

Chemical Bonding

Goal of bonding: Attainment of stable configuration

Chemical Bonding

accept electron easily

Ionic

Transfer of electrons

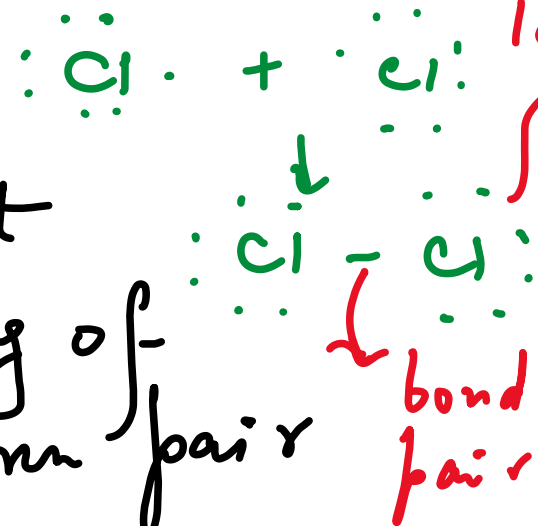
Electropositive (releases electrons)

Electronegative → bonding

Electrostatic attraction

Covalent

Sharing of electron pair



lone pair

Metallic

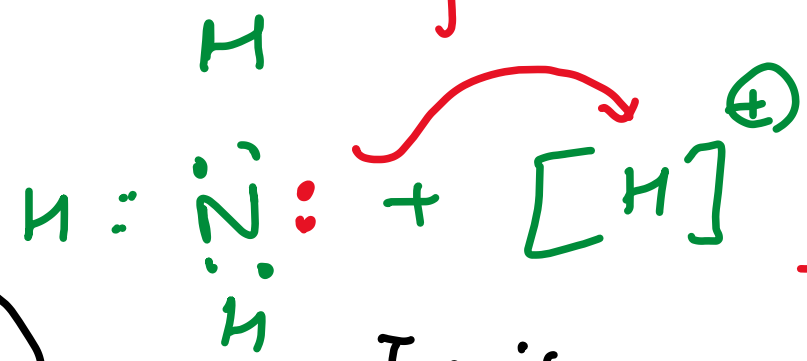
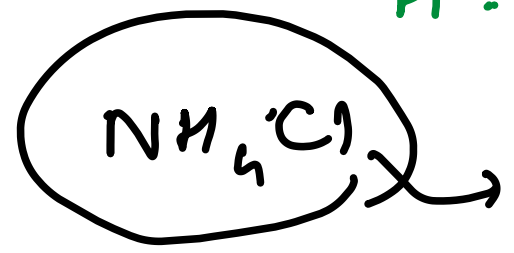
Made up of +ve ions packed together

Cubic close packed (C.C.P.) HCP BCC

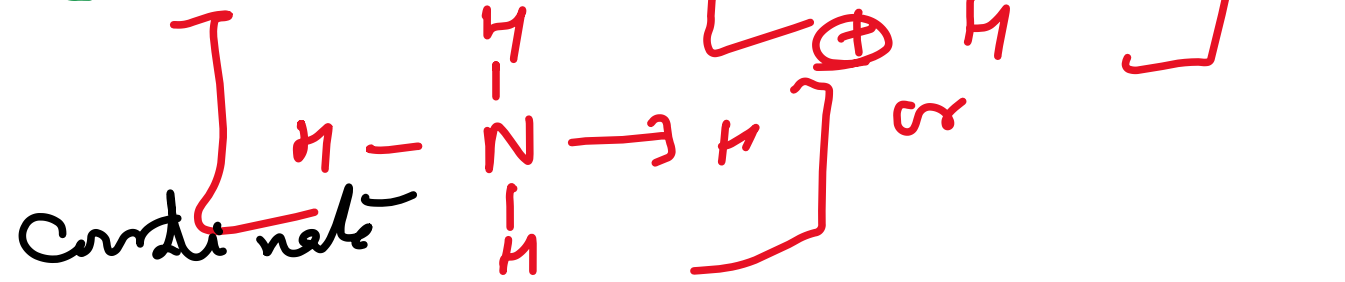
HCC = hexagonal close packed
BCC = body centered cubic

Coordinate bond \rightarrow Special case of covalency.

In normal / pure covalent compounds each atom contributes one electron to the bond. However, if both electrons originate from the same atom, dative or coordinate bonds are formed.



Ionic,
Covalent,
Coordinate



Ionic bonding : Electropositive + Electronegative

Covalent bonding : Electronegative + "

Metallic bonding : Electropositive + Electropositive

The Lewis Theory: Octet rule.

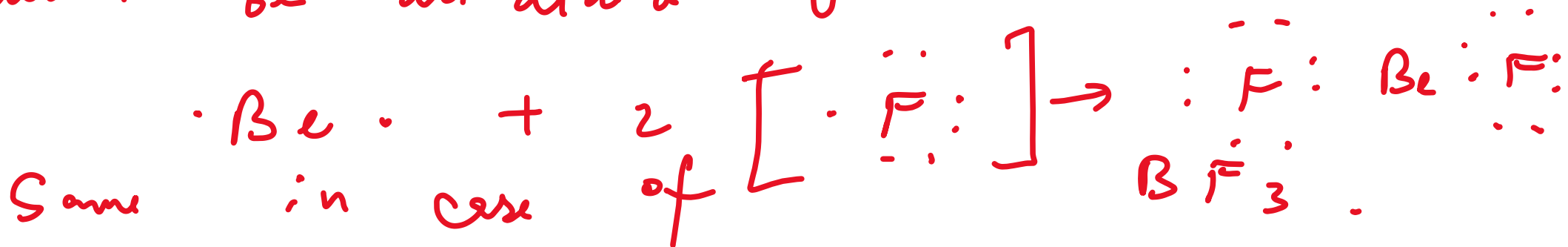
Atoms continue to form bonds until they have made up an octet of electrons.

any inert gas has 8 electrons in their outermost shell.

Hydrogen is stable with only 2 electrons as it assumes $1s^2$ configuration noble gas.

Exceptions to the octet rule:

- Atoms such as Be & B have less than 4 outer electrons. Even if all the electrons are used to form bonds octet cannot be attained.



2. PF_3 obeys octet rule but PF_5 does not.

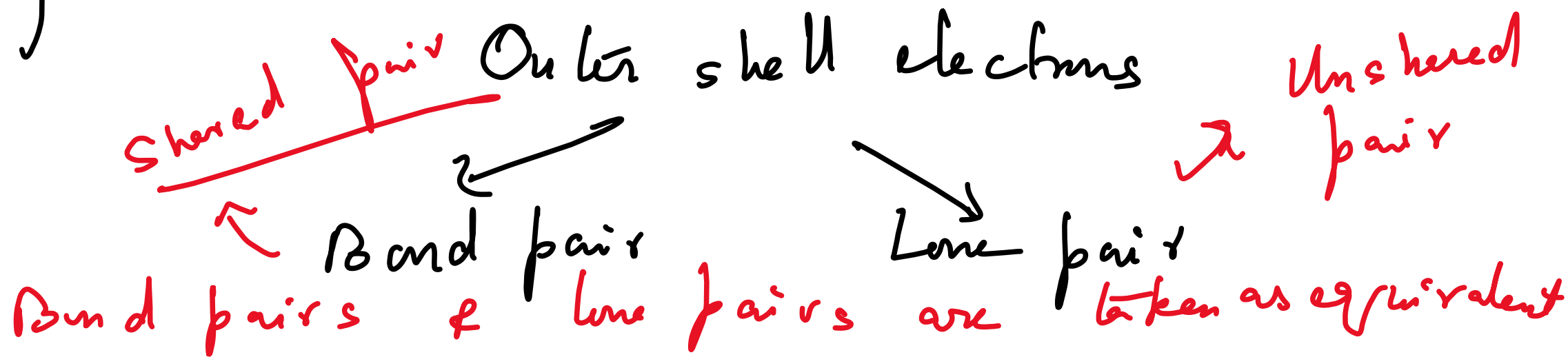
PF_5 has 10 outer electrons, & uses one 3s, three 3p & one 3d orbital.

Any compound with more than 4 covalent bonds will break the octet rule.

3. NO & ClO_2 → Octet rule does not work in molecules with odd no. of electrons
nor does it explain why O_2 is paramagnetic & has 2 unpaired electrons.

Sidgwick Powell Theory

For molecules and ions that contain only single bonds, the approximate shape can be predicted from the no. of electron pairs in the outer or valence shell of the central atom.


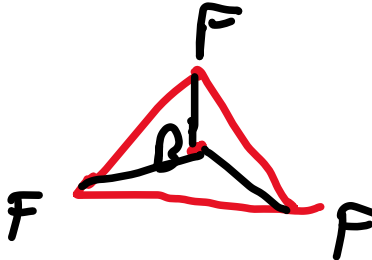
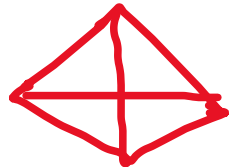
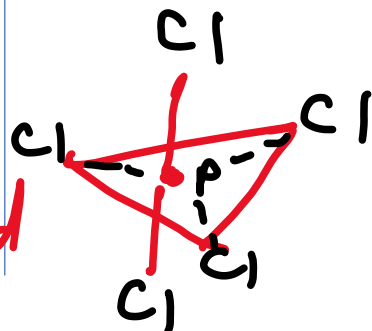



Since all electrons occupy space, they repel each other.

Goal: Minimization of repulsion.

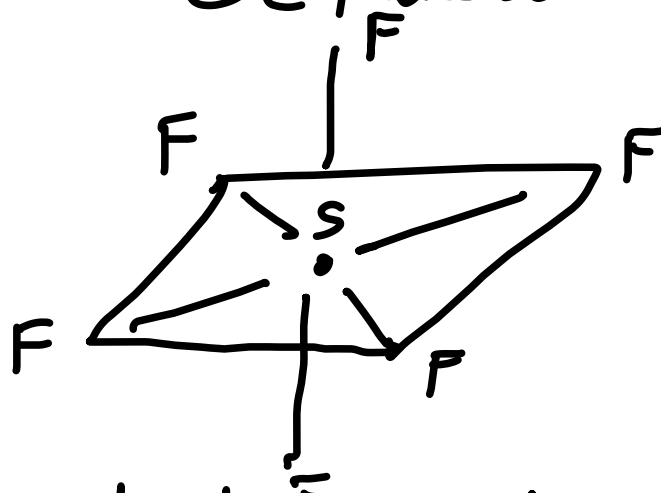
Repulsion is minimized if the electron pairs are oriented in space as far apart as possible.

Based on this theory, the following molecular shapes were suggested depending on no. of electron lone pairs in the valence shell.

	Molecular No. of electrons pair in outer shell	Shapes Shape of molecule	by Sidgwick-Powell Orientation	theory Bond angles-
1.	2	Linear	 $O=C=O$	Eg. CO_2 180°
2.	3	Trigonal planar		Eg. BF_3 120°
3.	4	Tetrahedral		Eg. CH_4 $109^\circ 28'$
4.	5	Trigonal Bipyramid		 120° 90°

5. No. of electron pairs = 6

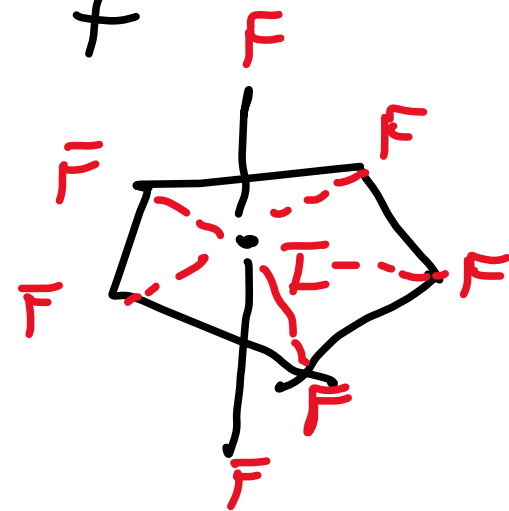
Shape Octahedron.



Bond angle
= 90°

6. No. of electron pairs = 7
Pentagonal bipyramid.

Bond angle: 72° & 90° .



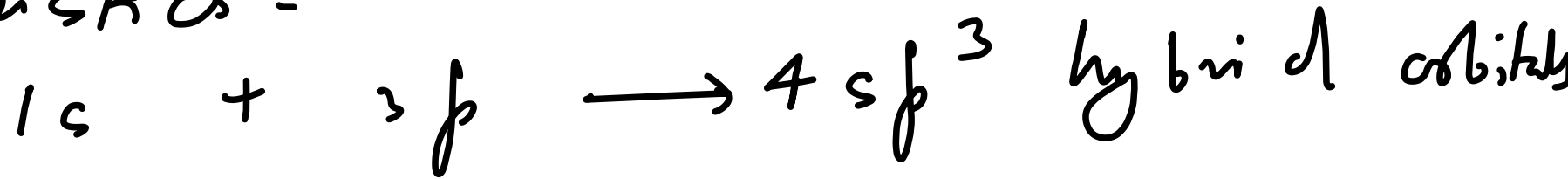
V. B.T: Valence Bond Theory.
Hybridization

Mixing of orbitals -

Features of hybrid orbitals:

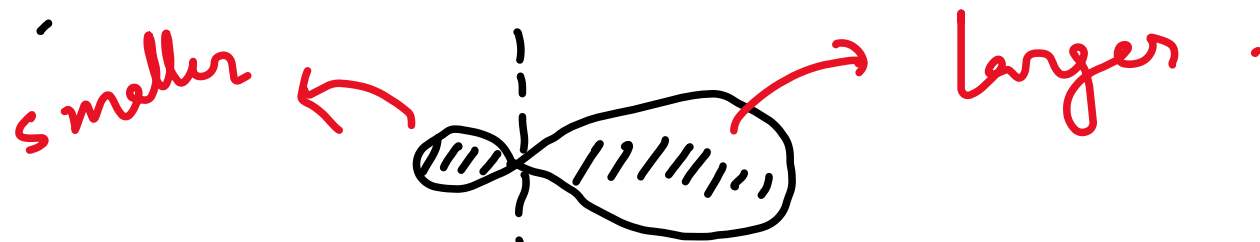
1. The no. of hybrid orbitals of equal energy formed is same as the no. of atomic orbitals that are mixed.

