

No: _____ Date: _____
Paper : Inorganic Chemistry (Sp- Th- I)
Course Code : CHEM - 406

Stoichiometry & Bonding in main group Compounds

Long Questions

Correlation Diagrams Approach

Past Paper \Rightarrow 2021, 2018 & 2017.

Introduction

The Walsh theory named, after the chemist Thomas A. Walsh, is a qualitative molecular orbital theory used to explain the geometrical changes in molecules as their bond angles are varied. Walsh diagram were first introduced in a series of ten papers. Here Walsh aimed to rationalize the shapes adopted by polyatomic molecules in the Gs as well as ES, by applying theoretical contributions made by J. Mulliken.

\Rightarrow Normally we determine the experimentally observed geometries of molecules by certain devised rules & concepts such as VSEPR theory, hybridisation etc.

But Walsh actually calculated the energies of molecular orbitals of a reference geometry and its several distortions for simple triatomic molecules.

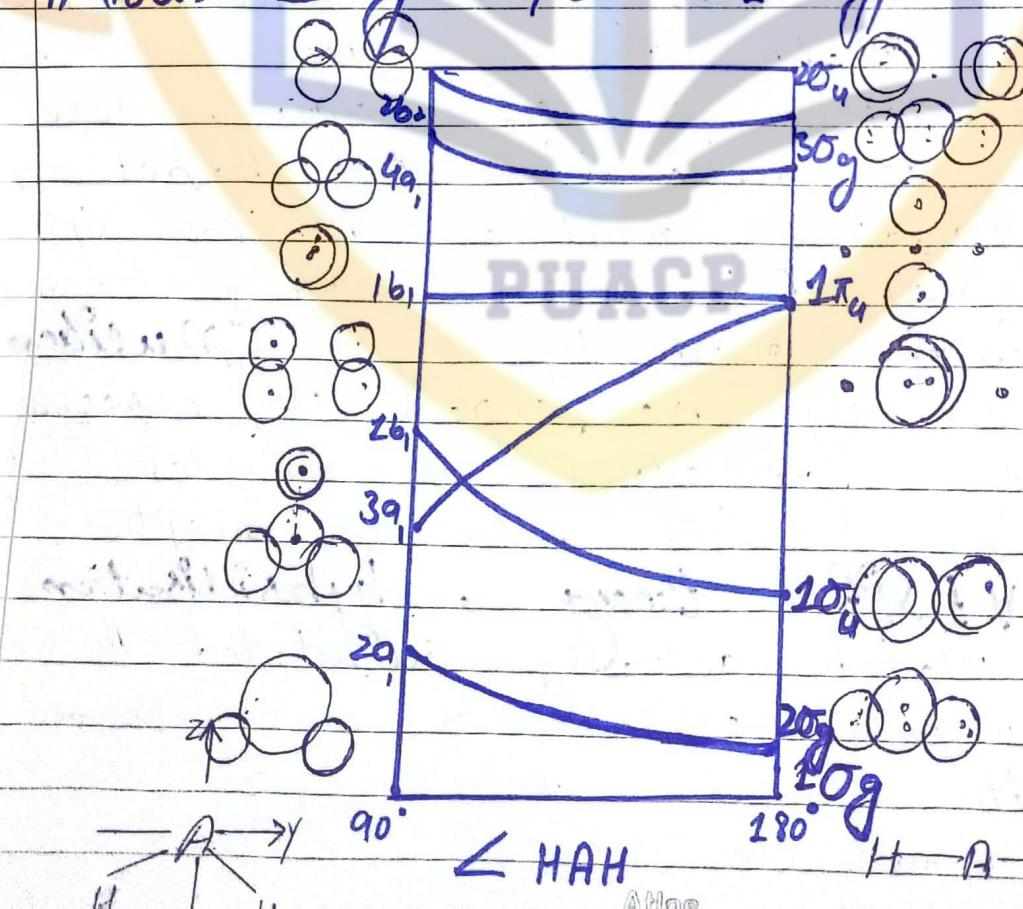
Concept of Walsh Diagrams

He correctly predicted the actual geometries of a number of simple triatomic molecules like H_2 , H_2O , BeF_2 etc by plotting a graph between the calculated energies of molecular orbitals of reference geometry and those of the distorted geometries of a molecule w.r.t. the distortion parameter i.e., bond angle.

"

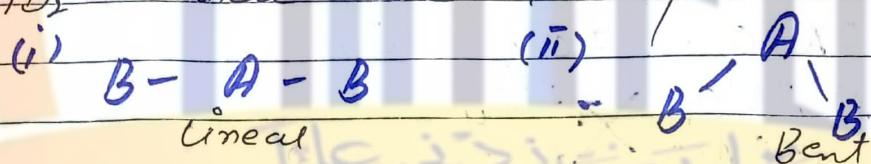
The position of the minimum energy of filled molecular orbitals in the graph indicates the most stable geometry of the molecule. Such graphs are known as **Walsh Diagram**.

Walsh Diagram For AH_2 Type Molecules



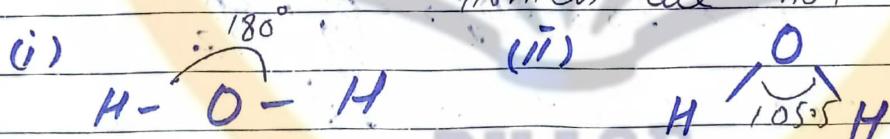
\Rightarrow Walsh involve "orbital binding energies plotted against bond angles. The basic idea is that the total energy is the sum of all the orbitals binding energies; therefore, by considering the stabilization or destabilization of all the orbital by a change in the angle, one can predict equilibrium BA for a given state of a molecule.

\Rightarrow Walsh diagram, often called angular coordinate diagrams or correlation diagrams, drawn on the basis of energy as bond angles vary. As J_{AB} , there are two possibilities;



And for $AB_4 \Rightarrow AB_2 \cdot F_2 \rightarrow H$

→ Here we consider it leatomatic bcz of 2 lone pairs which are not discussed



\Rightarrow Correlation b/w these two possible structures is described by M\"{o}ller-Plesset diagram; it calculates which one is more stable. It calculates energy of molecular orbitals and tells variations b/w these possible structures (actual geometry & distortions).

Energy ↑ Stability ↓

Examples

Here the triatomic molecules which we take as an example are BeH_2 , BH_3 , H_2O , BeCl_2 etc. the number of H atoms present are 2, let them H_a , H_b , thus the outer shell of these atoms are $1s\text{H}_a$, $1s\text{H}_b$.

In case of Be, B, O the OS are $2s$, $2p$, He

$2s$ has one orbital

$2p$ has three orbital ($2p_x$, $2p_y$, $2p_z$)

so total no of outer most shell are 6 namely $1s\text{H}_a$, $1s\text{H}_b$, $2s$, $2p_x$, $2p_y$, $2p_z$

6 AO combines to form 6 MO of which

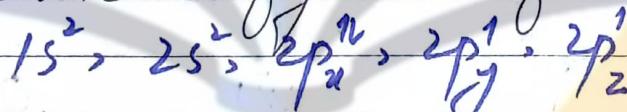
$$2 \text{ BNO} = 2 \text{Og}, 1\text{O}_4$$

