

M.Sc. Chemistry

Paper – I : INORGANIC CHEMISTRY

VSEPR Theory

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UNIT-1 STEREO CHEMISTRY IN MAIN GROUP COMPOUNDS

Structure:

1. Introduction
2. Objectives
3. Valence Shell Electron Pair Repulsion (VSEPR)
 - 3.1. Gillespie Laws
 - 3.2. Applications
 - 3.3. Comparison of CH_4 , NH_3 , H_2O and H_3O^+
 - 3.4. Comparison of PF_5 , SF_4 and $[\text{ICl}_2^-]$
4. Walsh Diagrams
 - 4.1. Application to triatomic molecules.
 - 4.2. Application to penta atomic molecules.
5. $d\pi - p\pi$ Bonds.
 - 5.1. Phosphorous Group Elements.
 - 5.2. Oxygen Group Elements.
6. Bent's rule and Energetic of hybridisation.
 - 6.1. III and IV groups halides.
 - 6.2. V and VI groups Hydrides halides.
 - 6.3. Isovalent hybridisation.
 - 6.4. Apicophilicity.
7. Some simple reactions of covalently bonded molecules.
 - 7.1. Atomic inversion.
 - 7.2. Berry pseudo rotation.
 - 7.3. Nucleophilic substitution.
8. Let Us Sum Up.
9. Check Your Progress: The key.

1. INTRODUCTION

The concept of molecular shape is of the greatest importance in inorganic chemistry for not only does it affect the physical properties of the molecule, but it provides hints about how some reactions might occur. Pauling and Slater (1931) in their Valence Bond Theory (VBT) proposed the use of hybrid orbital, by the central atom of the molecule, during bond formation. Thus, with the knowledge of the hybridisation used by the central atom of the molecule, one can predict the shape and also the angles between the bonds of a molecule. However, since then more advanced theories have come into existence. In this chapter we explore some of the consequences of molecular shape in terms of VSEPR theory and refine that concept into the powerful concept of molecular symmetry and the language of group theory, using Walsh diagrams and Bent's Theory, towards the end of the unit.

You may recall what you have already studied about the directional property of a covalent bond and the concept of hybridisation of orbital to predict molecular geometry.

2. OBJECTIVES

The main aim of this Unit is to study stereochemistry in main group compounds. After going through this unit you should be able to:

- discuss absolute shapes of various molecules;
- explain anomalies in bond angles present in some molecules;
- describe stability of molecular shapes in terms of energetics, and
- discuss simple reactions of covalently bonded molecules on the basis of the principles studied in this unit;

2. VSEPR THEORY (VALENCE SHELL ELECTRON PAIR REPULSION THEORY)

In order to predict the geometry of covalent molecules, Valence Shell Electron Pair Repulsion Theory is used. This theory was given by Gillespie and Nyholm. According to this theory the geometry of a molecule depends upon the number of bonding and non-bonding electron pairs in the central atom. These arrange themselves in such a way that there is a minimum repulsion between them so that the molecule has minimum energy (i.e. maximum stability).

2.1. Gillespie Laws

The following rules have been reported by Gillespie to explain the shape of some covalent molecules:

1. If the central atom of a molecule is surrounded only by bonding electron pairs and not by non-bonding electron pairs (lone pairs), the geometry of the molecule will be regular.

In other words we can say that the shape of covalent molecule will be linear for 2 bonding electron pairs, triangular for 3 bonding electron pairs, tetrahedral for 4 bonding electron pairs, trigonal bipyramidal for 5 bonding electron pairs:

Name of Compound	Bonding Electron Pairs	Shape
BeCl ₂	2	Linear
BeCl ₃	3	Triangular Planar
SnCl ₄	4	Regular Tetrahedral
PCl ₅	5	Trigonal bipyramidal
SF ₆	6	Regular Octahedral

2. When the central atom in a molecule is surrounded by both, bonding electron pairs as well as by lone pairs, then molecule will not have a regular shape. The geometry of the molecule will be disturbed. This alteration or distortion in shape is due to the alteration in bond angles which arises due to the presence of lone pairs on the central atom. How the presence of lone pairs causes an alteration in bond angles can be explained as follows:

At a fixed angle the closer the electric-pairs to the central atom, the greater is the repulsion between them. Since the lone-pair electrons are under the influence of only one positive centre (i.e. nucleus), they are expected to have a greater electron density than the bond-pair electrons which are under the influence of two positive centres. Thus lone pair is much closer to the central atom than the bond pair. Hence it is believed that lone pair will exert more repulsion on any adjacent electron pair than a bond pair will do on the same adjacent electron pair.

$$(lp - lp) > (lp - bp) \dots\dots\dots(i)$$

(lp = lone pair and bp = bond pair)

If the adjacent electron pair is a bond pair, then repulsive force between lone pair and bond pair will be greater than repulsive force between two bond pairs.

$$(lp - bp) > (bp - bp) \dots\dots\dots(ii)$$

On combining relations (i) and (ii) we get

$$(lp - lp) > (lp - bp) > (bp - bp)$$

Thus the repulsion between two lone pairs is maximum in magnitude, that between a bp and lp is intermediate while that between two bond pairs is the minimum.

