

Molecular Orbital Theory:-

- Conventionally, it was known that atoms having unpaired electron in their valence shell atomic orbitals, it was paramagnetic. The atom in which unpaired e^- is not present, it was considered as diamagnetic. For the quantitative explanation, the formula was given

$$\mu = \sqrt{n(n+2)} \text{ BM}$$

where, n = no. of unpaired e^-

- Later, for polyatomic molecule, magnetic nature was given.

The molecules having odd number of electron is assumed as paramagnetic & those having even no. of e^- is assumed as diamagnetic in nature.

e.g.

NO_2 (Para); CO_2 (Dia); CO (Dia); NO (Para)

- As per the given rule, oxygen should be diamagnetic but experimentally, it was found that it ~~was~~ is paramagnetic. To explain this nature of oxygen, molecular orbital theory was given.

- Some molecules having fractional bond order (without considering resonance), this was also explained by the theory of MOT.

Molecular Orbital Theory -

As per the MOT, pure atomic orbitals of different atom intermix with each other for the formation of equal no. of molecular orbitals having different energy.

Molecular orbital

Bonding Molecular Orbital (BMO)

- Has less energy
- More stable
- Near to nucleus

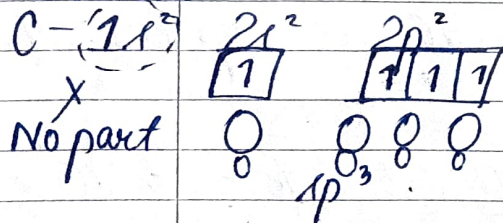
Anti-Bonding Molecular Orbital (ABMO)

- Have more energy
- Less stable
- Far from the nucleus

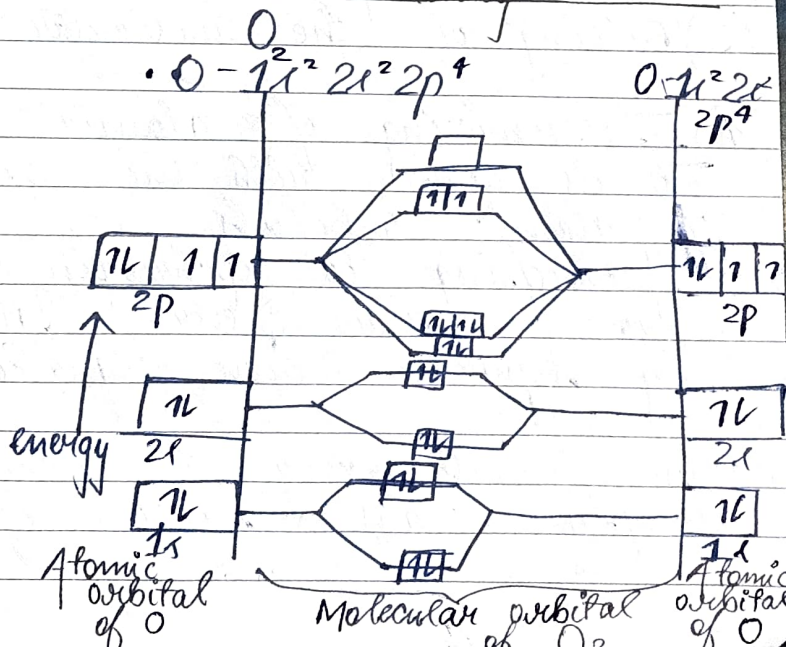
Difference b/w Mixing of Hybridisation & MOT:-

Hybridisation

- The intermixing of atomic orbital is done of the same atom belonging to valence shell atomic orbital.



Molecular orbital Theory



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Hybridisation

- Intermixing of atomic orbital is known as hybridisation.

- Orbitals which are present at different energy level & different shape are intermixed to get hybridised orbital having energy in between of pure atomic orbital.

Molecular Orbital Theory

- Intermixing of atomic orbital is known as LCAO (Linear Combination of Atomic orbital)

- The orbital which is being intermixed should be present at same energy level. After intermixing, they produce molecular orbital at different energy level.

MOI theory can be analysed by these 3 steps:

- (1) Intermixing of atomic orbital
- (2) Drawing of MOI
- (3) Filling of the molecular orbital

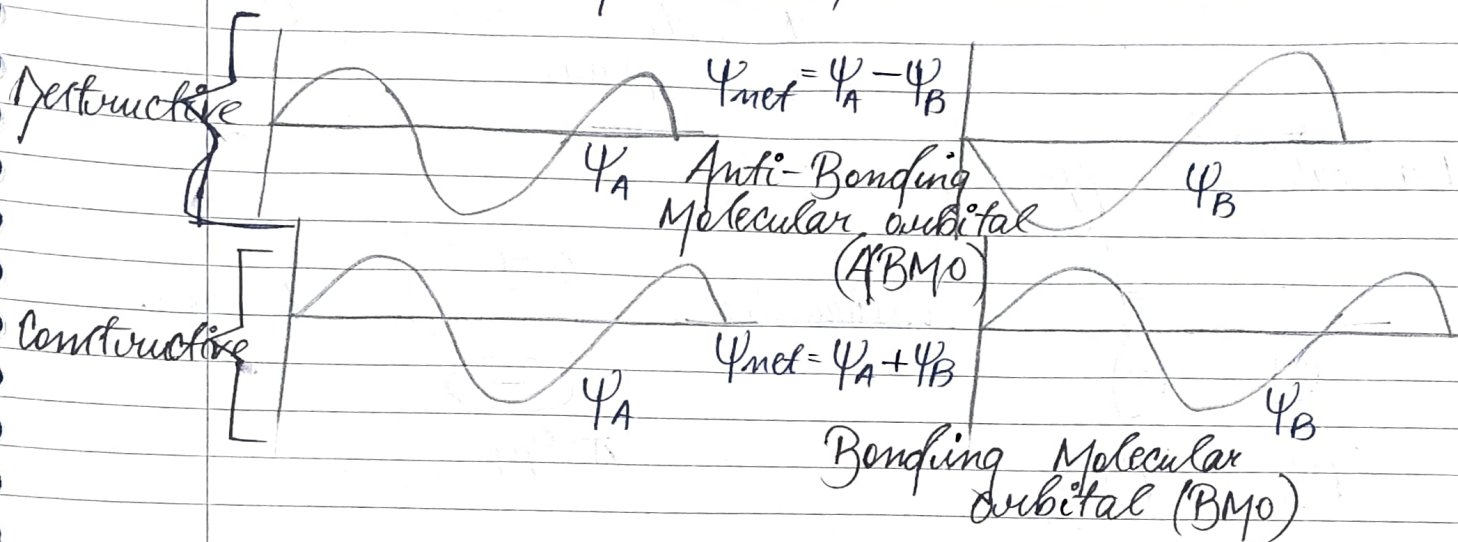
- (1) Intermixing of atomic orbital -

It is done with the help of linear combination of atomic orbitals.

- According to Schrodinger wave equation, electron have wave nature & every atomic orbital is represented by separate wave equation. ~~then~~

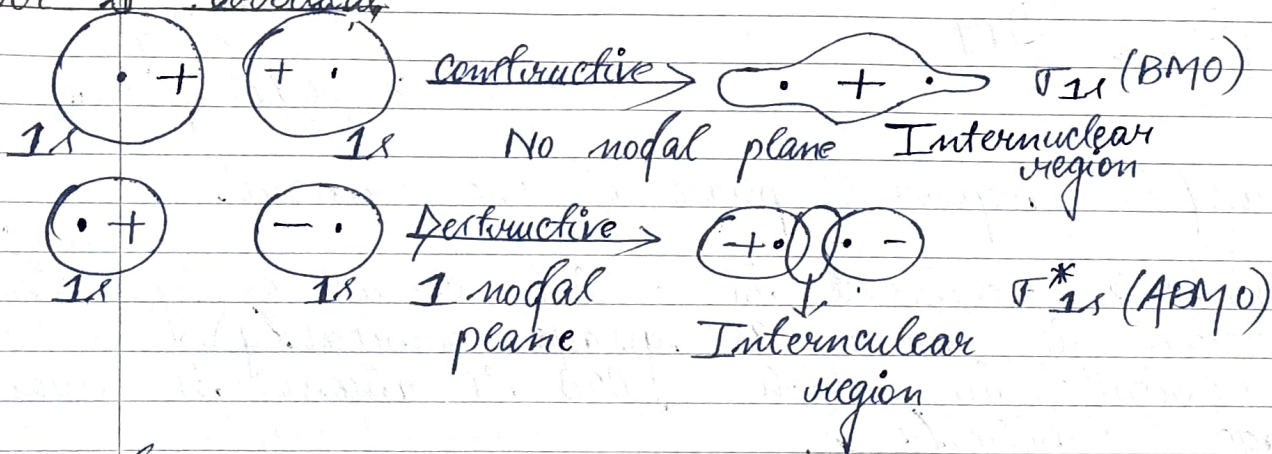
- When intermixing of atomic orbitals is done, that simply means mixing of wave. ~~to~~

- _/_/_
- The mixing of wave (interference) can be of 2 type -
Constructive or destructive, as shown.



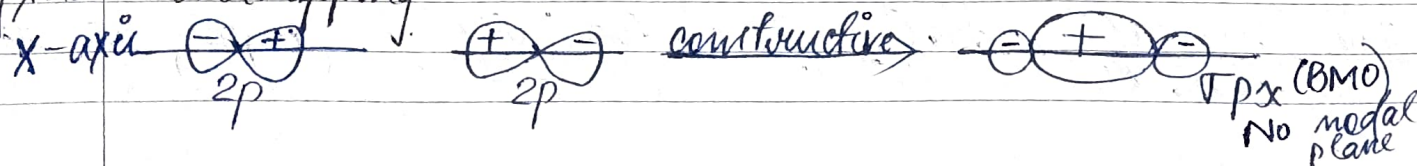
Intermixing by LCAO method:-

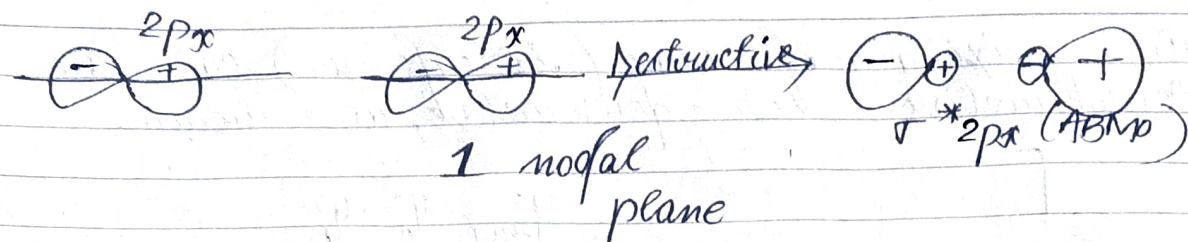
- For s orbital



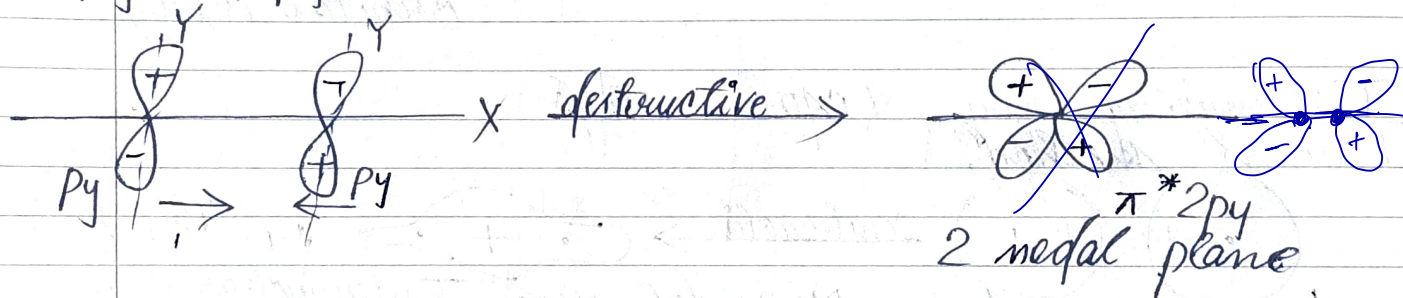
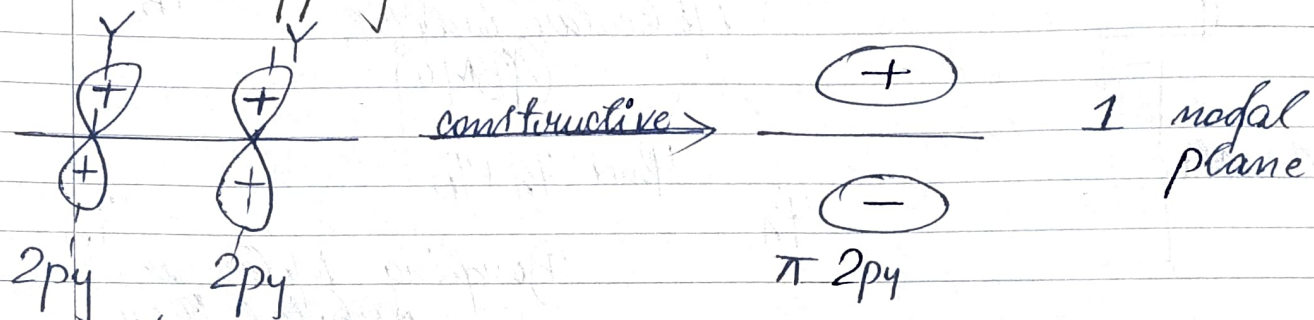
- The dot moves in opposite direction of motion of electron cloud.