$$2 \text{ ABMO}_5 = 1\text{Tu}_4$$

$$2 \text{ NBMO}_5 = 3\text{Og}, 2\text{O}_4$$

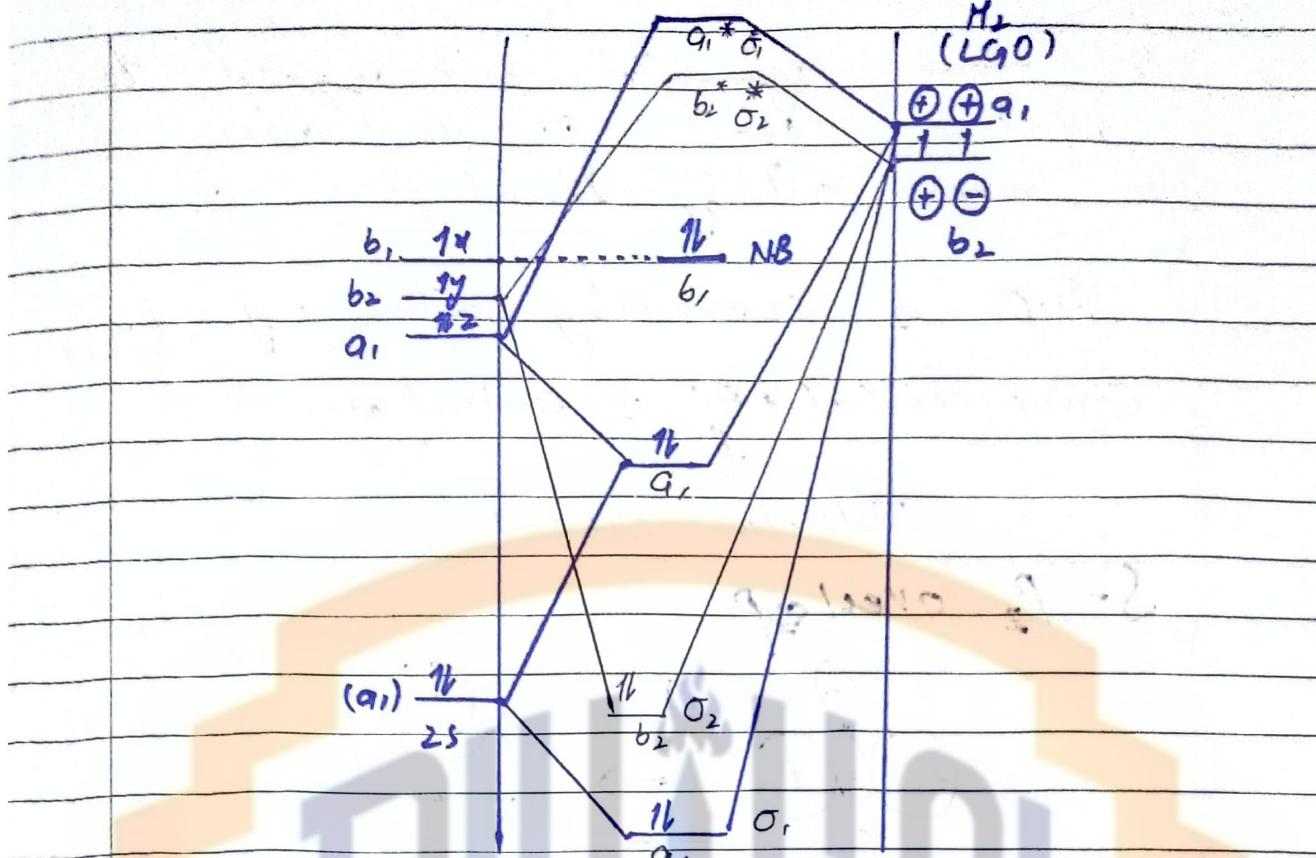
For H_2O Molecule

Electronic Configuration of O atom :-



EC for H atom - $1s^1$

O has six outermost es in $2s$ and $2p$ subshell, 2 H atoms have 2 ones in $2s$ \Rightarrow so total of 8 e-s in outermost shell and its molecular configuration $(2\text{Og}), (1\text{O}_4), (1\text{Tu}_4)$, (1Tu_{1g}) or $(2a_1, 1b_2, 3a_1, 1b_1)$. Because the formerly nonbonding 1Tu_4 orbital is greatly stabilized to $3a_1$ on bonding, the water has bent shape.



MO Diagram for the sake of understanding.

g = gerade (even) $\rightarrow \ominus\oplus \quad \oplus\ominus$ same

u = ungerade (uneven) $\rightarrow \ominus\oplus - \oplus\ominus$ opposite

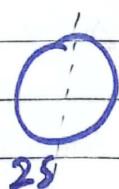
G_O = Ligand group orbital

$2H = \text{O O}$

$1 = \oplus\oplus$ same phase

$2 = \oplus\ominus$ diff phase

To determine symmetry of orbitals:-



E
no change
identity
 $2s$

rotation
along z -axis

cut

$6v$

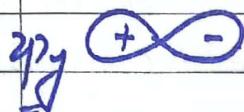
cut axis

$6v'$

cut axis

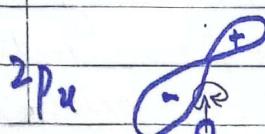
horizontally

$1 = a_1$



$1 \quad -1 \quad -1$

$1 = b_2$



$1 \quad -1 \quad 1$

$-1 = b_1$

$2p_u$

1

Atlas

1

$1 = a_1$

" a " means symmetric with regard to rotation about principle axis.

" b " means anti-symmetrical"

A_{1g} or surrounding "orbit" = group orbitals

Group orbital + AO of central atom

Molecular Orbital

S - P_z overlap



S - p_y overlap



S - p_x Overlap



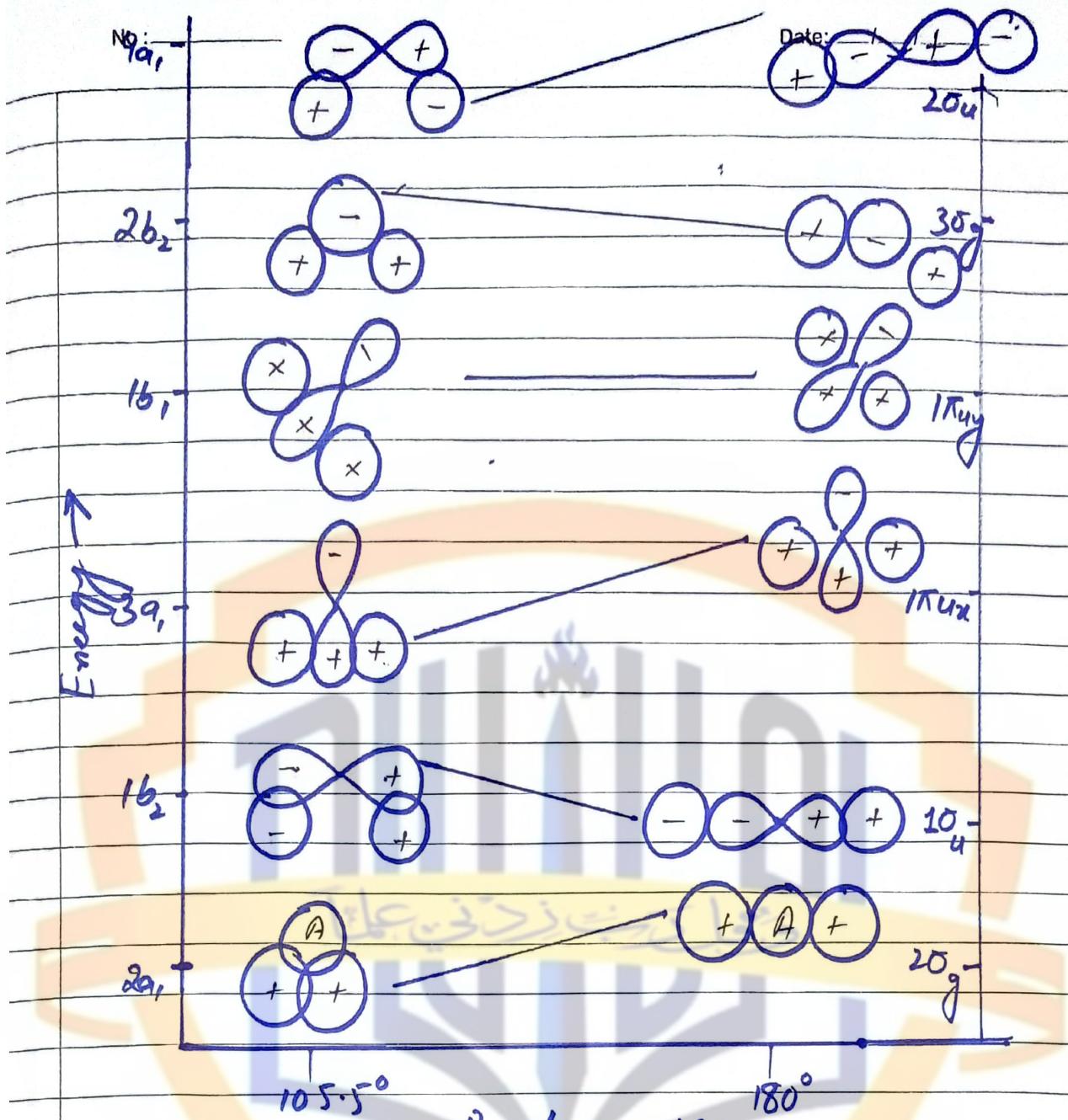
How to draw Walsh Diagrams:

→ Determination of point group of a molecule.

→ Coordinates assignment to the molecule (principle axis z for non-linear molecule).

→ Search for character table of reducible representation for the possible combination of valence orbitals of surrounding atoms.

→ Search for irreducible representations as per symmetry of group's "orbitals".



Bond angles →

- (symmetry adopted linear combination).
- Search for atomic orbit of central atom with the same symmetry.
- Combination of AOs with the group orbitals of the same symmetry and draw the MO diagram of these limiting structures.
- Walsh diagram correlates the energy of MOs of the limiting structure.

Question #02.

Briefly Discuss Stereochemistry with few examples. — (2020) a.

⇒ Stereochemistry in inorganic compounds deals with the spatial arrangement of atoms or groups of atoms within molecules without necessarily involving carbon atoms.

⇒ In contrast to organic chemistry, where stereochemistry often revolves around carbon-centered chirality, stereochemistry in inorganic compounds encompasses a wide range of structural aspects, including geometric isomerism, optical isomerism, and coordination isomerism. This field is essential for understanding the properties and reactivity of inorganic molecules, complexes and materials.