All the hybrid orbitals have identical characteristics -

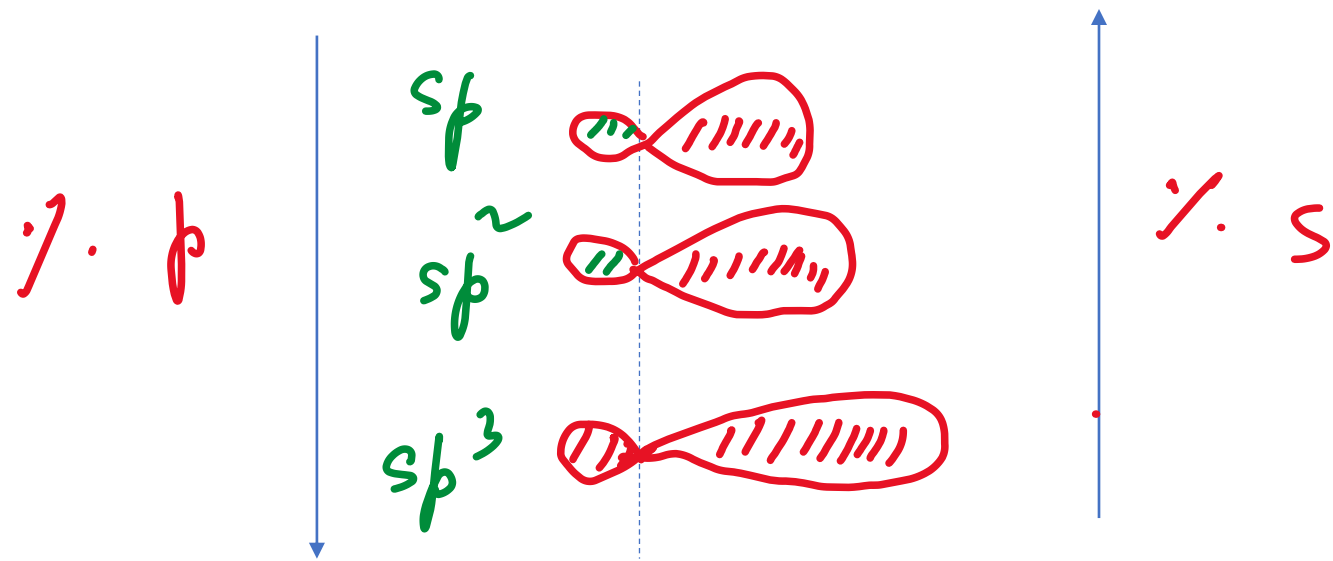


Each sp^3 orbital has identical character - is 1/4 s character + 3/4 p character. 25% s character + 75% p character.

2. Shape of each hybrid orbital is such that one lobe is smaller than the other lobe.



3. As the % s character increases, the hybrid orbital becomes bulkier & shorter.



3. As the % s character increases, the energy of the hybrid orbital decreases and as the % p character increases, the energy of hybrid orbital increases.

Hybridization type

% s % p % d

2	→	sp	50	50	—
3	→	sp ²	33.33	66.6	—
4	→	sp ³	25	75	—
5	→	sp ³ d	20	60	20
6	→	sp ³ d ²	~16.5	50	~33
7	→	sp ³ d ³	~14	~43	~43

Stenic no

no. of electron pairs in valence shell

How many bond pairs?
How many lone pairs?
actual shape

VS EPR theory

Gillespie - 1957

1. Electron pairs tend to minimize repulsion and these are in the order -

lone pair - lone pair > lone pair - bond pair
> bond pair - bond pair

Shape of molecules depend on pair repulsions between bond pair & lone pair electrons. a single bond refers to

2. The double bond needs more space than single bond. The repulsion order in relation to the bonds are as follows -

double bond - double bond > double bond - single bond > single bond - single bond.

3. Keeping the central atom (having lone pair) same, if the electronegativity of the surrounding atom increases, the bond angle will decrease provided

no other factors like size and back bonding play any role.

④ Keeping the surrounding atoms same, if the electronegativity of the central atom (having the lone pair) increases, the bond angle increases.

⑤ Sometimes the lone pair may be transferred from filled shell of an atom to unfilled shell of the adjacent bonded atom. This phenomenon

is known as back-bonding.

Effect of lone pair:

If the lone pair(s) are absent, the shape of the molecule is identical with the one proposed by Sidgwick-Powell theory.

Steric no. = The number of atoms bonded to a central atom of a molecule plus the no. of lone pairs attached

to the central atom.

For molecules/species having one central atom, the steps involved in calculation of steric no. are as follows -

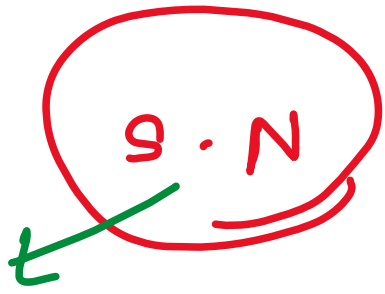
1. Calculate $n =$ no. of total valence shell electrons of all atoms + no. of negative charges (if any) - " " + ve " (if any)

N.B: a) It is considered that no. of valence shell electron of M atom is 7 (just to make calculation easier)

b) The value of n cannot be odd.

② Divide n by 8, which results in $Q + R$ (if any)
where $Q =$ no. of σ bond pairs
 $R =$ no. of unshared electrons on the central atom.

Hence $\frac{R}{2} =$ no. of lone pairs.



Steric no

$$= \left(Q + \frac{R}{2} \right)$$

Effect of lone pairs:

are present, the
distorted & the
molecule can be

If the lone pairs
bond angles get +
shape of the
visualized from.

the 3d figure obtained after placing the bond pairs & lone pairs in a manner such that the repulsion betw. them is minimized.

Shapes:

For sp hybridization.

Steric no. = 2.

The possible value of $Q + \frac{R}{2}$ are -

no. lone pairs

2 + 0 : Linear geometry.
e.g. BeH_2 , $BeCl_2$... etc.

$$s.n. = Q + \frac{R}{2}$$

$$= 1 + 1$$

\swarrow \searrow
 b.p. \quad \quad l.p.

Linear geometry.

2. sp^2 hybridization.

Steric no: 3

$$Q + \frac{R}{2} = 3 + 0$$

$$= 2 + 1$$

Trigonal planar
 BX_3 $AlCl_3$.

Bent / V shaped
 Angular

Valence Shell Electron Pair Repulsion

VSEPR

Theory

Gillespie

1957

Goal: Developed to improve the Sidgwick - Powell theory to predict and explain molecular shapes and bond angles more exactly.

VSEPR Theory: (Summary)

1. Electrons tend to minimize repulsion in the order of lone - pair - lone pair >

lone pair - bond pair > bond pair - bond pair.
(single bond)

Shapes of molecules depend on repulsion between l.p. & b.p. electrons.

(2)

Double bond needs more space than single bond

Repulsion order:

double bond - double bond > double bond - single bond > single bond - single bond.

③

Keeping the central atom (having lone pair)
same, if the electronegativity of the surrounding
atom increases, the bond angle will decrease
provided no other factors like size & back
bonding play any role -

④

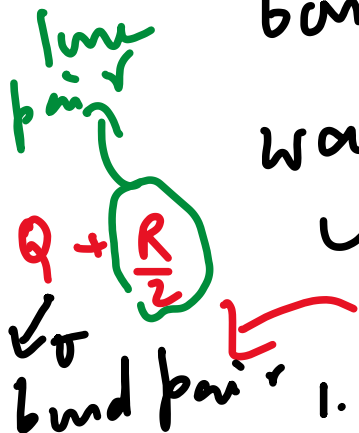
Keeping the surrounding atoms same, if
the electronegativity of the central
atom increases, the bond angle increases.

⑤ Sometimes 'back bonding' may occur when the lone pair is transferred from filled shell of an atom to unfilled shell of the adjacent atom.

Effect of lone pair.

If the lone pairs are absent, the shape of the molecule is identical with the electronic geometry of the central atom, as proposed by Sidgwick-Powell theory.

2. If the lone pair(s) are present, the bond angles get distorted and the shape of the molecule can be visualized from the 3d figure obtained after placing the bond pairs & lone pairs in such a way that the repulsion is minimized.



	Steric	no
	CB.P	+ L.P.)
1.	2	
2.	3	
3.	4	

Hybridization
sp
sp ²
sp ³

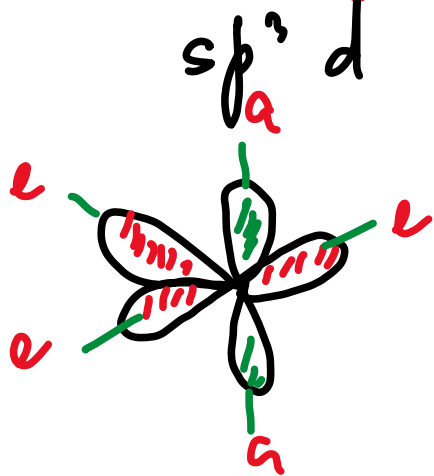
Geometry
Linear
Trigonal planar
Tetrahedral

Angles betw hybrid orbitals
180°
120°
109° 28'

Steric no

5

Hybridization



Geometry
Trigonal
Bipyramidal
(TBP)

Angles between
hybrid orbitals

Axial (a) &
Equatorial (e)

a - e : 90°
e - e : 120° ,
a - a : 180°

6.

sp^3d^2

Octahedral
(Oh)

Between two
adjacent orbitals

90° & opposite
orbitals 180°

7

sp^3d^3

Pentagonal
bipyramidal
PBB

a & a : 180° ,
a & e : 90° ,
e & e : 72°

Shapes of the species undergoing diff. hybridization.

1. For sp hybridization.

Steric no: 2

Possible values of $\sigma + \frac{\pi}{2}$ are:

$2 + 0 \Rightarrow$ Linear geometry

e.g. BeH_2 , $BeCl_2$, BH_2^+ , NO_2^+

$1 + 1 \Rightarrow$ Linear geometry

e.g. CO

2. For sp^2 hybridization:

Steric no: 3

Possible values of $A + \frac{R}{2}$ are

- i) $3 + 0 \Rightarrow$ Trigonal planar geometry.
 BX_3 , $AlCl_3$, $AlBr_3$, CH_3^+ , CO_3^{2-} , NO_3^-
- ii) $2 + 1 \Rightarrow$ Bent / V-shaped /
angular geometry. NO_2^- , $SnCl_2$, SO_2 etc.

For sp^3 hybridization.

Steric no: 4

Possible values of $a + \frac{R}{2}$ are -

- i) $4 + 0 \Rightarrow$ Tetrahedral geometry
e.g. BH_3^- , NH_3^+ , NH_3^+ , SiF_4 , PH_3 , CH_4
- ii) $3 + 1 \Rightarrow$ Pyramidal e.g. NH_3 , $SnCl_3^-$, etc.
 SO_3^{2-} , SeO_3^{2-} , etc.
- iii) $2 + 2 \Rightarrow$ Angular / Bent-shaped / V-shaped
e.g. H_2O , Cl_2O , NH_2^- etc.

Higher the no. of lone pairs, lesser will be the bond angle. Hence bond angle of CH_4 , NH_3 , & H_2O are $109^\circ 28'$, 107° & $104^\circ 5'$ respectively.

④ For sp^3d hybridization.

Steric no. = 5

Possible values of $q + \frac{r}{2}$:

i) $5 + 0 \Rightarrow$ TB P geometry e.g. PCl_5 , PF_5 , SbF_5 , PCl_2F_3 , PCl_3F_2 , XeO_3F_2 etc.

ii) $4+1 \Rightarrow$ See. saw geometry
e.g. SF_4 , SF_2Cl_2 , XeO_2F_2

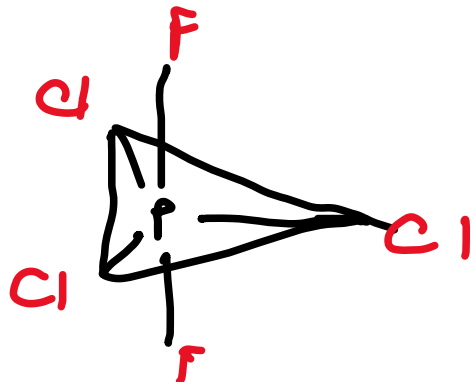
iii) $3+2 \Rightarrow$ T-shaped geometry. e.g. ClF_3 ,
 XeF_3^+ , BrF_3 , $XeOF_2$ etc.

iv) $2+3 \Rightarrow$ Linear geometry, e.g. XeF_2 ,
 ICl_2^- , $[CCN_2]^+$, etc.

The relative location of lone pair & bond pair is determined by Bent's rule.

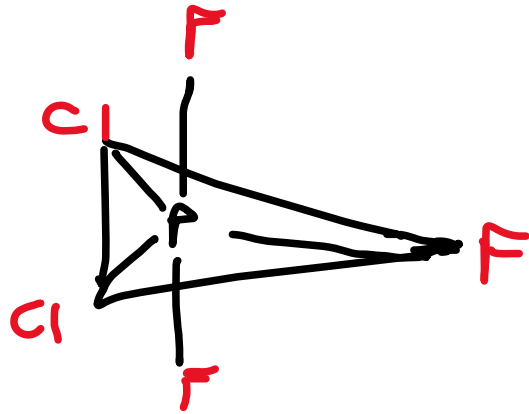
Bent's rule: The more electronegative atom prefers to stay in orbital having less s character, while the lone pair prefers to stay in orbitals with more s character.

For TBP geometry, the more electronegative atom prefers to stay in the axial position, while the lone pair prefers to stay in equatorial position.



PCl_3F_2
(5+0)

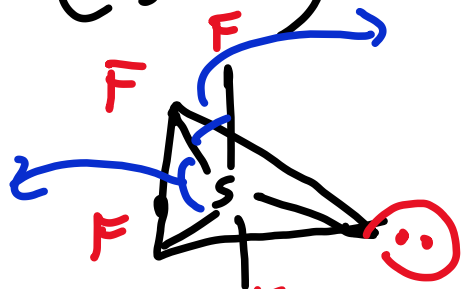
179°



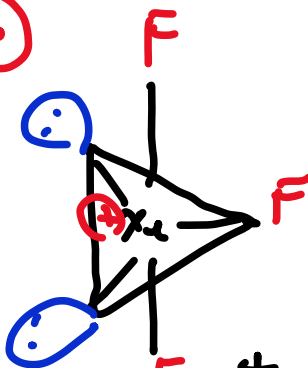
PCl_2F_3
(5+0)

Geometry of some molecules with sp^3d hybridization.