The more the numbers of lone pairs on a central metal atom, the greater is the contraction caused in the angle between the bonding pairs. This fact is clear when we compare the bond angles in CH_4 , NH_3 and H_2O molecules. (Table 1.1)

Table 1.1

Molecules	No. of Lone pairs on central atom	Bond Angle	Contraction in bond angle w.r.t. CH_4
CH_4	0	109.5°	0
NH_3	1	107.5°	2°
H_2O	2	105.5°	4°

3. B-A-B bond angle decreases with the increase in electro negativity of atom B in AB_2 molecule where A is the central atom.

Example: PI_3 (102°) > PBr_3 (101.5°) > PCl_3 (100°)

4. Bond angles involving multiple bonds are generally larger than those involving only single bonds. However, the multiple bonds do not affect the geometry of the molecule.
5. Repulsion between electron pairs in filled shells are larger than the repulsion between electron pairs in incompletely filled shells.

Examples: H_2O (105.5°) < H_2S (92.2°)

2.2. Applications of Gillespie Laws

Let us take some examples in support of these laws:

- (a) AX_2 molecule, which has only two bond-pairs, will be linear:



Examples in this groups will be BeCl_2 , CaCl_2 , CO_2 etc.

- (b) If the molecule is AX_3 (I) or AX_2 with a lone pair of electrons on the central atom A, i.e. AX_2E (II), then the molecule will be triangular (Fig 1.1):

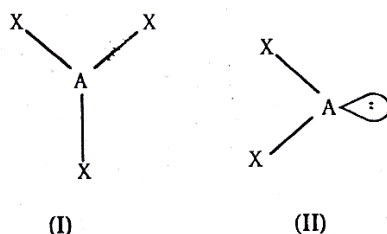


Fig 1.1 : (I) = BCl_3 , BF_3 etc.

(II) = SO_2 , $SnCl_2$ etc.

- (c) If the molecule is AX_4 (III) or AX_3E (IV) or AX_2E_2 , then AX_4 will be tetrahedral; AX_3E will be pyramidal and AX_2E_2 will be angular. (Fig. 1.2):

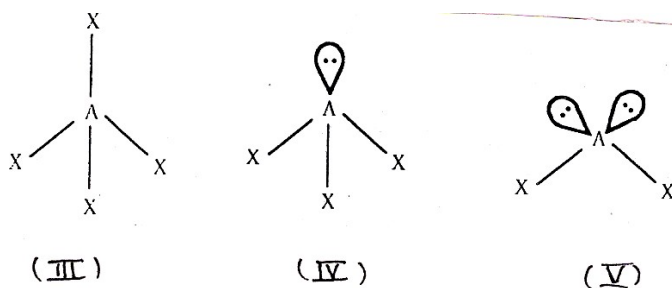
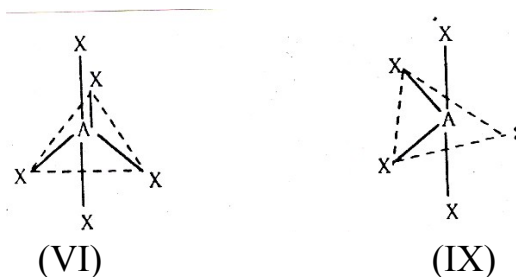


Fig 1.2 : (III) = CCl_4 , CH_4 , $SiCl_4$, $GeCl_4$ etc.

(IV) = NH_3 , PCl_3 , As_2O_3 etc.

(V) = H_2O , $SeCl_2$, etc.

- (d) If the molecule is AX_5 (VI) or AX_4E (VII) or AX_3E_2 (VIII) or AX_2E_3 (IX) then AX_5 will be triangular bi pyramidal; AX_4E will irregular tetrahedral; AX_3E_2 will be T-shaped,; and AX_2E_3 will be linear. (Fig. 1.3)



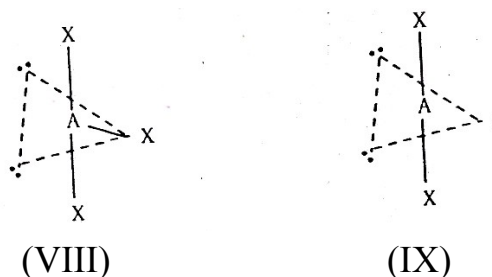


Fig 1.3 : (VI) = PCl_5 ; (VII) SF_4 , TeCl_4 etc.