"Stereochemistry is the study of the spatial arrangement of atoms within molecules and how this arrangement affects the properties and reactivity of the molecule."

⇒ Stereochemistry refers to finding relation b/w the structures of molecules and the nature of the chemical bonds that they contain. This has two aspects. The one to which we shall devote most attention concerns the shapes of the molecules, that is the angles b/w the bonds formed by a given atom. The second deal with certain aspects of multiple bonding, that is with

certain questions of bond length.
Here are few examples:

I am not sure if this is correct
 Isomerism topic in coordination compounds
 page # 315.

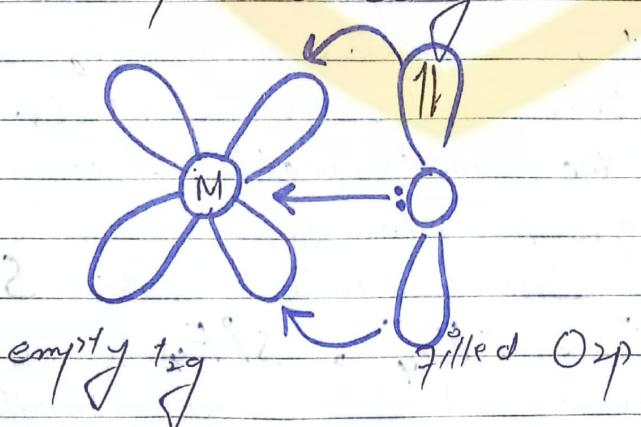
Q# 03 — (2019)

$\text{p}\pi - \text{d}\pi$ Bonding

This is a special type of bonding found in the molecular species having a central atom with d or p valence shell and surrounding groups with empty, partially or completely filled p or d orbitals.

In addition to direct overlap resulting in the σ bonding, $\text{d}\pi - \text{p}\pi$ bonds are formed by the sideways overlap.

If there is a bond between two atoms with one vacant orbital on one atom and one lone pair of electrons on the other atom, then this electron pair is donated to that corresponding unoccupied orbital, and the bonding is called $\text{p}\pi - \text{d}\pi$ bonding.



$\text{p}\pi - \text{d}\pi$ bond example

Atlas

indications of this are chiefly the high bond stretching constant and the shortness of bonds compared to the force constant and bond lengths to be expected for single bond containing a π - π overlap responsible for this anomaly.

Bond length

Bond length data in the series of ions SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} , ClO_4^- indicate that such π - π bonding actually does occur.

Ion	Obs. X-O dist in Å	Expt. X-O single bond dist. in Å	Shortening	π - π overlap
SiO_4^{4-}	1.063	1.076	0.13	0.33
PO_4^{3-}	1.054	1.071	0.17	0.46
SO_4^{2-}	1.049	1.069	0.20	0.52
ClO_4^-	1.046	1.068	0.22	0.57

As shown in table the X-O bond are all short relative to value reasonably expected for.

Examples

PUACP

The central atoms belonging to the third period has ns, np and nd orbitals in its valence shell. The combination of central and surrounding atoms s and p-orbitals form σ bond, which makes principle contribution for bonding.

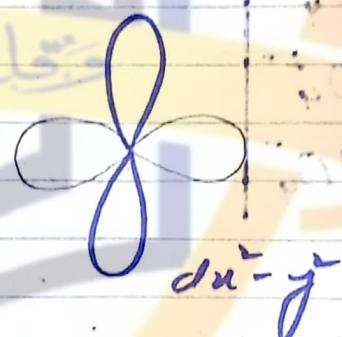
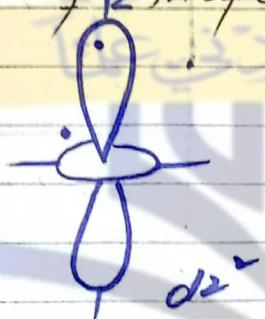
SiO_4^{4-} :

In SiO_4^{4-} , the silicon atom has vacant d orbitals which can participate in

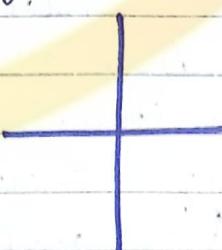
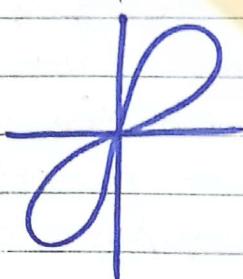
σ - π bonding with the oxygen atom. This σ - π bonding occurs when the π orbitals of oxygen overlap with the σ orbitals of silicon, resulting in additional bonding beyond the σ bond. Overall the combination of σ and π bonding in SiO_4^{4-} contributes to the stability and structure of the ion.

d -orbital

The "central" atoms belonging to the third period has d -orbitals (name) $d_{x^2-y^2}$ and d_{z^2} . denoted by e.g have electron density along the axes. The overlapping of appreciable magnitude required that orbital should be compact enough of z shape.



Two eg orbitals have different shape and point along the axes.



The remaining three have identical shape and point in between the x , y and z . The diffused shape of d -

leads to extreme overlap overlapping and weak bonding so σ and π are not involved in $\text{Si}-\text{O}$.

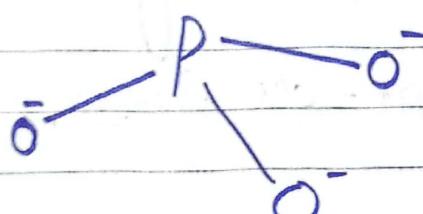
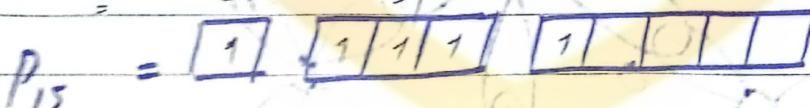
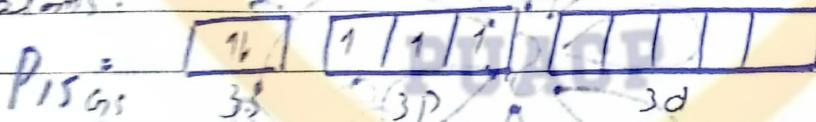


Si atom has vacant d orbital

and oxygen has two lone pair

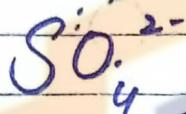
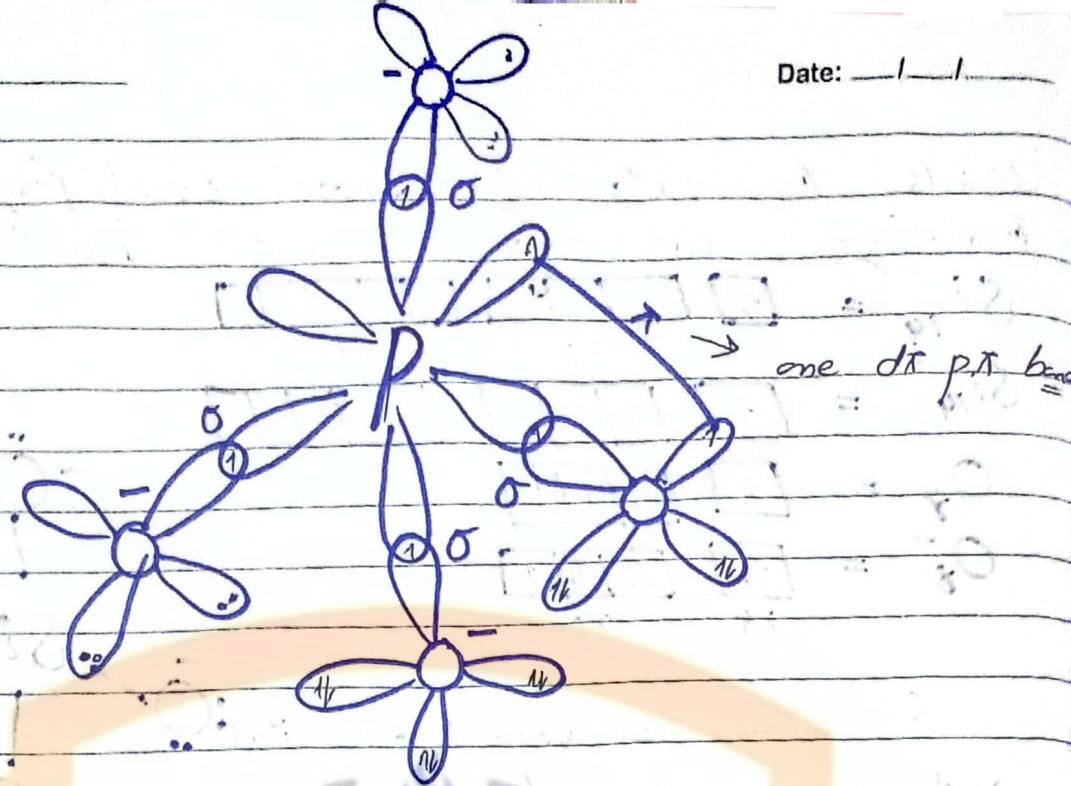
sp^2 hybridization so $\delta\pi$ present.

