

Subject :- Inorganic Chemistry - II

Subject Code :-

Semester :- II
Unit - I

Chemical * Bonding

(*) Methods of linear combination of atomic orbitals [LCAO]

→ Consider two atoms A and B which have atomic orbitals described by the wave function $\psi_{(A)}$ and $\psi_{(B)}$.

→ If the electron clouds of these two atoms overlap when the atoms approach, then the wave function for the molecule (molecular orbital $\psi_{(AB)}$) can be obtained by a LCAO;

$$\psi_{(AB)} = N (C_1 \psi_{(A)} + C_2 \psi_{(B)})$$

where N : Normalizing constant chosen to ensure that the probability of finding an electron in whole of the space is unity.

C_1, C_2 = constant chosen to give a minimum energy for $\psi_{(AB)}$.

→ So, the probability density for the combination of two atoms as above is related to the wave function squared:

$$\therefore \psi_{(AB)}^2 = [C_1^2 \psi_{(A)}^2 + 2 C_1 C_2 \psi_{(A)} \psi_{(B)} + C_2^2 \psi_{(B)}^2]$$

where; $\rightarrow C_1^2 \Psi_{(A)}^2$ is related to the probability of finding an electron on atom A if A is an isolated atom.

$\rightarrow C_2^2 \Psi_{(B)}^2$ is related to the probability of finding an electron on atom B if B is an isolated atom.

$\rightarrow 2 C_1 C_2 \Psi_{(A)} \Psi_{(B)}$ becomes increasingly important as the overlap between the two atomic orbitals increases, and this term is called overlap integral.

Rules for Linear Combination of Atomic Orbitals (LCAO)

\rightarrow In deciding which atomic orbitals may be combined to form molecular orbitals, three rules must be considered:-

(i) The atomic orbitals must be roughly the same energy. This is important when considering overlap between two different types of atoms.
i.e. 1s-1s, 2s-2s, 2p-2p.

(ii) The orbitals must overlap one another as much as possible. This implies that the atoms must be close enough for effective overlap.

(iii) In order to produce bonding and antibonding molecular orbitals, either the symmetry of the two atomic orbitals must remain unchanged when rotated about the intermolecular line. i.e. Same symmetry about the molecular axis.

* S-S combination of orbitals :-

→ Suppose the atoms A and B are hydrogen atom and the wave function ψ_A and ψ_B describe the 1s atomic orbitals on the two hydrogen atoms.

→ Two combinations of wave-functions are possible:

(a) Where the signs of the two wave functions are the same

(b) Where the signs of the wave functions are the different.

→ If one of the wave function ψ_A is arbitrarily assigned a \oplus ve sign, the other may be either \oplus ve or \ominus ve.

→ Wave functions which have the same sign may be regarded as waves that are in phase, which when combined add up to give a larger resultant wave by constructive interference.

→ Similarly, wave functions of different signs correspond to waves that are completely out of phase and which cancel each other by destructive interference.

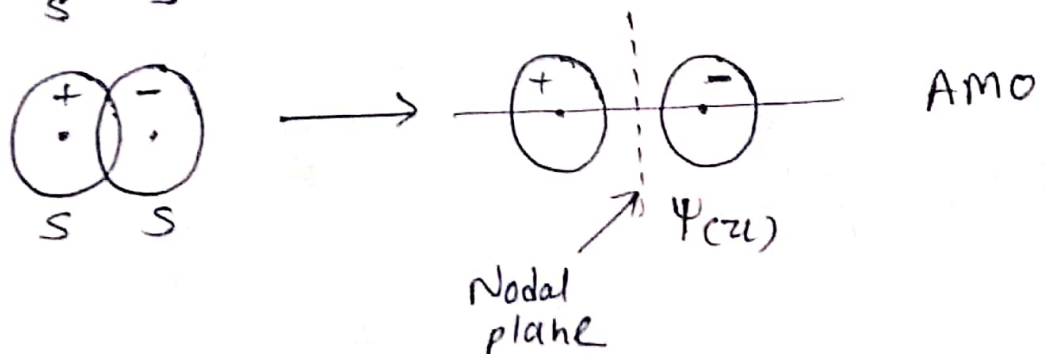
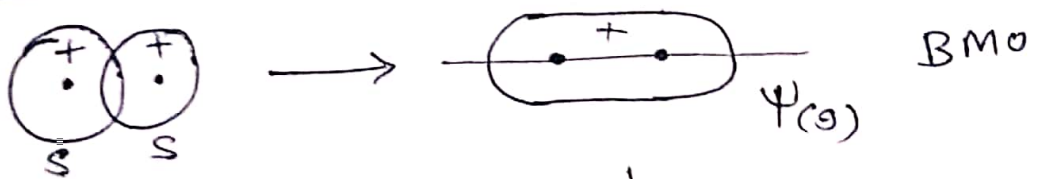


Fig (1). S-S combination

→ The two combinations are :

$$\Psi_{(g)} = N \{ \Psi_A + \Psi_B \}$$

$$\Psi_{(u)} = N \{ \Psi_A + (-\Psi_B) \}$$

→ When a pair of atomic orbitals Ψ_A and Ψ_B combine, they give rise to a pair of molecular orbitals $\Psi_{(g)}$ and $\Psi_{(u)}$.

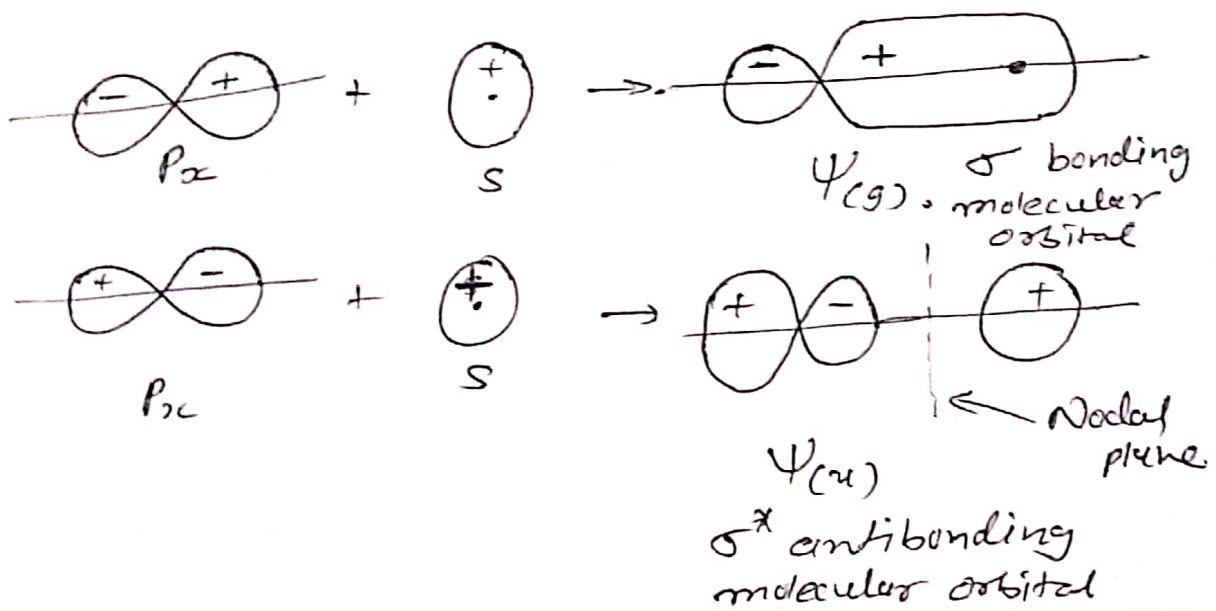
→ The function $\Psi_{(g)}$ leads to increased electron density in between the nuclei, and is therefore a bonding molecular orbital. It is lower in energy than the original atomic orbitals (Fig. (1))

→ Conversely, $\Psi_{(u)}$ results in two lobes of opposite sign cancelling and hence giving zero electron density in between the nuclei. This is an antibonding molecular orbital which is higher in energy than the original atomic orbitals. (Fig. (1))

→ The energy of the bonding-molecular orbital is lower than that of the atomic orbital by an amount ΔE . This is known as the stabilization energy.

