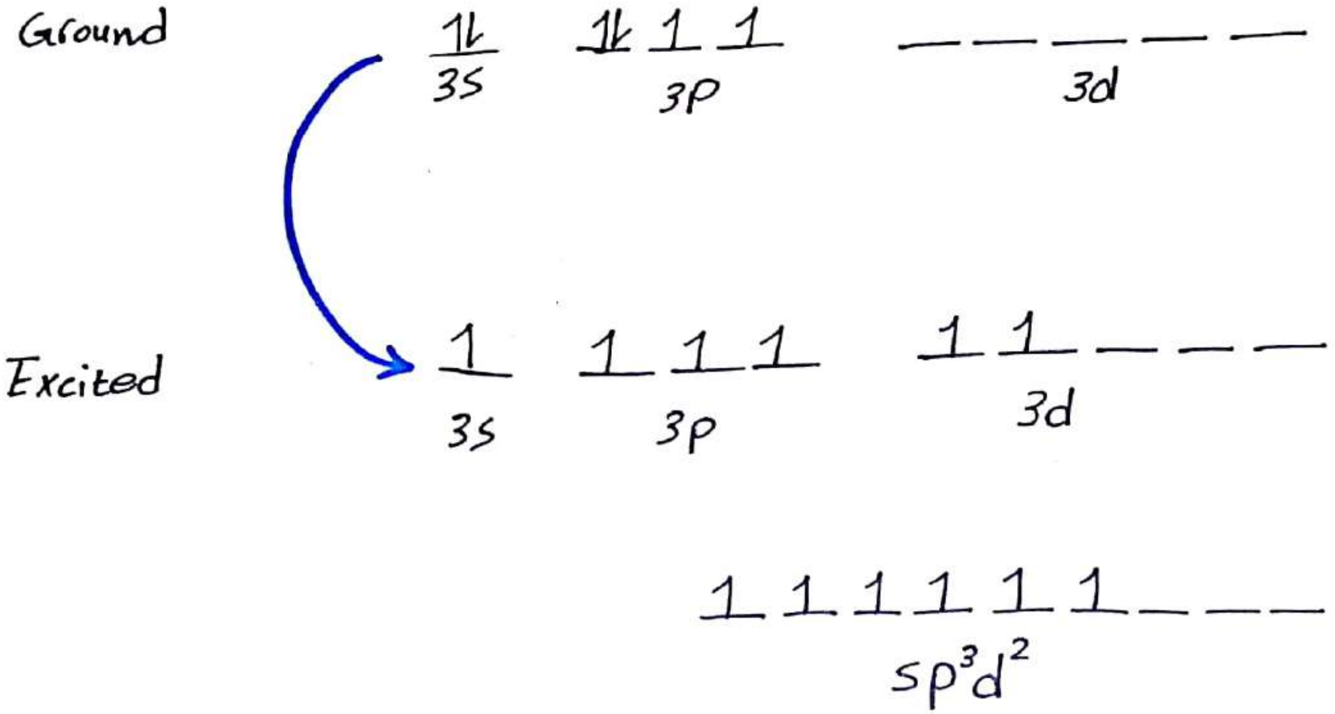
⇒ remember: more than 8ē we use the orbital d

Like in Trigonal Bipyramidal sp^3d
Octahedral sp^3d^2

Example:

S[redacted]

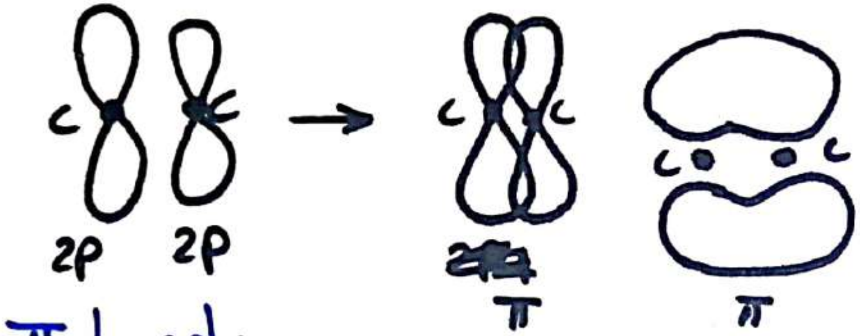
like: SF_6



* 10.4: Description of Multiple Bonding:

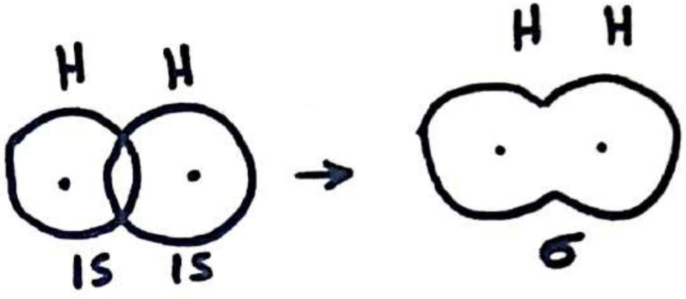
→ we described the overlap of one orbital from each bonding atoms.