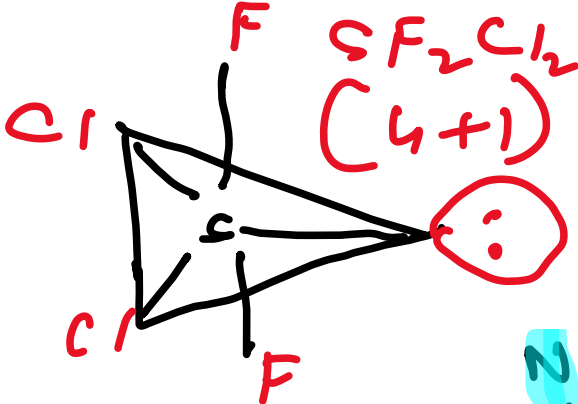
103°



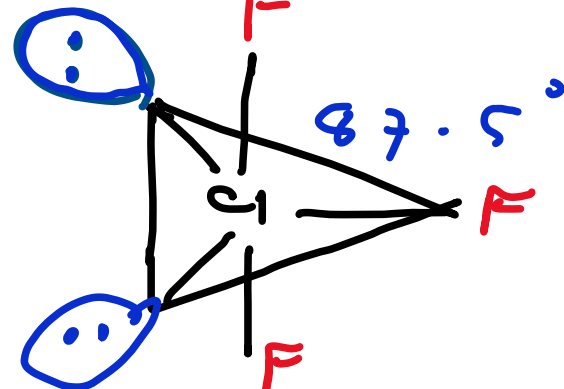
SF_4
(4+1)



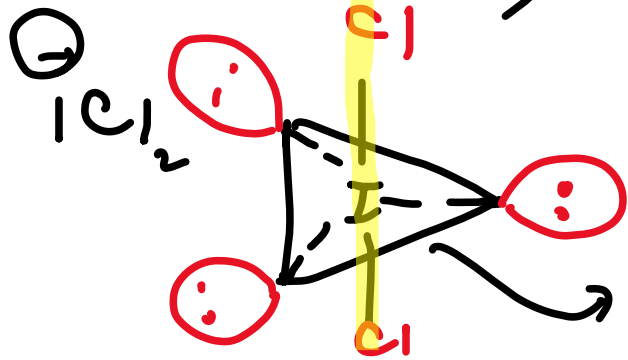
XeF_4
(3+2)



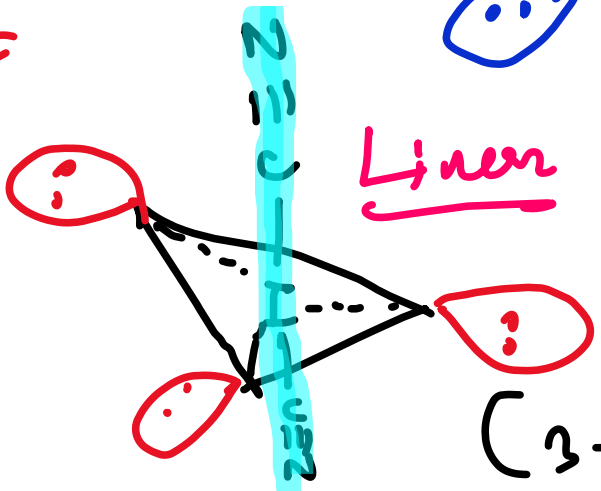
SF_2Cl_2
(4+1)



ClF_3
(3+2)



Linear



Linear

$[\text{I}(\text{CN}_2)]^-$
(3+2)

⑤ For $sp^3 d^2$ hybridization.

Steric no: 6

Possible values of $Q + \frac{R}{2}$:

i) $6 + 0 \Rightarrow$ Octahedral geometry.

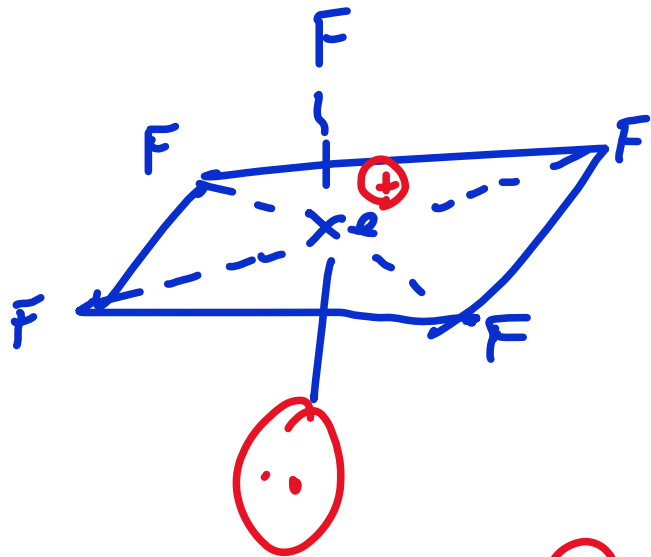
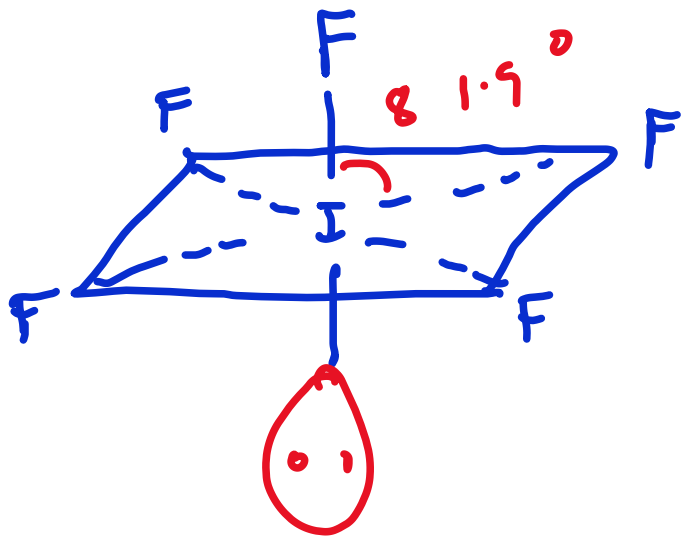
e.g. SF_6 , $TaCl_6$, XeO_6^{4-} , $XeO_2F_4^{2-}$ etc.

ii) $5 + 1 \Rightarrow$ Square pyramidal geometry.

e.g. IF_5 , XeF_5^+ , $XeOF_4$, etc.

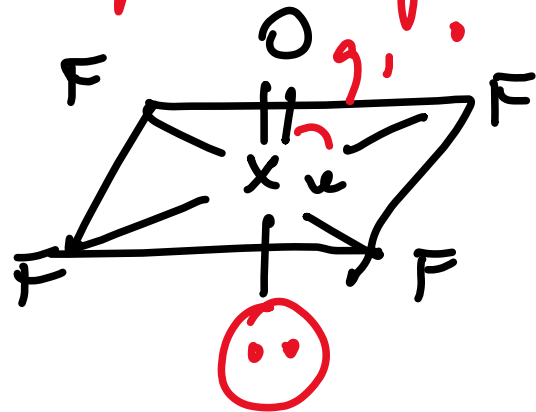
iii) $4 + 2 \Rightarrow$ Square planar

e.g. XeF_4 , $[ICl_4]^-$ etc.

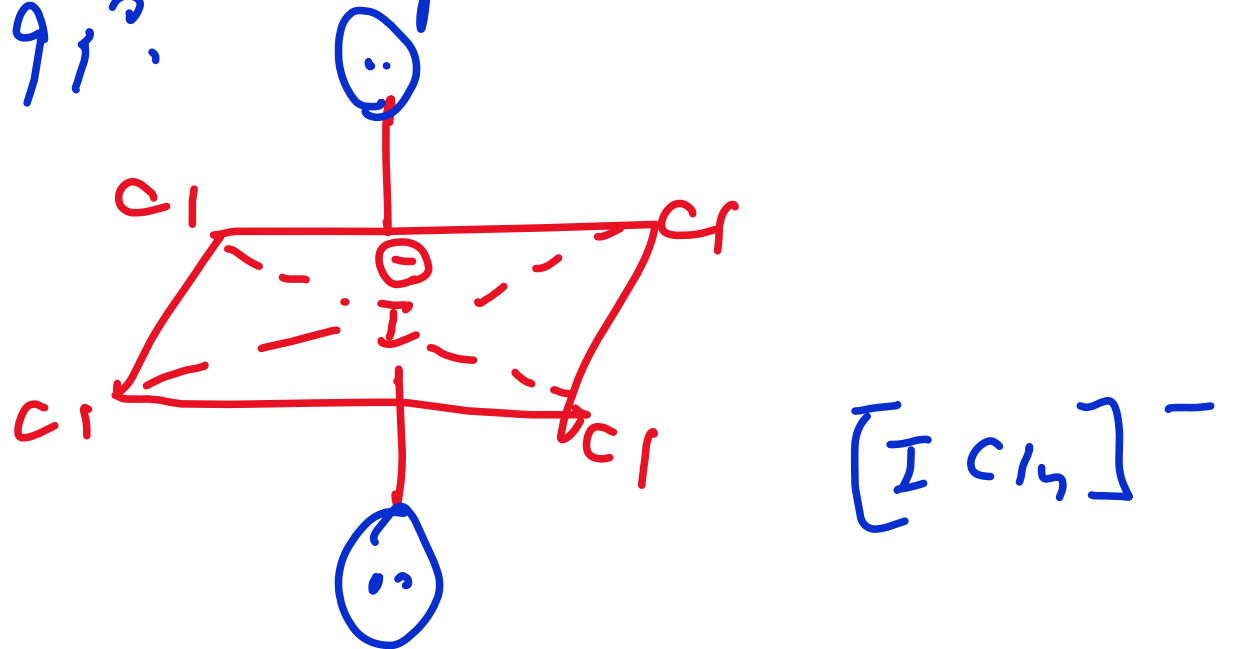
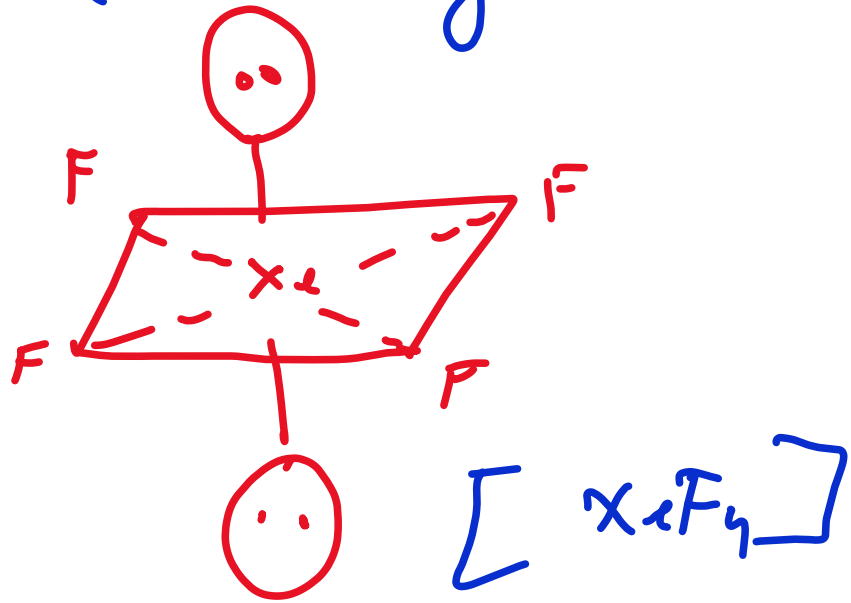


In case of IF_5^- & $[XeF_5]^+$, distortion is observed in shape because l.p. - b.p. repulsion is greater than b.p. - b.p. repulsion.

But in case of $XeOF_4$, the l.p. - b.p. repulsion is almost equal to the double



bond - single bond pair repulsion. Hence,
 the distortion is very less & the double
 bond repels slightly more here as
 compared to the lone pair, & the
 $\angle O \hat{x} F$ angle is 91° .



④ $sp^3 d^3$ hybridization

Steric no: ⑦

$$Q + \frac{R}{2} = \dots$$

- i) $7 + 0 \Rightarrow$ PBP e.g. IF_7
- ii) $6 + 1 \Rightarrow$ Two geometries are feasible.
- a) Distorted octahedral geometry
e.g. XeF_6 , IF_6^- etc
- b) Perfect octahedral geometry e.g. $[Cl_6]^-$, $[TeCl_6]^{2-}$, $[SbCl_6]^-$ etc

iii)

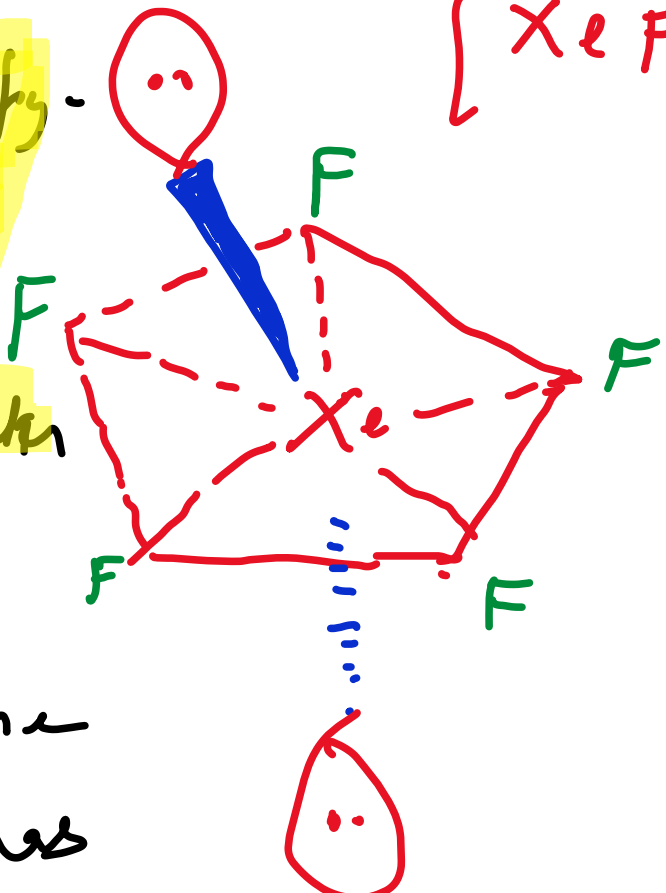
$5 + 2$

: Pentagonal planar geometry.

Bent's rule:



The orbital occupying more space around the central atom will have more s character.



PBB:

Axial orbital occupies more space & has greater s character.

TBB geometry:

Equatorial orbital occupies more space as compared to axial orbital & has more s character.

Lone pair occupies axial position in case of PBB.

Trouton's Rule

Trouton's rule states that entropy of vaporization is almost the same value, about $85-88 \text{ J K}^{-1} \text{ mol}^{-1}$ for various kinds of liquids at their boiling point.

The entropy of vaporization is defined as the ratio between the enthalpy of vaporization & the boiling temperature.

The success (partial success) of this rule can be attributed to the fact that

entropy of a gas is considerably larger than that of any liquid -

$$S_{\text{gas}} \gg S_{\text{liquid}}$$

$$\Delta S_{\text{vap}} = S_{\text{gas}} - S_{\text{liquid}} \quad \because S_{\text{gas}} \gg S_{\text{liquid}}$$

$$\therefore \Delta S_{\text{vap}} \approx S_{\text{gas}} \quad (\text{neglecting the entropy of the liquid})$$

When a liquid is converted to vapor/gaseous state, the entropy changes from a decent/moderate value to a significantly larger one

This is also related to the ratio of enthalpy of vaporization & temperature of transition.

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

Temp of transition.