For tetrahedral AB_4 molecule such as SiF_4 or PO_4^{3-} , each of the B atoms has two filled $\delta\pi$ orbitals perpendicular to the A-B bond axis and perpendicular to each other. A is central atom use its s and p orbitals for σ bonding. d orbitals of A overlap with the π orbitals on the B atoms, namely d_{z^2} , d_{xy} well with have much overlap with π of the 4 B atoms.

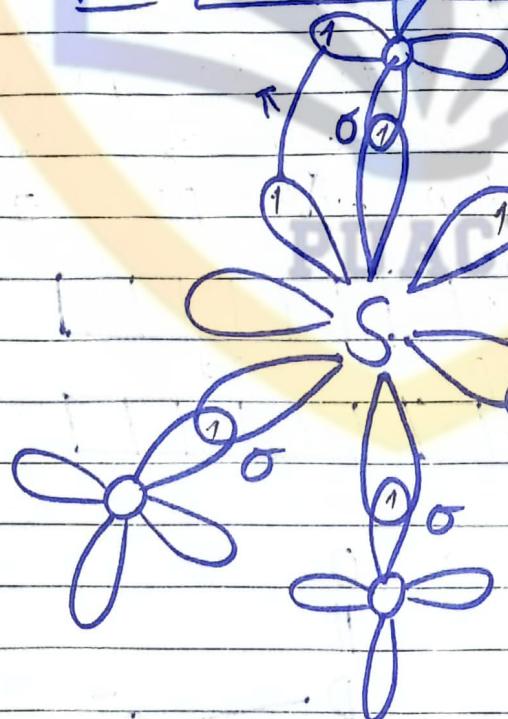


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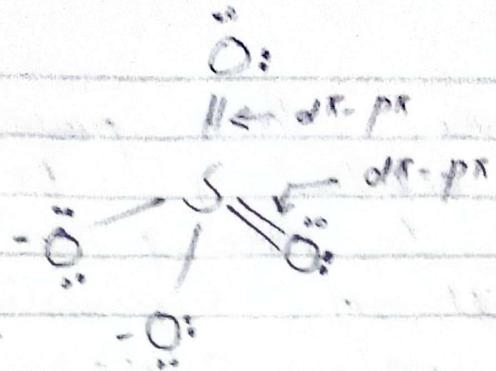
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Since S atom belongs to period 3 and O atom belongs to period 2, so it can form p π -d π multiple bond.



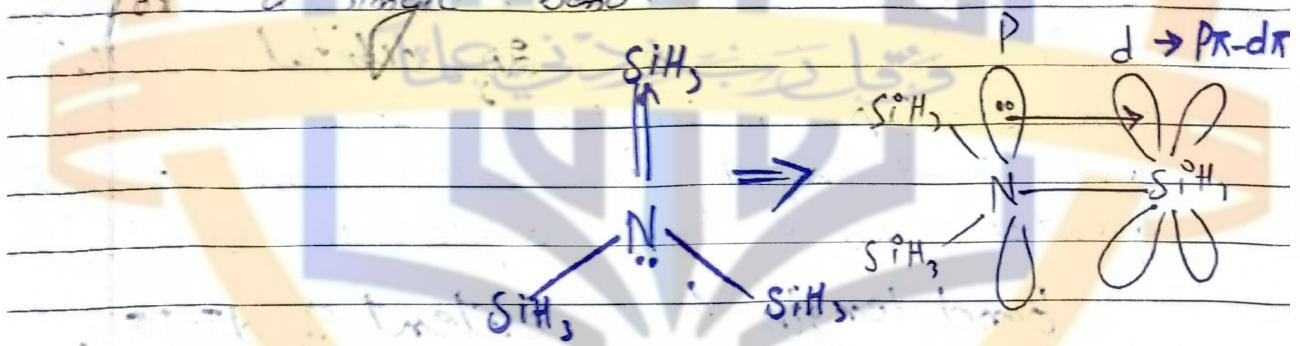
$2\pi - d\pi$ Bands



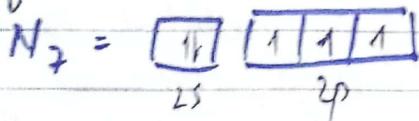
Q) There are molecules with central atom having d-valence shell for sideways overlap

Molecules with CA having p-VS for overlap

Sometimes, the existence of $\delta\pi-\delta\pi$ bonding can be viewed in terms of the molecular geometry. For example, Si_3N & Ge_3N (Skeletal) is planar. In $(\text{H}_3\text{Si})_3\text{N}$, $(\text{H}_3\text{Ge})_3\text{N}$ & $\text{Si}/\text{Ge}-\text{N}$ bond length is somewhat shorter than what is expected for a single bond.



In each case the Si-N or Ge-N bond are $0.05 - 0.15 \text{ \AA}$ shorter than expected for single bonds. These structural features can be accounted for by assuming that in the planar configuration about the N atom there is enough $\text{N}(2p) \rightarrow \text{Si}(3d)$ or $\text{Ge}(3d)$ π bonding to stabilize this configuration relative to pyramidal one found in most other Q_3N molecules.



However, the presence of partially filled p orbital of the central atom is prone to overlap with the empty d-subshell of surrounding groups. Yet it does not assure the sufficient dπ-pπ bonding leading to a planar structure in all cases.

Examples

The Si-A-Si bond angles in $P(SiH_3)_3$ & $As(SiH_3)_3$ are 96.5° & 93.8° respectively and both of these compounds exist pyramidal geometry like $P(GeH_3)_3$.

Reason:

This is due to the fact that $3p_z$ orbitals of P and As do not overlap with d-orbitals as efficiently as in the case w.r.t. $2p_z$ orbital of N. Less overlap, stretching force also less and bond length in either cases obviously greater, so bond angle shorter.

Bond length ↑ extent of dπ-pπ ↓
Bonding

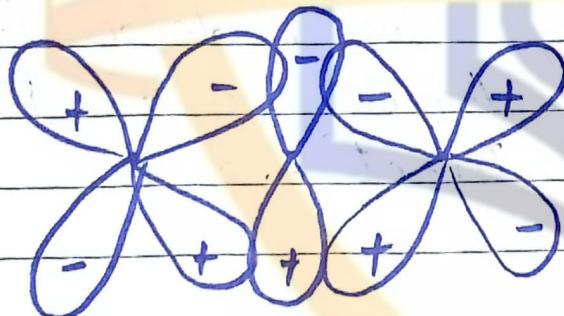
In the case of $N(SiH_3)_3$, N is smaller in size leading to high interelectrostatic repulsion, so ease to denote its lone pair to someone. In case of $P(SiH_3)_3$ and Si has vacant d-orbital, so needy for it if it is larger in size so opposite case, not face much interelectrostatic repulsion so don't den its lone pair to vacant d-orbital of silicon. This lone pair in $P(SiH_3)_3$ causes the SiH_3 group to arrange in a trigonal pyram

Other examples:

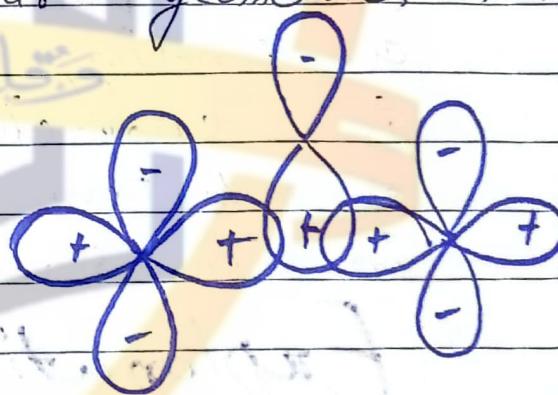
Furthermore, $\text{Si}(\text{SiH})_3$ is bent with a Si-A-Si bond angle of 98° resemble its tri-coordinated pyramidal analogs in terms of $d\pi-p\pi$ overlap. However $(\text{H}_3\text{Si})_2\text{O}$ is also bent in geometry with BL 144° but shows a small extent of $d\pi-p\pi$, which is also confirmed by the shortening of the Si-O bond length.

Note:

= The extent of $d\pi-p\pi$ overlap is much larger in flat and linear geometries than that of bent ones."



p_z overlap with d-orbitals
in linear molecules



p_z overlap with d-orbitals in bent

3 Center 4 Electron Bond

"3-center 4-electron bond is a model used to explain bonding in certain hypervalent molecules such as tetravacanic and hexaatomic interhalogen compounds, sulfur tetrafluoride, Xenon fluoride and bifluoride ion."

Definition

A 3-centered 4-e⁻ bond is a type of chemical bonding where three atoms share four electrons in a bonding orbital. This type of bond is characterized by the delocalization of electrons over three nuclei, resulting in a stabilizing interaction.