* S-p combination of orbitals:-

→

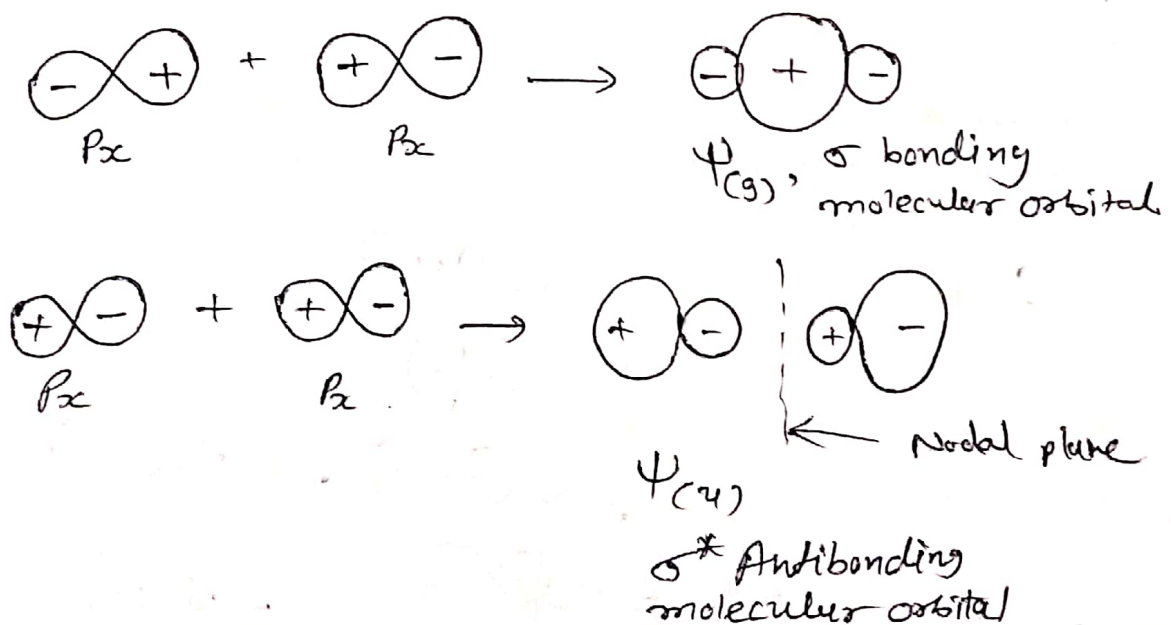


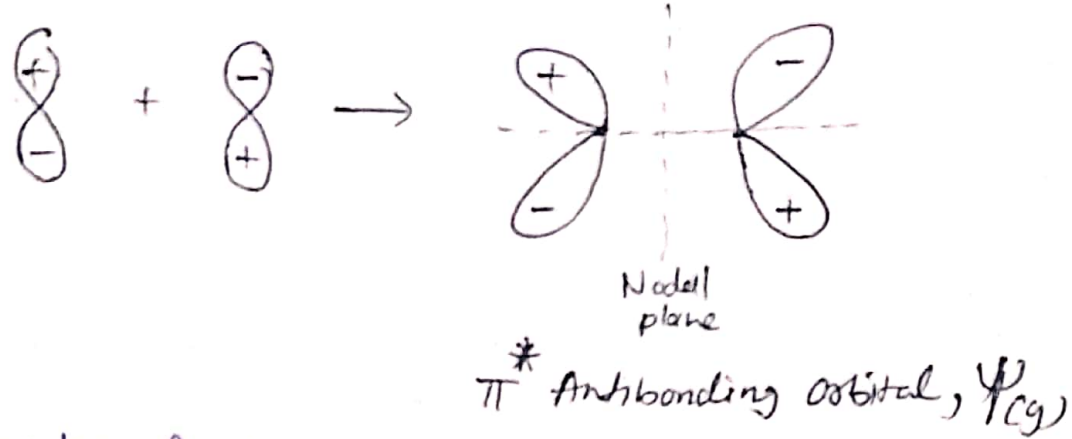
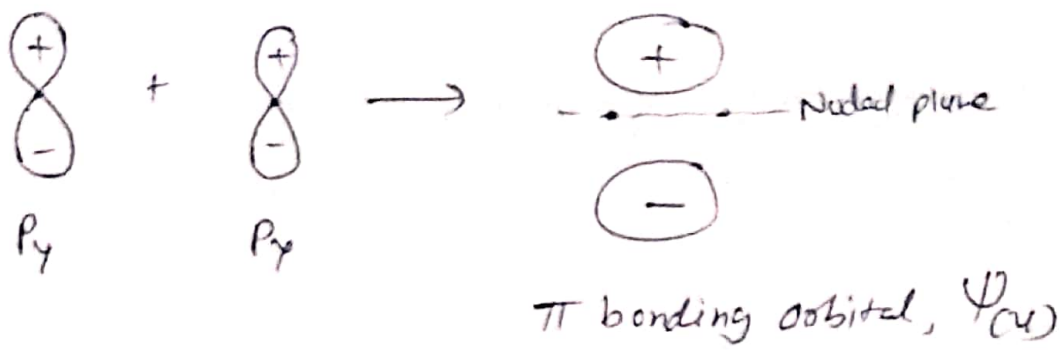
→ An s orbital may combine with a p-orbital provided that the lobes of the p orbital are pointing along the axis joining the nuclei.

→ When the lobes which overlap have the same sign this results in a bonding MO with an increased electron density between the nuclei.

→ When the overlapping lobes have opposite signs this gives an antibonding MO with a reduced electron density in between the nuclei.

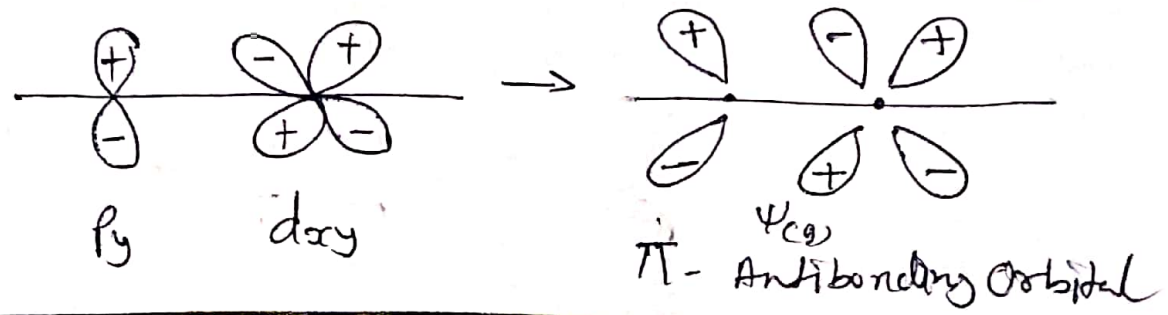
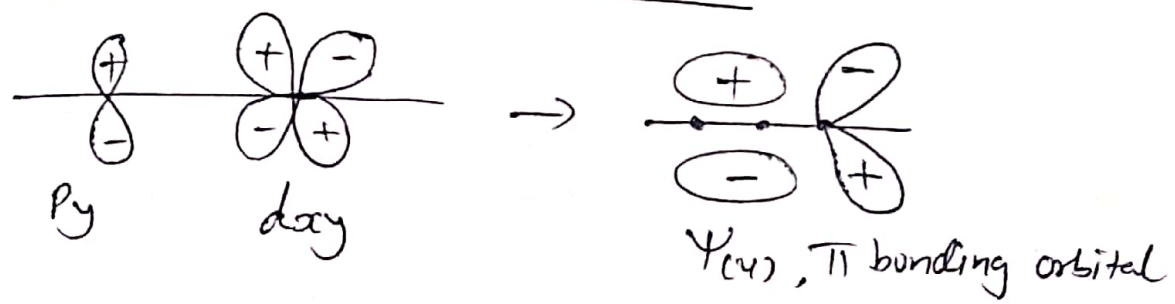
* P-p combinations of orbitals.





- Consider first the combination of two p orbitals which both have lobes pointing along the axis joining the nuclei.
- Both a bonding MO and antibonding MO are produced.
- Next consider the combination of two orbitals which both have lobes perpendicular to the axis joining the nucleus.
- Lateral overlap of orbitals will result in π bonding and π antibonding MO being produced.

* p-d combination of orbitals:-



* VSEPR [Valance Shell Electron Pair Repulsion] Theory.

→ The basic idea of this theory is that bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as far apart as possible.

~~→ Postulates~~

→ This theory gives information about molecular geometry.

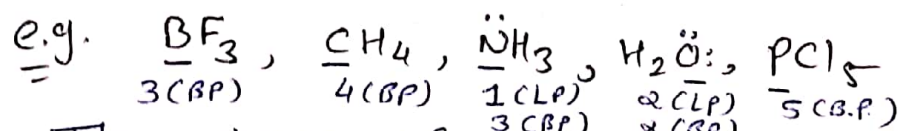
→ The basic concept of the theory was suggested by Sidgwick and Powell. (1940.)

→ It provides useful ideas for predicting shape and geometries of molecule.

→ Gillespie and Nyholm develop this concept as VSEPR Theory.

→ Postulates of VSEPR Theory:-

(1) For polyatomic molecules containing three or more atoms, one of the atoms is called the central atom.



(2) The shape of the molecule depends upon the number of valence shell electron pairs [Bonded or non-bonded] around the central atom.

