

## CHEMICAL BONDING

### QUANTUM THEORY (MODERN THEORY) OF COVALENT BOND AND OVERLAPPING

#### Introduction

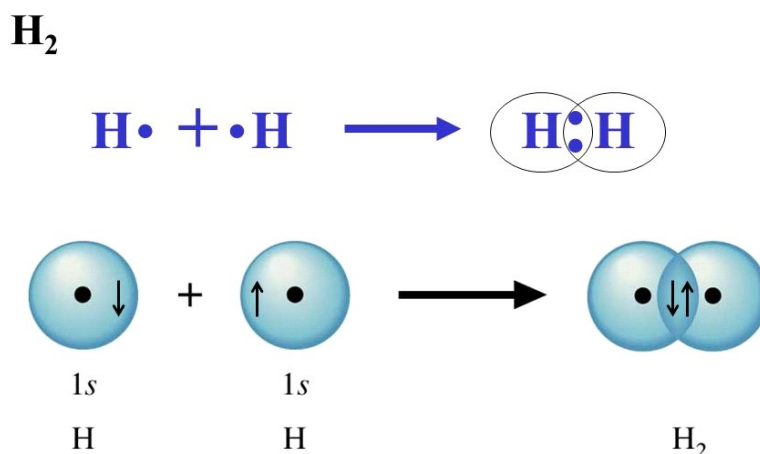
According to Lewis theory, Covalent bond is formed by the sharing of electron but Lewis theory couldn't explain about how the sharing of electrons takes place during the formation of covalent bond.

In order to rectify the drawbacks of Lewis theory, Quantum theory (Modern theory) of Covalent bond formation is proposed

#### A modern Approach for covalent bond (Valence bond theory or VBT)

##### (i) Heitler and London concept.

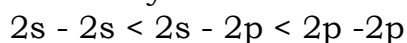
- To form a covalent bond, two atoms must come close to each other so that orbitals of one overlaps with the other.
- Orbitals having unpaired electrons of anti spin overlaps with each other.
- After overlapping a new localized bond orbital is formed which has maximum probability of finding electrons as shown in the following figure.



- Covalent bond is formed due to electrostatic attraction between nuclei and the accumulated electrons cloud and by attraction between spins of anti spin electrons.
- Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high.

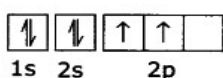
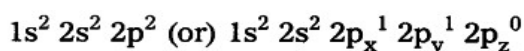
##### (ii) Pauling and Slater extension

- The extent of overlapping depends upon: Nature of orbitals involved in overlapping, and nature of overlapping.
- More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high.
- Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy :



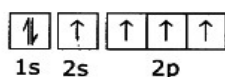
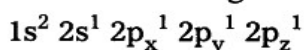
(d) S-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand,  $p$ -orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping.

Electrons which are already paired in valency shell can enter into bond formation if they can be unpaired first and shifted to vacant orbitals of slightly higher energy of the same main energy shell (valency shell). This point explains the trivalency of boron, tetravalency of carbon, pentavalency of phosphorus, hexavalency of sulphur and heptavalency of halogens (Cl, Br, I) inspite of the fact that these atoms have paired orbitals in the valency shell.



### Carbon (ground state)

Electronic configuration of carbon (excited state) :



### Carbon (excited state)

- Between two orbitals of the same stability (i.e., having same energy) one more directionally concentrated would form a stronger bond. Dumb-bell shaped  $p$ -orbitals will form stronger bond as compared to spherically symmetrical  $s$ -orbital. It is formed by head on or axial overlap.
- Two types of bonds are formed on account of overlapping. These are (a) Sigma ( $\sigma$ ) and (b) pi ( $\pi$ )

#### (a) Sigma ( $\sigma$ ) Bond:

A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma ( $\sigma$ ) bond. In such a bond formation, maximum overlap is possible between electron cloud of this bond is symmetrical about the line joining the two nuclei of the two atoms. Sigma bond can, thus, be defined as :