- For p orbital, Axial overlapping -





Lateral overlapping -



• (+ve) and (-ve) represent phase of the orbital.

• The molecular orbital in which centre of symmetry ^(COS) is present is known as gerade orbital (g). The orbital in which COS is absent is known as ungerade orbital (un).

• There is another method to analyse gerade and ungerade orbital.

If orbital contain even no. of nodal plane, then this is known as gerade orbital & if orbital contain odd no. of nodal plane, then it is ~~un~~ ungerade orbital.

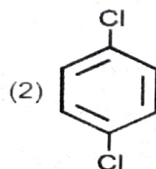
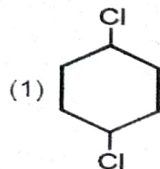
15. Consider the following statements :

- The percentage ionic character according to Hannay-Smith equation in X-Y bond is 46% if electronegativity of X and Y are 1.4 and 3.4 respectively
- Bond angle of PF_3 is more than PH_3 .
- In PCl_2F_3 , all P-F bond lengths are equal.

The correct statement(s) is(are)

- I only
- II only
- I and II only
- I, II and III

16*. Which of the compounds do not have zero dipole moment?



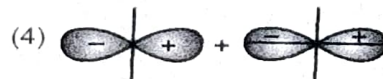
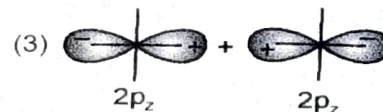
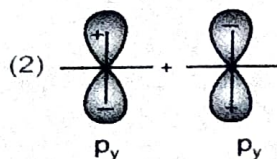
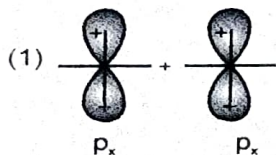
17. Select the incorrect statement about $(\text{NO}_2)^\ominus$.

- All the N - O bonds are equivalent
- It has two resonating structure
- Both resonating structures have equal contribution towards resonance hybrid.
- Formal charge on nitrogen atom in both resonating structure is +1

18. The compound in which sp mixing is present

- N_2
- O_2
- C_2
- Both (1) & (3)

19*. Which of the following representation leads to π^* molecular orbital, (z is considered as internuclear axis)?



20. During oxidation, in which of the following bond order will increase?

- N_2
- CO
- O_2^-
- Both (2) & (3)

21. The correct order of pair regarding nodal surface

- $\sigma 2s > \sigma^* 2s$
- $\sigma 2s < \sigma^* 2p_z$
- $\sigma^* 2s > \sigma^* 2p_z$
- $\sigma^* 2p_z < \pi 2p_x$

SECTION - B

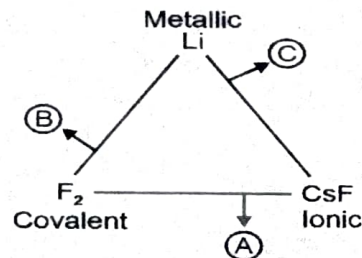
Multiple Choice Type Questions

(One or more than one option(s) is/are correct)

1. Which of the following can show variable valency?

- F
- Cl
- Br
- I

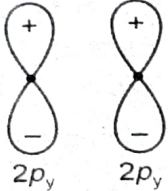
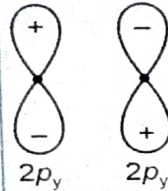
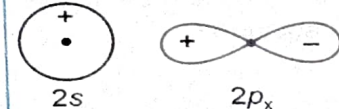
2. Given below is a triangle illustrating the transition between ionic, metallic and covalent bonding



where (A), (B) and (C) respectively are compounds which have more ionic, covalent and metallic character respectively. Which combination go well for (A), (B) and (C)?

- MgF_2 , I_2 , Na_3Bi
- IF_7 , ClF , Na_3N
- BeF_2 , S_8 , Na_3Sb
- OF_2 , ClF , NF_3

5. Match the following.

	List-I Orbital overlap (Assume x-axis or inter nuclear axis)		List-II (M.O. formed)
(P)	 $2p_x$ $2p_x$	(1)	Bonding $\sigma 2p$
(Q)	 $2p_y$ $2p_y$	(2)	Bonding $\pi 2p$
(R)	 $2p_y$ $2p_y$	(3)	Anti bonding $\pi 2p_y$
(S)	 $2s$ $2p_x$	(4)	Bonding σsp
		(5)	Anti bonding $\sigma 2p$

(1) (P $\rightarrow$ 1); (Q $\rightarrow$ 2); (R $\rightarrow$ 3); (S $\rightarrow$ 4)(2) (P $\rightarrow$ 3); (Q $\rightarrow$ 1); (R $\rightarrow$ 5); (S $\rightarrow$ 5)(3) (P $\rightarrow$ 2); (Q $\rightarrow$ 3); (R $\rightarrow$ 4); (S $\rightarrow$ 5)(4) (P $\rightarrow$ 1); (Q $\rightarrow$ 3); (R $\rightarrow$ 1); (S $\rightarrow$ 2)**SECTION - E****Assertion-Reason Type Questions**

This section contains 10 questions. Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (1), (2), (3) and (4) out of which **ONLY ONE** is correct.

- (1) Statement-1 is True, Statement-2 is True; Statement-2 **is** a correct explanation for Statement-1
- (2) Statement-1 is True, Statement-2 is True; Statement-2 **is NOT** a correct explanation for Statement-1
- (3) Statement-1 is True, Statement-2 is False
- (4) Statement-1 is False, Statement-2 is True

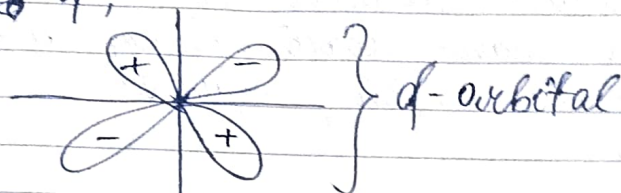
1. STATEMENT-1 : PCl_5 has trigonal bipyramidal shape.**and**STATEMENT-2 : Length of all P-Cl bonds in PCl_5 is equal.2. STATEMENT-1 : PH_3 and PF_3 are pyramidal in shape with one lone pair on P. But PF_3 has greater bond angle than PH_3 .**and**STATEMENT-2 : Back bonding is present in PF_3 but absent in PH_3 .

3. STATEMENT-1 : Polarisation is the distortion of the shape of an anion by an adjacently placed cation.

and

STATEMENT-2 : Maximum polarisation is brought about by a cation of high charge.

Q How many of the following are gerade orbital?
 (A) s (B) p (C) d (D) $\sigma^* 1s$ (E) $\sigma 1s$ (F) $\pi^* 2p$
 (G) $\pi 2p$ (H) $\sigma^* 2p$ (I) $\sigma^* 2p$
 Gerade: (A), (E), (H), (I)



- CO is the point from which going backward & forward gives same phase/sign.
- In hybridisation, σ mixing occurs but in LCAO, s-d mixing does not occur.
- s-p mixing occurs in both.

BMO

- BMO is near to the nucleus, contains more electron and is relatively stable.
- BMO is formed by constructive interference.
- Ionisation of e^- from BMO requires more energy.

• The wave function of BMO orbital can be $\psi_{BMO} = \psi_{AO} + \psi_{AO}$

ABMO

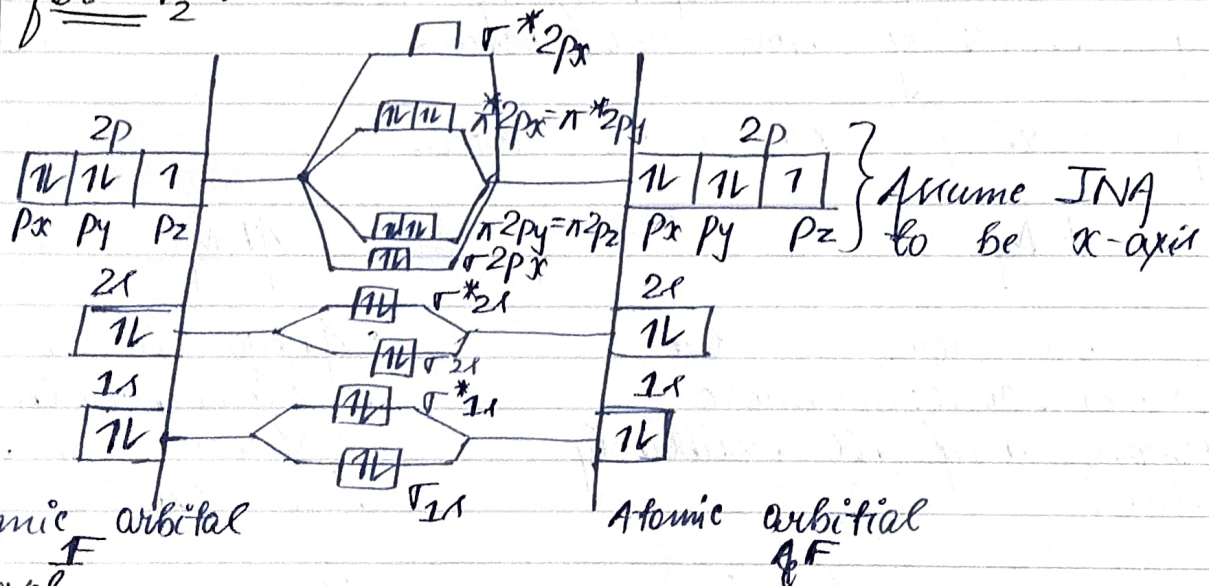
- ABMO is far from the nucleus, contains less electron and is relatively less stable.
- ABMO is formed by destructive interference.
- Ionisation of e^- from ABMO requires less energy.

• The wave function of ABMO is $\psi_{ABMO} = \psi_{AO} - \psi_{AO}$

(2) Drawing MO diagram -

- MO diagram is formed in increasing order of energy of the molecular orbital in which the molecular orbital which have least energy are kept at down & molecular orbital which have more energy are kept at the top.
- The molecular orbital are filled with the help of Aufbau, Hund's & Pauli's principle.

MO for F_2 :-



Energy level $\sigma_{1s}^2, \sigma_{1s}^{*2}; \sigma_{2s}^2, \sigma_{2s}^{*2}, \sigma_{2p_x}^2, \pi_{2p_y}^2 = \pi_{2p_z}^2, \pi_{2p_y}^{*2} = \pi_{2p_z}^{*2}$

* LUMO - Lowest Unoccupied Molecular Orbital

* HOMO - Highest Occupied Molecular Orbital

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- Filling of electron in molecular orbital is simply redistribution of electron from atomic orbital to molecular orbital.