Explanation

This type of bond is commonly found in certain molecular structures such as boron hydrides & certain metal complex. 3 Center 4-e⁻ bond is formed from a p-orbital of the central atom and the s-orbital of two outer atoms. It is also known as "Pimentel-Rundle three-center model" after the work published by George C. Pimentel in 1951, which built on concepts developed earlier by Robert E. Rundle for e⁻ deficient bonding.

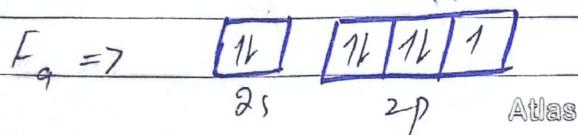
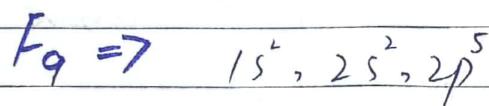
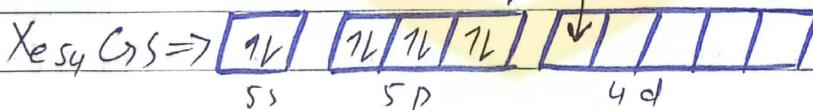
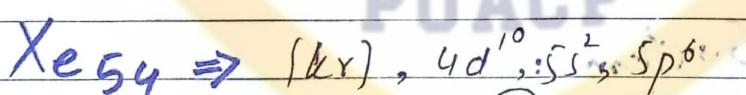
→ An extended version of this model is used to describe the inshore class of hypervalent molecules such as,

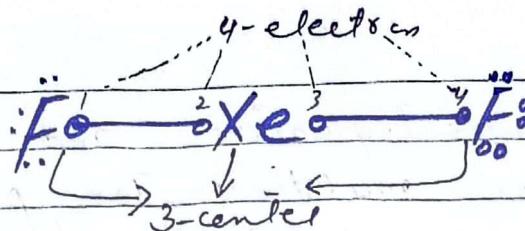
phosphorous pentafluoride and sulfur hexafluoride as well as multi-center pi-bonding such as ozone and sulfur trioxide.

Description:

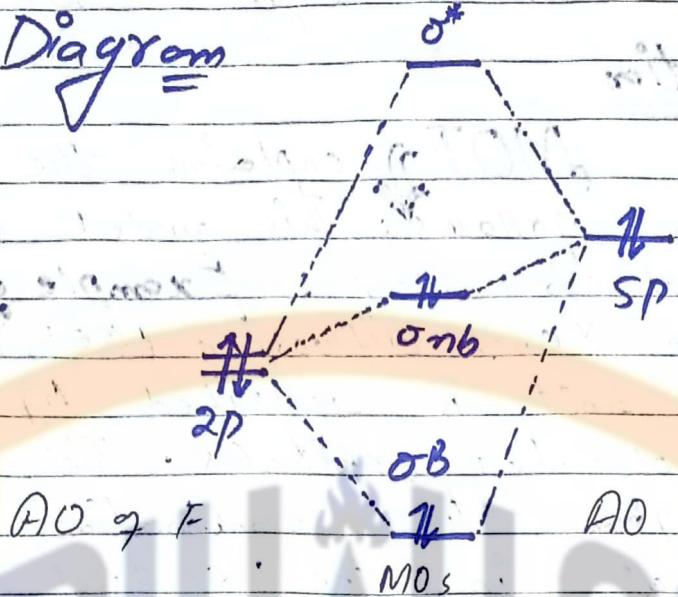
MOT explains the 3C-4e bond as follows; this model considers bond of 3 collinear atoms; Example: in Xenon difluoride (XeF_2), the linear F-Xe-F unit is described by a set of three molecular orbitals. The Xe-F bonds result from the combination of a filled p-orbital in the central atom (Xe), with two half-filled p-orbitals on the axial atoms (F), resulting in a filled bonding orbital, a filled non-bonding orbital and an empty anti-bonding orbital. The two lower energy MO's are doubly occupied. The BO is $\frac{1}{2}$. since the only bonding orbital is delocalized over the 2 Xe-F bonds.

XeF_2 :

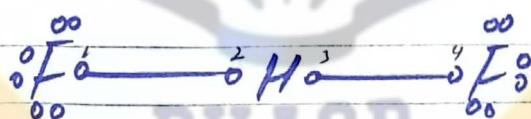




MO Diagram

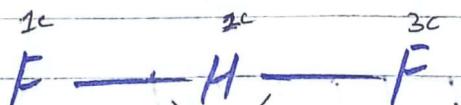


The linear F-A-F axis of the molecule SF_3 and ClF_3 is also described as 3c-4e bond. In XeF_2 all bonds described with 3c-4e model. Molecules without s-orbital lone pair such as PF_3 and SF_4 are described by extended version of 3c-4e model of hypervalent molecules.



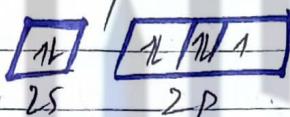
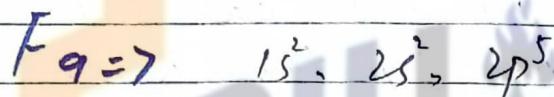
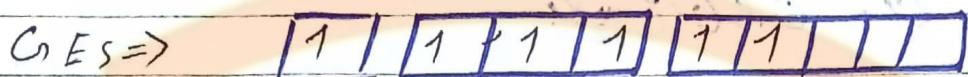
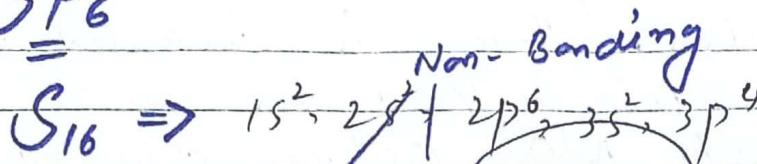
Other System :

F^- = 3 center. 4e⁻ interactions
 can also be considered in the transition state of S_2 reactions and in some (resonant) hydrogen bonding as in the bifluoride anion discussed above.

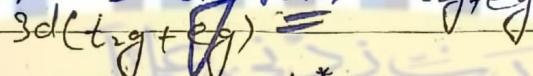


Hydrogen Bonding

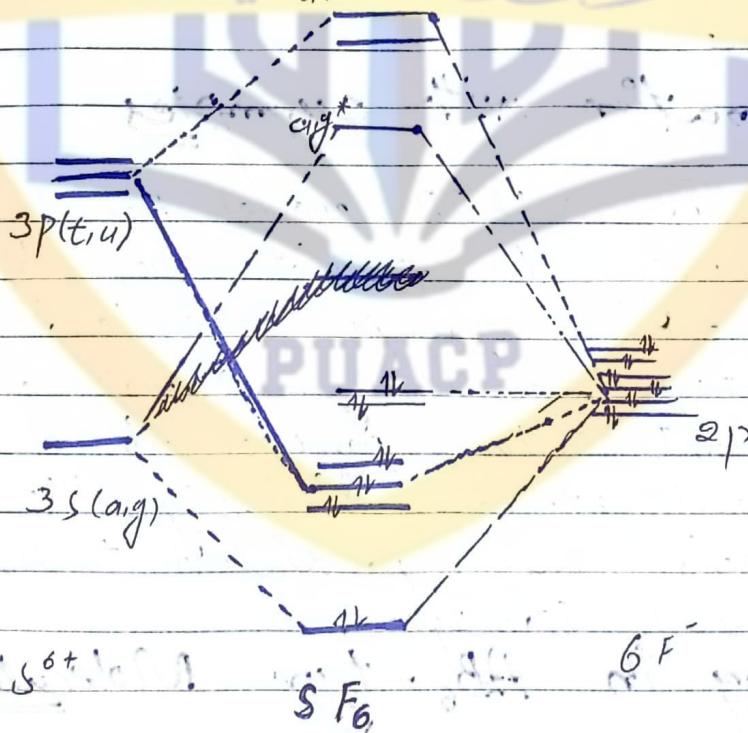
Six fluorine ligands approach to the central sulfur or phosphorous atom along the x, y & z axes forming an octahedral str.