(VIII) = ClF_3 , BrF_3 etc.

(IX) = XeF_2 , ICl_2^- , or I_3^- etc.

- (e) If the molecule is AX_6 (X) or AX_5E (XI) or AX_4E_2 (XII) then AX_6 will be octahedral, AX_5E will be square pyramidal; and AX_4E_2 will be square planar. (Fig. 1.4)

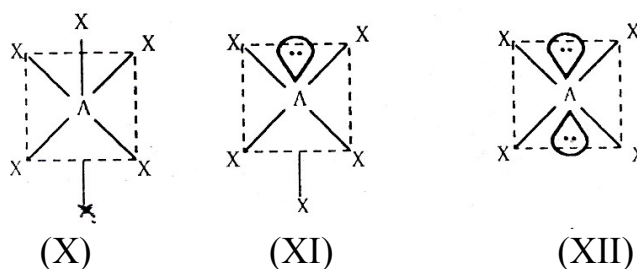


Fig 1.4 : (X) = SF_6 , WF_6 , etc.

(XI) = BrF_5 , IF_5 etc.

(XII) = ICl_4^- , XeF_4 etc.

2.3. Comparison of CH_4 , NH_3 , H_2O and H_3O^+

In table 1.1 bond angles in CH_4 , NH_3 and H_2O molecules are given. In all these molecules, the central atom (C, N and O respectively) is sp^3 hybridised. But they differ in the number of lone pair (s) present on the central atom, being zero in CH_4 , one in NH_3 and two in case of H_2O . Thus the repulsive force between electron pairs gradually increases in these molecules from CH_4 to H_2O , resulting in the change of geometry and the bond angles. This CH_4 (Four bond pairs) is tetrahedral with the

characteristic bond angle of 109.5° . NH_3 is pyramidal (Three bond pairs and one lone pair) and has a bond angle of 107° . While H_2O is angular (Two bond-pairs and two lone-pairs) and has bond angle of 105° . The increasing lp-lp repulsion decreases the bond angles from 109.5° to $\sim 107^\circ$ in NH_3 and $\sim 105.5^\circ$ in H_2O . On comparing H_3O^+ with these molecules, we notice that it resembles with NH_3 molecule. As the central atom of H_3O^+ (Oxygen) is also sp^3 hybridised and has 3bp+1 lp. Thus H_3O^+ will also be pyramidal with a bond angle of $\sim 107^\circ$. (Fig 1.5)

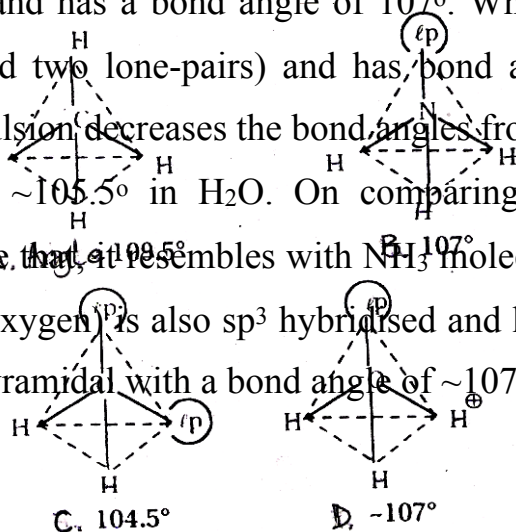


Fig 1.5 :A- CH_4 , Tetrahedral, bond angle 109.5°

B- NH_3 , Pyramidal, bond angle $\sim 107^\circ$

C- H_2O , Angular, bond angle $\sim 105^\circ$

D- H_3O^+ , Pyramidal, bond angle $\sim 107^\circ$

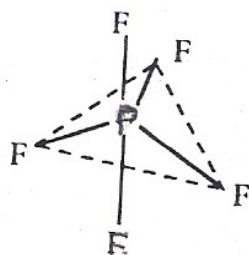
2.4. Comparison of PF_5 , SF_4 , ClF_3 and $[\text{ICl}_2]^-$

A comparison of PF_5 , SF_4 , ClF_3 and $[\text{ICl}_2]^-$ species clearly indicates that each of these molecules have 10 electrons in the valence shell of the central atom, being P, S, Cl and I respectively. In addition to this, the central atom in each case is sp^3d hybridised, and has 0, 1, 2 and 3 lone pairs (lp) respectively. In PF_5 , all the five electron pairs (= 10 electrons) are bond pairs and are housed in the five sp^3d hybrid orbital; resulting in the trigonal bipyramidal geometry of the molecule. (Fig 1.6 (a)).