At the boiling point,

ΔS_{vap} is found to be roughly / approximately constant.

$$\Delta S_{\text{vap}} \approx 85 \text{ J mol}^{-1} \text{ K}^{-1}$$

Toluene - $\Delta S_{\text{vap}} \sim 87.30 \text{ J K}^{-1} \text{ mol}^{-1}$
 Benzene - $\Delta S_{\text{vap}} \sim 89.45 \text{ J K}^{-1} \text{ mol}^{-1}$
 Chloroform - $\Delta S_{\text{vap}} \sim 87.92 \text{ J K}^{-1} \text{ mol}^{-1}$

Trautman's rule does not apply to structured liquids

Trautman's rule does not work for high-ordered substances exhibiting hydrogen bonding. Other factors like the enthalpy of vaporization for a long chained organic

low entropy

molecule of Vander Waals may also play some significant role -

The experimentally determined enthalpy of vaporization of water is 40.7 kJ mol^{-1} .

Does water follow Trouton's rule in predicting the enthalpy of vaporization -

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} \approx 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

This predicts that (since H_2O boils at

373 K (under atm. pressure)

$$\Delta H_{\text{vap}} \approx (85 \text{ J K}^{-1} \text{ mol}^{-1}) (373.15 \text{ K})$$

$$\approx 31.7 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{Deviation} = 40.7 - 31.7 \approx 9 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\% \text{ deviation: } \frac{9}{40.7} \times 100 \approx 22\%$$

Trouth's rule is not applicable to water - ^{boundary}

$$\Delta S_{\text{vap}} = 109.1 \text{ J K}^{-1} \text{ mol}^{-1} > 85 \text{ J K}^{-1} \text{ mol}^{-1}$$

Chemical Bonding

There is a common misconception that hybridization is the cause of a particular molecule shape. This is not true.

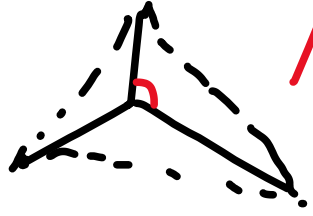
The reason why any particular shape is adopted is its energy. We should keep in mind that the hybridized state is a theoretical step in going from an atom to a molecule, and the hybridized state never

actually exist^s. It cannot be even detected spectroscopically, so the energy of hybrid orbitals cannot be measured & can only be estimated theoretically.

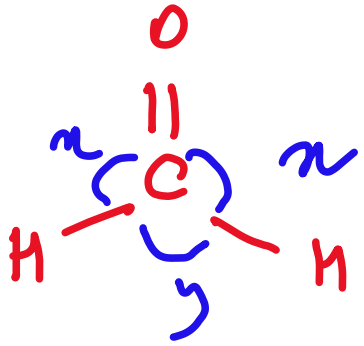
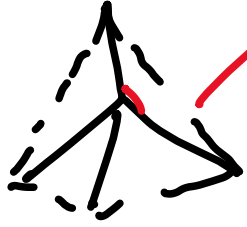
Effect of double bond.

Double bond - double bond repulsion is greater as compared to double bond - single bond & single bond - single bond repulsion.

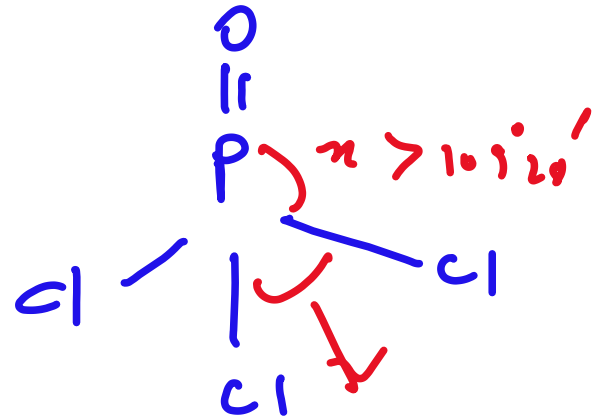
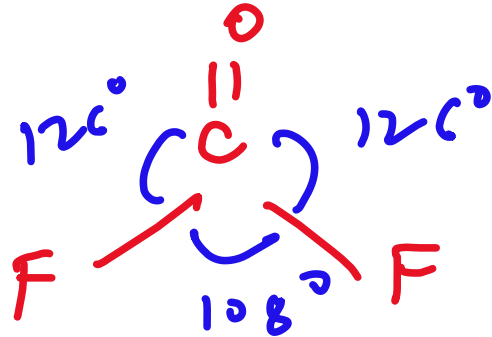
Trigonal planar: Normal bond angle: 120°



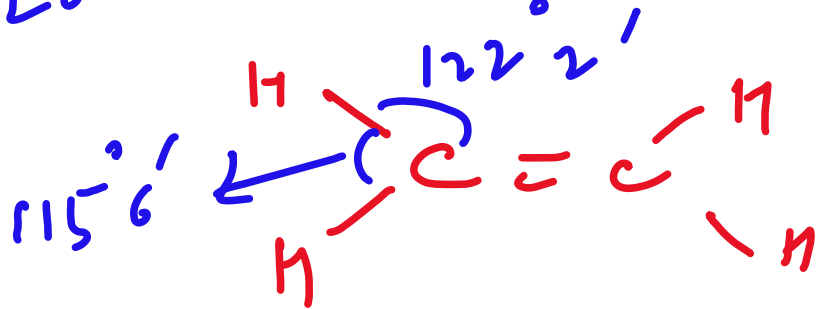
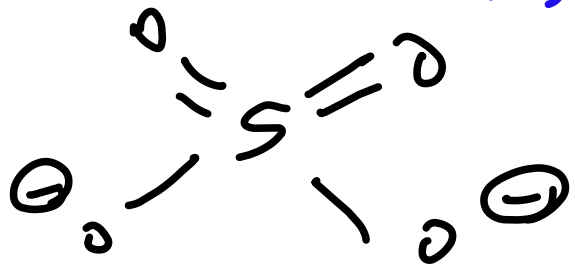
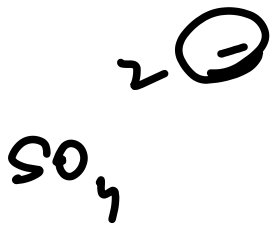
Tetrahedral: $109^\circ 28'$



$\alpha > \gamma$
 $\alpha > 120^\circ$
 $\gamma < 120^\circ$



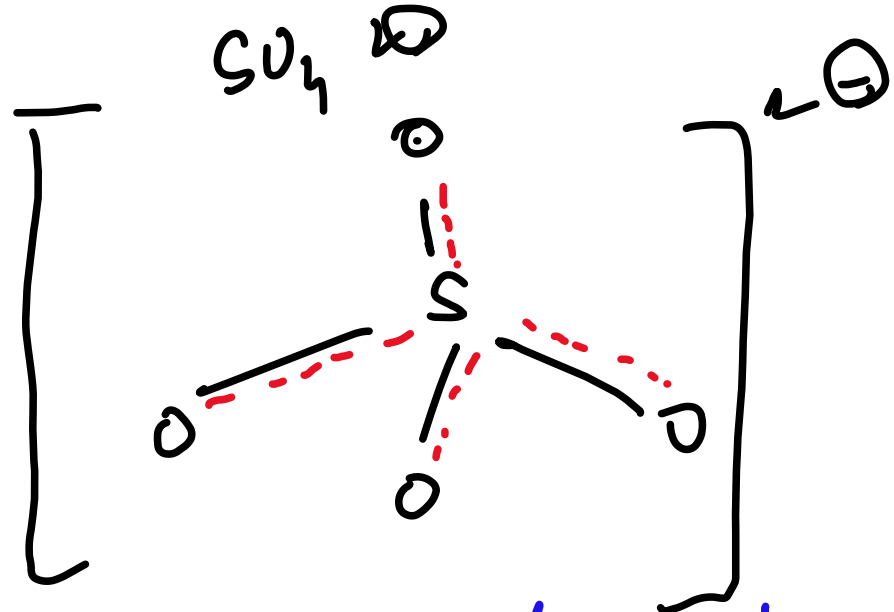
$103^\circ 3'$
 $109^\circ 28'$



All are

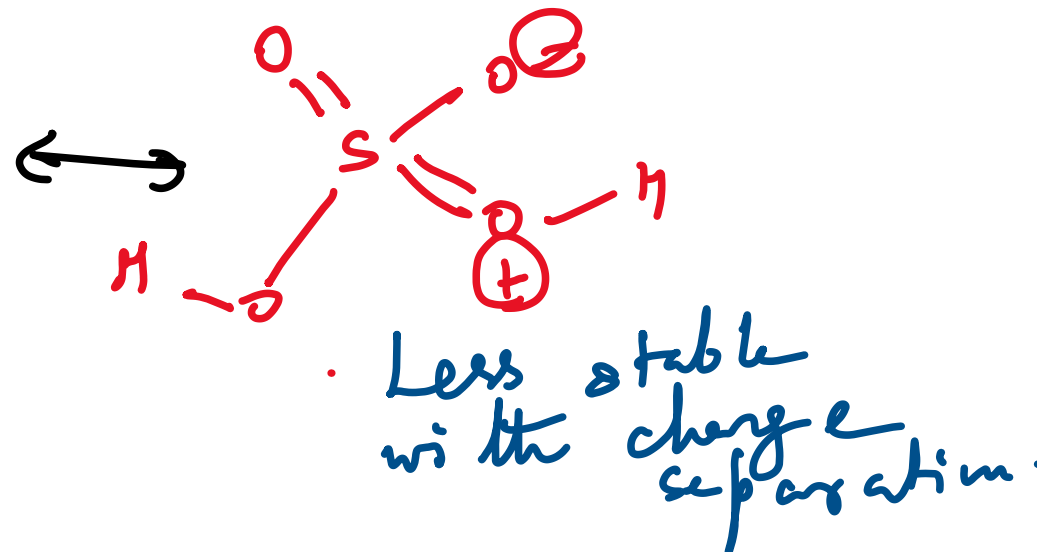
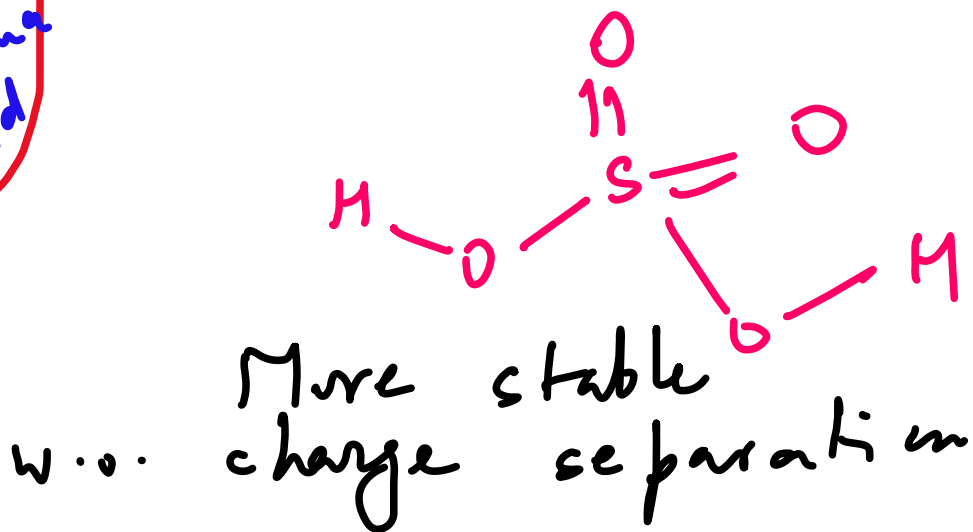
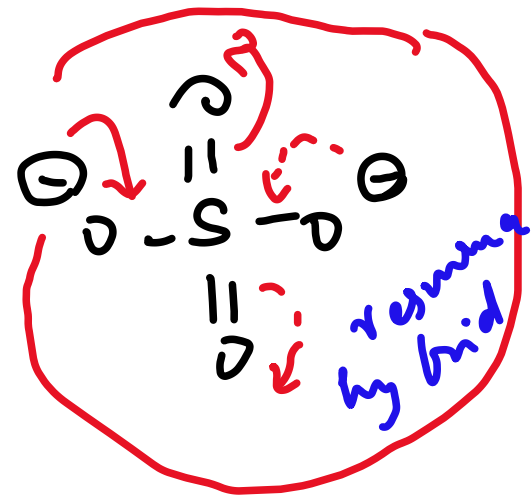


bond angles
 identical

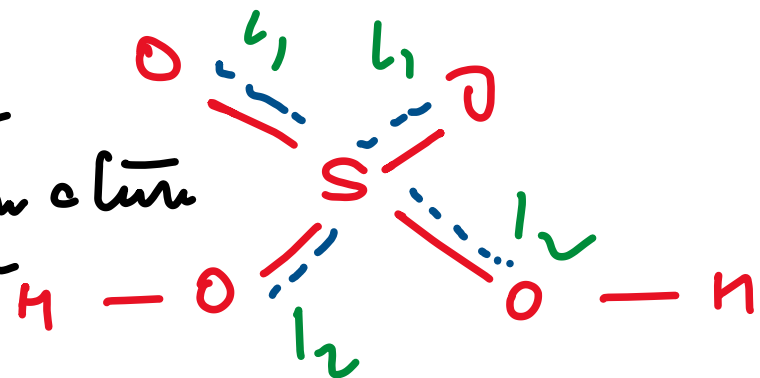


resonance hybrid -

In H_2SO_4 , all $\widehat{\text{OSO}}$ angles are not identical because resonance structures are not identical as in SO_4^{2-} , and their contribution is also not identical.



H_2SO_4 -
Resonance
hybrid structure



$$l_1 < l_2$$

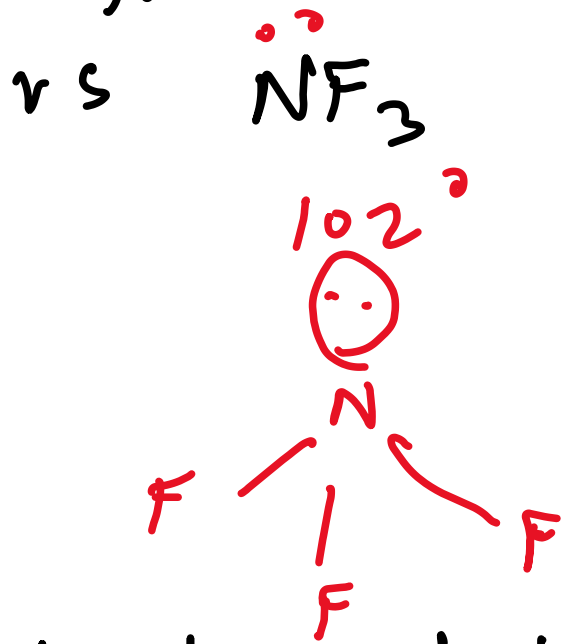
\therefore D.B - D.B repulsion $>$ P.B - S.B
& S.B - S.B repulsion \widehat{OSO} bond
angles in H_2SO_4 are non identical.

Also there are two kinds of S-O bond length.

Similar explanation is also applicable to
 HCO_2^- & $HCOOH$, NO_3^- & HNO_3 , NO_2^- & HNO_2 ,
 PO_4^{3-} & H_3PO_4 etc.