MOT Diagram

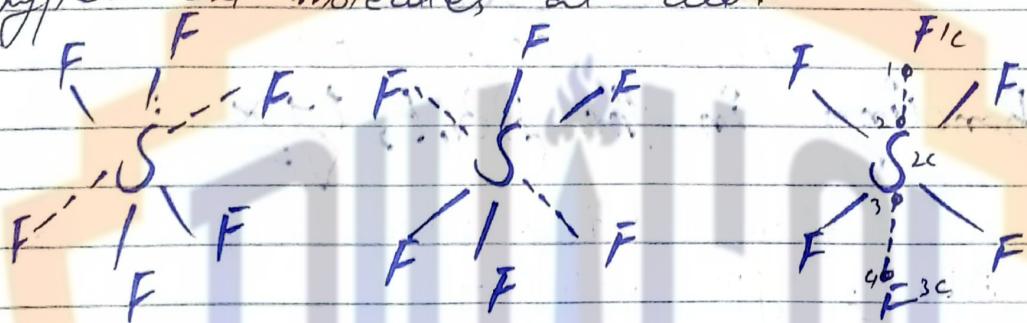


t_{2g}^*



Look at how much higher in energy the 3d orbitals are than the other

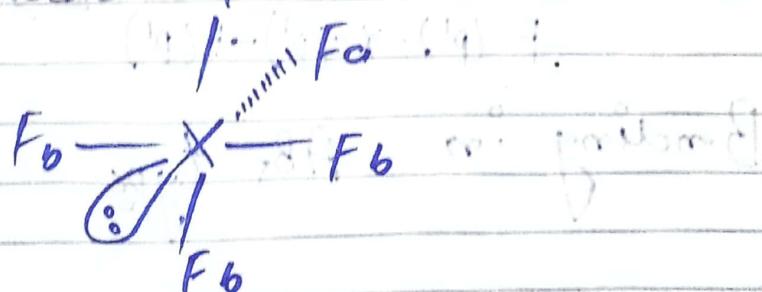
hand they are also diffused which form weak bonding. They are not significantly involved in bonding. In this case we have 2 non bonding pairs. This means we have a situation where sulfur has formed 4 single bond to F⁻ and 2 F ions that are attached to S²⁺ center. That's what this simplified model is saying anyway. In fact it is not necessary to explain by hypervalent molecules at all.

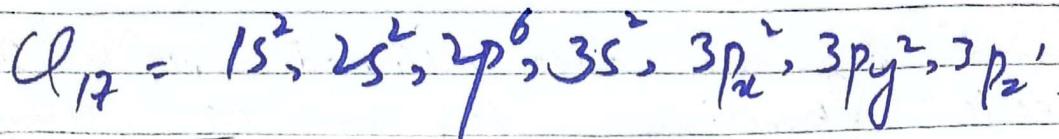


3c-4e Bond

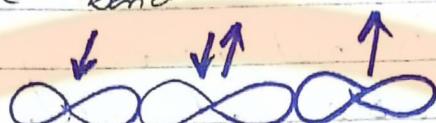
Bonding in the AB₅E type:

The halogen pentafluoride XF₅ (X = Cl, Br, or I) belongs to the AB₅E type molecule. A square pyramidal structure with a lone pair in the central halogen atom. In all the XFs molecules the basal X-F_b bonds (all are equivalent) are about 0.1 Å longer than axial X-F_a bond. This shows that bonding in basal and axial positions must be different. F_b is longer than F_a.





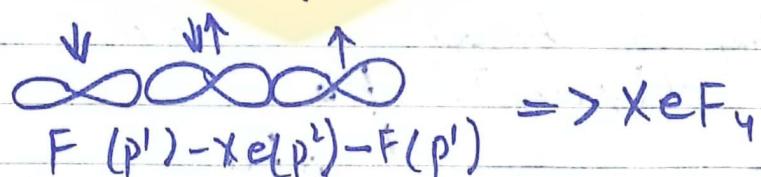
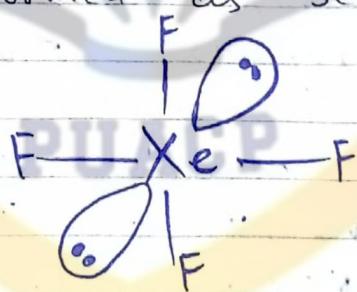
~~F₂-X-F₂~~ bonds are reasonably formed by the overlap of unhybridized, orthogonal p_x and p_y orbitals respectively, with the terminal fluorine p orbitals leading to a 3c 4e bond.



Bonding in the AB₄E₂ type:

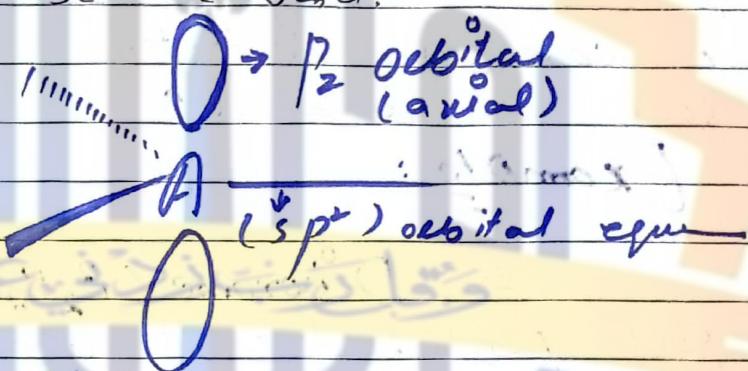
Xenon tetrafluoride XeF₄ is an example of AB₄E₂ type molecules.

A square planar structure with 2 lone pair in the central atom. In XeF₄, 2 sp hybrid could reasonably form one lone pair pointing toward the axial positions and holding a lone pair in each of them. 2 sets of linear F-Xe-F bonds are formed as 3c 4e as same as above.



Bonding in AB₅ type:

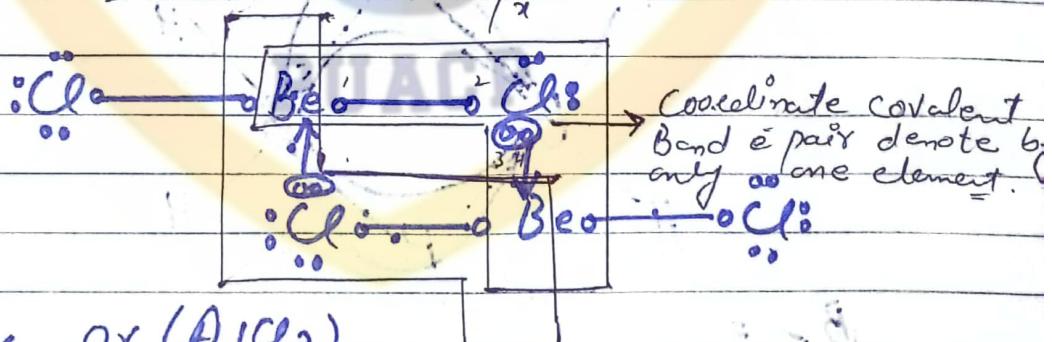
An alternative model that does not involve d-orbitals in bonding in the pentacoordinated AB_5 -type such as phosphorus pentabhalides PX_5 ($X = \text{F}, \text{Cl}$). Instead, three sp^2 hybrid orbital (each contains a single electron) are formed on the CA overlapping with ligands orbital in the equatorial positions. Longer axial bonds are formed via overlap of the unhybridized p orbital (containing 2 electrons) and the CA and the 2 terminal ligands orbitals, resulting in $3c - 6e$ bond.



Other Examples

Be_2Cl_4 or $(\text{BeCl}_2)_n$

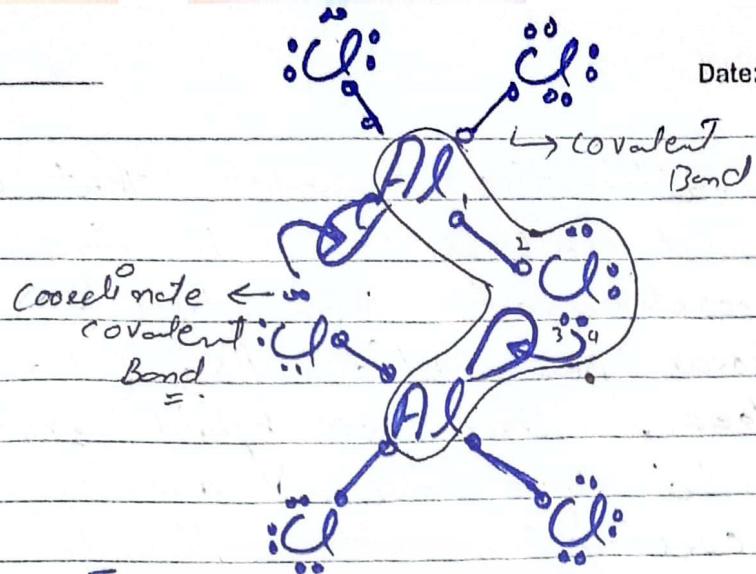
$$\text{Be}_4 = 1s^2, 2s^2 \Rightarrow 1s^2, 2s^1, 2p_1^1$$



Al_2Cl_6 or $(\text{AlCl}_3)_n$

$$\text{Al}_{13} \Rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^1 \Rightarrow \boxed{1} \boxed{1} \boxed{1}$$

AAA
HHH

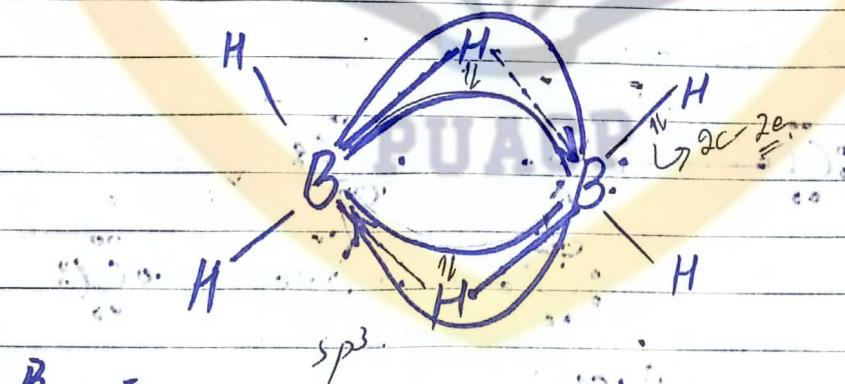


3 center 2 Electron

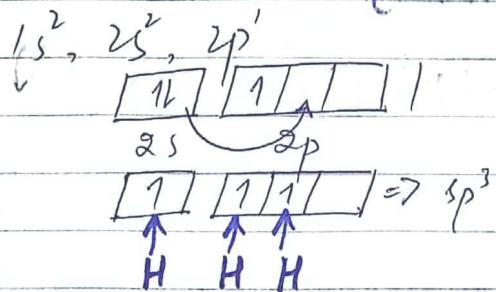
"3 centered 2-electron bond" is a chem bond in which 2 electrons are shared between 3 atoms. This type of bonds are found in case of electron deficient molecules such as boranes.