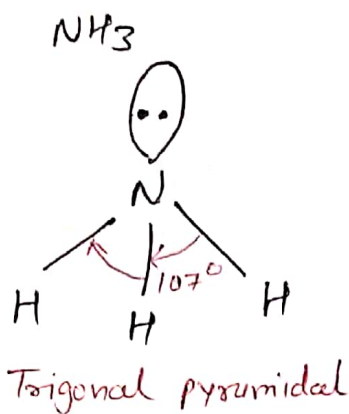
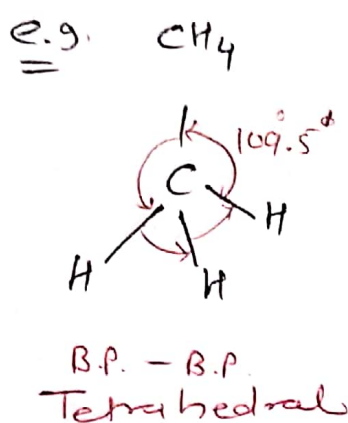
(3) If the central atom is surrounded by bond pairs only, it gives symmetrical shape to the molecules.

Sr. No.	Hybridization	Shape	Bond Angle	Example
1	SP	Linear	180°	CO ₂ , BeCl ₂
2	SP ²	Trigonal planar	120°	BF ₃
3	SP ³	Tetrahedral	109.5°	CH ₄ , SO ₄ ⁻²
4	SP ³ d	Trigonal bipyramidal	90°, 120°	PCl ₅
5	SP ³ d ²	Octahedral	90°	SF ₆
6	SP ³ d ³	Pentagonal bipyramidal	72°, 90°	IF ₇

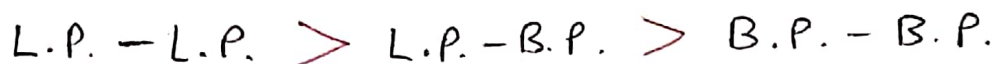
(4) If the central atom is surrounded by lone pairs as well as bond pairs of electrons, then molecule has distorted (irregular) geometry.

Types of electron pairs in central atom		Shape	Example
Lone pair	Bond pair		
1	2	Bent	SO ₂
1	3	Trigonal pyramidal	NH ₃
2	2	Bent	H ₂ O
1	4	See-saw	SF ₄
2	3	T-shaped	ClF ₃

(5) The position of electron pairs in space around central atom are such that minimise repulsion and thus maximize distance between them.



(6) The relative order of repulsion between electron pairs is as follow.



- Repulsive forces decrease sharply with increasing bond angle between the electron pairs.
- They are strong at 90° , weaker at 120° and weakest at 180° .

⇒ Limitations of VSEPR Theory :-

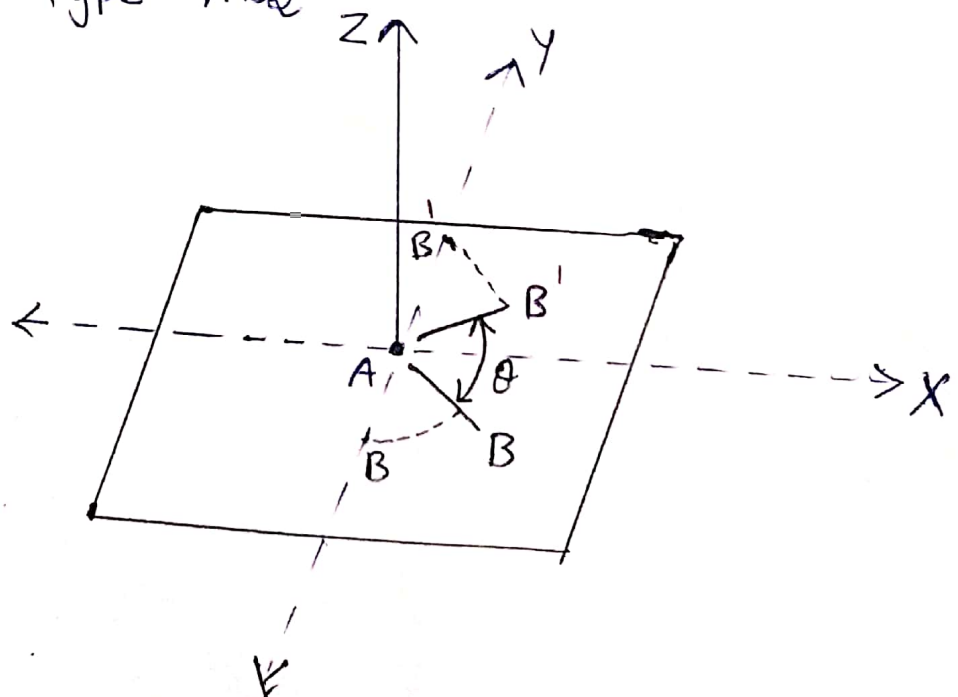
- It is applicable to only simple covalent molecule and is not useful for ionic compound.
- It does not predict the exact bond angles in molecule such as H_2O and NH_3 having distorted geometries.
- It does not make any distinction between the electrons present in different type of orbital (s, p, d, f) of the valance shell.
- It does not explain the shape of molecule or ions which have extensive delocalized π -electron system.

* Walsh diagram :-

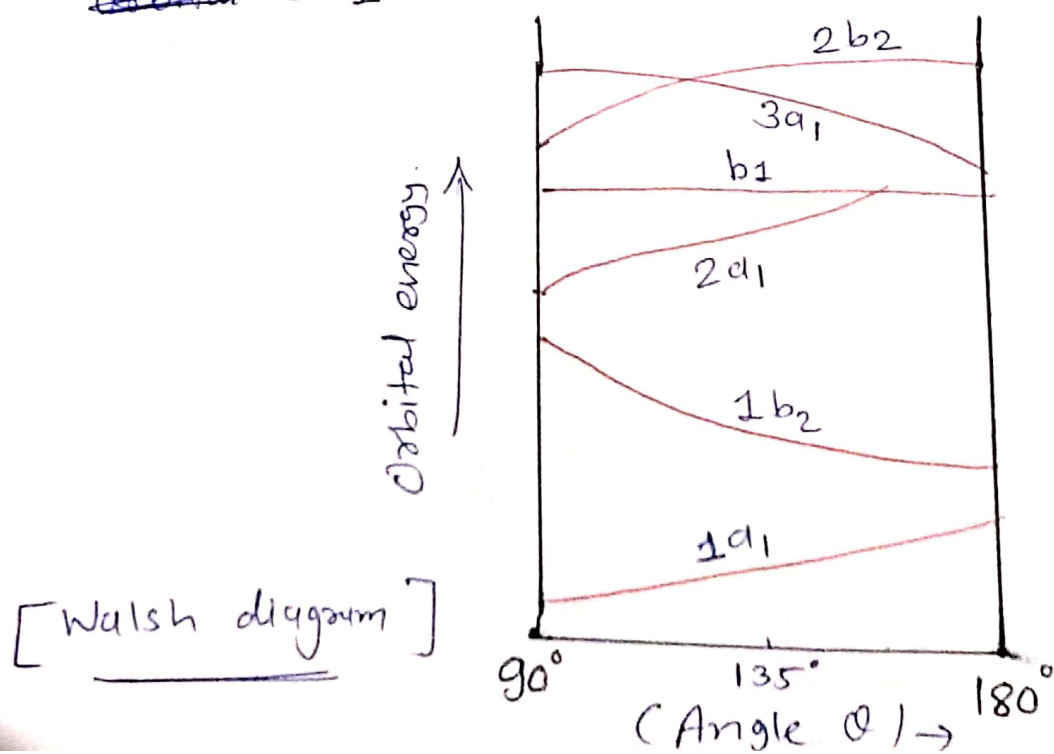
- All the systems want to be in a stable state, and the stable state is one in which it has the minimum possible energy.
- The VSEPR theory considered that the most stable configuration of a molecule is one in which repulsive forces between the valance electron pair is minimum.
- The MOT (Molecular orbital theory) considers that the stable geometry of a molecule can be determined on the basis of the energy of molecular orbitals formed as a result of LCAO.
- In 1953, A.D. Walsh proposed a simple approach to determine the geometry of a molecule considering and calculating the energies of molecular orbitals of the molecule.
- The Walsh's rules which related to the shape of triatomic molecules to their electronic structure. It is used to calculate energies of bond angles.