- The no. of molecular orbital = no. of atomic orbital intermixed

• Filling of electron in molecular orbital is simply redistribution of electron from atomic orbital to molecular orbital.

• The no. of molecular orbital = no. of atomic orbital intermixed

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~~Significance of~~

• For molecular species in which total no. of electrons ≤ 14 ,

$$\sigma 2p_x < \pi 2p_y = \pi 2p_z \quad \times$$

$$\pi 2p_y = \pi 2p_z < \sigma 2p_x \quad (\text{Due to } sp \text{ mixing})$$

Total no. of $e^- > 14$

$$\sigma 2p_x < \pi 2p_y = \pi 2p_z$$

• We can find out bond order, with the help of M.O.

$$BO = \frac{N_b - N_a}{2}$$

where,

N_b = No. of bonding e^-

N_a = No. of antibonding e^-

e.g.

$$O_2 = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^2 < \pi 2p_y^2 = \pi 2p_z^2 < \pi^* 2p_y = \pi^* 2p_z$$

$$N_b = 10 ; N_a = 6$$

$$BO = \frac{N_b - N_a}{2} = \frac{10 - 6}{2} = 2$$

$$N_2 = \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_y^2 = \pi 2p_z^2 < \sigma 2p_x^2$$

$$N_b = 10 ; N_a = 4 ; BO = \frac{10 - 4}{2} = 3$$

If $BO = 0$, then molecule does not exist.

e.g. Let He_2 :- $\sigma 1s^2 < \sigma^* 1s^2$
 $BO = \frac{2-2}{2} = 0$

Bond order maybe +ve integral or fractional. In some cases, it has -ve value, also.

• Higher the number of bonding electron, greater will be the stability (BO should be same).

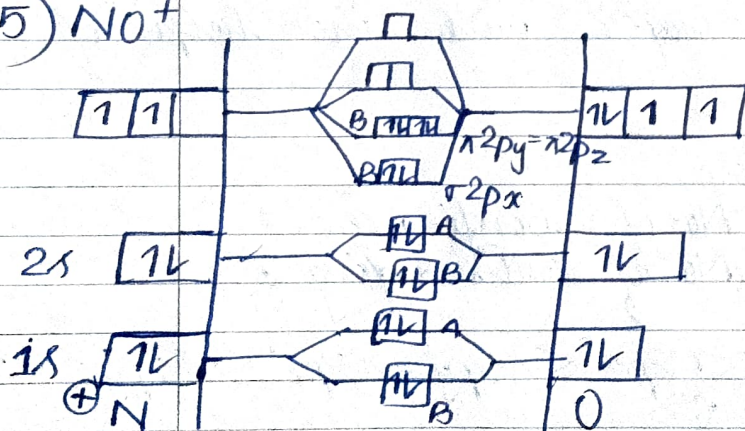
Q) Write the electronic configuration for:

- (1) Li_2 (2) B_2 (3) C_2 (4) NO (5) NO^+ (6) O_2^+ (7) O_2^-
 (8) O_2^{2-}

(1) $Li_2 = 6e^-$
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2$
 $BO = \frac{4-2}{2} = 1$

Diamagnetic

(5) NO^+



$BO = \frac{10-4}{2} = 3$ Diamagnetic

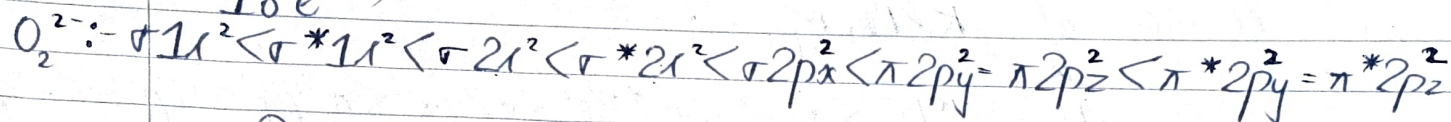
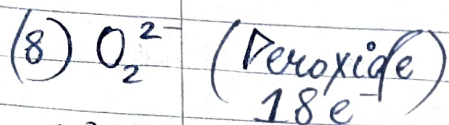
(3) $C_2 = 12e^-$
 $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2py^2 = \pi 2pz^2$
 $BO = \frac{8-4}{2} = 2$
 Diamagnetic

(7) $O_2^- = 17$
 Superoxide

$O_2^-: \sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2pz^2 < \pi 2px^2 = \pi 2py^2$

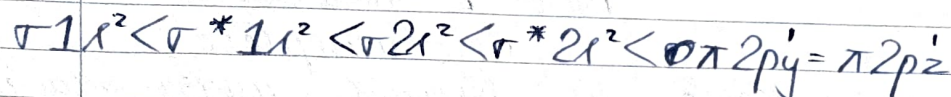
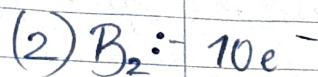
$BO = \frac{10-7}{2} = 3/2$

Paramagnetic
 (Unpaired e^-)



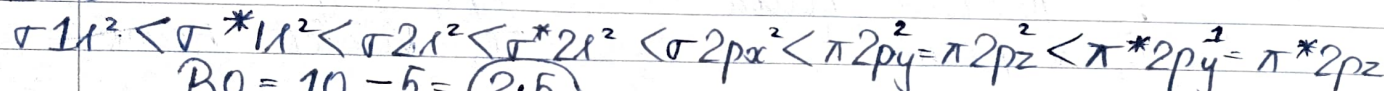
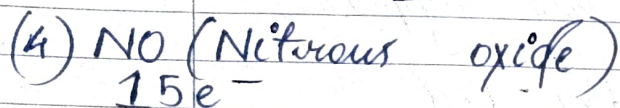
$$BO = \frac{10 - 8}{2} = (1)$$

Diamagnetic (No unpaired e⁻)

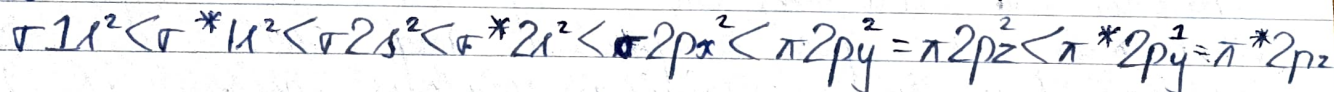
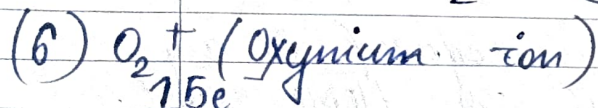


$$BO = \frac{6 - 4}{2} = (1)$$

Paramagnetic



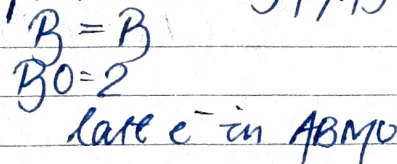
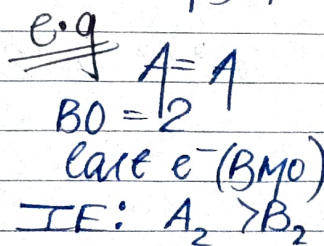
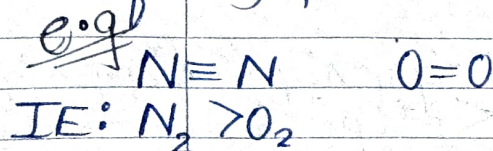
$$BO = \frac{10 - 5}{2} = (2.5)$$



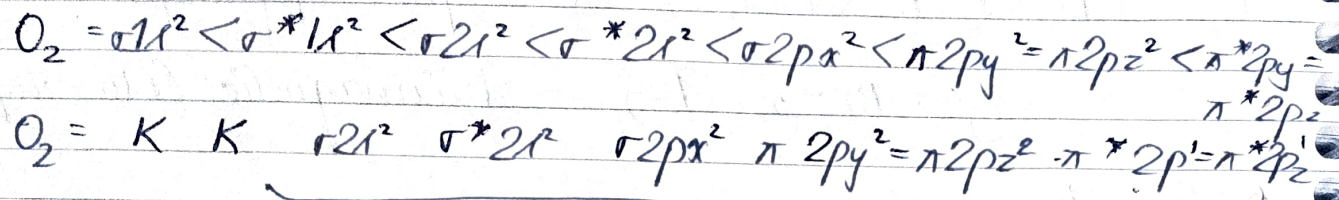
$$BO = \frac{10 - 5}{2} = (2.5)$$

• Higher the bond order, greater will be the ionisation energy.

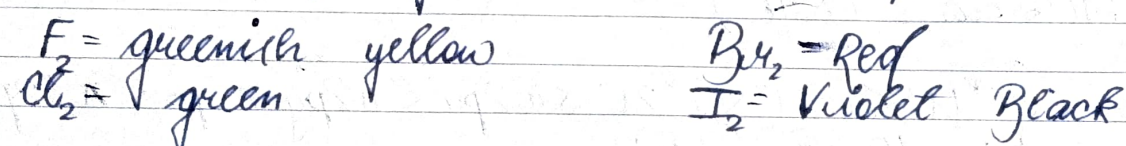
If bond order is same, then ionisation energy if BMO is higher than ABMO. (When last e⁻ is present in BMO/ABMO)



The electronic configuration can also be written in terms of K, L, M, ...



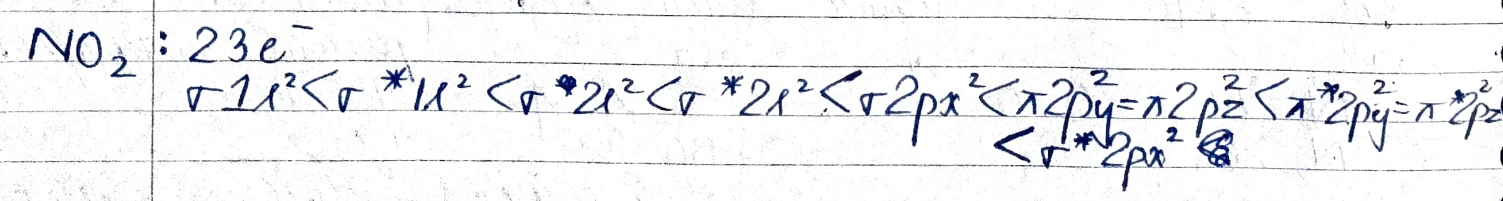
When the gaseous molecule is brought under radiation, HOMO - LUMO transition take place & due to HOMO - LUMO transition, colour of gaseous molecule appear.