Example:

In Diborane (B_2H_6), there are two such bonds: Two H atoms bridge the two B atoms, leaving two additional H atoms in ordinary B-H bonds on each B.



$B_5 =$



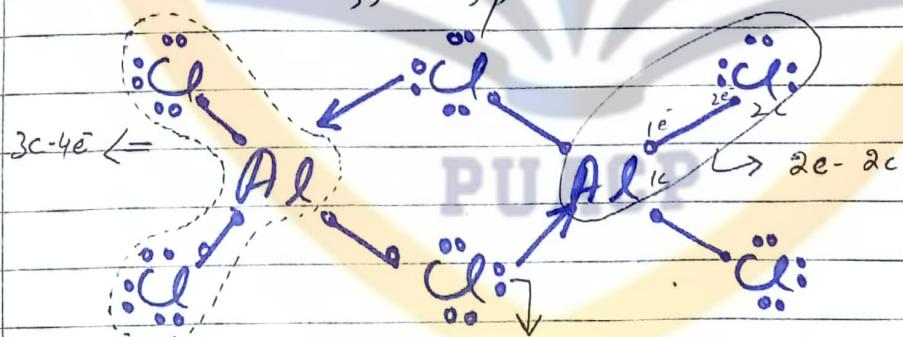
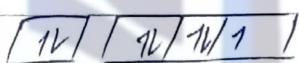
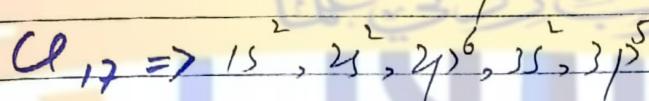
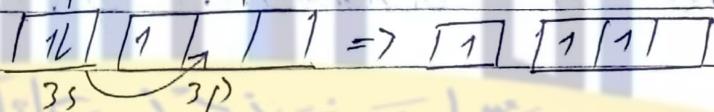
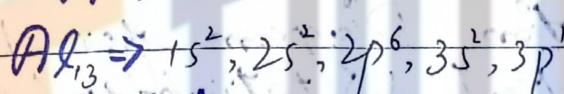
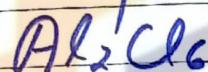
2 centered 2 Electron:

"2c- 2e" refers to chemical bonds in which two atoms share two electrons.

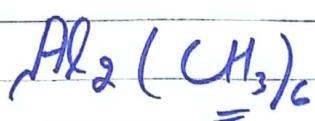
These types of bonds are commonly found in organic chemistry and are known as:

These types of bonds are often found in compounds with delocalized electrons and can exhibit unique bonding and reactivity properties.

Examples

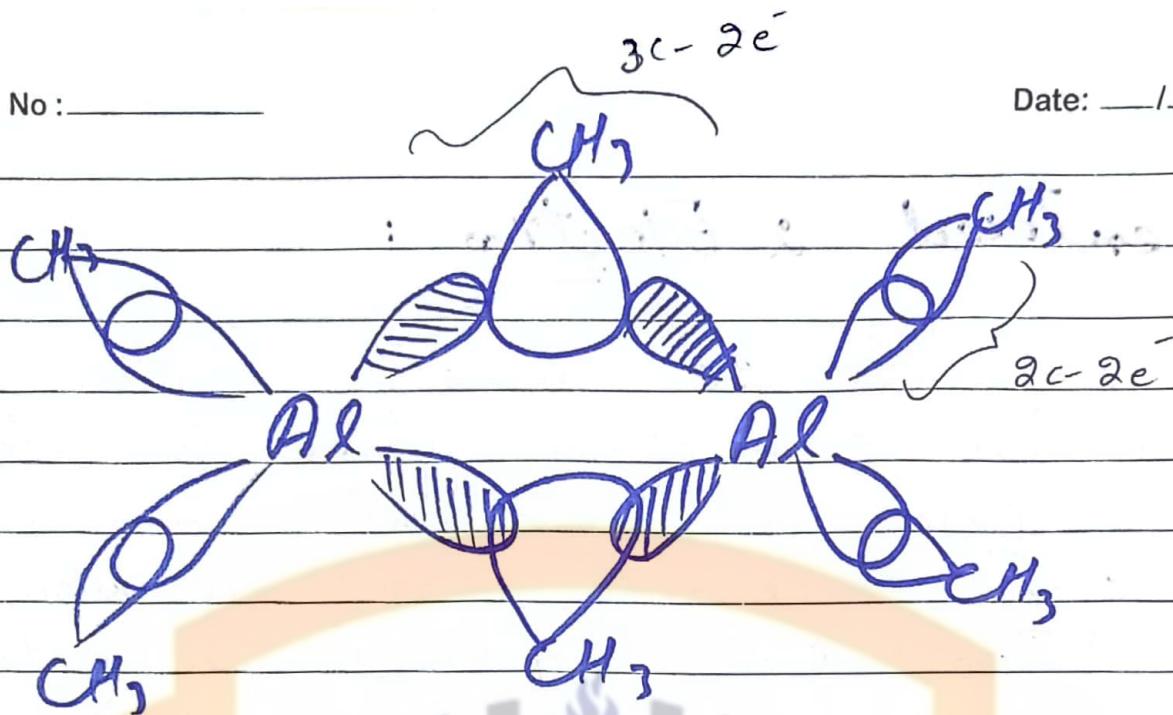


Represents a dative covalent bond or coordinate covalent bond, where an e-pair that only comes from one of the atom.



No : _____

Date: ___ / ___ / ___



Short Questions.

TSQs - (2017) -

(i)

Draw Correlation Diagram for d^5 & d^8 octahedral & tetrahedral comp.

PUACP

(ii) - 2017

Write 2 point of difference b/w VBT and MOT

Books page no # 194 - 195.

(iv)

What is 3c-4e bond? Give one example?

Previously explained on register.

Short Questions - 2018-

(ii)

Mention your points of similarity b/w VBT and MOT?

Books page # 194

(v) What is 3 center 2 electron?

(vi) Give one example?

Previously explained on Register.

(vii) 2 advantages & 2 drawbacks of VSEPR theory?

Drawback in Register.

Applications

⇒ Lewis structures only tell the number and types of bonds between atoms as they are limited to two dimensions. The VSEPR model predicts the 3-D shape of molecules and ions but is ineffective in providing any specific information regarding the bond length or bond itself.

⇒ VSEPR models are based on the concept that electrons around a central atom will configure themselves to minimize repulsion and that dictates the geometry of the molecule.

\Rightarrow It can predict the shape of nearly all compounds that have a central atom, as long as the central atom is not a metal. Each shape has a name and an idealized bond angle associated with it.

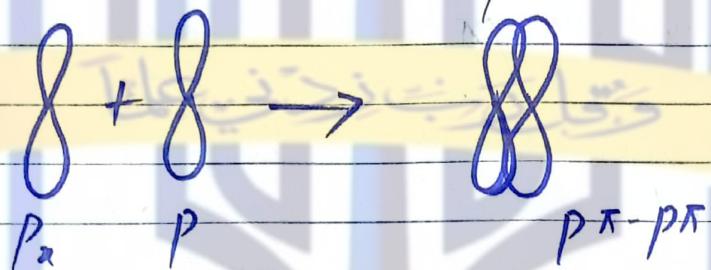
Short Questions 2019

Give 2 failure of VBT.

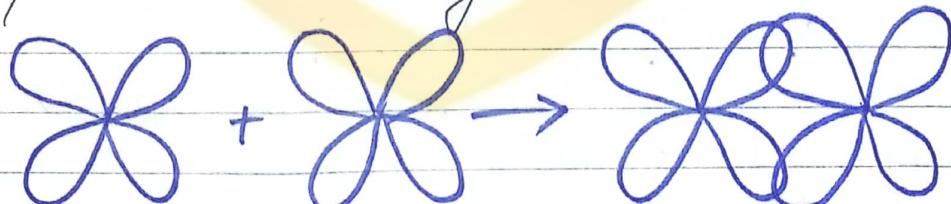
Explained on Register.