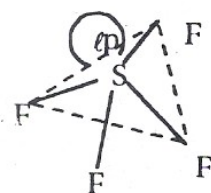
SF_4 molecule has 4 bond-pairs and one lone pair on the central S atom. The lp in this molecule has two options- it can sit in a axial or in an equatorial orbital. In the axial position (Fig. 1.6 (b)(i)) it has three bps at 90° and one bp directly opposite to itself. While in equatorial position (Fig. 1.6 (b)(ii)) it has two bps at 90° and two bps at 120° . As in the equatorial position lp-bp repulsion is less and expansion is easy the lp prefers the equatorial position and the molecule is therefore irregular tetrahedral.

In ClF_3 , the two lps may be axial-axial (Fig 1.6(c)(i)), or axial-equatorial (Fig 1.6(c)(ii)), or equatorial-equatorial (Fig 1.6(c)(iii)) positions. As the axial position will result in maximum repulsion hence the axial position for the lp is ruled out. Thus the molecule will have T. shaped geometry, according to the Fig. 1.6(c)(ii).

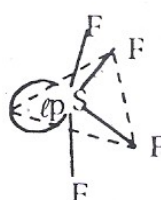
Similarly, due to reduced lp-lp repulsions and a larger volume that a lp can occupy at equatorial positions, the $[\text{ICl}_2]^-$ ion will be linear. The three lps occupy the three equatorial positions, leaving the axial positions for the Cl atoms (Fig. 1.6(d)).



(a) PF_5 , Trigonal bipyramidal

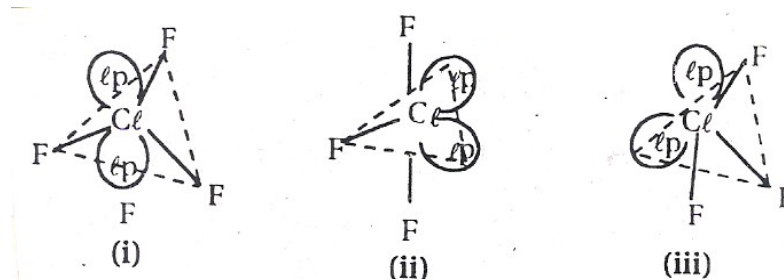


(I)

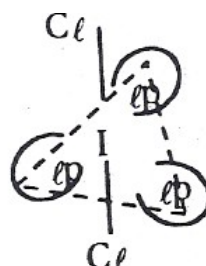


(II)

(b) SF_4 , Irregular tetrahedral



(c) ClF_3 , T-Shaped



(d) $[\text{ICl}_2]^-$, Linear

Fig. 1.6 : Structures of PF_5 , SF_4 , ClF_3 and $[\text{ICl}_2]^-$

Limitations of VSEPR Theory

1. This theory is not able to predict the shapes of certain transition element complexes.
2. This theory is unable to explain the shapes of certain molecules with an inert pair of electrons.
3. This theory is unable to explain the shapes of molecules having extensive delocalised π -electron system.
4. This theory can not explain the shapes of molecules which have highly polar bonds.

Check Your Progress-1

Notes: (i) Write your answers in the space given below;

(ii) Compare your answers with those given at the end of the unit.

(a) Identify and write the shapes of the following molecules.

(i) BeCl_2 (iv)

ClF_3 (ii)

PCl_3 (v)

XeF_2

(iii) SF_4 (vi)

BrF_5 (b) Arrange the following

species in the order of increasing bond-angle, considering the repulsive forces due to lone pair:

$\oplus\text{NO}_2$, NO_2 and NO_2^\ominus

> _____ > _____ > _____

3. WALSH DIAGRAMS

We know all the systems want to be in a stable state, and the stable state is one in which it has the minimum possible energy. Same is true for the stereochemistry or the geometry of a molecule. The VSEPR theory considered that the most stable configuration of a molecule is one in which repulsive forces between the valence electron-pairs is minimum. In contrast, the molecular orbital theory (MOT) 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 linear combination of atomic orbitals (LCAO). In 1953 A.D. Walsh proposed a simple pictorial-approach to determine the geometry of a molecule considering and calculating the energies of molecular orbitals of the molecule.

The basic approach is to calculate the energies of molecular orbitals for two limiting structures, say linear or bent to 90° for an AB_2 molecule, and draw a diagram showing how the orbitals of one configuration correlate with those of the other. Then depending on which orbitals are occupied, one or the other structure can be seen to be preferred. By means of approximate MO Theory implemented by digital computers, this approach has been extended and generalized in recent years.