→ Triatomic molecules :-

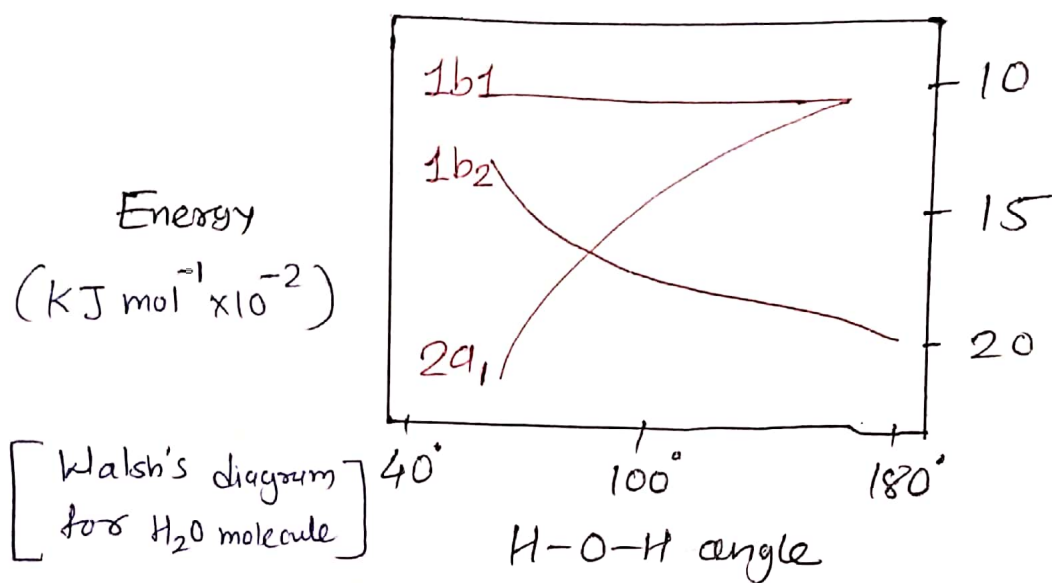
- Let us consider a triatomic molecule of the type AB_2 .



- Co-ordinate axes used for linear and bent AB_2 molecules.
- The AB_2 molecule has ~~C_{2v}~~ C_{2v} symmetry when it is bent and ~~D_{2h}~~ D_{2h} symmetry when the molecule is linear.
- The atom A of the molecule AB_2 will be supposed to have only s, p_x, p_y and p_z orbitals in its valence shell, and each B atom has only a single orbital which form σ bond with A.
- In the linear configuration p_x^A and p_z^A are equivalent non-bonding orbitals labelled $2a_1$, and b_1 respectively.
- The orbitals s^A and p_y^A interact with σ_1^B and σ_2^B , σ orbitals on the B atoms, to form one very strongly bonding orbital, $1a_1$, one less strongly bonding orbital, $1b_2$, one less strongly bonding ~~orbital~~ $3a_1$ and $3b_2$.



- From this diagram, it is seen that an AB_2 molecule is more stable when linear than when bent.
- The $1b_2$ orbital drops steadily in energy from $\theta = 90^\circ$ to 180° , while the energy of the $1a_1$ orbital is fairly insensitive to angle.
- The H_2O molecule :-



- A correlation diagram calculated specially for H_2O as shown in fig. The general purpose diagram pertains to a situation in which there is only a small energy difference between the ns and np orbitals of the central atom.
- In the diagram calculated expressly for H_2O the lowest level's is practically pure $2s$ and its energy is essentially constant for all the angles.
- It can be determined from this diagram that the energy is minimized at an angle of 106° , essentially in accord with the experimental value of 104.5° .

⇒ For penta-atomic molecules:-

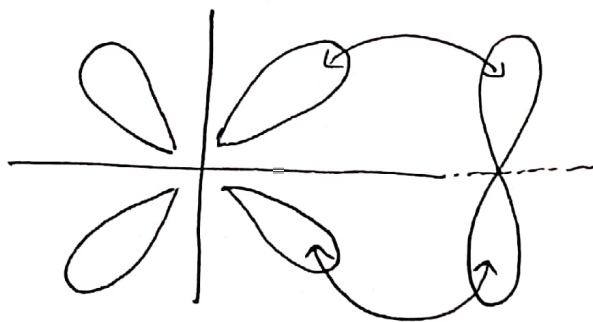
- For penta-atomic molecules example of CH_4 and SF_6 may be taken for consideration.
- For these molecules, two geometries are possible:
: One a symmetrical tetrahedral and the other, a distorted tetrahedral geometry.

→ CH_4 - molecule:-

- Methane CH_4 , has eight valance electrons. During bonding, four orbitals [$2s$ & $2p$] of carbon, and one [$1s$] orbital of each four hydrogen atoms take part.
- Overlapping of these 8 orbitals, eight molecular orbitals are formed, the four bonding and four antibonding.
- In the tetrahedral geometry due to overlapping with the orbitals of hydrogen atom, the energy of orbital is reduced.
- In contrast, in the distorted geometry, comparatively less overlapping of orbitals with the hydrogen orbitals, the energy of molecular orbitals increases.
- Thus, the geometry of CH_4 molecule is symmetrical tetrahedral, rather than a distorted tetrahedral.

* $d\pi - p\pi$ Bonds :-

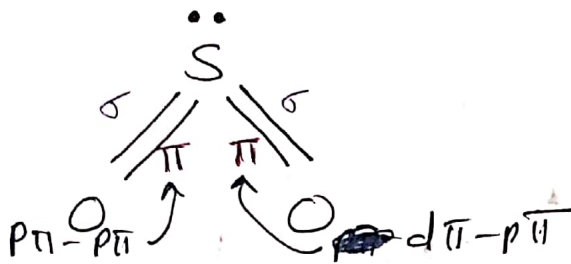
- IF there is bonding between two atoms where one atom is having one vacant orbital and another is having one lone pair of electrons, then this electron pair is donated to that respective vacant orbital. This type of bonding is called $p\pi - p\pi$ or $p\pi - d\pi$ depending on the orbital to which the electron pair is donated.
- Generally $d\pi - p\pi$ bonds are formed by the elements of 1st period & 2nd period.
- We have 5 d-orbitals, but only 3 of them formed $d\pi - p\pi$ bond.
- In order to form π bond, the d orbitals selected are d_{xy} , d_{yz} , d_{zx} .
- In these d orbitals, the probability of finding an electron is at an angle of 45° with their respective co-ordinate axis.



d -orbital p -orbital

- d-orbital undergoes side wise overlapping & parallel overlapping with the p-orbital to form $d\pi - p\pi$ bond.

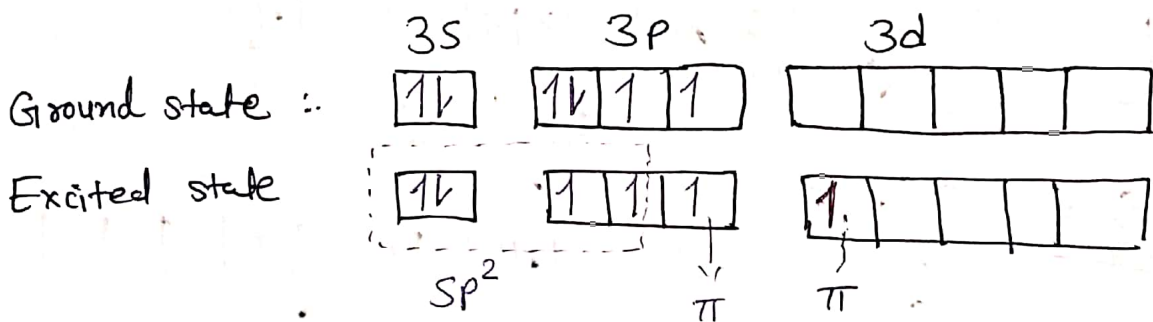
→ Example: ① SO_2



- In SO_2 , we have 2 σ bonds & 2- π bonds.
- We have to identify the nature of π bond
- First we should know about the hybridization in sulphur.