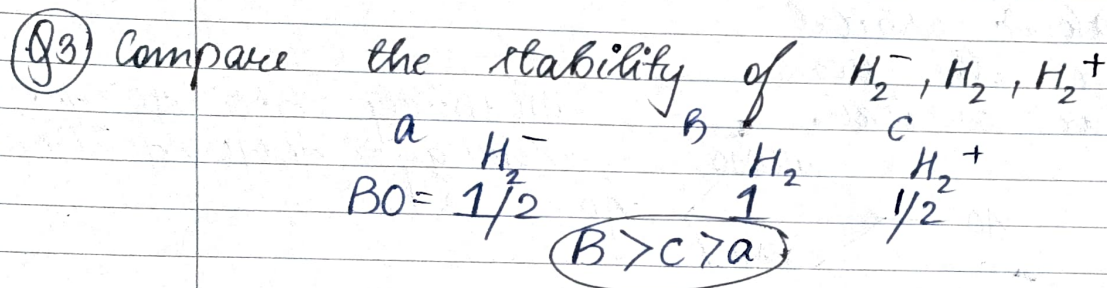
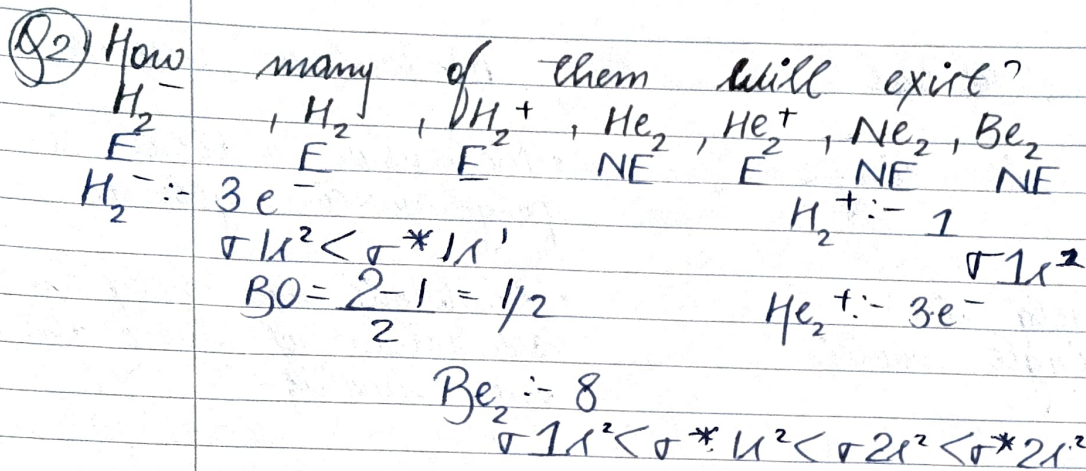


HOMO - LUMO transition:

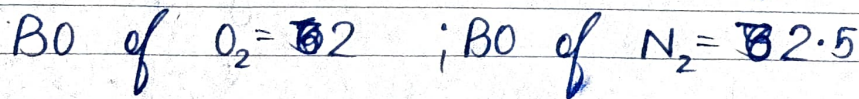
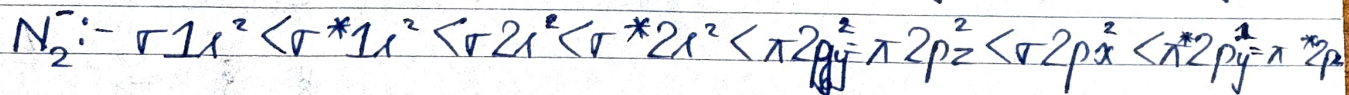
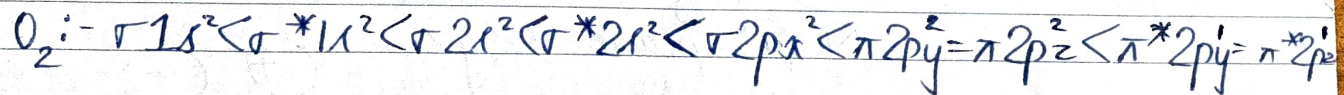
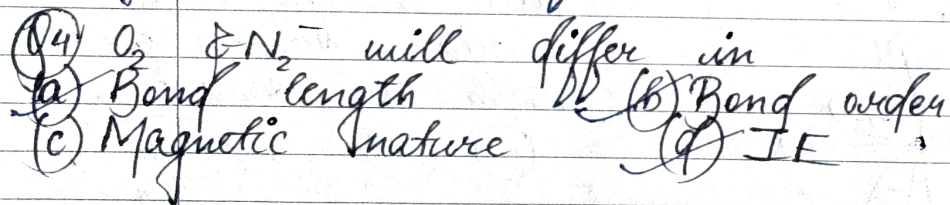
When a source of radiation introduced to any gaseous molecule, the e^- present in HOMO orbital absorb a specific photon and excite to higher orbital. Due to remaining photons, colour of the gaseous molecule appear.

Q1) How many of them are paramagnetic in nature?
 $B_2, O_2^{2-}, NO, NO_2, O_2^-, O_2$





• Higher the no. of ABMO e^- , lesser will be stability.



Both paramagnetic

SECTION - G

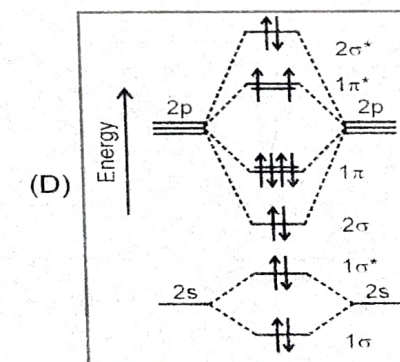
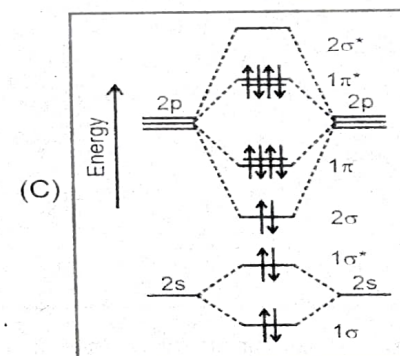
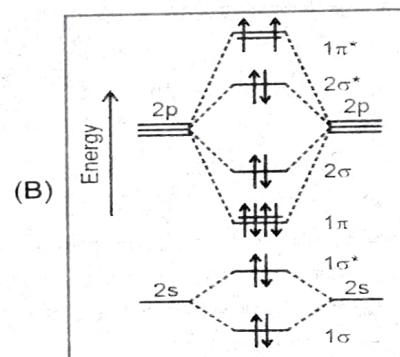
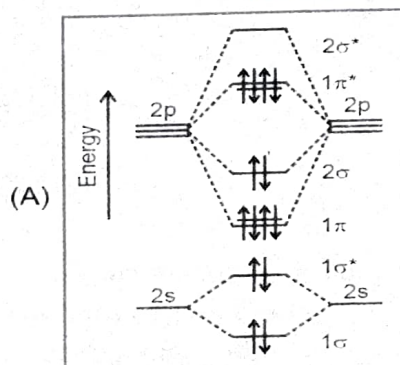
(Previous Years Questions)

Multiple Choice Type Question
(Only One Option Correct)

- The species having bond order different from that in CO is [IIT-JEE-2007 (Paper-1)]
(A) NO^-
(B) NO^+
(C) CN^-
(D) N_2
- Among the following, the paramagnetic compound is [IIT-JEE-2007 (Paper-1)]
(A) Na_2O_2
(B) O_3
(C) N_2O
(D) KO_2
- The structure XeO_3 is [IIT-JEE-2007 (Paper-1)]
(A) Linear
(B) Planar
(C) Pyramidal
(D) T-shaped
- Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is [IIT-JEE-2010 (Paper-2)]
(A) 1 and diamagnetic
(B) 0 and diamagnetic
(C) 1 and paramagnetic
(D) 0 and paramagnetic
- The species having pyramidal shape is [IIT-JEE-2010 (Paper-2)]
(A) SO_3
(B) BrF_3
(C) SiO_3^{2-}
(D) OSF_2
- The shape of XeO_2F_2 molecule is [IIT-JEE-2012 (Paper-2)]
(A) Trigonal bipyramidal
(B) Square planar
(C) Tetrahedral
(D) See-saw
- Assuming $2s$ - $2p$ mixing is **NOT** operative, the paramagnetic species among the following is [JEE (Adv)-2014 (Paper-2)]
(A) Be_2
(B) B_2
(C) C_2
(D) N_2

The correct molecular orbital diagram for F_2 molecule in the ground state is

[JEE (Adv)-2023 (Paper-2)]



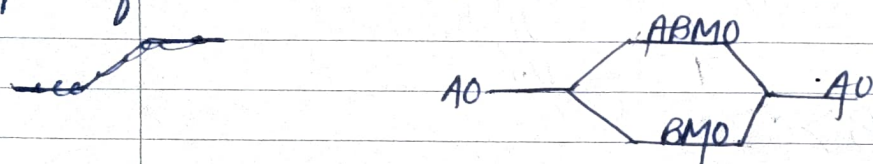
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Atomic Orbital

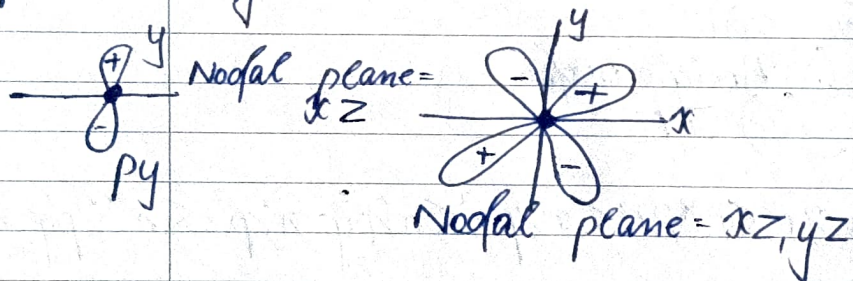
• Atomic orbital is single nuclei system.

• Electrons are held in attraction of single nuclei.

• Stability of atomic orbital is in between the two type of molecular orbital.



• The nodal plane always pass through nucleus.



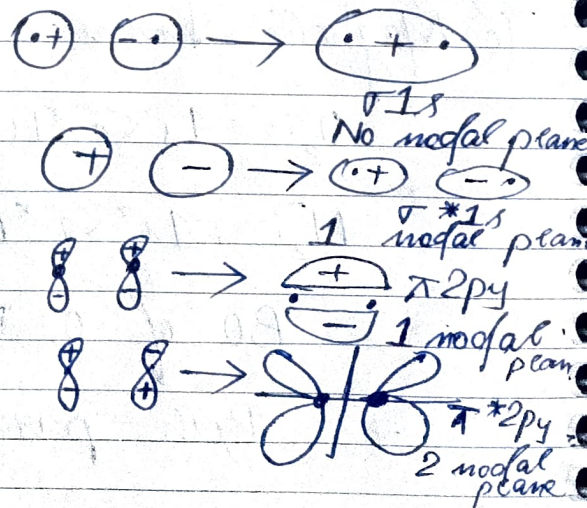
Molecular Orbital

• Molecular orbital is poly-nuclei system.

• Electrons are held in attraction of more than one nuclei.

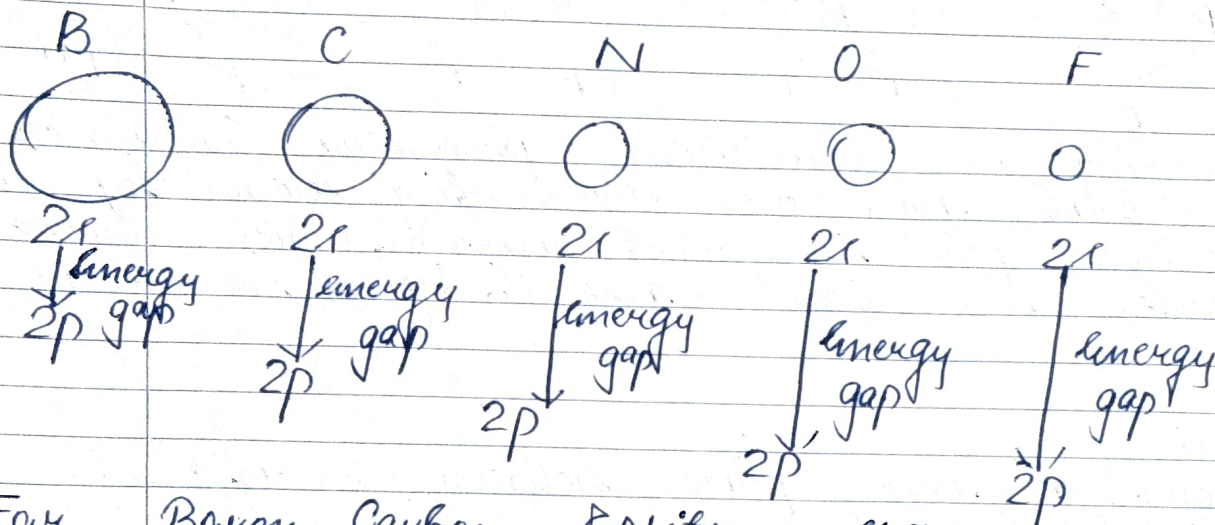
Stability $\Rightarrow$ BMO $>$ AO $>$ ABMO
 Energy $\Rightarrow$ ABMO $>$ AO $>$ BMO

• The nodal plane should pass through inter-nuclear region or from both the nucleus.



s-p mixing:-

When we move from left to right in periodic table, atomic size decreases and difference between energy gap between 2s and 2p orbital increases.