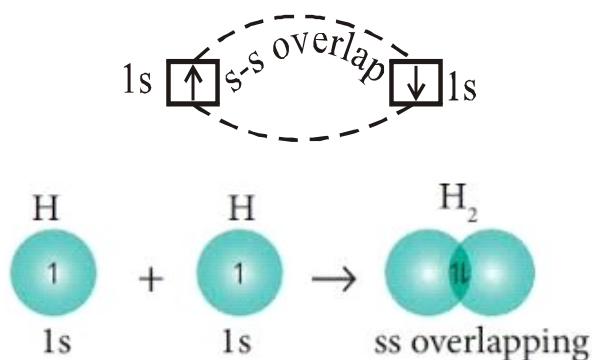
“Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond.” It is formed by head on or axial overlap.

Sigma bonds are formed by three types of overlapping:

#### (i) s-s overlapping (Formation of hydrogen molecule):

Each hydrogen atom has one electron in  $1s$ -orbital which is spherical.  $1s$ -orbital of both the hydrogen atoms approach each other closely and when they reach a

point of maximum attraction by the two nuclei, they overlap and form a sigma bond.



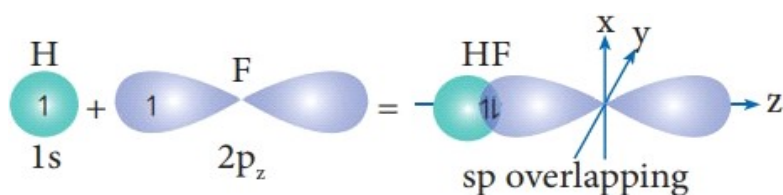
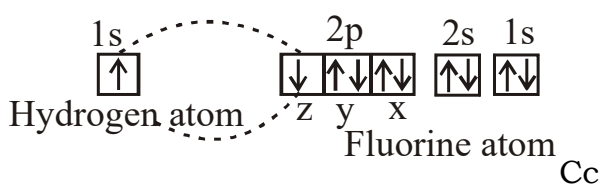
The bond has two electrons which have opposite spins. The probability of finding these electrons is

maximum in the region between the two nuclei on the molecular axis. The electron density of the bond is distributed symmetrically about the molecular axis.

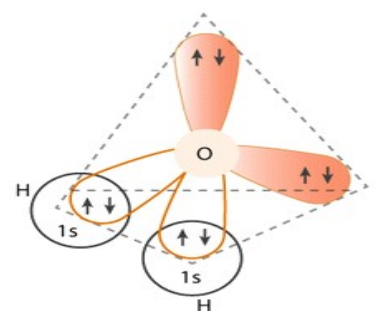
**(ii) s-p overlapping (Formation of HF, H<sub>2</sub>O, NH<sub>3</sub> molecules):**

**(a) Formation of HF molecule:**

In the formation of HF molecule the 1s-orbital of hydrogen overlaps with the p-orbital of fluorine containing unpaired electron.



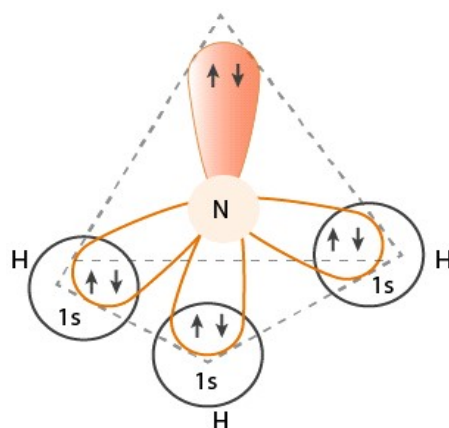
**(b) Formation of water molecule:** Oxygen atom has the configuration of valency shell  $1s^2 2p_z^2 2p_y^1 2p_x^1$ , i.e., it has two orbitals singly occupied. These two orbitals overlap with 1s-orbital of two hydrogen atoms forming sigma bonds.



Since the two orbitals of oxygen are at right

angle to each other an angle of  $90^\circ$  is expected between two sigma bonds but actual bond angle observed is  $104.5^\circ$ .