Effect of electronegativity

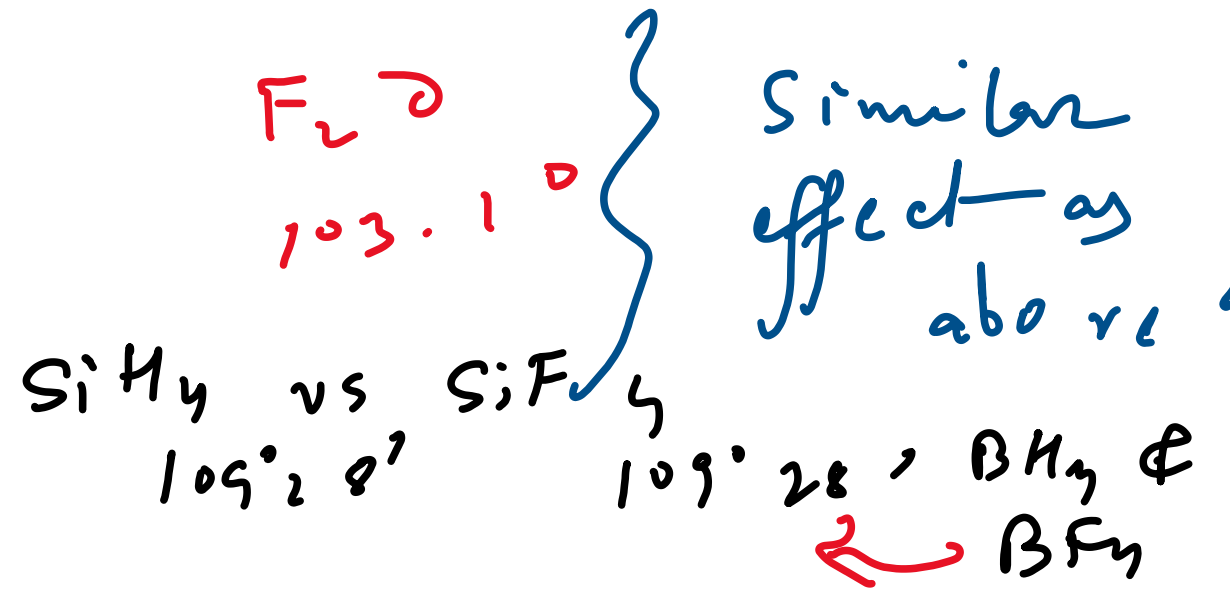
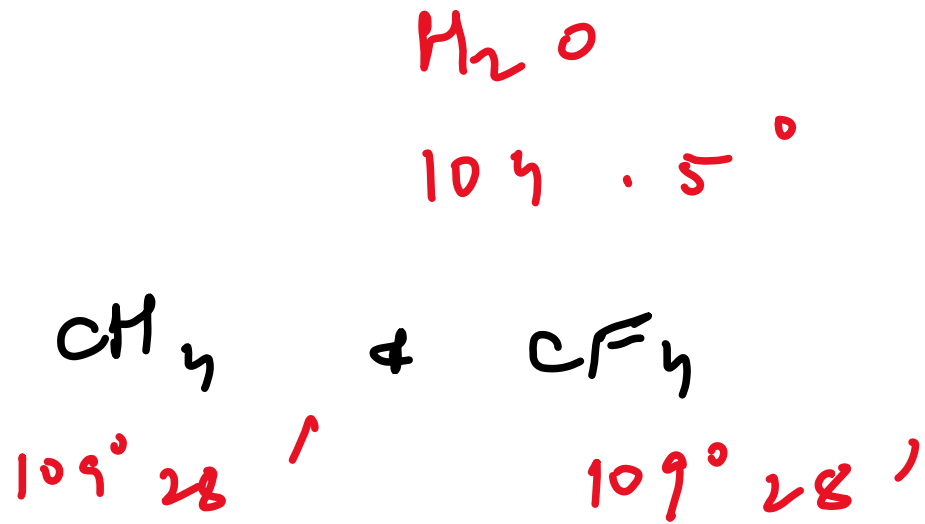
1. When the central atom having lone pair is same with different surrounding atoms.



NH_3 & NF_3 both have structures based on a tetrahedron with one of the corners occupied by the l.p. The high E.N. of

F pulls the bonding electrons further away from N than in case of NH_3 . Thus, repulsion

between bond pairs is less in NF_3 than in NH_3 .
 Hence the l.p. in NF_3 causes a greater distortion from ideal tetrahedral structure than NH_3 .



In absence of l.p., the effect of electronegativity is not observed.



102°



101°



100.3°

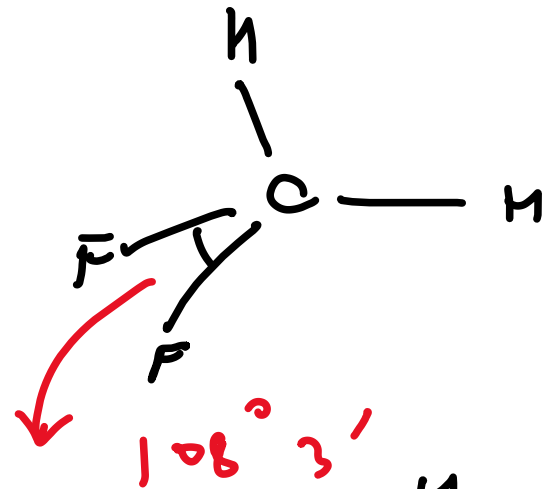
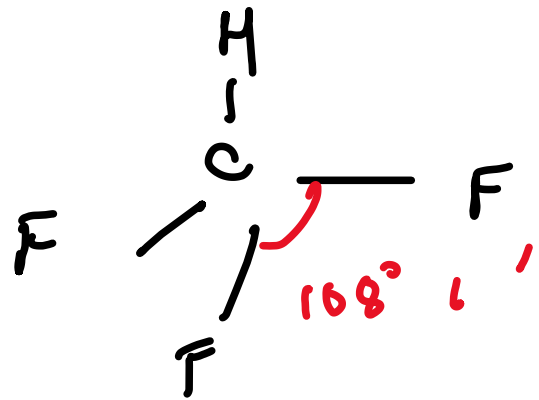


97.8°

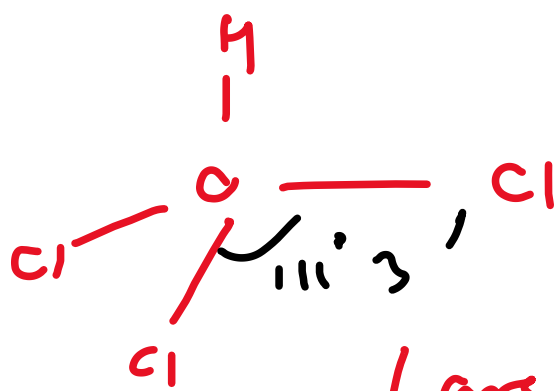
Bond angles are distorted in this case due to decrease in steric crowding.

More electronegative atom not only prefers to stay in orbital having more p character but also can increase the p character in its attached orbital from the central atom depending on the circumstances.

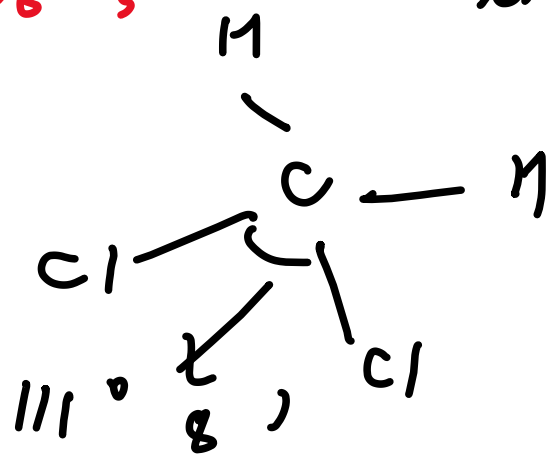
This rule can be applied to explain the effect of bond length & bond angle.



The increase in electronegativity of surrounding atoms affect the bond angle.

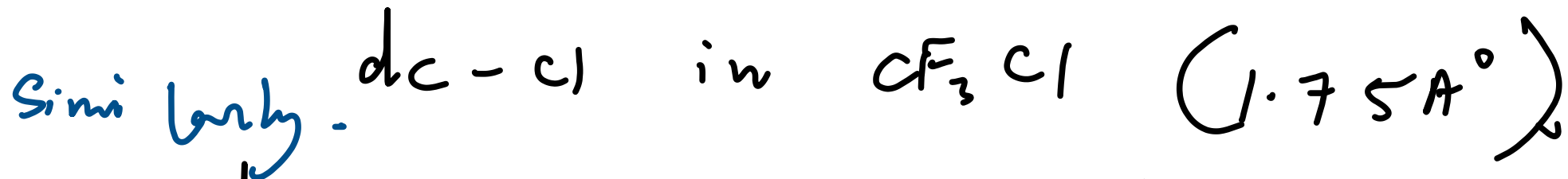
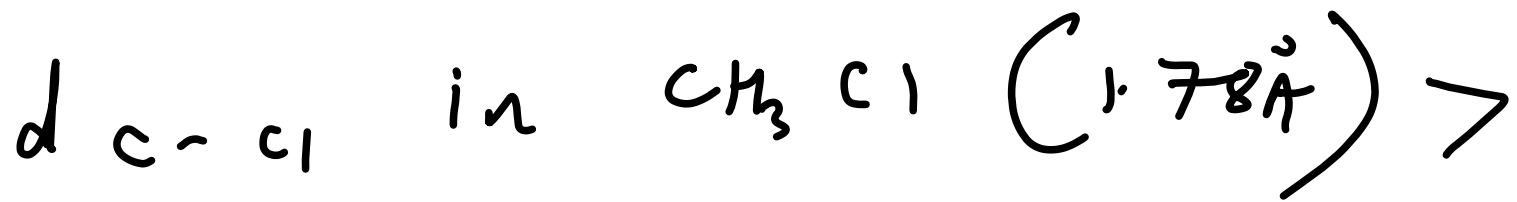


Larger size of Cl atom



increases the bond angle.

With increase in p character in an orbital, bond length increases, while with increase in s character in an orbital bond length will decrease.



When the surrounding atom is same with diff cent central atom having l.p.

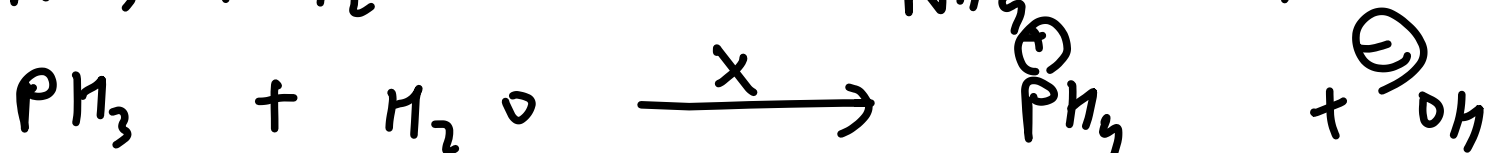
NH_3	PH_3	AsH_3	SbH_3
107°	93.8°	91.8°	91.3°
H_2O	H_2S	H_2Se	H_2Te
104.5°	92°	91°	89.5°

Higher the electronegativity of central atom, greater is the bond angle.

Chemical Bonding -

1. PH_3 has much lower solubility in water as compared to that of NH_3

2. The formation of PH_4^+ is difficult as compared to that of NH_4^+ :



When $[\text{H}^+]$ increases in the presence of strong acids like HX [$\text{X} = \text{Cl}, \text{Br}, \text{I}$],

① PH_4 is formed more readily.

② The complexing ability of NH_3 is much higher as compared to PH_3 .

Explain the above observations -

All the three observations can be explained on the basis that lone pair donating ability for P in case of PH_3 is much less because the lone pair resides at almost pure s orbital. In case of NH_3 , the lone pair is

present in one sp^3 hybrid orbital & can be donated easily.

Drago's rule: Empirical rule compatible with energetics of hybridization.

If the central atom is in the third row or below in the periodic table, the lone pair will occupy a stereochemically inactive s orbital, & the bonding will be through p orbitals, if & bond angles will be close to 90° if the electronegativity of the

surrounding atom ≤ 2.5

This rule is based on the relationship between hybridization & bond angle for 2 or more equivalent s-p hybrid orbitals, where the fraction of s character or p character is given by

$$\cos \theta = \frac{s}{s-1} = \frac{p-1}{p}$$

when $90^\circ < \theta < 180^\circ$)

Eg: For AsH_3 $\angle \text{HAsH} = 91.8^\circ$
From calculation, it can be shown,

$$\cos \theta = \frac{s}{s-1}$$

$$\text{If } \theta = 21.8^\circ, \quad \cos \theta = -0.0314$$

$$\Rightarrow -0.0314 = \frac{s}{s-1}$$

$$\Rightarrow -0.0314s + 0.0314 = s$$

$$\Rightarrow s(1 + 0.0314) = 0.0314$$

$$\Rightarrow s = \frac{0.0314}{1.0314}$$

$$\% \quad s = \frac{0.0314}{1.0314} \times 100 = 3.04 \approx 3\%$$

$$\cos \theta = \frac{p-1}{p}$$

$$\Rightarrow -0.0314 = \frac{p-1}{p}$$

$$\Rightarrow -0.0314 p = p-1$$

$$\Rightarrow p + 0.0314 p = 1$$

$$\Rightarrow 1.0314 p = 1$$

$$\Rightarrow p = \frac{1}{1.0314}$$

$$\% p = \frac{1}{1.0314} \times 100 = 96.95$$

$$\sim 97\%$$

Each As - H bond consists of almost 97% p character & 3% s character.

So, we can conclude that the extent of hybridization is practically nil or very less in PH_3 , AsH_3 , SbH_3 , H_2S , H_2Se & H_2Te .

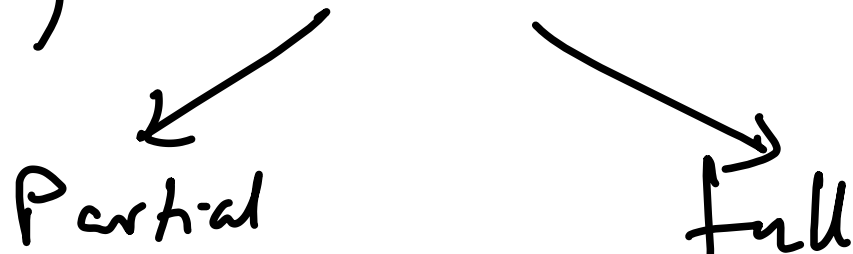
In case of P, the energy required for hybridization is about 600 kJ mol^{-1} , which is not compensated by the energy released from bond formation using

hybrid orbitals. From the viewpoint of energetics, the most stable arrangement would be utilizing pure p orbitals in bonding with the lone pair confined into a pure s orbital.

Back bonding:

Back bonding is a process / phenomenon in which a lone pair is transferred from filled shell of an atom to the unfilled shell of the adjacent bonded atom.

It is a type of coordinate π bonding



Depends on - Relative donating & accepting ability of the donor & acceptor atoms.