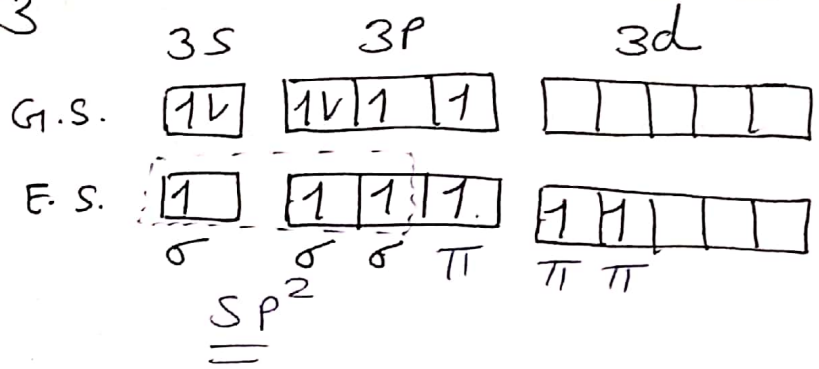
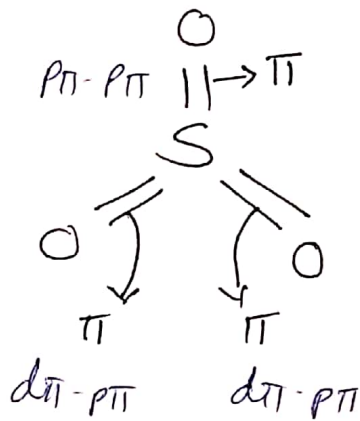
σ bond pair + Lone pair gives hybridization

For Sulphur: $2 + 1 = 3 \rightarrow \text{SP}^2$

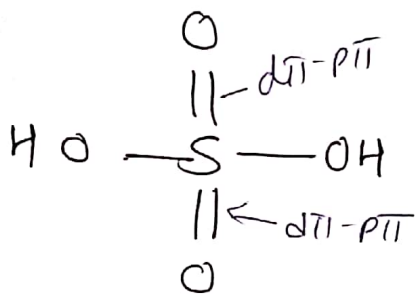


- The first π bond is formed by the unhybridized p-orbital of the sulphur, with the unhybridized p-orbital of oxygen. So it is known as $\text{p}\pi\text{-p}\pi$ bond.
- The second π -bond is formed by the unhybridized d-orbital of the sulphur with the unhybridized p-orbital of oxygen. So it is known as $\text{d}\pi\text{-p}\pi$ bond.

example - (2) :- SO_3



(3) H_2SO_4



Hybridization : sp^3

= The hybridization is sp^3 , so all the p-orbitals participating in hybridization and no p-orbital left unhybridized. It means all π bonds are $d\pi$ - $p\pi$ bonds.

* Bent Rule & Energetics of hybridization.

- Bent rule may be stated as follows :-

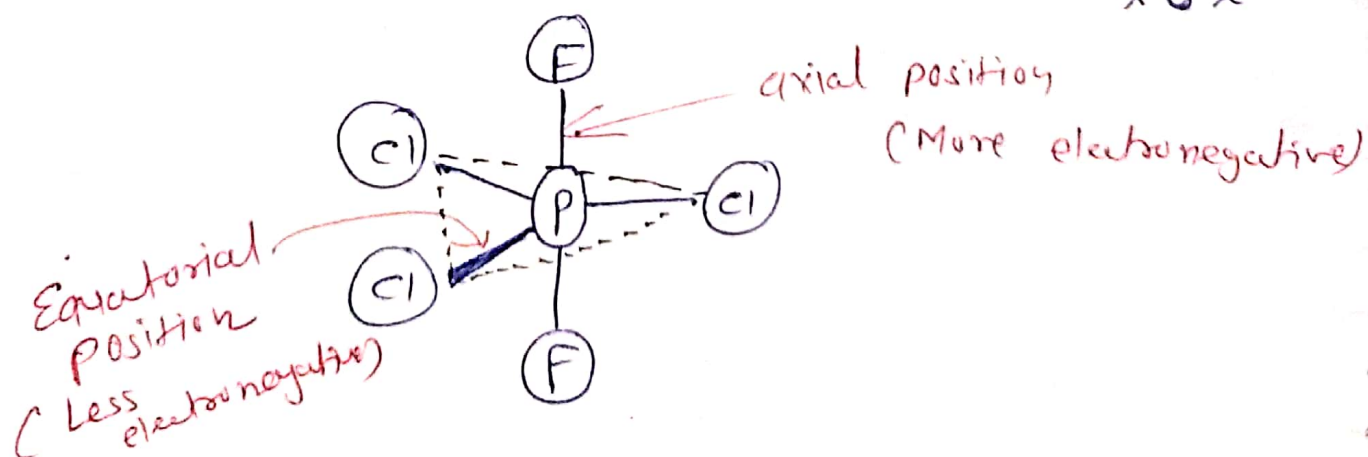
" More electronegative constituents prefer hybrid orbital having less 's' character and more electropositive substituents 'prefer' hybrid orbitals having more 's' character.

- s-character means small bond angle.

- Example: In fluoromethanes, CH_2F_2 , the F-C-F bond angle is less than 109.5° , indicating less than 25% s character, but the H-C-H bond angle is larger and C-H bond has more s character.
- The atomic s character tends to concentrate in orbitals that are directly towards electropositive group and ~~atomic~~ atomic p character tends to concentrate in orbitals that are directed towards electronegative groups.
- s orbitals have low energy than p orbital.
- More s character decrease the energy of bonding orbitals and hence they have shaped more like a s-orbital.
- More p character increase the energy of bonding orbitals and hence they have shaped more like a p-orbitals.
- s orbitals are closer to the nucleus, so it stabilize the lone pair. Due to more s character less repulsion and less hybridisation energy.
- The most stable arrangement would be to utilize pure p orbitals for bonding and letting the lone pair into the pure s orbital.

⇒ Energetics of Hybridization:-

- ① According to hybridization model, bond directions are determined by a set of hybrid orbitals on the central atom which are used to form bonds to the ligand atoms and to hold unshared pairs.
- Thus AB_2 molecules are linear due to the use of linear sp hybrid orbitals.
- AB_2 molecule should be equilaterally triangular, while AB_2E molecule should be angular, due to use of trigonal sp^2 hybrids.
- For AB_4 , AB_3E and AB_2E_2 molecule should be tetrahedral, pyramidal and angular.
- For AB_5 , AB_4E , AB_3E_2 , AB_2E_3 molecules the hybrid must now include orbitals in their formation.
- The hybrid orbital used must be of the sp^3d^2 leading to trigonal bipyramidal geometry.
- For example: sp^3d hybridisation in PCl_xF_{5-x}



- In sp^3d Hybridisation one s, three p and one d orbitals ~~are~~ form 5 sp^3d hybridised orbital.
- All these 5 hybridised orbitals are not of the same type, so they can be divided into two non-equivalent sets.
- The first set is known as equatorial set of orbitals. It is formed from one s, one p_x and one p_y orbitals.
- The second set is known as axial set. It is formed from one p_z and d orbitals.
- It is experimentally observed that the more electronegative substituents occupies the axial position. (as it has less s-character) i.e. F and less electronegative substituents is equatorially situated that is Cl.

→ Less bond angle in CH_2F_2 .

- In case of sp^3 hybridisation, CH_4 or CCl_4 formed tetrahedral geometry with bond angle 109.5° .
- But in the case of CH_2F_2 , the F-C-F bond angle is less, this explained on the basis of Bent's rule.

- F is more electronegative than H, so F-C-F s-character is less than 25%. while H-C-H, It is more than 25%. Due to less s-character bond angle is less in CH_2F_2 .

Lone pair \rightarrow Equatorial position

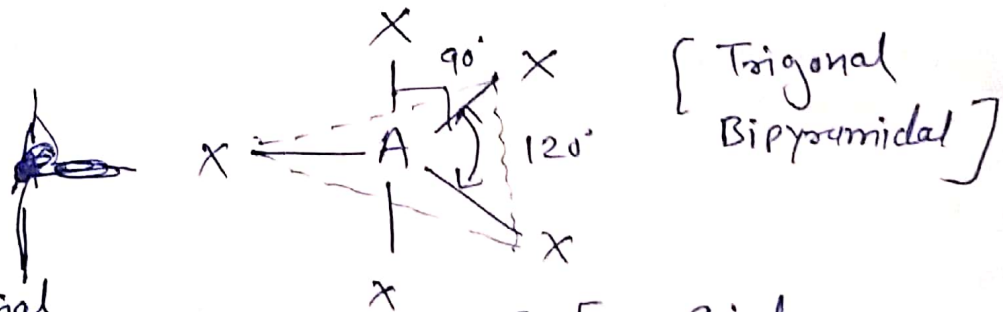
high electro-
negative \rightarrow axial position

$$sp^3d = sp^2 + pd$$

\downarrow \downarrow
 Equatorial axial
 (More-s character) (Less-s character)

- For Calculating % s-character;

$$\cos \theta = \frac{s}{s-1}, \text{ where } \theta \text{ is bond angle.}$$



\rightarrow Equatorial

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

$$\cos 120 = \frac{s}{s-1}$$

$$-\frac{1}{2} = \frac{s}{s-1}$$

$$2s = 1-s$$

$$3s = 1$$

$$s = 1/3 \therefore s = 33.3\%$$

\rightarrow For axial

$$\cos 90 = \frac{s}{s-1}$$

$$0 = \frac{s}{s-1}$$

$$\boxed{s = 0} \text{ 0\%}$$

% s-character \propto closeness to the molecule

" " \propto Electronegativity

" " \propto Bulkiness

% p-character \propto length of thinness.

\Rightarrow Apicophilicity:-

" The tendency of more electronegative substituents to seek out the low electronegativity $Pz d_z^3$ apical orbital in tetragonal bipyramidal structure is often termed "apicophilicity".