- (c) **Formation of ammonia molecule:** Nitrogen atom has the configuration of valency shell  $2s^2 2p_x^1 2p_y^1 2p_z^1$ , i.e., three singly occupied orbitals are present. These orbitals overlap with 1s-orbitals of three hydrogen atoms forming three sigma bonds.

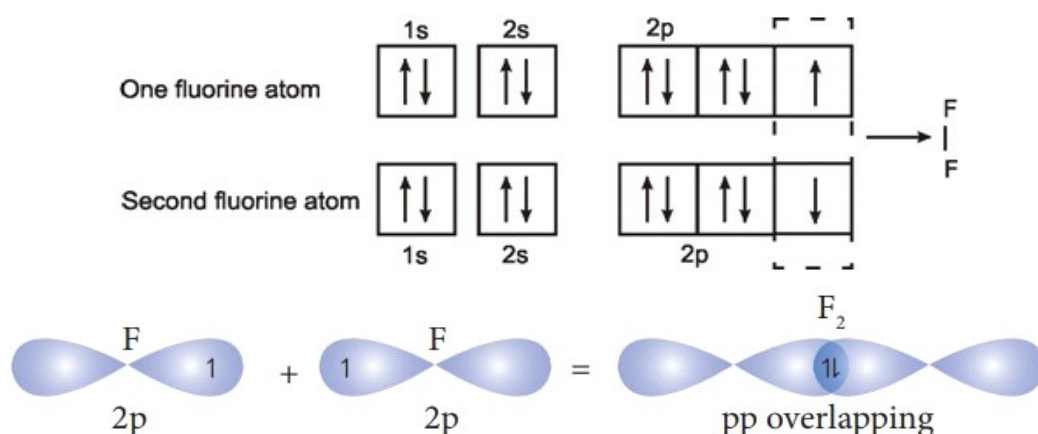


Orbital overlap in  $\text{NH}_3$

Since the three orbitals of nitrogen are at right angle to each other, the expected angle between two sigma bonds should be  $90^\circ$  but actual bond angle observed is  $107^\circ$ .

- (iii) **p-p overlapping (Formation of fluorine molecule):**

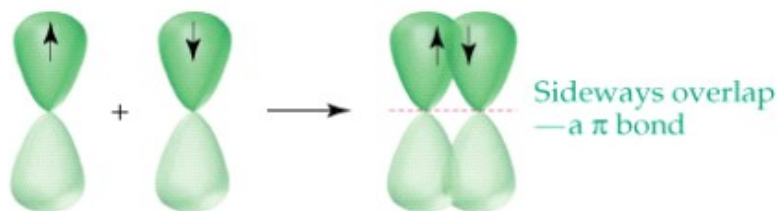
This is illustrated by the formation of fluorine molecule. The electronic configuration of fluorine atom is  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ , i.e., one orbital is singly occupied. When p-orbitals of two fluorine atoms approach each other with their heads directly towards one another, they overlap and form a sigma bond.



- b) **Pi ( $\pi$ ) Bond:**

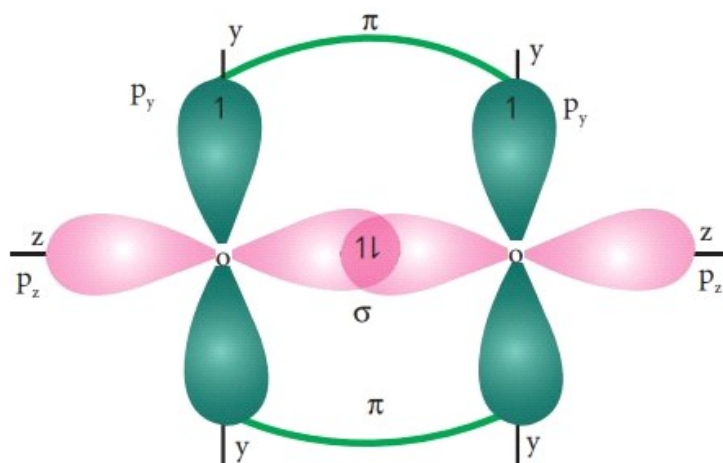
$\pi$ -bonds are formed by the sidewise or lateral overlapping of p-orbitals. The overlapping takes place at the side of two lobes and hence, the extent of overlapping

is relatively smaller. Thus,  $\pi$ -bond is a weaker bond in comparison to sigma bond. The molecular orbital is oriented above and below the plane containing nuclear axis.