Donor atoms: Second period elements carrying lone pairs, such as F, O, N, C etc

Cl, Br, I, P, S , \longrightarrow act as donor atoms depending on circumstances -

1. Back bonding with F as donor atom.



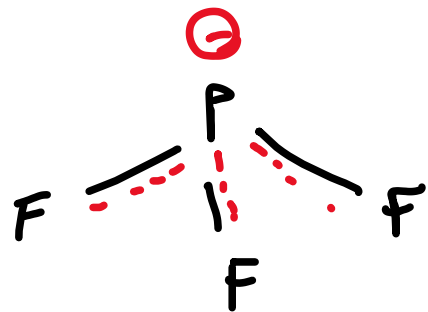
Considering the electronegativity of the surrounding atom, expected bond angle order is -



In reality, $\text{PH}_3 < \text{PF}_3$

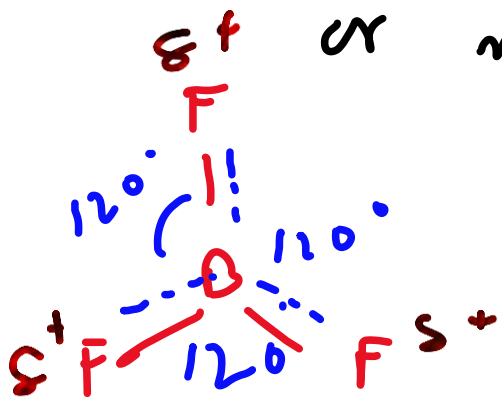
This is due to back bonding in PF_3 .





resonance hybrid -

Due to back bonding, partial double bond character develops in a bond causing decrease in the bond length; bond angle may or may not increase but it never decreases -



vs



91.8°

96.2°

} Same explanation.

In case of BF_3 , the extent of back bonding is more than that

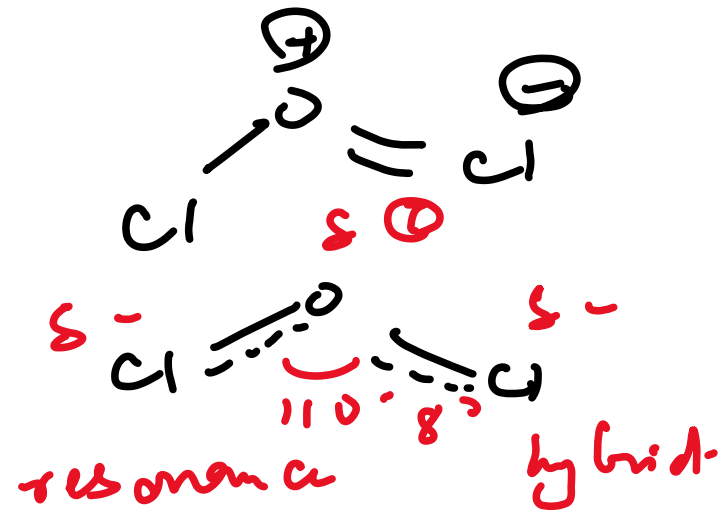
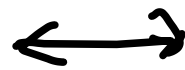
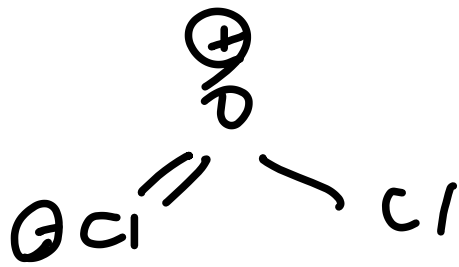
observed in PF_3 because of $2p\pi - 2p\pi$ overlap
 in case of BF_3 , while \downarrow that in $P-F$
 bond is $3d\pi - 2p\pi$. However, there
 is no change in bond angle due to the absence
 of lone pairs.

2. \downarrow Back bonding with O atoms.

Cl_2O :

Bond angle order:

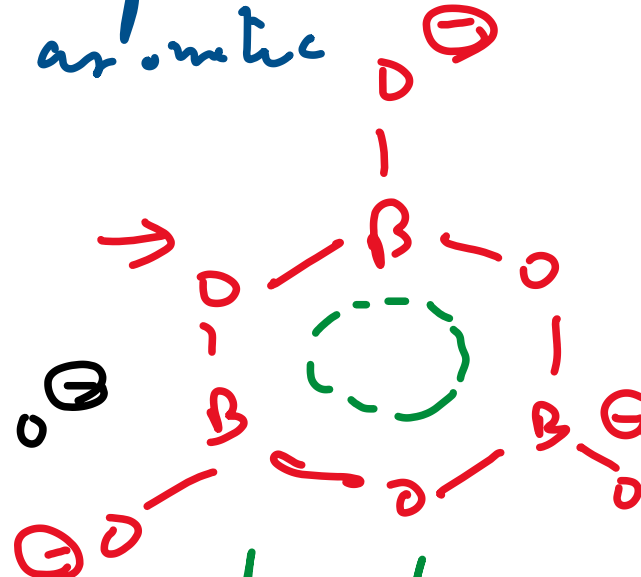
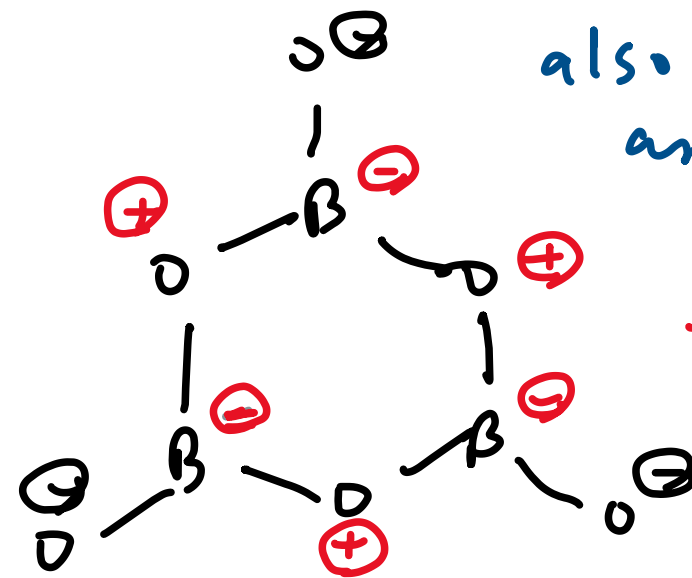
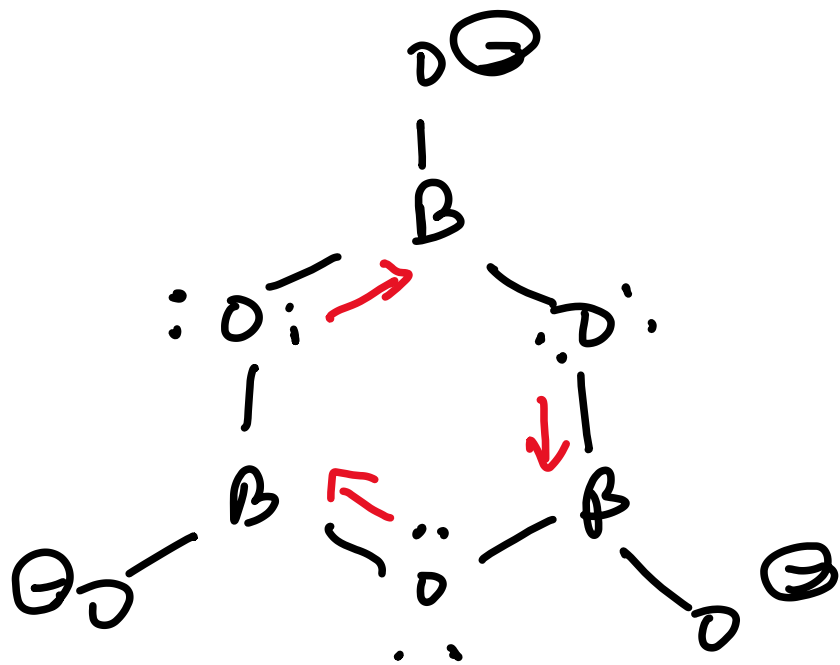
Cl_2O ($110^\circ 8'$) $>$
 H_2O ($104^\circ 5'$) $>$ F_2O ($103^\circ 2'$)



Back bonding in Cl_2O !

Boroxine (B_3O_6) ring is planar due to back bonding and aromatic in nature

$B_3N_3H_6$ is also planar & aromatic



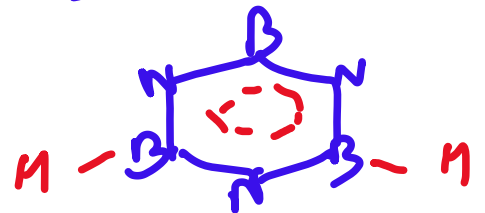
Here, the back bonding is considered as a full coordinate π bond in a particular resonance structure

③ Back bonding with N as donor atoms -



This is due to very slight back bonding in NCl_3 from $2p$ orbital of N \rightarrow $3d$ orbital of Cl, the extent of which is very less due to the distribution of only one l.p. over three Cl atoms

due to back bonding from N \rightarrow B atom in the form of $2p\pi - 2p\pi$.



$(\text{CH}_3)_3\text{N}$ is pyramidal whereas $(\text{SiH}_3)_3\text{N}$ is planar.

$(\text{SiH}_3)_3\text{P}$ is pyramidal & $(\text{GeH}_3)_3\text{N}$ is planar -

$(\text{CH}_3)_3\text{N} :$ No back bonding

$(\text{SiH}_3)_3\text{N} :$ $2p\pi - 3d\pi$ back bonding

$(\text{GeH}_3)_3\text{N} :$ $2p\pi - 4d\pi$ " "

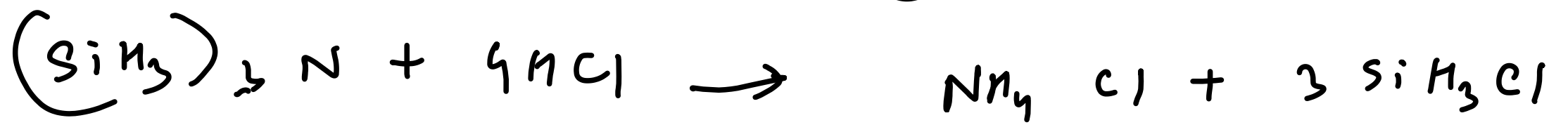
N atom is forced to adopt sp^2 planar hybridization

$P(SiH_3)_3 \rightarrow$ Intermolecular distance is large & P atom has its own vacant d orbital. Hence the tendency to donate lone pair is very less & it adopts pyramidal structure & P atom is sp^3 hybridized.

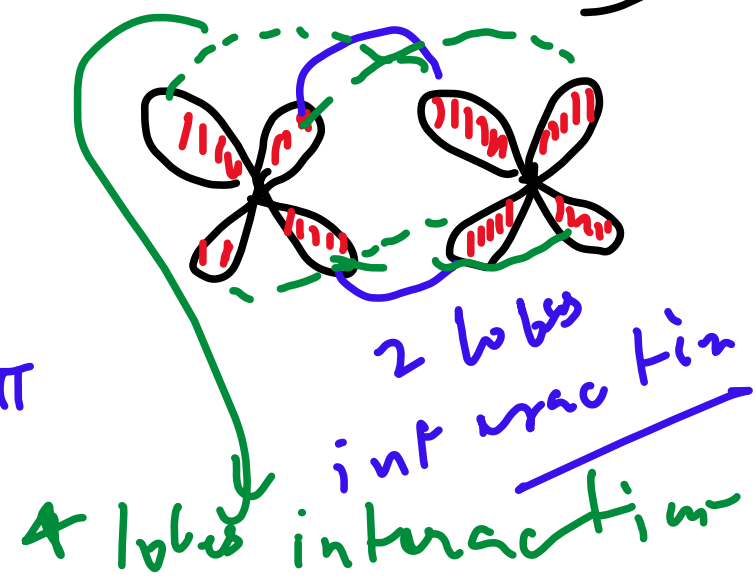
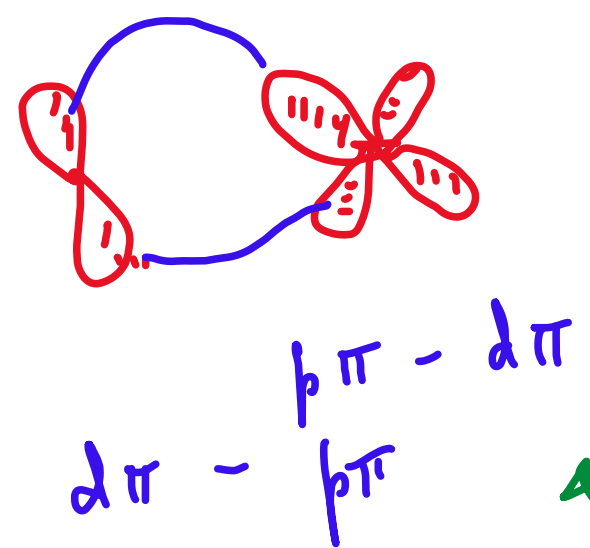
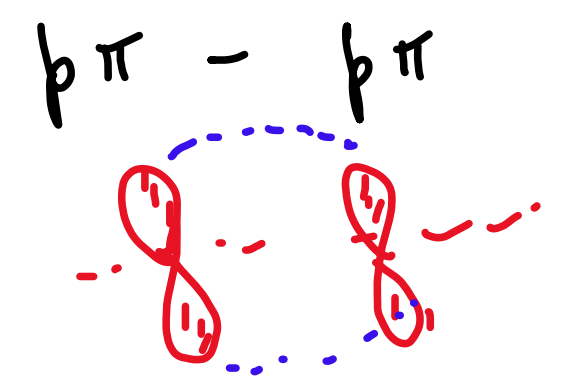
$(CH_3)_3N$ is more basic than $(SiH_3)_3N$ due to the same reason & they behave differently with HCl.