For Boron, Carbon & Nitrogen, energy gap is small & before formation of molecular orbital, 2s & 2p orbital intermix. and then this phenomena is known as s-p mixing.

Now, this s-p orbital intermix for the formation of molecular orbital.

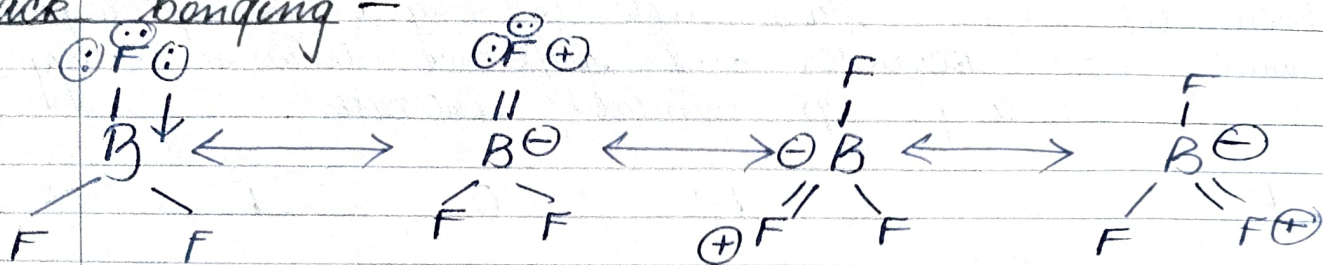
Due to s-p mixing, σ_{2p_x} orbital become more energetic than π_{2p_y} or π_{2p_z} , i.e., $\pi_{2p_y} = \pi_{2p_z} > \sigma_{2p_x}$.

Q) If we don't consider s-p mixing, which of the following will change their magnetic property?

- (i) $B_2 = 10e^-$ (ii) C_2 (iii) N_2 (iv) O_2
- Para before Dia now
- $\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x$
- (ii) $C_2 = 12e^-$ Para (iv) O_2 no change
- (iii) $N_2 = 14e^-$ Dia before
Dia now

Special Type of Bonding:

(1) Back bonding -



Back bonding is stabilising phenomena in which either central atom or surrounding atom disperse their electron pair in slight amount, which increases bond order in slight amount. Hence, increases bond energy.

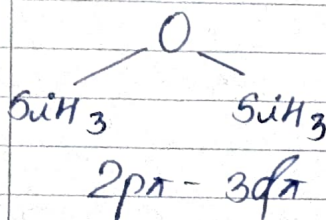
Condition:

- Back bonding take place between 2 adjacent covalently bonded atom.
- The atom which donate electron pair should belong to second period, because as atomic size increases tendency for lateral overlapping decreases (as back bond is a type of π -co-ordinate bond).
- The atom which accept electron pair should belong to second or third period.
- When both the atom belongs to 3rd period, then no back bonding is observed, as 3p-3p lateral overlapping is not effective.

Q In which of the following effective back bonding is observed?

- (1) PCl_3 (2) BeCl_2 (3) BeF_2 (4) H_2O (5) OF_2
 (6) SO_2 (7) PF_3 (8) NH_3 (9) OCl_2 (10) $\text{O}(\text{CH}_3)_2$
 (11) $\text{O}(\text{SiH}_3)_3$ (12) NCl_3 (13) $\text{N}(\text{SiH}_3)_3$ (14) CCl_3^- (15) CF_3^-
 (16) $\text{CH}_2^+ - \text{OH}$

- OF_2 doesn't have vacant orbitals. Both don't have tendency to accept e^- pair.
- OCl_2 In OCl_2 , Cl has vacant d -orbital.

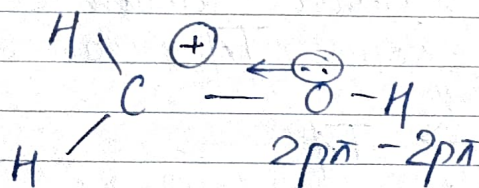
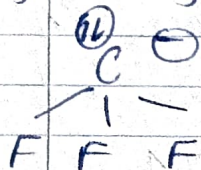
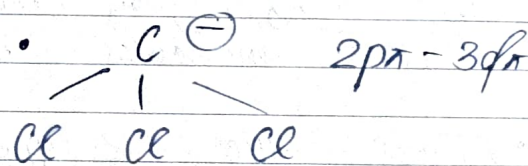
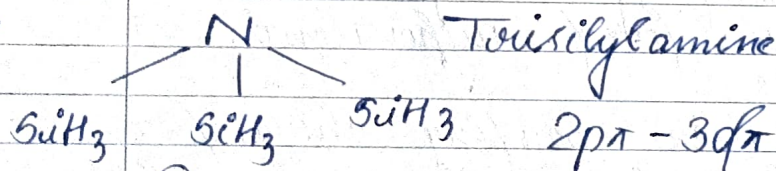


- In SO_2 , back bonding called $2p\pi - 3d\pi$.

- In BeF_2 , $2p\pi - 2p\pi$

- In PF_3 , $2p\pi - 3d\pi$

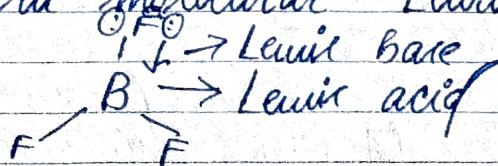
- In OCl_2 , $2p\pi - 3d\pi$



Characteristics:

- It is a type of π -coordinate bond.

- It is intra-molecular Lewis acid-base interaction.



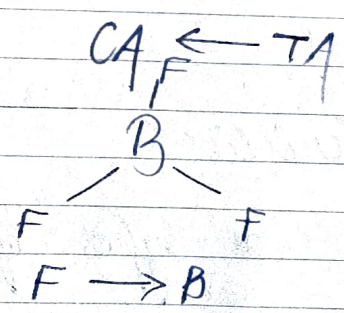
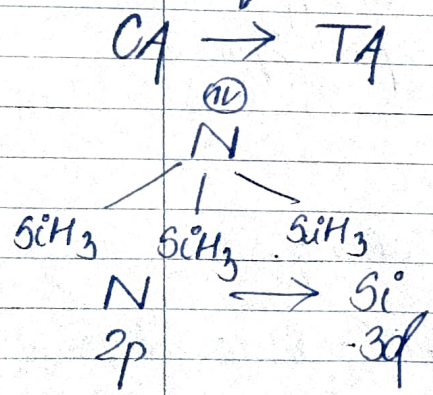
- Higher the size of atom, lesser is the tendency of back bonding.
- There are 2 type of back bonding - $2p\pi - 2p\pi$ and $2p\pi - 3d\pi$

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- $2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi$
 occur in less extent
 e.g. BCl_3

$\begin{array}{c} \text{Cl (3p)} \\ \downarrow \\ \text{B (2p)} \\ \uparrow \\ \text{Cl} \end{array}$

- In BF_3 , BCl_3 , back bonding is present but still these molecules are considered hypovalent.
- There are 2 type of back bonding observed in which electron transfer take place: from CA to TA or from TA to CA.



When back bonding is observed from by donation of electron from CA to TA, the following observation of

//_

will take place:-
- lp which is present in hybridised orbital will have tendency to move in pure 'p' orbital.
- Due to loss of lp, the trigonal pyramidal geometry will slightly convert into trigonal planar.

In transfer of e^- from TA to CA, the back bond be formed ~~will have~~ ~~following~~ & structure of molecule does not change.

Application of Back bond:-

(1) Bond length -

Since back bond is a type of π -coordinate bond, slight amount of bond order increases due to back bonding. b/w 2 adjacent atom

So, bond ~~then~~ length decreases.

(2) Hybridisation -

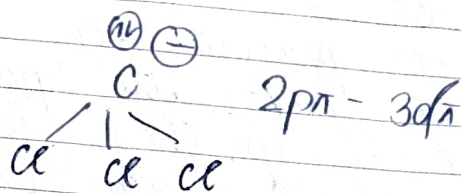
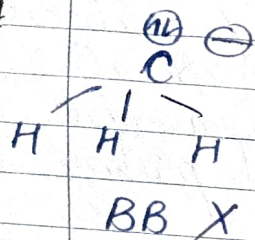
Hybridisation of some molecule changes in slight amount only when electron transfer take place from central atom to terminal atom. Also, the lp should be present in hybridised orbital.

While back bonding, lp have tendency to move in pure p orbital.

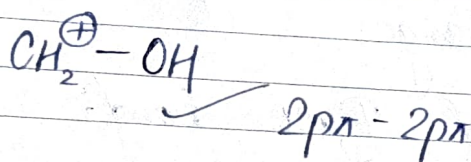
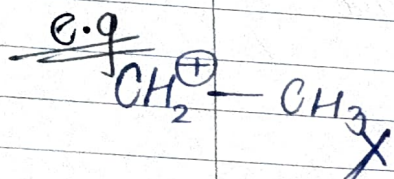
(3) Stability of Carb anion -

Localised negative charge on any atom or +ve ~~atom~~ charge makes the molecule unstable. When this -ve charge become delocalised by any means, then this

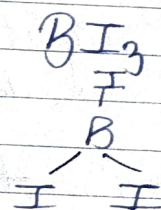
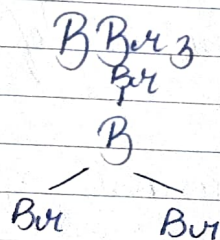
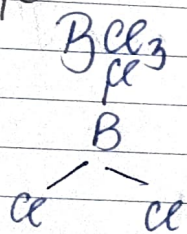
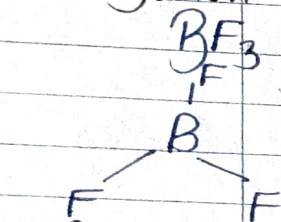
becomes stable.



Due to back bonding, the -ve charge delocalizes throughout the molecule & carbanion becomes stable.



(4) To compare the Lewis acidic nature of Boron trihalide -



Need: $2e^-$
Donated: 0.1
by halide:

$2e^-$
 0.01

$2e^-$
 0.001

$2e^-$
 0.0001

Remaining need: 1.90

1.99

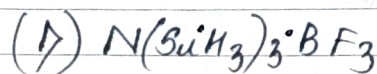
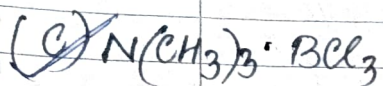
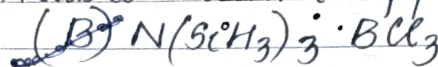
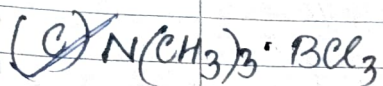
1.999

1.9999

BI_3 is best Lewis acid as it requires more electron.

Acidic strength. $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$

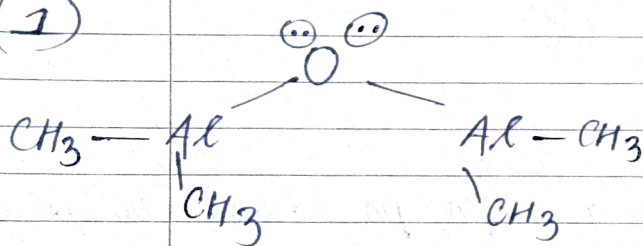
Q Which will form most stable ~~add~~ adduct?



For $N(CH_3)_3$, lp is still present
 So, it is stronger Lewis base.
 In $N(SiH_3)_3$, lp is used in back bonding.