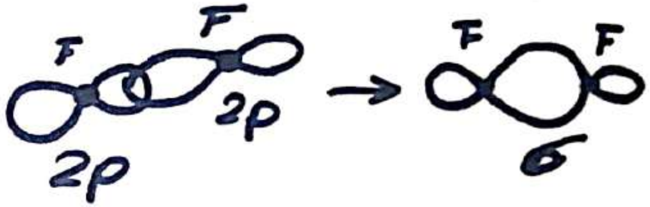
→ Now we consider the possibility that more than one orbital from each bonding atom might overlap.



π bond:

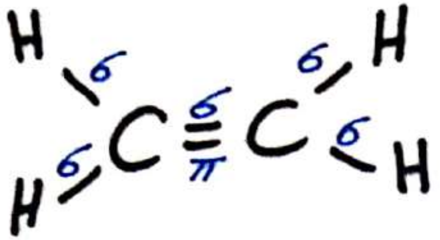
→ (Pi) bond, has an electron distribution above and below the bond axis.





σ bond:

→ (sigma) bond, has a cylindrical shape about the bond axis.



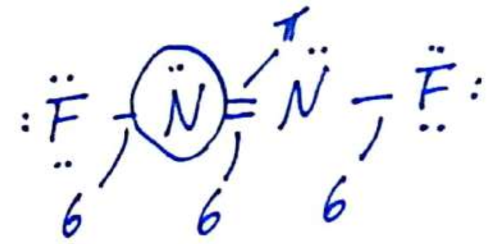
ethylene molecule

→ the double bond consists of one σ and one π.

→ the triple bond consists of one σ and two π.

***Example:** describe the bonding on a given N atom in dinitrogen difluoride, N_2F_2, using valence bond theory: Bent

10 + 14 = 24



$N: 1s^2 2s^2 2p^3$

2p ↑ ↑ ↑

2s ↑↓

1s ↑↓

N

ground

→

2p ↑

sp^2 ↑↓ ↑ ↑

$1s^2$ ↑↓

N

hybridized

→

2p ↑↓ – $\overset{\pi}{N=N}$

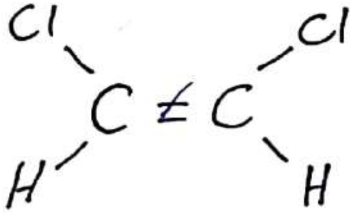
sp^2 ↑↓ ↑↓ ↑↓

Lone Pair, $\underset{\sigma}{N-F}$, $\underset{\sigma}{N-N}$

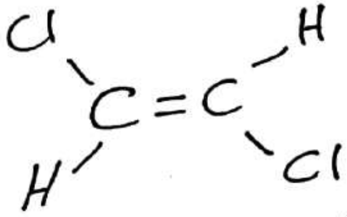
$1s^2$ ↑↓

N

* Isomers: compounds of the same molecular formula but with different arrangements of the atoms.

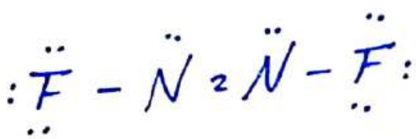


cis-1,2-dichloroethene



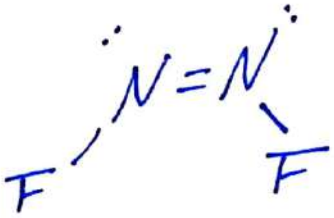
trans-1,2-Dichloroethene.

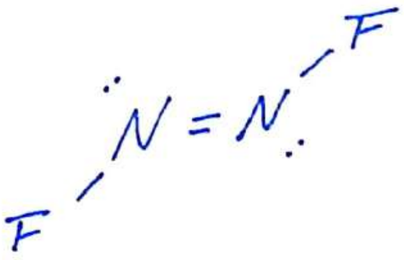
*** Example:** determine cis and trans isomers of N_2F_2:



Bent

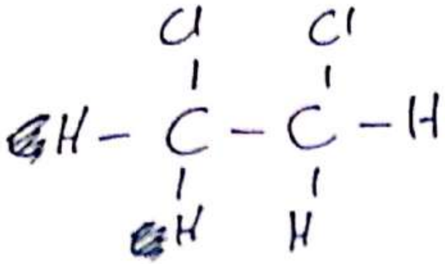
trans has lower dipole





cis

→ lack of isomers in 1,2-dichloroethane ($CHCl_2\,CH_3$)



$$H-\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-H$$

→ geometric isomers are not possible.

→ they can be twisted easily togive the orientation.