(Lewis acid base-adduct)

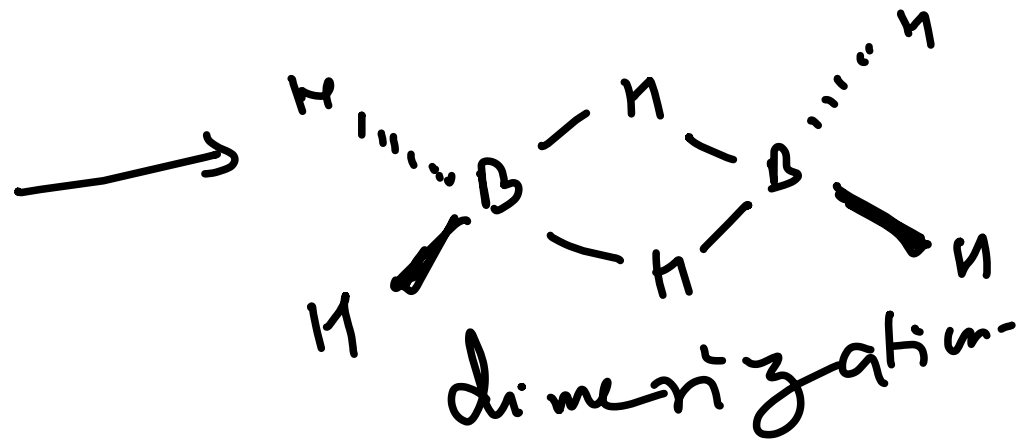
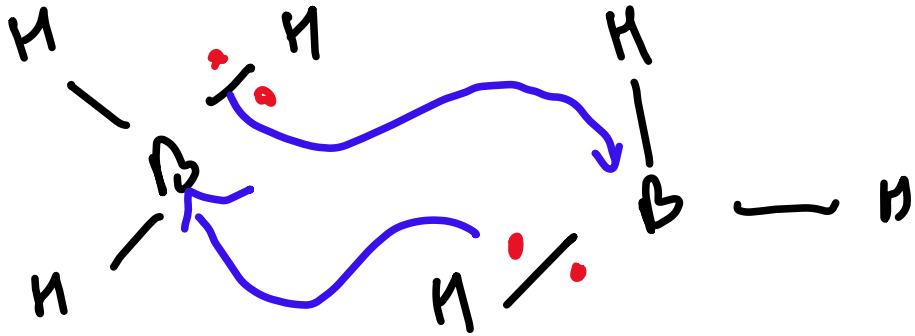


Cl bond cleavage through S_N2 mechanism



Bridge Bonding

BH_3 molecules do not exist as monomers at ordinary conditions and exist as dimers.

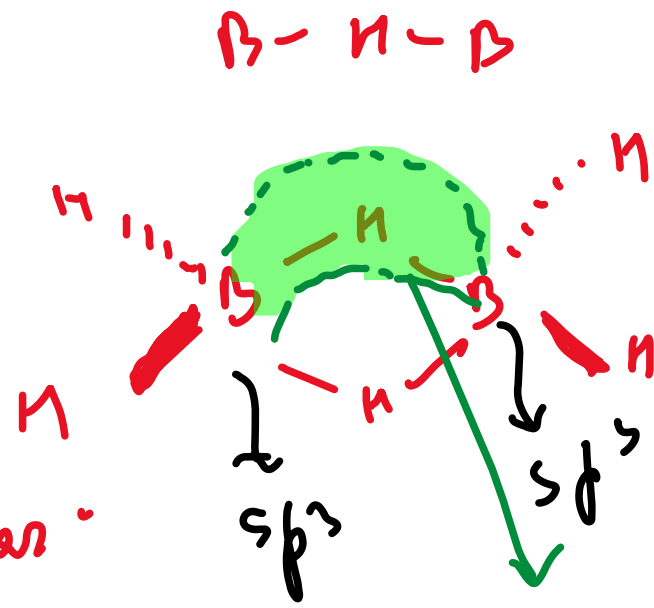


Driving force: of Completion of octet of B atoms of permanent

B₂H₆ :

1. Hybridization of B atoms :

Hybridization of both B atoms is sp^3 & overall molecule is non planar.



The electronic distribution of B-H-B has a banana like appearance & is therefore called banana bond.

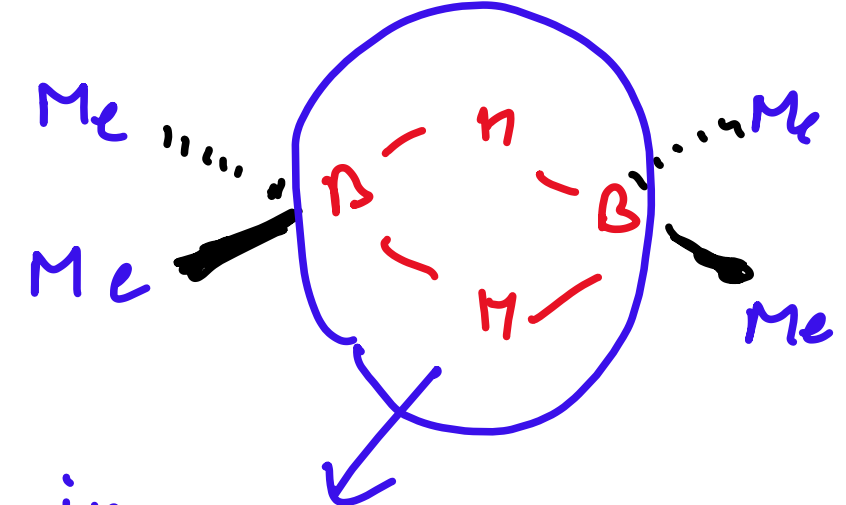
The bridge bond is also called three centered - two electron $3c-2e$ bond.

because only two electrons are responsible
for attracting 3 e^- center or nucleus

2. Bond length - & bond strength in B_2H_6 :

i) d_{B-H} (terminal bonds) $<$ d_{B-H} (bridge bonds)

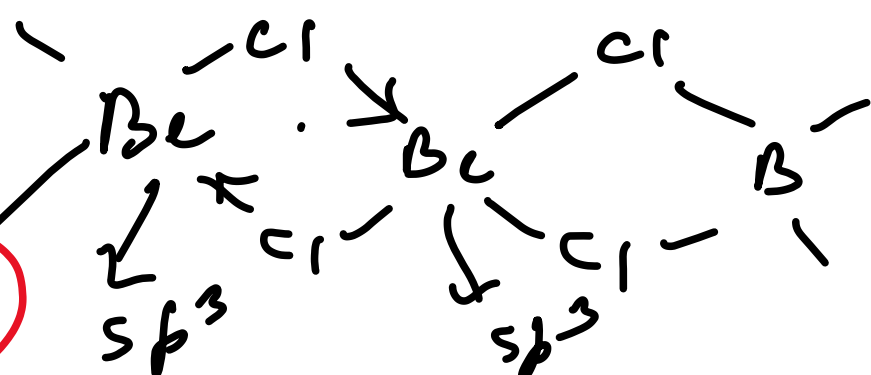
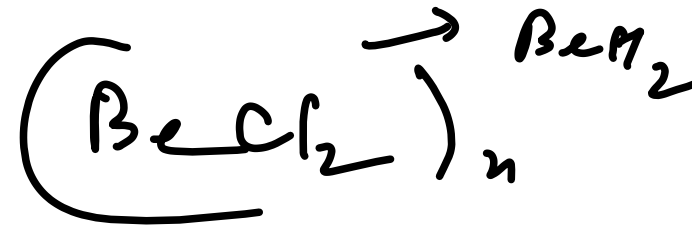
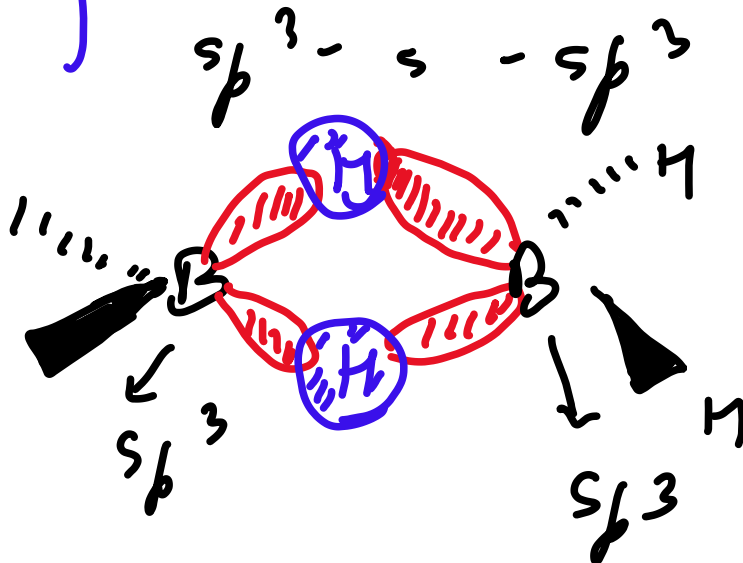
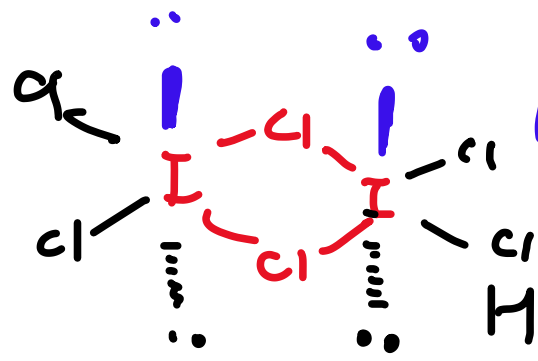
ii) Energy required to replace H atoms
in the bridged position is more than
that needed for the terminal position



Terminal H are replaced by -CH₃ group in preference to the bridged H atoms.

not labile. atoms.

overlap



Molecular Orbital Theory

Developed by F. Hund & R.S. Mulliken in
1932

Salient features of M.O. theory.

1. Electrons of molecules are present in various molecular orbitals.
2. Molecular orbitals are formed by the combination of atomic orbitals, having same or nearly same energy level.

- ③ In a molecular orbital, an electron is influenced by two or more nuclei or M.O. is polycentric
- ④ No. of M.O. formed = No. of atomic orbitals.
- ⑤ When two atomic orbitals combine they form two new M.O. This means that when two atomic orbitals combine they form one bonding & one antibonding orbitals.
- ⑥ Bonding M.O. has lower energy or higher

Stability whereas antibonding M.O. has higher energy or lower stability.

7) The electron probability distribution around a group of nuclei in a molecule is given by a M.O.

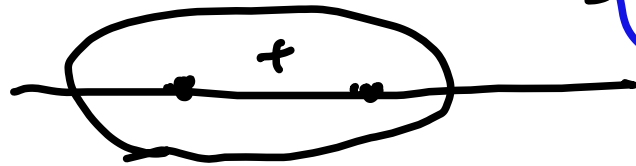
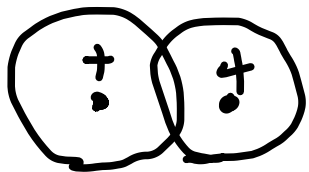
8) Filling of electrons in molecular orbital is in accordance with Aufbau Principle, Pauli's principle, & the Hund's rule.

Formation of molecular orbital.

Linear combination of atomic orbital -

L.C.A.O \Rightarrow an approximation method to write Schrodinger eqn. for any molecule.

gerade (g)
= even



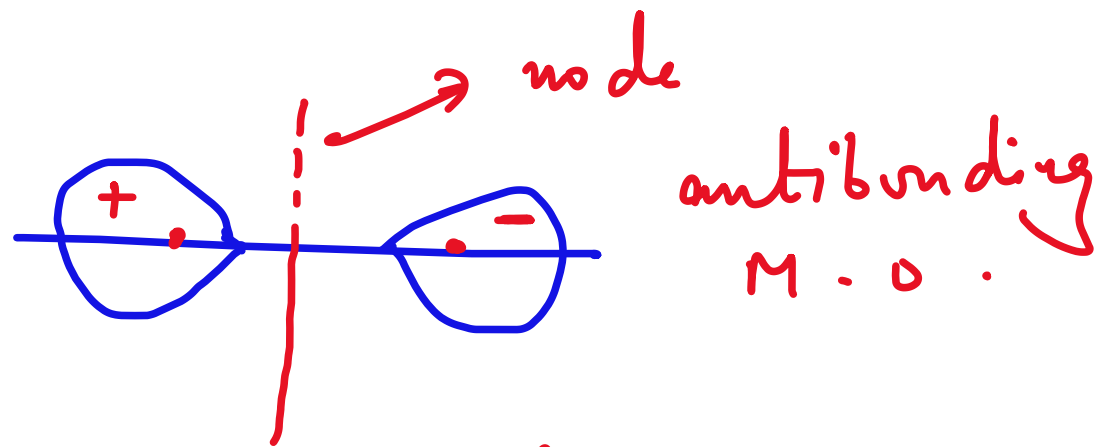
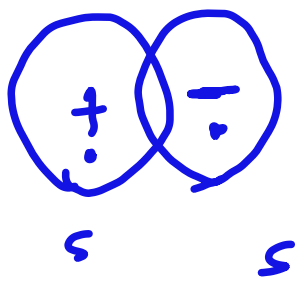
Molecular orbitals **Bonding M.O.**

$\sigma(g)$

g = gerade
u = ungerade

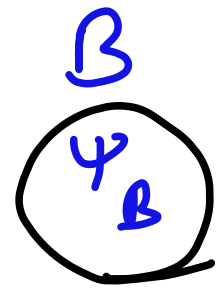
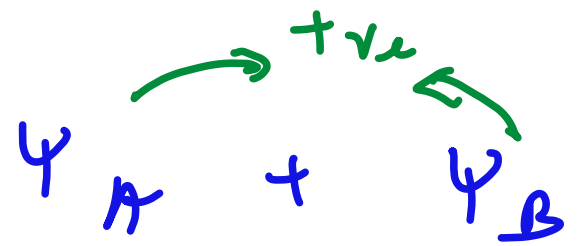
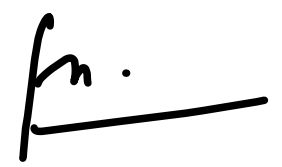
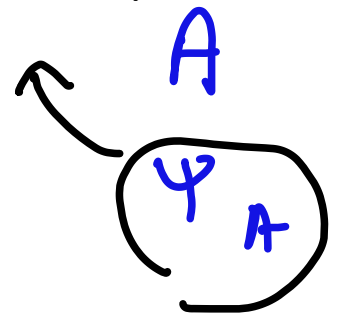
ungerade (u)
= odd

If the signs of the lobes remains the same, the orbital is gerade (g), & if the sign changes, the orbital is ungerade (u).

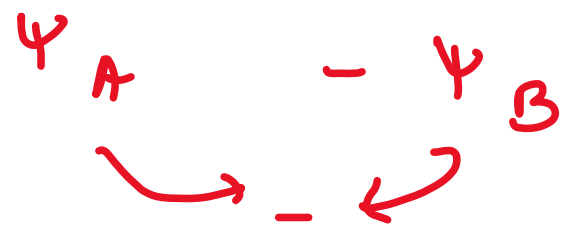


s - s combination of atomic orbitals

orbital / wave fn.



→ bonding



→ antibonding

L.C. A.D.

(Energy)

1. The atomic orbitals must be roughly of the same energy. This is important when considering overlap between two different types of atoms.

2. The orbitals must overlap one another as much as possible. This implies that the atoms must be close enough for

Proximity of orbitals

effective overlap & that the radial distribution functions of the two atoms must be similar at this distance

③

Symmetry

In order to produce bonding & antibonding M.O., either the symmetry of the two A.O. (atomic orbitals) must remain unchanged when rotated about the inter-nuclear line, or both the atomic orbitals must change symmetry in an identical manner.

Homonuclear diatomic molecules:

O_2 , H_2 → i) Orbitals of lowest energy are filled first. ii) Each orbitals can accommodate

iii) maximum of 2 electrons.

It follows Aufbau principle.