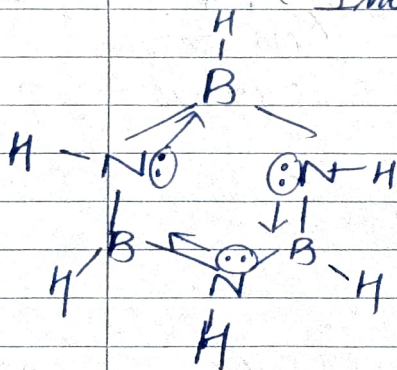
Some Important Points:-

(1)

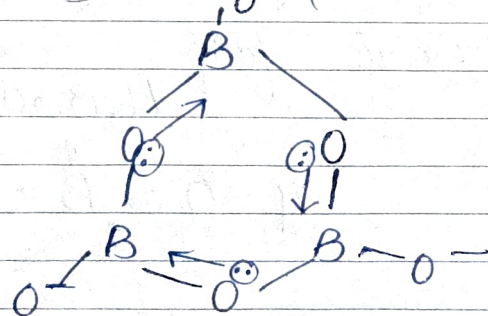


The structure should be angular but it is linear due to back bonding as well as NBEPR.
 Angle = 173° (Almost linear)

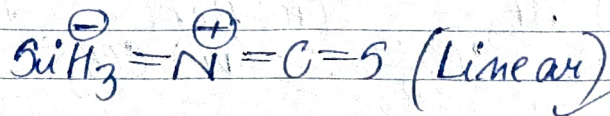
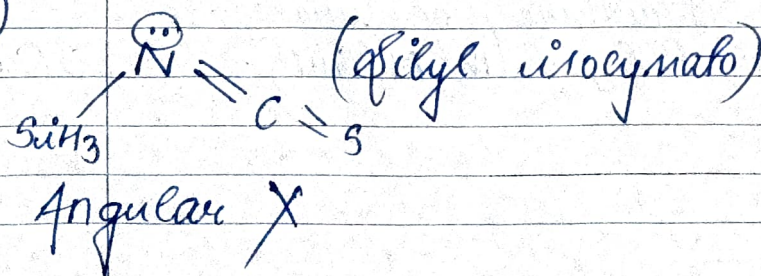
(2) $B_3N_3H_6$ (Borazine / Inorganic benzene)

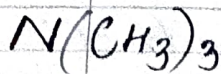


(3) $B_3O_6^{3-}$ (Boroxine)



(4)



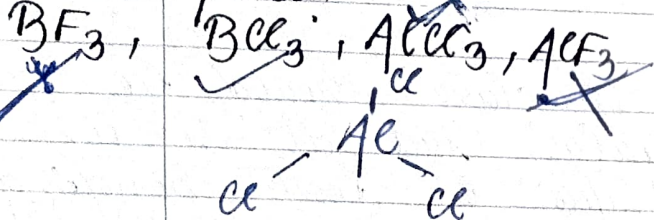


- Pyramidal
- lp of 'N' is present in sp^3 hybridised orbital.



- Almost trigonal planar.
- lp of N is present in pure $2p$ orbital.

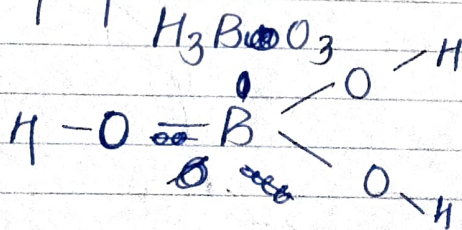
Q In how many of the following back bonding will take place?



③ ②

Q In how many of the following $\pi-\pi$ back bonding will be observed?

- (I) Boric acid
(II) Borazine
(III) Methyl isocyanate
(IV) ~~Methyl~~ silyl isocyanato
(V) OCC_2
(VI) OF_2
(VII) $\text{CH}_2\text{-OH}$
- (1) Boric Acid
No vacant orbital



Q In which of the following back bonding will not affect the existing structure of molecule?

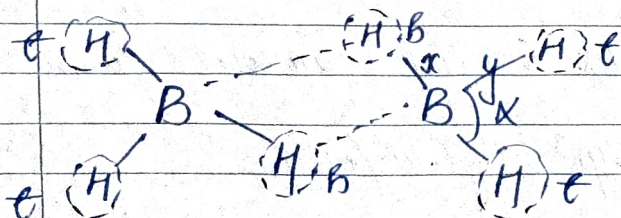
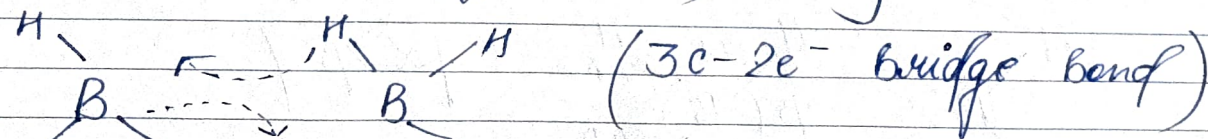
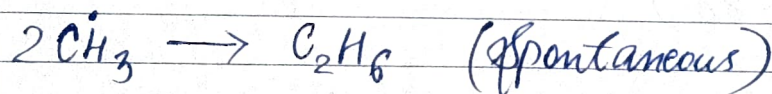
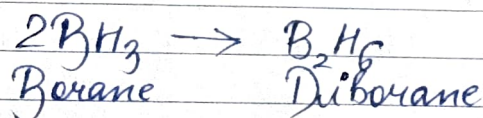
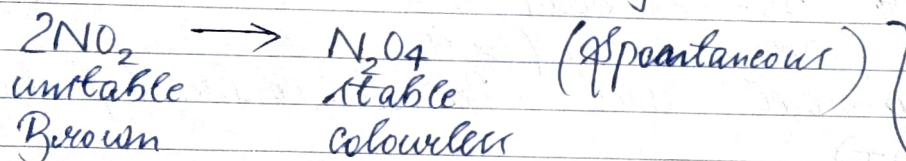
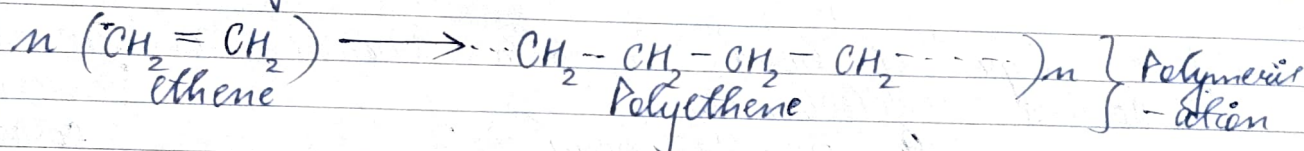
- (i) BF_3 (ii) BeF_2 (iii) BCl_3 (iv) $\text{N}(\text{SiH}_3)_3$ (v) $\text{O}(\text{SiH}_3)_2$
(vi) CCl_3^+ (vii) CCl_3^-

(2) Bridge bond -

The molecule in which back bonding is not present, the molecule have bridge bond.

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- Unstable molecules have tendency to dimerise or polymerise to get a stable molecule.



Ht = Terminal hydrogen
Hb = Bridged hydrogen

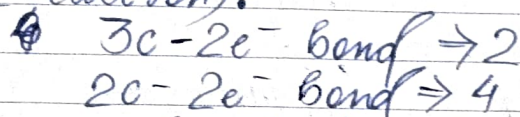
} Dimerisation

Some Important Points of Diborane:

- (1) x = Bond length of bridge bond
 y = Bond length of terminal bond
 $x > y$

Electron present in bond x is utilised for the bridge bond formation (in slight amount). So, bond x will become slightly weak & will elongate.

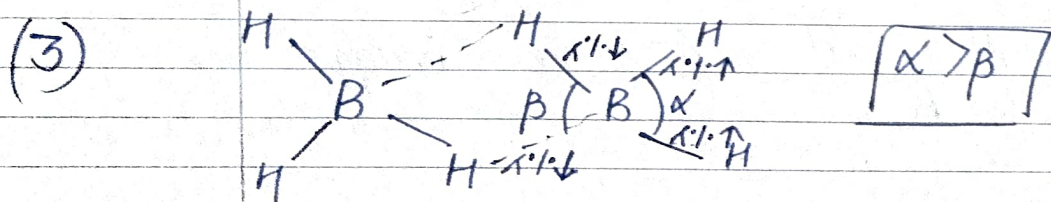
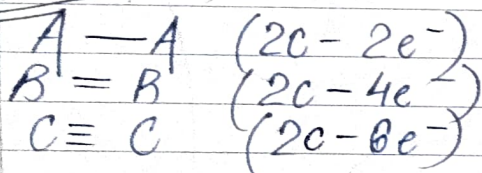
- (2) This type of bond is also known as $3c-2e^-$ bond (3 centres - 2 electrons).



non-conventional

$3c-2e^-$ represent that $2e^-$ is controlled by 3 nucleus.

Conventional (VBT)



- (4) Borane & diborane both exist in gaseous form.

- (5) Both of the Boron is sp^3 hybridised.

- (6) All terminal atoms lie in 1 plane but bridged atom lie above & below the plane.

Max. 6 co-planar atom is present in the molecule.

- Q In which of the following there is tendency to form bridge bond?
- (A) $\text{Al}(\text{CH}_3)_3$ (B) BF_3 (C) AlCl_3 (D) BCl_3 (E) CH_3
 (F) BeCl_2 (G) BeF_2 (H) BeH_2

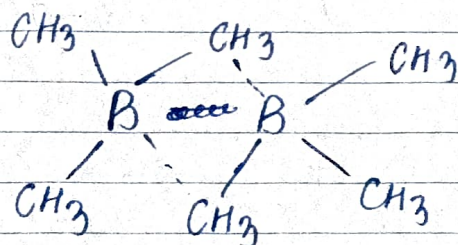
- (A) Octet of Al is not complete.
 (B) Back bonding will take place.
 (C) No back bonding as 3p-3p overlapping.
 (D) There will be back bonding. In the molecule, back bonding. So, it is 3p doesn't have tendency to dimerise. And, bridge bond isn't B 2p formed due to bulky nature of chlorine.

(E) The molecule dimerise but not bridge bonding. It just overlaps.

(F) In BeCl_2 , back bond is present due to 3p-2p. This is weak lateral overlapping. So, molecule also have tendency to dimerise.

(G) Back bond will take place.

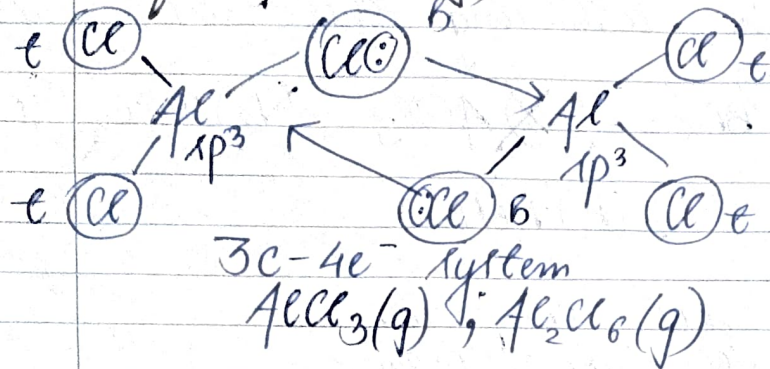
Q Max. co-planar atom in $\text{B}_2(\text{CH}_3)_6$?