Walsh's approach to the discussion of the shape of an AB_2 triatomic molecule (such as BeH_2 and H_2O) is illustrated in Fig. 1.8. The illustration shows an example of a Walsh diagram, a graph of the dependence of orbital energy on molecular geometry. A Walsh diagram for an B_2A or AB_2 molecule is constructed by considering how the composition and energy of each molecular orbital changes as the bond angle changes from 90° to 180° . The diagram is in fact just a more elaborate version of the correlation diagram.

3.1. Application to Triatomic Molecules

The coordinate system for the AB_2 molecule is shown in Figure 1.8. The AB_2 molecule has C_{2v} symmetry when it is bent and, when linear D_{2h} symmetry. To simplify notations, however, the linear configuration is considered to be simply an extremum of the C_{2v} symmetry. Therefore the labels given to the orbitals through the range $90^\circ \leq \theta < 180^\circ$ are retained even when $\theta = 180^\circ$. The symbols used to label the orbitals are derived from the orbital symmetry properties in a systematic way, but a detailed explanation is not given here. For present purposes, these designations may be treated simply as labels. (Fig. 1.7).

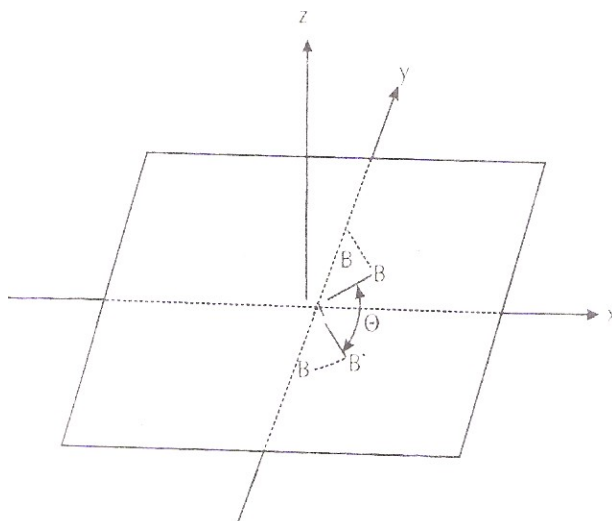


Fig. 1.7

The A atom of AB_2 molecule will be assumed to have only s, p_x , p_y and p_z orbitals in its valence shell, whereas each of the B atoms is allowed only a single orbital oriented to form a σ bond to A. In the linear configuration P^A_x and P^A_z are equivalent non-bonding orbitals labelled $2a_1$ and b_1 respectively. The orbitals S^A and P^A_y 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 $3a_1$ and $3b_2$. The ordering of these orbitals and in more detail, the approximate values of their energies can be estimated by an MO calculation. Similarly, for the bent molecule the MO energies may be estimated. Here only p_z^A is non bonding, spacing and even the order of the other orbitals is function of the angle of bending θ . The complete pattern of orbital energies, over a range of θ , is obtained with typical input parameters. This is shown in the figure 1.8. Calculations in the Huckel approximation are simple to perform and give the correct general features of the diagram but for certain cases (e.g. AB_2E_2) very exact computations are needed for an unambiguous prediction of structure.

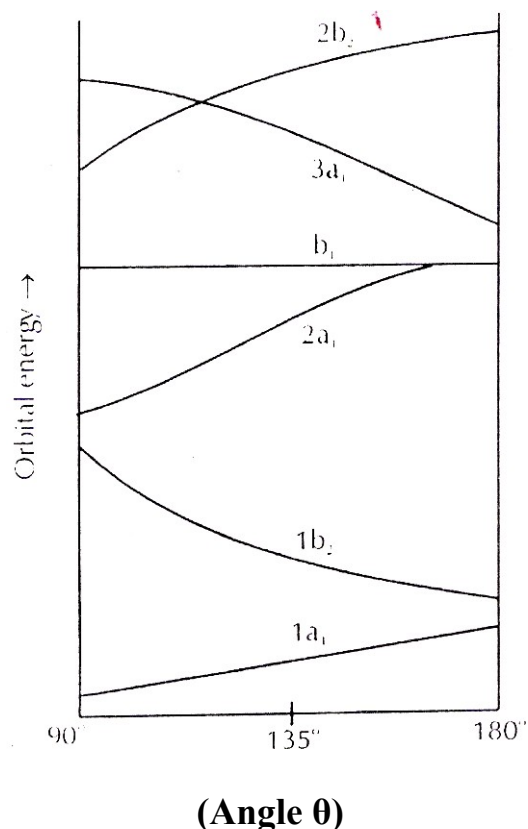


Figure 1.8 Orbital Correlation Diagram For AB₂ Triatomic Molecules Where A uses only s and p orbitals

From the approximate diagram (Fig. 1.8) it is seen that an AB₂ molecule (one with no lone pairs) is more stable when linear than when bent. The 1b₂ orbital drops steadily in energy from $\theta = 90^\circ$ to 180° ; while the energy of the 1a₁ orbitals is fairly insensitive to angle.