* Some simple reactions of covalently bonded molecules.

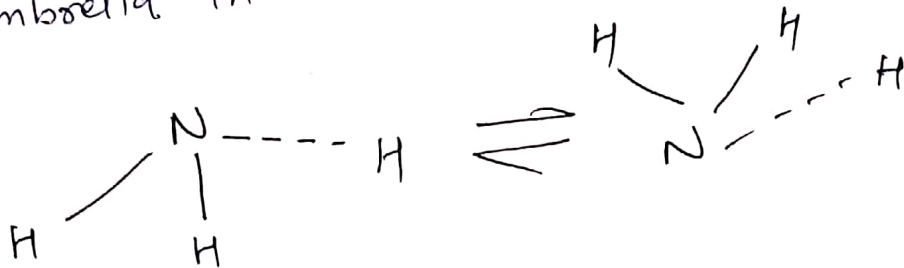
\rightarrow One of the major differences between organic and inorganic chemistry is the relative emphasis and reactivity.

\rightarrow Structural organic chemistry is relatively simple, as it is based on diagonal, trigonal or tetrahedral carbon.

\rightarrow Few simple reactions of covalent molecules will be discussed here

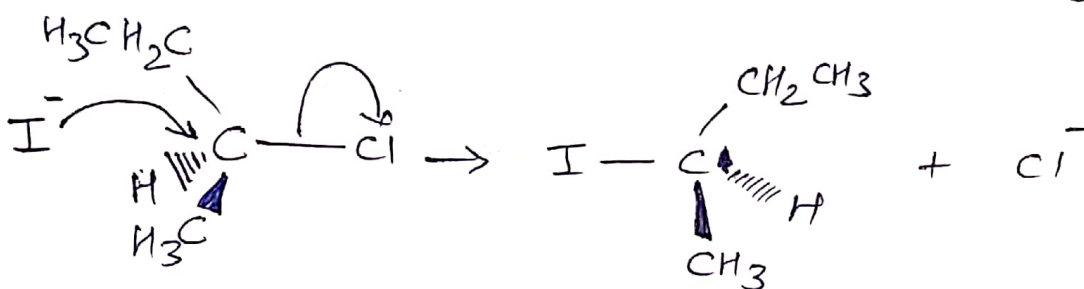
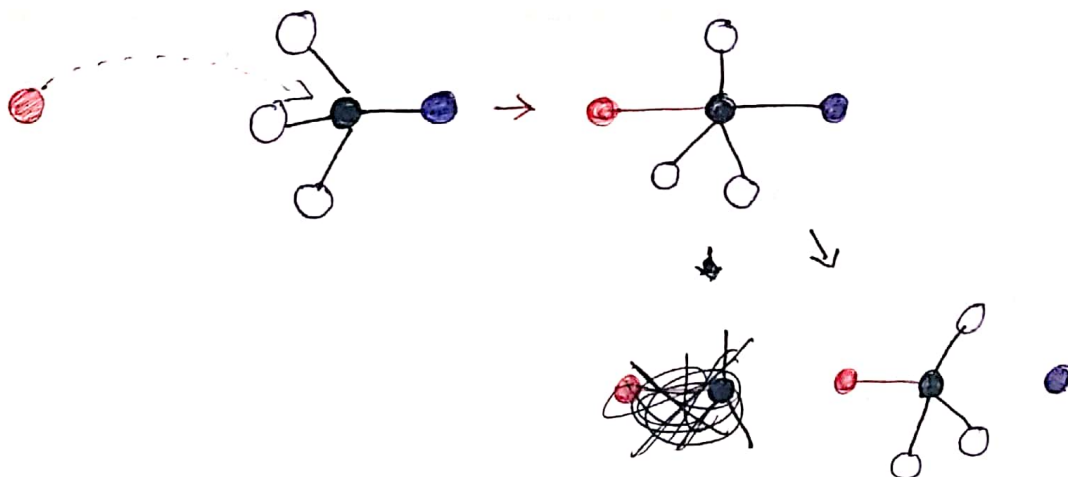
① Atomic Inversion :-

- The simplest reaction is seen in a molecule of Ammonia. This can undergo the simple inversion of the hydrogen atoms about the nitrogen atom.
- This is analogous to the inversion of an umbrella in a high wind.



- ~~Consider the~~ Atomic inversion reaction is defined as, the spatial rearrangement of atoms or group of atoms in a dissymmetric molecule, giving rise to a product with a molecular configuration that is a mirror image of the original molecule.
- The reaction is usually one in which an atom or a group of atom in the molecule is replaced by another atom or group. The phenomenon of inversion is also known as Walden inversion.

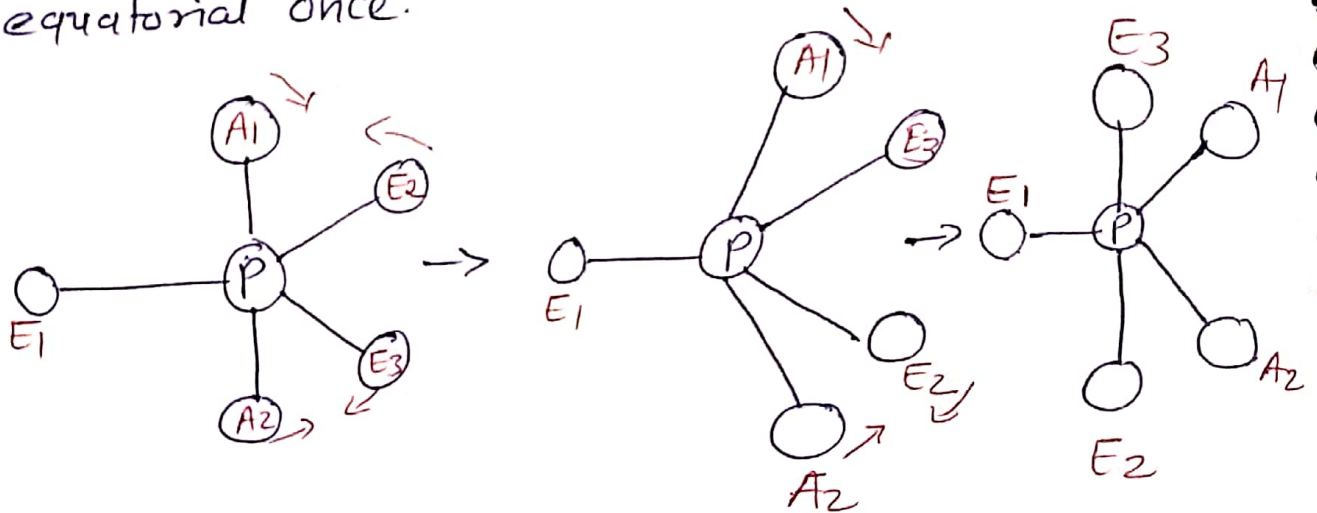
example :



- A molecule can form two enantiomers around a chiral centre, the walden inversion converts the configuration of the molecule. From one enantiomer to the other.
- For example, in an S_N2 reaction, walden inversion occurs at a tetrahedral carbon atom. It can be visualised by imagining an umbrella turned inside-out.
- In the walden inversion, the backside attack by the nucleophile in an S_N2 mech. gives rise to a product whose configuration is opposite to the reactant.

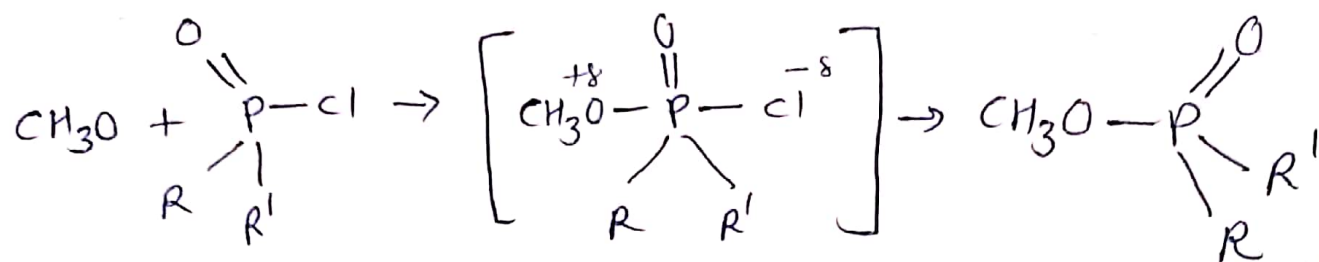
⇒ (2) Berry pseudo rotation:-

- It is a type of vibration causing molecules (inter-molecular force) of certain geometries to isomerize by exchanging the two axial ligands for two of the equatorial ones.