(10)

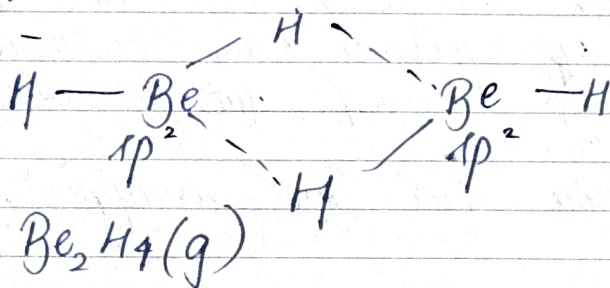
Structure of some Important compound:-

(1) Dimer of $AlCl_3$ (g)

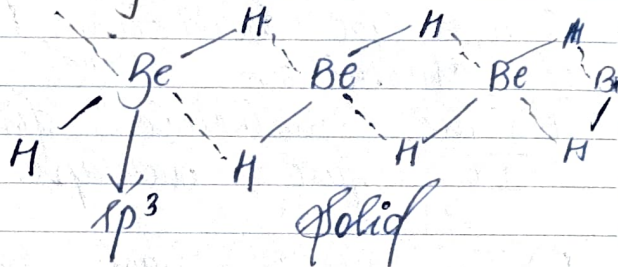


(2) BeH_2 (g)

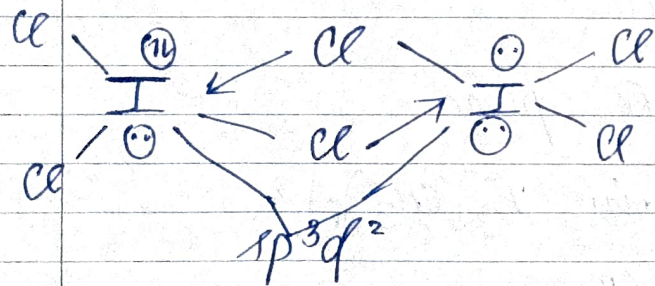
Dimer -



Polymer -



(3) I_2Cl_6 -



~~All~~ all atoms are co-planar

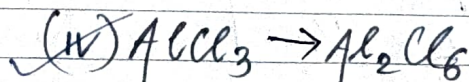
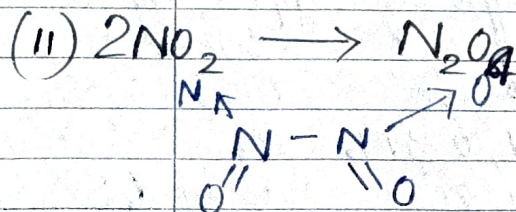
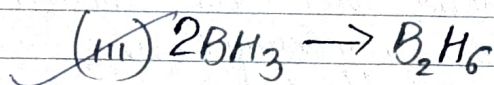
Some Important Points —

- After back bonding or bridge bond, molecule still remain hypovalent.
- Borane does not dimerise in presence of ether. Since, ether is Lewis base & have tendency to form co-ordinate bond with Borane. Now, the Borane will not dimerise as it is no more hypovalent.

Q In which of the following molecule 3c-2e⁻ bond is present?

- (1) Dimer of BeH_2
- (2) Polymer of BeH_2
- (3) Al_2Cl_6 3c-4e⁻²
- (4) C_2H_6 2c-2e⁻
- (5) Si_2H_6 2c-2e⁻
- (6) B_2H_6

Q In which of the following molecules formation occurs in which completion of octate is not a driving force?



If octate completion is driving force, then octate will be completed.

Q Which of the following does not exist?

- (i) B_2F_6 (ii) B_2Cl_6 (iii) B_2Br_6 (iv) B_2I_6 (v) Be_2F_4 (vi) Be_2Cl_4
- X X X X X exists

Back bonding. ϕ ,
no need of dimer

Weak Chemical Force:-

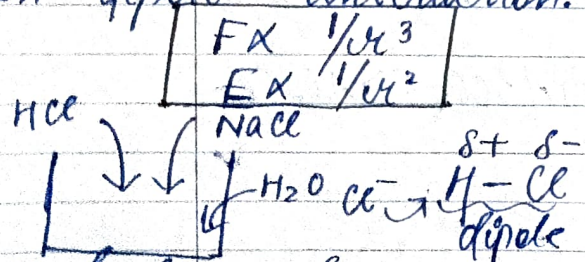
- The chemical forces exist between two different chemical species, either ionic species or covalent species.
- The chemical force is responsible for physical state of any substance.

Weak Chemical Forces

Non-Van der Waal force

(a) Ion-dipole interaction-

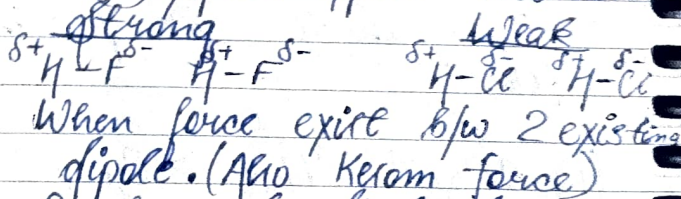
When interactive force exist between any ion and existing dipole, then this is known as ion-dipole interaction.



Hydration phenomena occurs due to this.

Van der Waal force

(a) Dipole-dipole interaction-

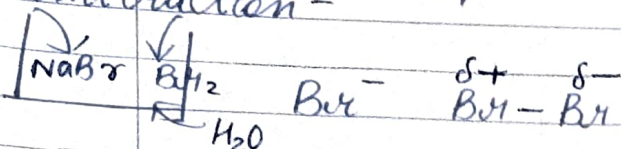


2 type of dipole-dipole -
Strong Weak

When electro-ve atom is F, O & N. When electro-ve atom is other than F, O & N.

$$F \propto \frac{1}{r^3}; E \propto \frac{1}{r^4}$$

(b) Ion induced dipole interaction -

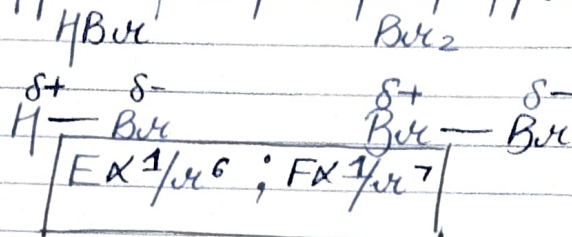


$$\boxed{F \propto \frac{1}{r^5} \quad E \propto \frac{1}{r^4}}$$

The force between ion & induced dipole is known as ion induced dipole interaction.

(b) Dipole-instantaneous induced dipole interaction (Debye force)

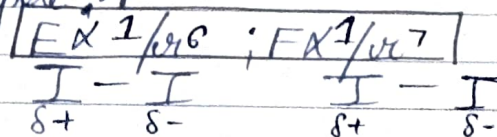
When force exists b/w an existing dipole & ~~induced~~ induced dipole.



(c) Instantaneous induced dipole interaction (London-dispersion force)

L-D force

When force exists b/w two induced dipoles.

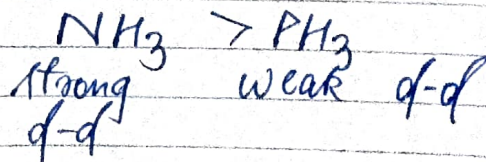
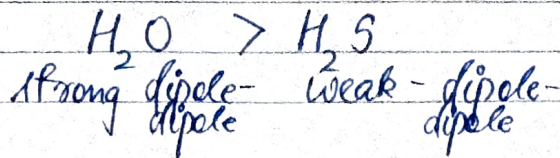
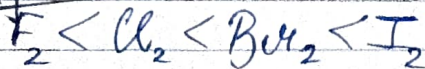


Extent of attraction of above force -

Ion dipole > dipole-dipole > ion-induced dipole > dipole induced dipole > instantaneous induced dipole

Some Important Points:-

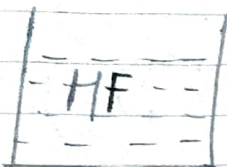
- Higher the molecular mass, greater will be the extent of L-D force & higher will be the boiling point.



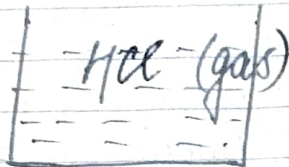
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Hydrogen Bond:-

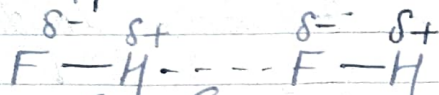
It is a strong dipole-dipole interaction in which electronegative atom is mostly F, O, and N, and sometime Cl and C also.



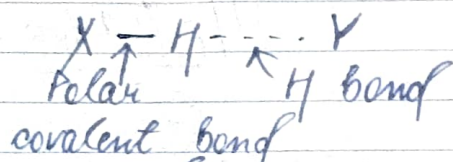
Strong dipole-dipole



Weak dipole-dipole

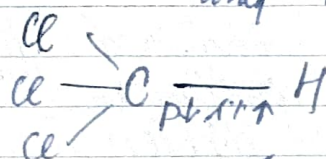


Hydrogen bond is represented by $\text{X} - \text{H} \cdots \text{Y}$ may or may not be same.



Where, X could be F, N, O, CCl_3 , CF_3 , $\text{C} \equiv \text{CH}$ and Y

EN of sp
C is more than N

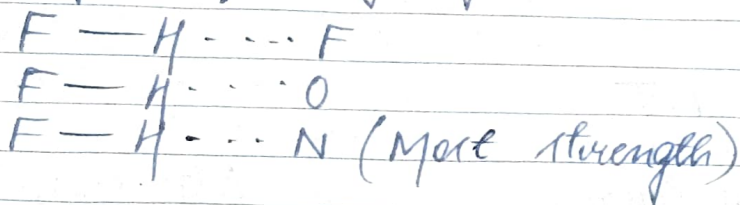


In the given diagram, we can see that due to increased s.p., carbon act as an electronegative atom. In the given diagram, group electronegativity of carbon is defined.

Due to smaller size of hydrogen ~~atom~~ in bonded form & electropositive nature, it have tendency to form multiple hydrogen bond in the given molecules.

• Almost 8-42 kJ of energy is released in the formation of 1 hydrogen bond.

• Higher the electronegativity of x, greater will be the strength of hydrogen bonding.
Lower the electronegativity of y, greater will be the strength of hydrogen bond.



• Due to absence of lp in hydrogen, it forms hydrogen bond more effectively.

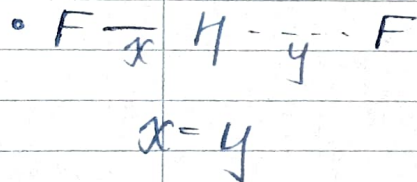
• When X and Y are same, this is known as symmetrical hydrogen bond.

In this case, hydrogen lies in b/w X & Y.

When X and Y are different, it is known as unsymmetrical hydrogen bond.

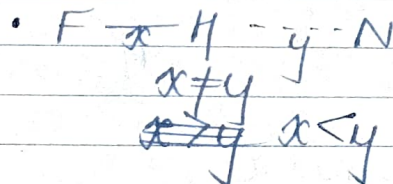
In this case, hydrogen lies near X.

Symmetrical



• Homonuclear hydrogen bond

Unsymmetrical



• Heteronuclear hydrogen bond

Any particular electronegative atom can form more than one hydrogen bond. The number of hydrogen bond formed by any atom depends on following factor —

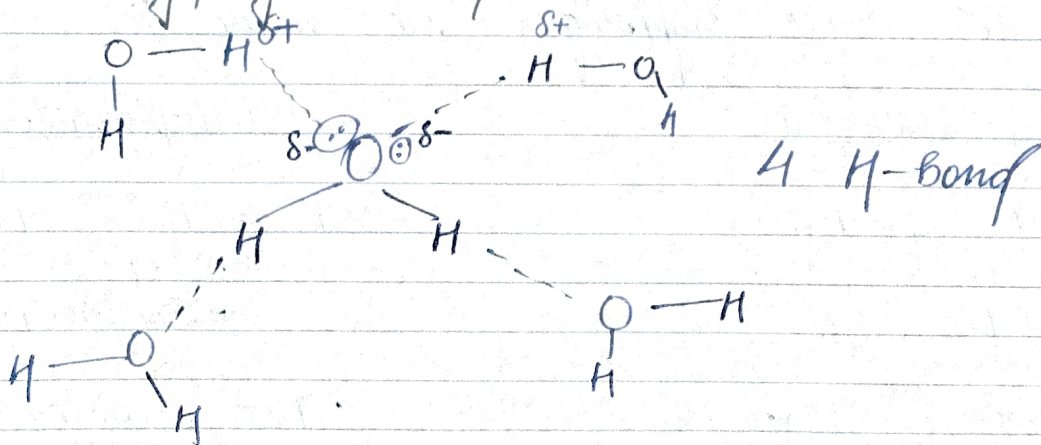
- (1) Number of lp
- (2) Electronegativity of the atom.
- (3) VBT

★ According to VBT,

	Covalency	Max. covalency
Be	2 ($BeCl_2$)	4 ($BeCl_4^{2-}$)
B	3 (BH_3)	4 (BH_4^-)
C	4 (CH_4)	4 (CH_4)
N	3 (NH_3)	4 (NH_4^+)
O	2 (H_2O)	3 (H_3O^+)
F	1 (HF)	1 (HF)

e.g.