For an AB₂E molecule the results are ambiguous, because the trend in the energy of the 2a₁ orbital approximately offsets that of the 1b₂ orbital.

For AB₂E₂ molecules, the result should be the same as for AB₂E. Since the energy of b₁ orbital is independent of the angle. Thus it is not clear in this approach that AB₂E₂ molecules should necessarily be bent, but all known ones are.

The H₂O Molecule:

Because of its unique importance, this molecule has been subjected to more detailed study than any other AB₂E₂ molecule. A correlation diagram calculated specially for H₂O is shown in the figure. Although it differs in detail for the general AB₂E₂ shown in the figure it is encouraging to see that the important qualitative features are the same. 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. As stated in discussing that general purpose diagram, it is not clear whether an AB₂E₂ molecule ought necessarily to be bent.

In the diagram calculated expressly for H₂O the lowest level's is practically pure 2s and its energy is essentially constant for all 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°. (Fig. 1.9).

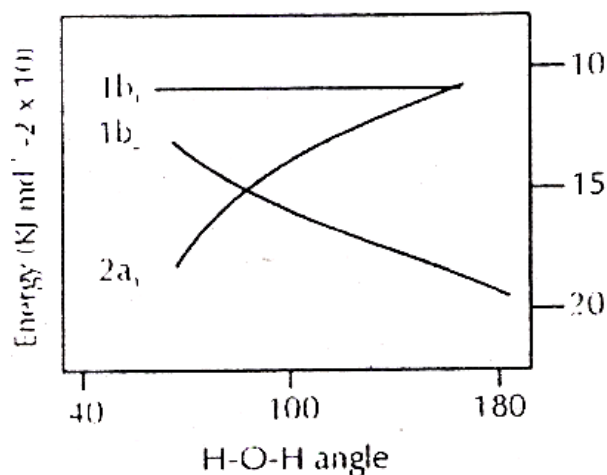


Fig. 1.9

BeH₂ - Molecule

The simplest AB₂ molecule in Period 2 is the transient gas-phase BeH₂ molecule (BeH₂ normally exists as a polymeric solid), in which there are four valence electrons. These four electrons occupy the lowest two molecular orbitals. If the lowest energy is achieved with the molecule angular, then that will be its shape. We can decide whether the molecule is likely to be angular by accommodating the electrons in the lowest two orbitals corresponding to an arbitrary bond angle in Fig. 1.7. We then note that the HOMO decreases in energy on going to the right of the diagram and that the lowest total energy is obtained when the molecule is linear.

Hence, BeH₂ is predicted to be linear and to have configuration $1\sigma_g^2 2\sigma_u^2$. In CH₂, which has two more electrons than BeH₂, three of the molecular orbital must be occupied. In this case, the lowest energy is achieved if the molecule is angular and has configuration $1a_1^2 2a_1^2 1b_2^2$.

The principal feature that determines whether or not the molecule is angular is whether the 2a₁ orbital is occupied. This is the orbital that has considerable A-2s character in the angular molecule but not in the linear molecule.

3.2. Application to Penta Atomic Molecules

For penta-atomic molecules examples of CH₄ and SF₄ may be taken for consideration. For these molecules, two geometries are possible: one a symmetrical tetrahedral and the other, a distorted tetrahedral geometry (or a tetragonal geometry of relatively lower symmetry).

CH₄ - Molecule

Methane, CH₄, has eight valence electrons. During bonding, for orbitals [a_{1g} (2s) and t_{1u} (2p)] of carbon, and one [a_{1g} (1s)] orbital of each

four hydrogen atoms take part. Overlapping of these eight orbitals, eight molecular orbitals are formed, the four bonding ($2\sigma_g$ or $2a_1$ and $2t_\sigma$ or $2t_1$) and the four antibonding ($2\sigma_g^*$ and $2t^*\sigma$). The eight valency electrons of CH_4 molecule are distributed in the four bonding molecular orbitals (Electronic Configuration, $2\alpha_1^2 2t_1^2$). In the tetrahedral geometry due to overlapping with the orbitals of hydrogen atom the energy of $2a_{1g}$ and $2t_{1u}$ orbitals is considerably reduced. In contrast, in the distorted geometry, comparatively less overlapping of t_{1u} orbitals with the hydrogen orbitals (as compared to that in the tetrahedral geometry) the energy of $2t_1$ molecular orbitals increases. Thus the geometry of CH_4 molecule is symmetrical tetrahedral, rather than a distorted tetrahedral.