- The process results in complete scrambling of fluorine atoms at the equatorial and axial position in phosphorus pentafluoride.
- If all of the substituents are the same as in PF_5 , the two trigonal bipyramidal arrangements are related to each other by simple rotation. The entire process is called a Berry pseudorotation.
- The mechanism for this exchange is believed to take place through conversion of the ground state and ~~back~~ trigonal bipyramidal into a square pyramidal transition state.

→ (3) Nucleophilic Substitution



- The simplest $\text{S}_{\text{N}}2$ path for nucleophilic displacement may be illustrated by solvolysis of a chlorodialkylphosphine oxide.
- We would expect the $\text{S}_{\text{N}}2$ to proceed with inversion of configuration of the phosphorus atom. This is observed generally when the entering and leaving groups are highly electronegative and is thus favorably disposed at the axial positions, and when the leaving group is one that is easily displaced.
- In contrast, in some cases when the leaving group is poor one, it appears as though front side attack takes place because there is a retention of configuration.

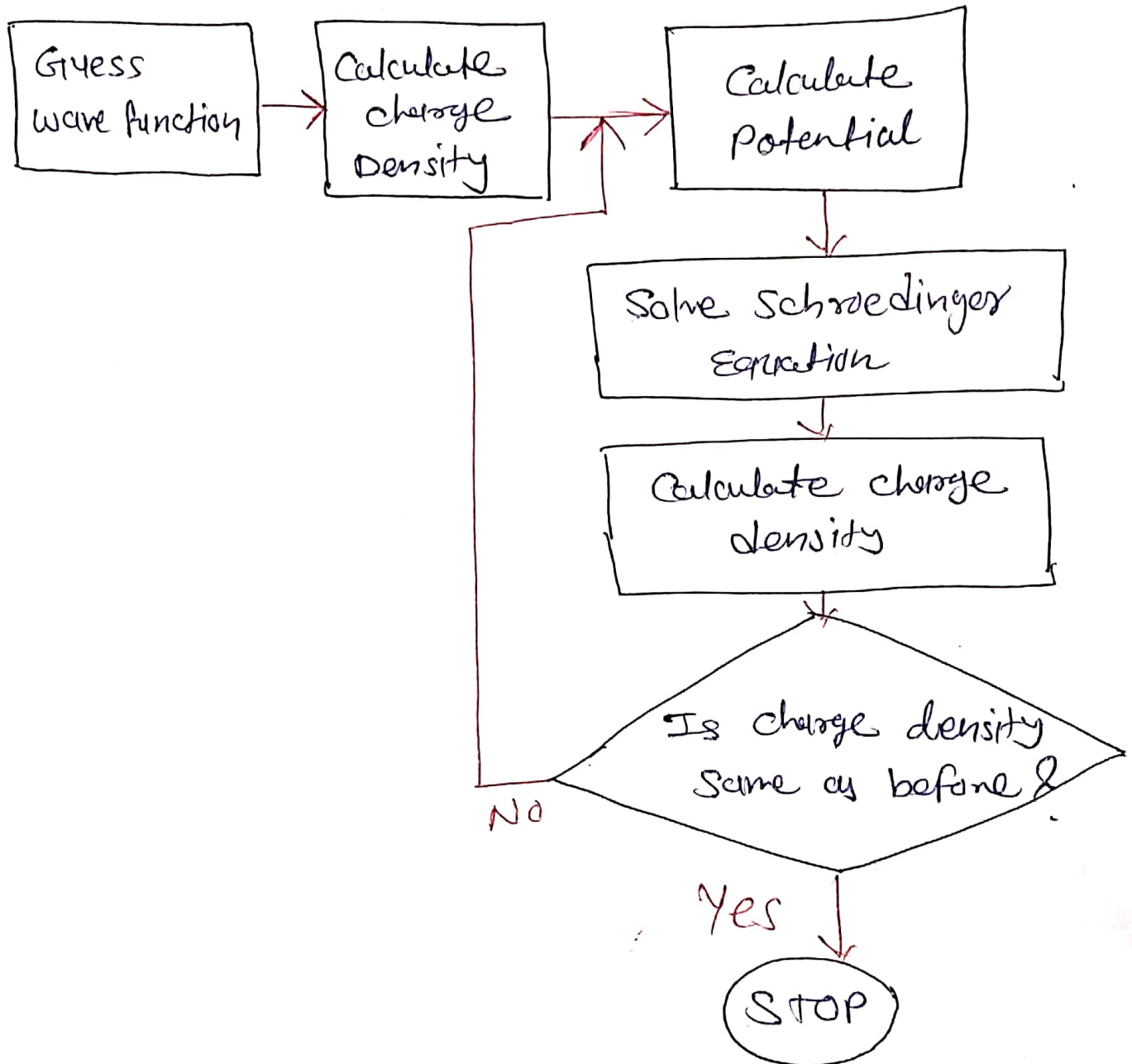
* Self-consistent field theory:-

- An important unsolved problem in quantum mechanics is how to deal with indistinguishable, interacting particles - in particular electrons which determine the behaviour of almost every object in nature.
- The basic problem is that if particles interact, that interaction must be in Hamiltonian. So until we know where the particles are, we can not write down the Hamiltonian, but until we know the Hamiltonian, we can not tell where the particles are.

⇒ Hartree-Fock theory:-

- The idea is to solve the Schrodinger equation for an electron moving in the potential of the nucleus and all the other electrons.
- We start with a guess for the trial electron charge density, solve $Z/2$ one particle Schrodinger equations to obtain Z electron wave functions.
- Then we construct the potential of each wave function from that of the ~~nucleus~~ nucleus and that of all the other electrons, symmetrise it, and solve $Z/2$ Schrodinger equations again.
- Fock improved on Hartree's method by using the properly antisymmetrised wave function. Instead of simple one electron wave function. Without this, the exchange interaction is missing.

- This method is ideal for a computer, because it is easily written as an algorithm.



[Algorithm for Self-consistent field theory]

- Although we are concerned here with atoms, the same methodology is used for molecules or even solids.

- The full set of equations are:

$$\begin{aligned}
 E_i \psi_i(\mathbf{r}) = & \left(-\frac{1}{2} \nabla^2 + V_{\text{ion}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) \\
 & + \sum_j \int d\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) \\
 & - \sum_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r})
 \end{aligned}$$

- The first term is the kinetic energy & electron ion potential.
- The second term is Hartree term, is the electrostatic potential from the charge distribution of N electrons, including an unphysical self interaction of electrons when $j=i$.
- The third, "exchange term", acts only on electrons with the same spins and comes from the wavefunction.

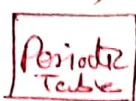
* Valence State Ionization Potential :-

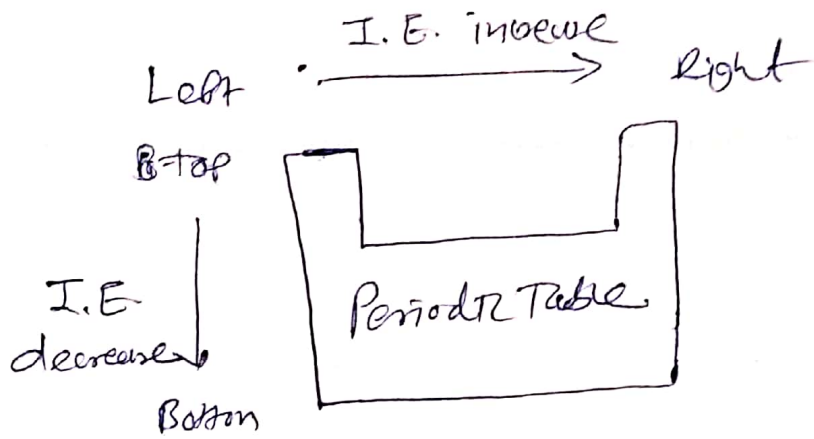
- The ionization potential is the measure of the amount of energy required to remove an electron from a neutral atom or ground state (gaseous or isolated).
- The first electron can be removed from the valence shell and can be noted as the first ionization potential.

→ Factors affecting the ionization energy (I.E.)

- Larger the nuclear charge, greater the I.E.
- Greater the shielding effect, less the I.E.
- Greater the distance betⁿ nucleus and outer electrons → less the I.E.
- Tends to increase across a period.
 - As radius decrease across a period, the electron you are removing is closer to the nucleus and harder to remove.
- Tends to decrease down a group.
 - Outer electrons are further from the nucleus and easier to remove.

→ Atomic no. increases → Nuclear charge increases → Atomic size decreases → Electrons are held tightly, hence greater energy is required to remove the electrons. → I.E. energy increases

[When we move left to right in periodic table.]
Left → Right




→ We move from top to bottom, the atomic size increases, distance to loosen electrons which are away from the nucleus, lesser amount of energy is required to remove them, So the I.E. is decreases.

F.e. $IE_1 < IE_2 < IE_3$

First electron Second electron Third electron.