Filling in order of energy of orbitals

He: $1s^2$

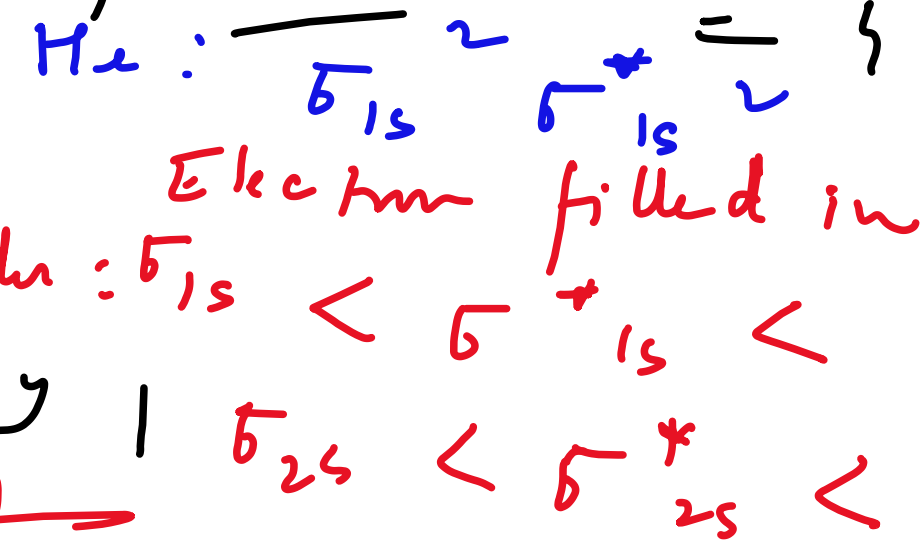
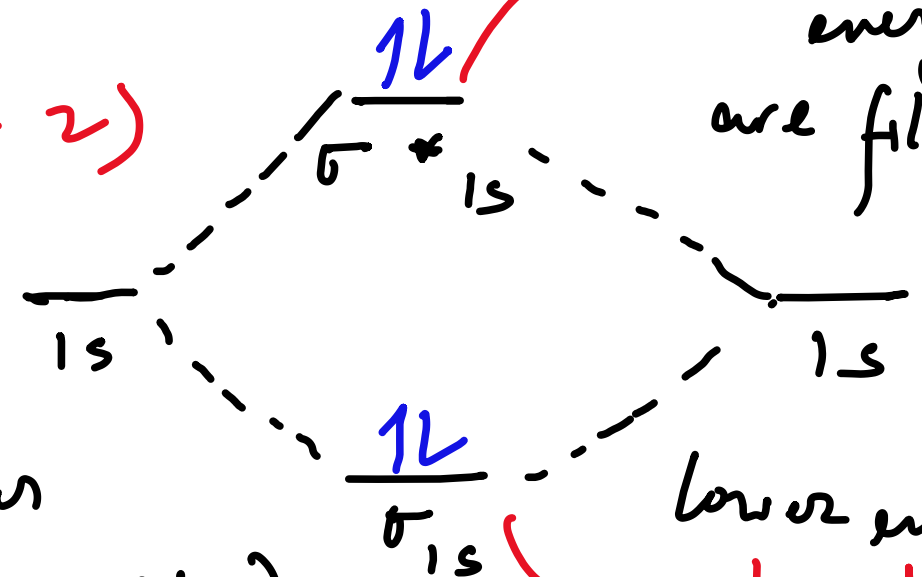
inert gas

a.o. Lower energy orbitals are filled first

He₂: Total electrons = 4

B.O: $\frac{1}{2} (2 - 2) = 0$

He₂ does not exist



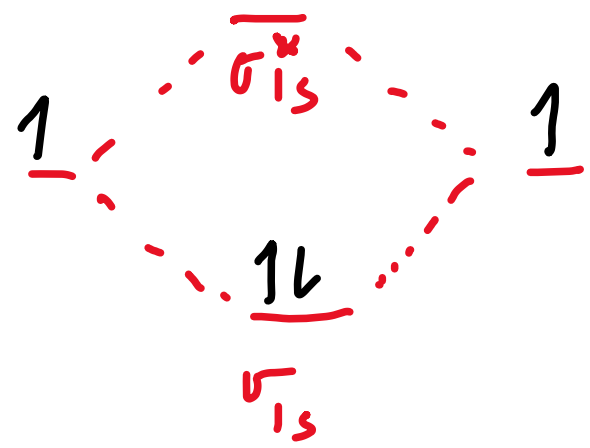
Bond order

$= \frac{1}{2} (N_b - N_a)$

where N_b = no. of electrons in bonding orbitals, N_a = " " " " a.o. orbitals



¹H :



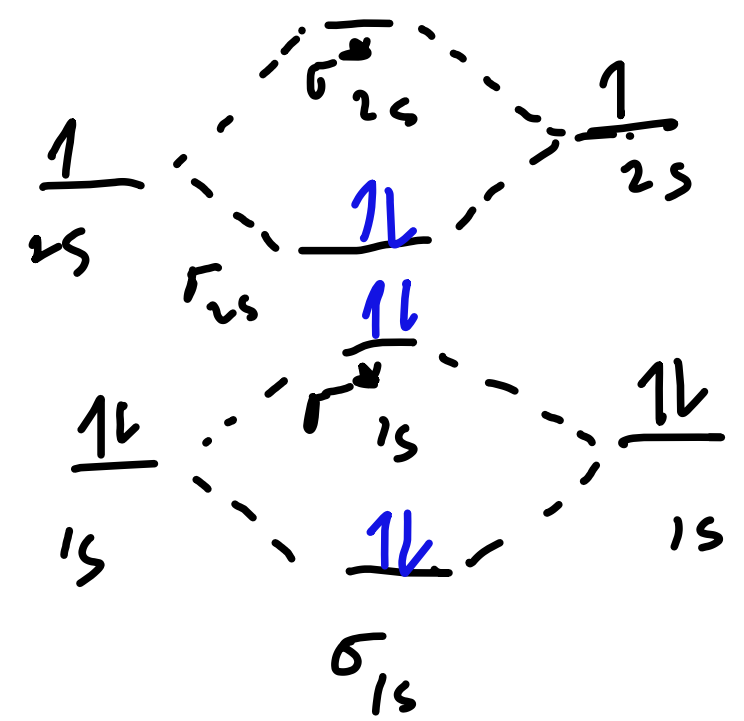
Total $e = 2$

B.O. = $\frac{1}{2} (2 - 0) = 1$



σ_{1s}^2

³Li :



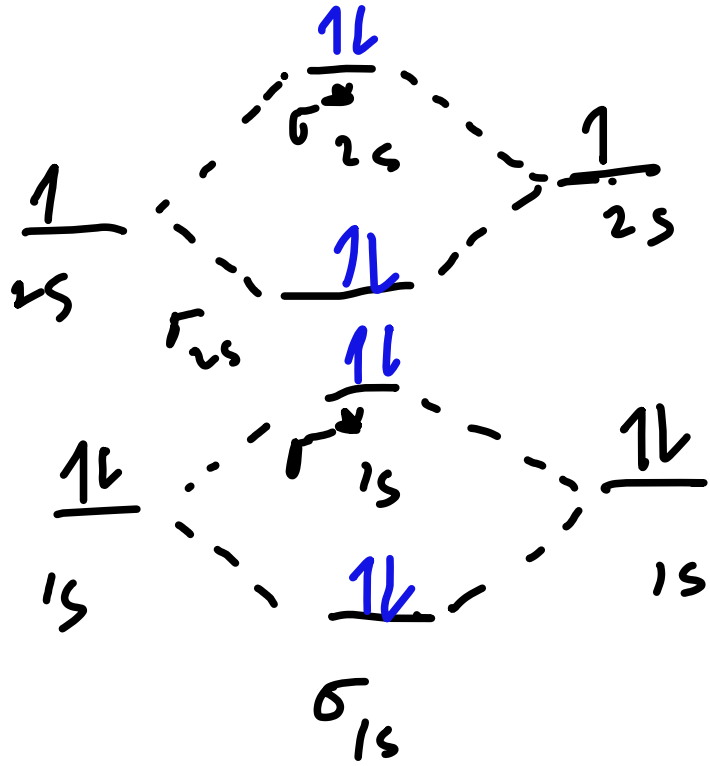
Total $e = 6$

B.O. = $\frac{1}{2} (4 - 2)$

= $\frac{1}{2} \times 2 = 1$



4
Be

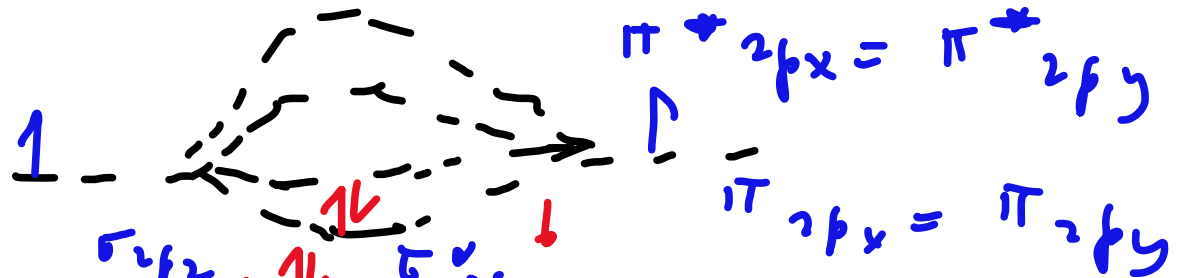


B.O.

$$= \frac{1}{2} (4 - 4) = 0$$

Be₂ molecule

does not exist.



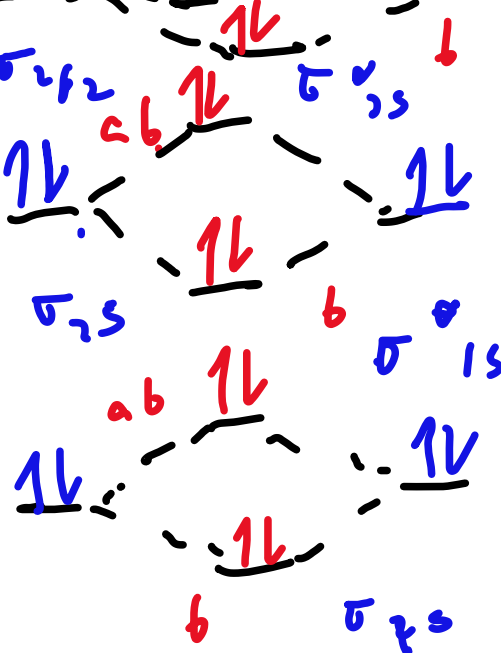
B:

B.O.:

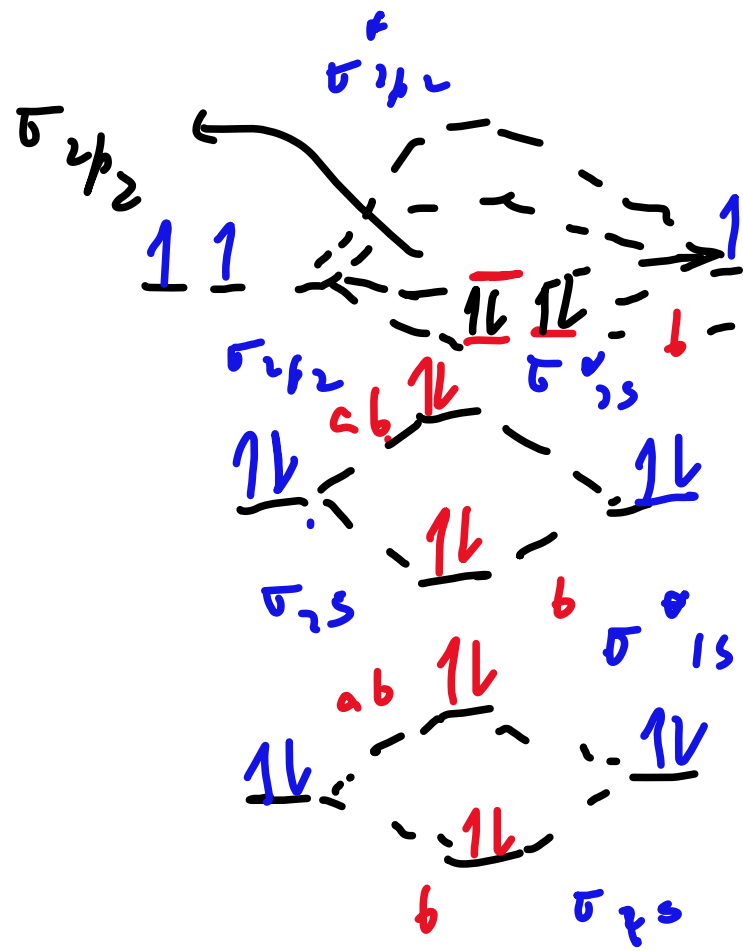
Bond order = 1

$$\frac{1}{2} (6 - 4)$$

$$= \frac{1}{2} \cdot 2 = 1$$



C:



Total = 12 e (c + c)

B: 0 = 1/2 (8 - 4)

$\pi_{2p_x} = \pi_{2p_y}$

$(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^2$

$(\pi_{2p_x}^2 = \pi_{2p_y}^2)$

Für Li₂, Be₂, B₂, C₂,

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < (\pi_{2p_x} = \pi_{2p_y}) < \sigma_{2p_z} < (\pi^*_{2p_x} = \pi^*_{2p_y}) < \sigma^*_{2p_z}$

N: 7

F: $\frac{1}{2}(10-8) = 1$ (circled)

N₂: 14

F₂ = 0 (circled)

invert

Ne: (circled)

B: 0 = $\frac{1}{2}(10-10) = 0$

$\frac{1}{2}(10-7) = \frac{3}{2} = 1.5$

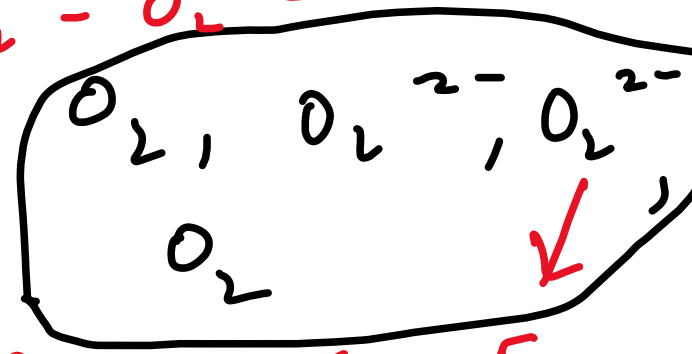
O₂ diamagnetic

O:

O = 0 O₂ (circled)



$\pi_{2p_x} = \pi_{2p_y}$



B.O.: 1
B: 0 = $\frac{1}{2}(10-4) = \frac{1}{2} \times 6 = 3$

N ≡ N (circled)

paramagnetic

(10-6) = 2

paramagnetic O₂⁺ $\frac{1}{2}(10-5) = 2.5$