SF_4 - Molecule

In the valence shell of sulphur atom, in SF_4 molecule, in addition to $3s$ (α_{1g}) and $3p$ (t_{1u}) orbitals, $3d$ (t_{2g} and e_g) orbitals are also present. During the bonding, $2p_z$ orbital of each of the four fluorine atoms take part. As a result four bonding ($2a_1$ and $2t_1$) and four antibonding ($2\alpha_1^* 2t_1^*$) molecular orbitals formed; while the d-orbitals [$a_1(dz^2)$, $b_1(dx^2 - y^2)$ and t_2 (d_{xy} , d_{xz} , d_{yz})] are present as non-bonding molecular orbitals. Ten valency electrons of SF_4 molecule remain distributed in the four bonding and one non-bonding molecular orbitals, resulting in $2\alpha_1^2 2t_1^2 3a_2^1$ configuration.

As in the distorted geometry, overlapping of $2t_1$ orbitals is comparatively greater (thus reducing their energy) and the filling in $3a_1$ orbital considerably reduce the energy of the system as compared to that in the regular tetrahedral structure. Hence SF_4 molecule has a distorted tetrahedral geometry, rather than a regular tetrahedral structure.

Thus we can say 'Walsh Diagrams' are complementary to the VSEPR concept.

Check Your Progress 2

- Notes: 1. Write your answers in the space given below.
2. Compare your answers with those given at the end of this unit.
- (a). Predict the shape of an H_2O molecule on the basis of a Walsh Diagram for an AB_2 molecule.

- (b) Is any AB_2 molecule, in which A denotes an atom of a period 3 element, expected to be linear? If so, which

4. $d\pi - p\pi$ BONDS.

There are several structural phenomena that have traditionally been attributed to the formation of $d\pi - p\pi$ Bonds. Recent work has raised some doubts. The phenomena in questions are exemplified by:

1. The fact that for amines such as $(\text{R}_3\text{Si})_2\text{NCH}_3$, $(\text{R}_3\text{Si})_3\text{N}$ and $(\text{H}_3\text{Ge})_3\text{N}$, the central NSi_2C , NSi_3 and NGe_3 skeletons are planar.
2. Many tetrahedral species such as SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} and ClO_4^- have bond lengths shorter than those predicted from conventional tables of single bond radii. In silicates the Si-O-Si units also show what were considered to be Si-O distance that are "too short" for single bonds.

Recent re-examinations of these phenomena by both theoretical and experimental methods together with earlier arguments now suggest that the $d\pi - p\pi$ contributions to these effects are at best small. Thus, in reading literature written prior to 1985, where such interactions are often accorded great importance, one should now be sceptical of all but the facts themselves.

This is not to say that $d\pi - p\pi$ bonding in main group compounds is never important. Probably in the case of $-S-N=S$ units, and in $F_3F \equiv N$, where the $S-N$ distances are very short indeed. However, it is always dangerous to attribute all structural effects to simple orbital overlaps, even if the explanation seems to fit, and the rise and fall of the $d\pi - p\pi$ overlap hypothesis is a case in point.

In a multiple bonded molecule having bond pairs + lone pairs = 4, 5 or 6, the π bonds will be $p\pi - d\pi$ bond. In this case the central atom uses all its p-orbitals for hybridisations and has only d-orbitals available to overlap with p-orbitals of the adjacent atom to give $d\pi - p\pi$ bond.

The formation of $d\pi - p\pi$ bond is common for all the second period elements and is not important for the elements of third and higher periods. The $p\pi - d\pi$ bonding is more favourable than the $d\pi - p\pi$ bonding for higher atoms of third and higher periods.

4.1. $d\pi - p\pi$ Bonding in Phosphorous Group Elements

Phosphine Oxide, $R_3P=O$, presents an important example of the participation of d-atomic orbitals of nonmetallic elements in π bonding. Presence of π bonding is defected with the help of the evidences, such as reduction in the bond length, increase in the bond strength and the stabilisation of charge distribution. On these grounds, compared to

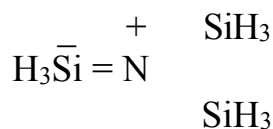
amine oxide, phosphine oxide presents a strong evidence of the presence of $d\pi - p\pi$ bond, in a very high stability of $P = O$.

Similarly the fact that almost all π -phosphines are readily oxidised into $R_3P = O$, also indicates that $d\pi - p\pi$ bond is present in the $P = O$ bonding. This is supported by the lower dipole moment of triethyl phosphine oxide (1.4×10^{-3} Cm. cf 16.7×10^{-3} Cm. of trimethyl amine oxide), higher dissociation energy of $P = O$ bond (500-600 KJ, cf 200-300 KJ of $N=O$ bond) and the smaller P-O bond lengths in phosphoryl compounds.