→ Ionization energy is only for isolated gaseous atom.

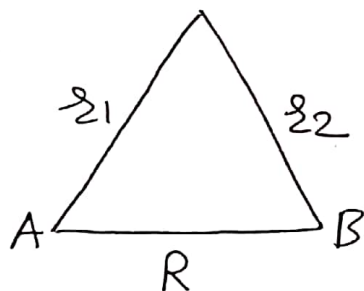
- because
- e.g., $A_{(s)} \rightarrow A_{(s)}^+ + e^- \rightarrow$ Not I.E., solid state
- $A_2(g) \rightarrow A_2(g)^+ + e^- \rightarrow$ Not I.E., molecule
- $A_2(g) \rightarrow A_2(g)^{2+} + 2e^- \rightarrow$ Not I.E., molecule
- $A(g) \rightarrow A(g)^{2+} + 2e^- \rightarrow$ Not I.E., $2e^-$ remove at a time
- ✓ $A(g) \rightarrow A(g)^+ + e^- \rightarrow$ Yes I.E., it follow definition

* LCAO-MO theory for diatomic molecule

→ Let us consider H_2^+ molecule ion, contains two hydrogen atoms A & B. the trial function may be written as,

$$\Psi_{MO} = C_1 \Psi_A + C_2 \Psi_B \quad \text{--- (1)}$$

→



→ The Schrodinger equation for this system is

$$\hat{H} \Psi_{MO} = E \Psi_{MO} \quad \text{--- (2)}$$

where $\hat{H} = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + R$

→ According to linear variation theorem, energy can be calculated by the eqⁿ:

$$E = \frac{\langle \Psi_{MO} | \hat{H} | \Psi_{MO} \rangle}{\langle \Psi_{MO} | \Psi_{MO} \rangle} \quad \text{--- (3)}$$

→ substituting value of Ψ_{MO} in eqⁿ (3);

$$\therefore E = \frac{\langle C_1 \Psi_A + C_2 \Psi_B | \hat{H} | C_1 \Psi_A + C_2 \Psi_B \rangle}{\langle C_1 \Psi_A + C_2 \Psi_B | C_1 \Psi_A + C_2 \Psi_B \rangle}$$

$$E = c_1^2 \langle \psi_A | \hat{H} | \psi_A \rangle + c_2^2 \langle \psi_B | \hat{H} | \psi_B \rangle + c_1 c_2 \langle \psi_A | \hat{H} | \psi_B \rangle + c_1 c_2 \langle \psi_B | \hat{H} | \psi_A \rangle$$

$$c_1^2 \langle \psi_A | \psi_B \rangle + c_2^2 \langle \psi_B | \psi_B \rangle + 2c_1 c_2 \langle \psi_A | \psi_B \rangle$$

→ As the \hat{H} is hermitian operator,

$$\langle \psi_A | \hat{H} | \psi_B \rangle = \langle \psi_B | \hat{H} | \psi_A \rangle \quad \text{--- (4)}$$

& if, atomic orbitals are normalized,

$$\langle \psi_A | \psi_B \rangle = \langle \psi_B | \psi_B \rangle = 1 \quad \text{--- (5)}$$

→ Put the value of eqⁿ (4) & (5) in above eqⁿ,

$$E = c_1^2 \langle \psi_A | \hat{H} | \psi_A \rangle + c_2^2 \langle \psi_B | \hat{H} | \psi_B \rangle + 2c_1 c_2 \langle \psi_A | \hat{H} | \psi_B \rangle$$

$$c_1^2 + c_2^2 + 2c_1 c_2 \langle \psi_A | \psi_B \rangle$$

As in the above eqⁿ:

$$\langle \psi_A | \hat{H} | \psi_B \rangle = \alpha_A$$

$$\langle \psi_B | \hat{H} | \psi_B \rangle = \alpha_B$$

$$\langle \psi_A | \hat{H} | \psi_B \rangle = \beta_{AB}$$

$$\langle \psi_A | \psi_B \rangle = S_{AB}$$

$$\therefore E = \frac{c_1^2 \alpha_A + c_2^2 \alpha_B + 2c_1 c_2 \beta_{AB}}{c_1^2 + c_2^2 + 2c_1 c_2 \cdot S_{AB}}$$

$$c_1^2 + c_2^2 + 2c_1 c_2 \cdot S_{AB}$$

→ The integrals α_A & α_B are coulomb integrals. The values of α_A & α_B are close to E_A & E_B . represents the energy of an electron in ψ_A & ψ_B in isolated H-atoms. The integral β_{AB} is resonance integral whose value is the measure of exchange of an electron from one atom to another. The integral S_{AB} is known as overlap integral

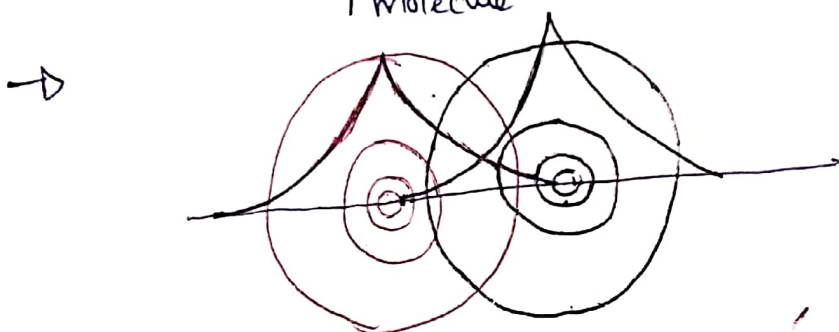
* Valance Bond treatment for diatomic molecules :

→ Consider formation of bond in H_2 diatomic. Label the atom A and B, each with one electron.

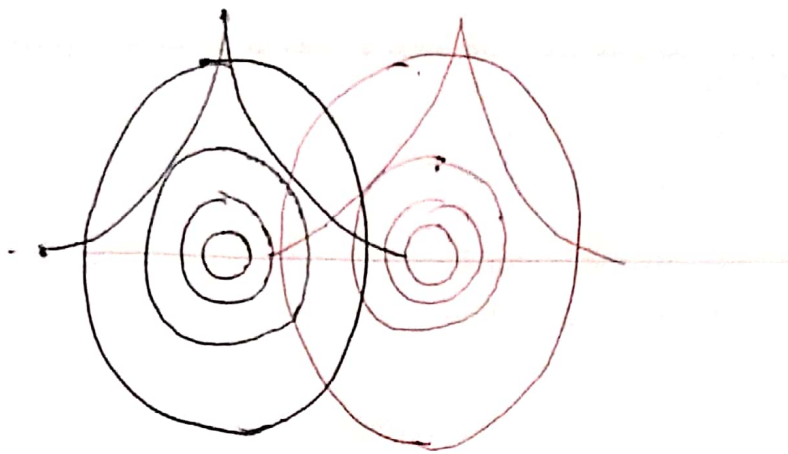
→ At large distance, $\psi_{molecule} = A(1)B(2)$. where, $A(1)$ & $B(2)$ are atomic orbitals i.e. 1s.

→ As atoms begin to interact at short distance, it is impossible to distinguish whether electron 1 is on A, or electron 2. An equally valid description would be :

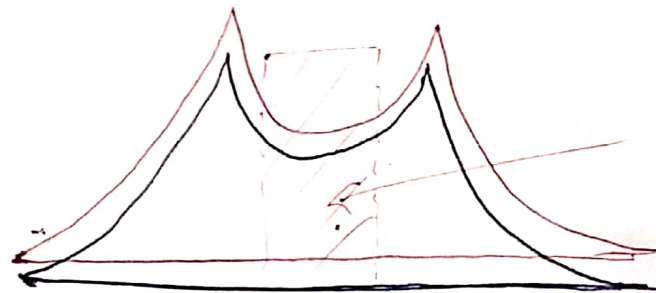
$$\psi_{molecule} = A(2)B(1)$$



$A(1)B(2)$



$$A(2)B(1)$$



$$A(1)B(2) + A(2)B(1)$$

→ The true wave function is a superposition of these two possibilities, so in quantum mechanics we construct two linear combinations.

$$\psi_{\pm} = A(1)B(2) \pm A(2)B(1)$$

→ The combination with (+) sign is the lower energy one, so that becomes the valence bond wave function for H_2 .

→ The electron distribution is called a sigma (σ) bond, meaning it has cylindrical symmetry around the bond axis.

→ The Valence Bond wave function

$\Psi_{\sigma} = A(1)B(2) + A(2)B(1)$ is only the spatial part of the wave function, and is symmetric with respect to interchange of electron labels 1 and 2.

→ Pauli principle requires a total wave function which is antisymmetric, so the spin part of wave function must be antisymmetric.

→ Therefore, the spin wave function we saw before must be used, and that means spins paired. [one up & one down]