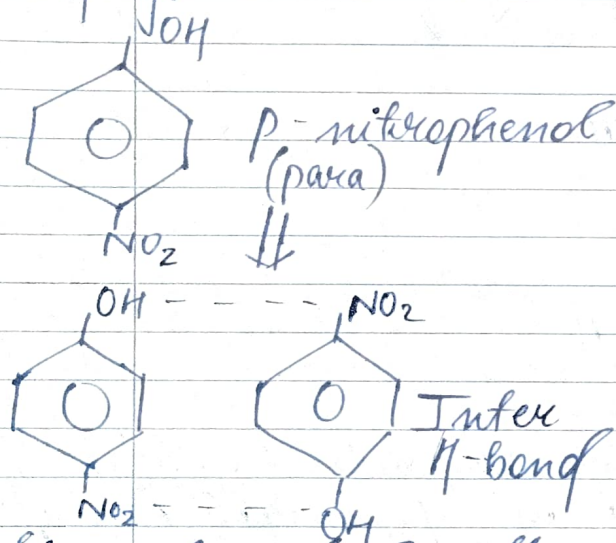
H_2O hydrogen bond



- There are 2 type of hydrogen bonding-
- Intermolecular hydrogen bond
 - Intramolecular H-bond

Intermolecular H-bond

- When H-bonding take place b/w 2 different molecule, then this phenomena is known as inter-molecular hydrogen bonding.

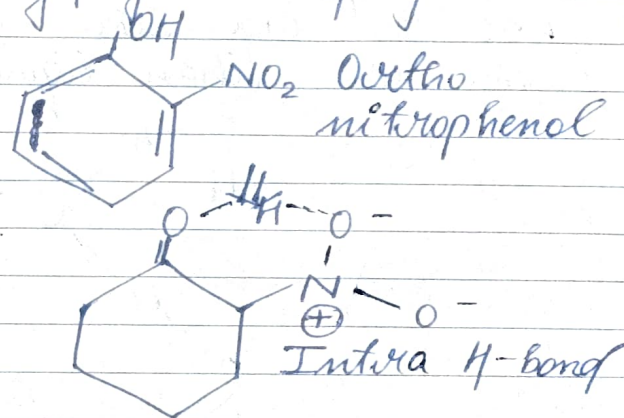


- Since 1 molecule attracted towards another molecule due to H-bonding, so net attractive force dominate which increases the boiling point.

It have ~~more~~ less vapour

Intramolecular H-bond

- When H-bonding take place within the molecule, then this phenomena is known as intramolecular hydrogen bonding.



- H-bonding take place within the molecule, so 1 molecule does not have tendency to combine with another molecule. So, it have escaping tendency & have lower boiling point.

Comparatively, it have more

pressure, comparatively.

vapour pressure.

• Less volatile

• More volatile

★ Oxygen form 2 hydrogen bond.

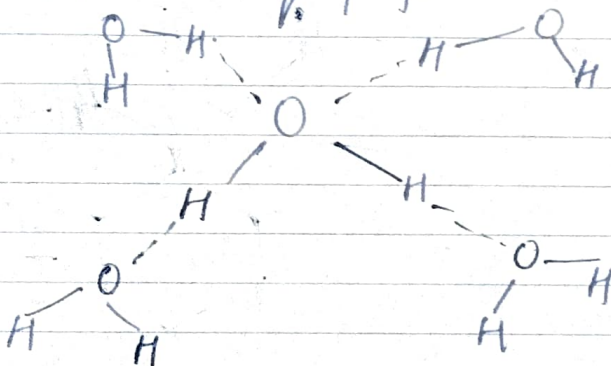
Fluorine form 1 and Nitrogen also 1 H-bond.

Hydrogen Bond in some important molecule:-

(a) H_2O -

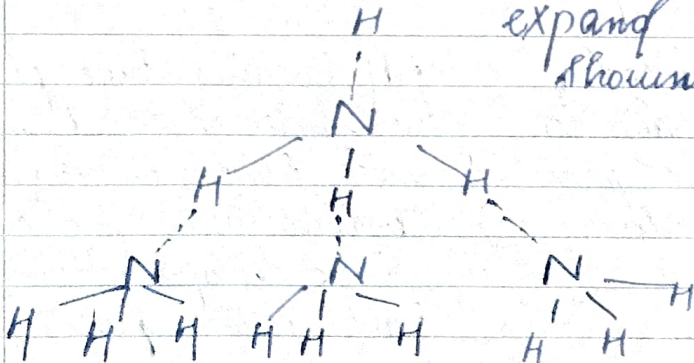
Due to H-bond, H_2O molecule form cage-like structure when present in bulk.

Due to cage-like structure, density of H_2O in solid form become less than liquid form.

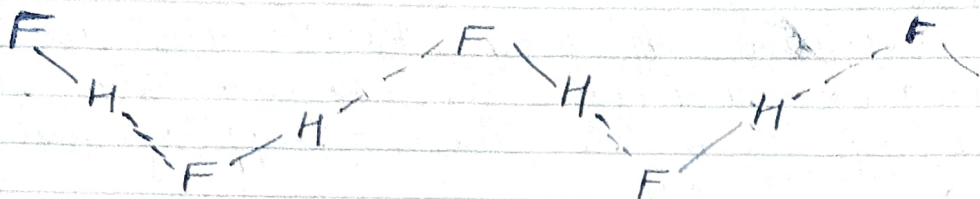


(b) NH_3 -

When ammonia solidify, it expand in pyramidal shape, as shown.



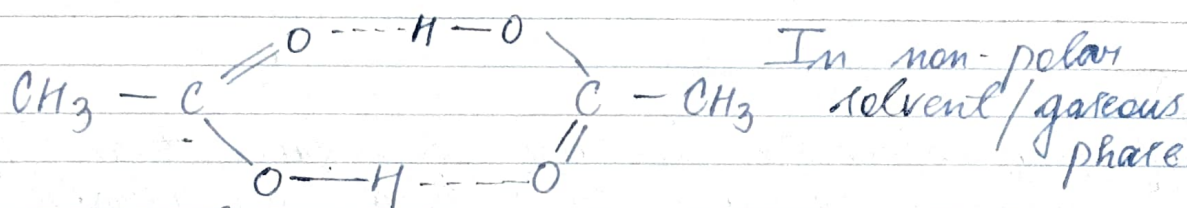
(C) HF -



~~The~~ Due to lp present in Fluorine, lp-lp repulsion will take place. To minimise the repulsion, it exist as shown.

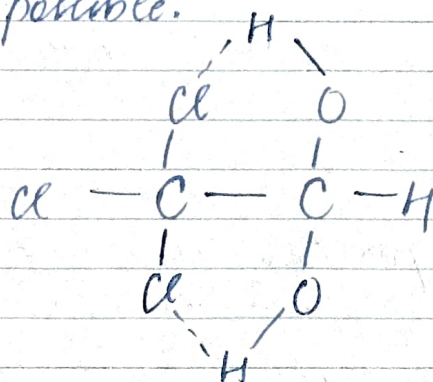
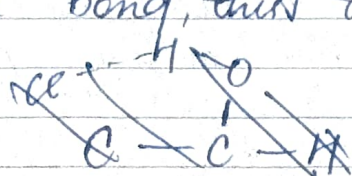
(d) CH_3COOH -

Due to H-bond, carboxylic acid, in general, exist in dimer form in gaseous phase, or in non-polar solvent. But in polar solvent, it exist in ionised form.



(e) Chloral Hydrate -

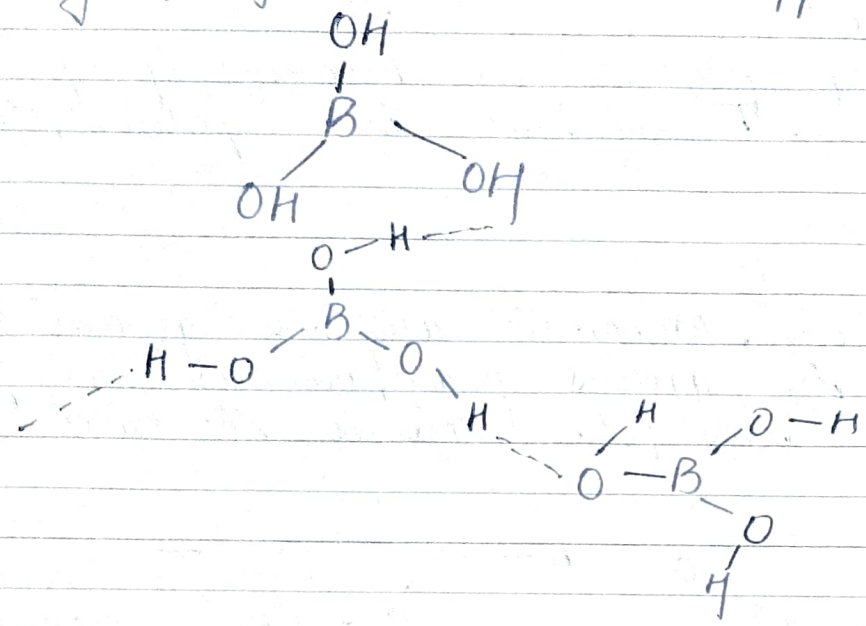
In sp^3 carbon, 2 hydroxy group is not present, in general, due to NBEPR. But, in chloral hydrate, due to intramolecular hydrogen bond, this is possible.



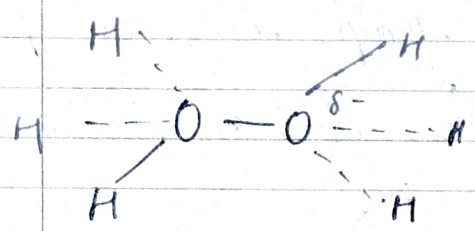
$\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$

(f) Boric acid -
Due to extensive H-bond, Boric acid forms 2-D layer structure and exist in layered form. Due to this layered form, it has slippery nature.

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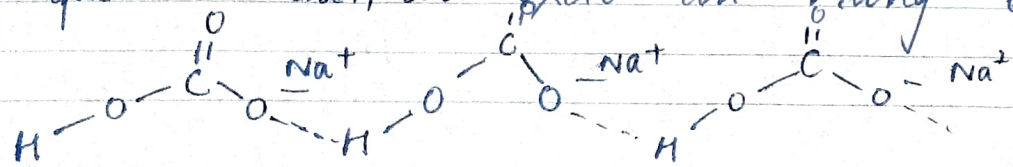
(g) H_2O_2 -
H-bond strength in H_2O_2 is weaker than H-bond strength in H_2O , but number of H-bond in peroxide is more than water.



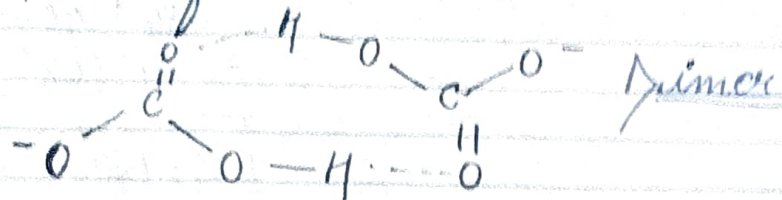
Boiling point of peroxide is more than water.

★ No. of H-bond is deciding factor in boiling point.

(h) $NaHCO_3$ -
 HCO_3^- ion present in the salt forms hydrogen bond & due to this, it exist in long chain.



For this reason, NaHCO_3 exists in solid crystal.
 In KHCO_3 , ~~ion~~ HCO_3^- ion does not form long chain but it exists in dimer form.



★ H_2SO_4 , H_3PO_4 , HNO_3 and H_2O_2 is more viscous liquid than water due to excess number of H-bond.