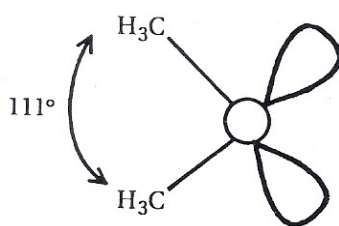
4.2. $d\pi - p\pi$ Bonding in Nitrogen, Oxygen and Sulphur Compounds

There are number of examples, which show $d\pi - p\pi$ bonding in nitrogen, oxygen and sulphur compounds:

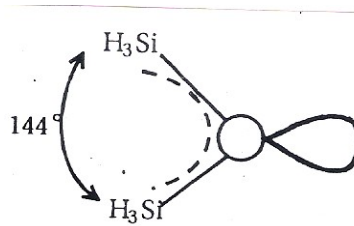
- (i) Mobile π bonding in trisilyl amine results in the resonance in the molecule :



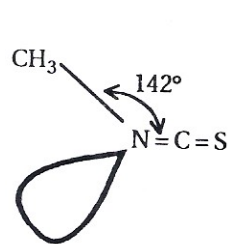
- (ii) The bond angles in disiloxane, $H_3SiOSiH_3$, and silyl isothiocyanate, $H_3Si-N=C=S$ indicates $p\pi - d\pi$ back-bonding (in comparison to ether and methyl isothiocyanate) :



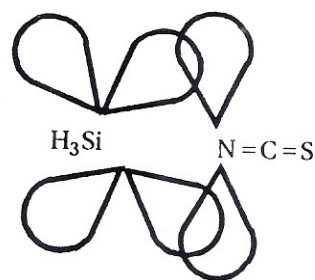
Dimethyl ether
(sp^3 -hybridised. 0 + 2 lp)
Addition compound with BF_3



Disiloxane
(sp^3 -hybridised. 0 + 1 lp)
No addition compound with BF_3



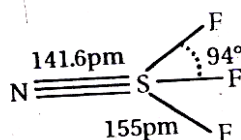
Methyl isothiocyanate
(one lp on N; Angular)



Silyl isothiocyanate
lp used in π bonding, Linear

The argument given against the use of d atomic orbitals in bonding by non-metallic elements is that a very high excitation energy is required for the same. Hence it may be concluded that the use of d-atomic orbitals in bonding by non-metallic elements will be possible only in their higher oxidation states and when they are linked with strong electronegative elements, eg. PF_5 , SF_6 , OPX_3 etc.:

- (i) The N - S bond length in $\text{N} \equiv \text{SF}_3$ indicates. The bond order = 2.7 indicating $d\pi - p\pi$ bonding:

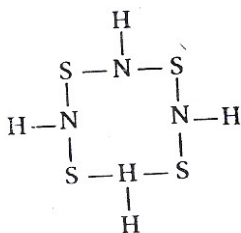


Thiazytrifluoride

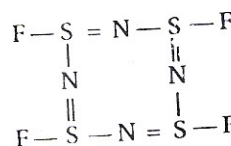
N - S bond length = 141.6 pm; Bond order = 2.7

(cf N - S = 174 pm, b.o = 1, N = S = 154 pm; b.o = 2)

- (ii) In $\text{S}_4\text{N}_4\text{F}_4$ also there is indication of $d\pi - p\pi$ bonding (compare with $\text{S}_4\text{H}_4\text{N}_4$):

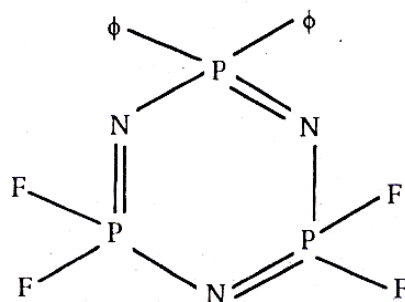


Tetra Sulphur tetramide
(Isoelectronic and
Isomorphous with S_8)



Tetra sulphur tetramide fluoride
(Alternate S = N bond)

- (ii) In diphenyl phosphonitrilic fluoride, there is evidence of π bonding in the ring:



Check Your Progress-3

- Notes: 1. Write your answers in the space given below.
2. Compare your answers with those given at the end of this unit.
- (a). In which of the following molecule there is a possibility of $d\pi-p\pi$ bonding?

$S_4N_4F_4$, $S_4H_4N_4$, $N \equiv SF_3$, $H_3SiOSiH_3$, $CH_3N = C = S$ and Et_3NO .

Ans: (i) _____ (ii) _____
(iii) _____

- (b) Which are the evidences in favour of $d\pi-p\pi$ bonding in R_3PO molecule?

Ans: (i) _____
(ii) _____
(iii) _____