(iii) Which type of bonding is stronger $\pi\pi$ - $\pi\pi$ and $d\pi-d\pi$? Why?

In $\pi\pi$ - $\pi\pi$ bonding, the overlapping lobes are parallel, and as a result there occurs a pure sideways ($\neq 180^\circ$) overlap, on the other hand, in $d\pi-d\pi$



\Rightarrow In $d\pi-d\pi$ bonding the lobes of the overlapping d-orbitals are at an angle $\angle 180^\circ$ to the lobes of the p-orbital. Hence $\pi\pi$ - $\pi\pi$ bonding is less significant than the $d\pi-d\pi$ bonding.



Better overlapping
Bond strength is more.

\Rightarrow The $d\pi-d\pi$ bond strength is more than $p\pi-p\pi$ bond strength due to shape of the orbitals. The tilted shape of d-orbitals

gives better attraction b/w the nucleus and the electron hence better overlapping.

→ The $p\pi/p\pi$ bond is stronger than the $d\pi/d\pi$ bond. This is because the extent of overlap is more in the $p\pi/d\pi$ bond, due to the higher level of overlap in the electron clouds, leading to a lower energy bonding MO.

Short Question 2020

- i) Write 2 drawbacks of VSEPR theory.
Explained on Pege 11.
- ii) Discuss one experimental evidence for $d\pi - p\pi$.

The $d\pi - p\pi$ bond, also known as the dative π bond, is a type of covalent bond formed by the overlap of a unfilled d orbital from one atom with a filled p orbital on another atom, typically involving transition metals.

→ Experimental evidence for $d\pi - p\pi$ bond comes from various spectroscopic techniques and computational studies.

X-ray Crystallography

This technique provides direct structural evidence of bond formation. By analyzing crystal structures of transition metal complexes, researchers can identify bonding geometries indicative of $d\pi - p\pi$ interactions.

UV - Vis Spectroscopy :

Allas

UV-vis spectroscopy can provide information about the electronic transitions within a molecule. In transition metal complexes, characteristic absorption bands can be observed, which are often attributed to dπ or pπ interaction.

NMR Spectroscopy

Nuclear Magnetic Resonance Spectroscopy can provide information about the electronic environment around nuclei. Shifts in NMR signals can indicate the presence of dπ or pπ bonding.

Computational Studies

Quantum mechanical calculations such as density functional theory (DFT) or MOT, can predict & analyse the nature of dπ or pπ bonds. These calculations can provide insights into bond energies, bond lengths, and electron density distributions associated with dπ or pπ bonds.

Magnetic Susceptibility

Can provide information about the electronic structures of transition metal complexes. Anomalous magnetic properties can be indicative of the presence of dπ or pπ bonds.

(iii)

Mention 2 differences b/w hybrid orbital and molecular orbital.

Molecular Orbitals

Hybrid Orbitals

Formation

Result from the overlap and mixing of atomic orbitals.

Formed through hybridization of atomic orbitals.

Source of orbitals

Atomic orbitals from different atoms. Atomic orbitals from the same atom.

Geometry

No specific geometry. Determined by the distributed over the molecular geometry based on the hybridization.

Bonding

Participate in bonding by overlapping with other atomic orbitals.

Participate in bonding and determine the type and number of bonds formed.

Energy level

Have varying energy levels depending on the type of molecular orbital.

Examples

Bonding & antibonding non bonding, sigma and pi orbitals.

Atlas

sp , sp^2 , sp^3 orbitals.

No: _____

Date: ___/___/___

(iv)

Q. 3c-4e: Bond? Give example

Repeated

Short Questions 2021

- (i) Difference b/w VBT and MOT.
- (ii) $3c-2e^-$ bond ?: Give example.
- (iv) Which bonding is stronger $\sigma\pi$ and $\pi-\pi$.

1)

Drawbacks of VSEPR Theory / Criticism :

VSEPR model is a useful tool for predicting the shapes of molecules based on repulsion between electron pairs around a central atom.

However, it has some limitations and can fail to explain certain molecular geometries accurately:

1) Transition metal complex:

This theory is unable to explain the shapes of molecules certain transition metal complex, where d-orbitals play a significant role in bonding and shape. This theory cannot explain the shapes of molecules having any polar bonds e.g;

LiO_2 should have the same structure as H_2O but in fact it is linear.

(2) Inability to account for e^- 's Delocalization

This is unable to explain the shapes of molecules having extensive delocalized π -electron system.

does'

- It doesn't account for the distribution of electrons over multiple atoms, which can influence molecular geometry.

e.g;

Such as delocalized π electron system in aromatic compounds.

Assumes purely Electrostatic Repulsions:

This theory is solely based on the idea of repulsion b/w e⁻s pairs, without considering other factors such as orbital hybridization or bonding interaction. In reality the shapes of molecules are influenced by a combination of factors beyond simple electrostatic repulsion.

Lack of explanation for bent structure:

This predicts linear structures for molecules with 2 e⁻s pairs around the central atom and trigonal planar for molecules with 3 e⁻s pairs. However it fails to explain why certain molecules, have bent structure despite having 2 e⁻s pairs.

e.g; H₂O have bent structures despite having only two e⁻s pairs.

2)

VBT Drawback / Criticism :

Criticism of VBT regarding the stereochemistry of inorganic compounds primarily revolves around its limitation in accurately predicting the geometries and bonding in complex molecules. Some key points of criticism include:-

Neglect of Orbital Hybridization

VBT doesn't explicitly consider orbital hybridization, which is crucial for understanding the geometries and bonding in many inorganic compounds.

e.g;

This limitation becomes particularly evident when describing molecules with sp^3d , sp^3d^2 or other hybridized orbitals.

Lack of Predictive Power:

VBT lacks predictive power compared to more advanced theories like MOT. It provides qualitative insights into bonding but often fails to accurately predict bond strengths, energies

and spectroscopic properties.

بِلْبَرْجِيَّةٍ

Inability to describe molecular Orbitals:

VBT primarily focuses on the ~~overlap~~ of AOs to form to form localized bonds. It doesn't adequately describe the formation of delocalized molecular orbitals, which are essential for understanding electronic structure and stereochemistry of molecules.

Bonding in e⁻ deficient molecules

Doesn't explain the bonding in electron deficient molecules e.g; Diborane

Magnetic properties

This is unable to explain magnetic properties

e.g; paramagnetic behaviour of O₂ molecule.

Dificulty in describing Stereoisomers:

VBT may struggle to explain the differences between stereoisomers, such as geometric isomers (cis-trans) and optical isomers (enantiomers & diastereomers). These differences arise from the spatial arrangement of atoms around stereocentres, which VBT not fully

2) Drawbacks of MOT

is its complexity and difficulty in directly predicting certain stereochemical features of molecules, particularly those involving geometric arrangement and chirality.

Limited power for Geo-isomers

MOT provides insight into the electronic structure of molecules, it may not always directly correlate with the spatial arrangement of atoms around = bond leading to challenges in predicting geometric isomerism.

Complexity in analyzing chirality

Face difficulty in directly analyzing the chirality of molecules, especially those with multiple chiral centers or complex structures.

Stereoelectronic Effect :

MOT does not consider stereoelectronic effects, such as steric hindrance and hyperconjugation, which play crucial roles in determining molecular geometry and stereochemistry.

Complex molecules:

- MOT becomes increasingly complex when applied to molecules with large numbers of atoms or transition metal complexes, where no. of orbital involved in bonding interaction can be abundant.

Intermolecular interactions:

- MOT primarily focuses on intermolecular bonding interactions within a molecule and not fully describe the influence on stereochemistry.

4

Criticism on hybridization or directed Valence theory

Commonly used to explain the shapes of inorganic compounds, can fail to provide accurate descriptions of molecular shapes in certain cases :-

Transition Metal complexes :

Transition metal complexes often exhibit complex geometries that cannot be easily explained by simple hybrid theories. The involvement of d-orbitals in bonding leads to a variety of geometries.

Equivalent hybrid Orbital

A set of hybrid orbitals need not be equivalent e.g.; A trigonal bipyramidal hybridization gives two axial orbitals perpendicular to the three equatorial orbitals. Thus PCl_5 has two chlorine atoms different from the other 3

Steic effect :

Hybridization theory assumes that orbitals align

- and overlap to form bonds, but it doesn't always account for steric effect, such as the repulsion by lone pairs or bulky substituents. This influence the actual geometry, deviating from what is predicted by HT

Electronegativity

- The distribution of electron density can be influenced by the electronegativity of atoms, leading to deviations from the predicted hybridization scheme.

Experimental discrepancies:

- In some cases, experimental observations deviate from the predictions made by hybridization theory, indicating its limitations in accurately describing molecular shapes.