- **Formation of oxygen molecule:** Oxygen atom has two p-orbitals singly occupied in the valency shell. When two oxygen atoms approach each other, one set of p-orbitals experiences head on overlaps and other p-orbitals sideways to form a  $\pi$ -bond. Thus, oxygen molecule has one  $\sigma$ -and one  $\pi$ -bond.

		$\pi$ bond	$\sigma$ bond
Oxygen 1	1↓ $2s^2$	1↓	1
		$2p_x^2$	$2p_y^1$ $2p_z^1$
Oxygen 2	1↓ $2s^2$	1↓	1
		$2p_x^2$	$2p_y^1$ $2p_z^1$



Similarly, the formation of nitrogen molecule can be explained. It has one sigma bond and two  $\pi$ -bonds.

<b>Differences between <math>\sigma</math> and <math>\pi</math> bonds</b>	
<b>Sigma (<math>\sigma</math>) bond</b>	<b>Pi (<math>\pi</math>) bond</b>
It results from the end to end overlapping of two <i>s</i> -orbitals or two <i>p</i> -orbitals or one <i>s</i> and one <i>p</i> -orbital.	It result from the sidewise (lateral) overlapping of two <i>p</i> -orbitals.
Stronger	Less strong
Bond energy 80 <i>kcal</i> s	Bond energy 65 <i>kcal</i> s
More stable	Less stable
Less reactive	More reactive
Can exist independently	Always exist along with a s-bond
The electron cloud is symmetrical about the internuclear axis.	The electron cloud is above and below the plane of internuclear axis.

### Important points related to $\sigma$ and $\pi$ bonds

- ' $\pi$ ' bond is formed only after the formation of ' $\sigma$ ' bond.
- Any type of orbitals can involve in ' $\sigma$ ' bond formation.
- Only 'p' or 'd' - orbitals can involve in ' $\pi$ ' bond information.
- Single bond is equal to one ' $\sigma$ ' bond.
- Double bond is a combination of one ' $\sigma$ ' bond and one ' $\pi$ ' bond.
- Triple bond is a combination of one ' $\sigma$ ' bond and two ' $\pi$ ' bonds.
- $\sigma$  bond is stronger than ' $\pi$ ' bond.
- Strength of the bonds follows the order
 
$$\sigma_{p-p} > \sigma_{s-p} > \sigma_{s-s} > \pi$$
- ' $\sigma$ ' bond between '1S' orbitals is exceptionally stronger .
- Strength of the bonds follows the order  
triple bond > double bond > single bond.

### Workedout Examples

**Example-1: Four bonds are never formed between two atoms. Why ?**

**Solution :**

There are three axes (x, y and z) perpendicular to each other. A maximum of two p bonds can be formed by collateral overlapping and one s bond is formed by coaxial overlapping. Thus, highest bond order between two atoms can be three and never four.

**Example-2:** A s bond is formed in  $O_2$  by overlapping of :

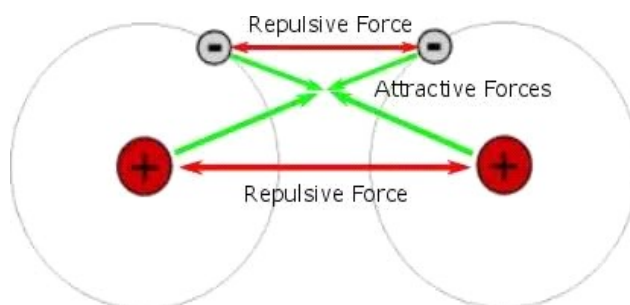
- (1)  $2p_y - 2p_z$       (2)  $2p_y - 2s$       (3)  $2p_z - 2s$       (4)  $2p_z - 2p_z$

**Solution : Ans. (4)**

Extent of  $p_y - p_z$  and  $p_y - s$  overlapping is zero.

**(iii) Energy concept**

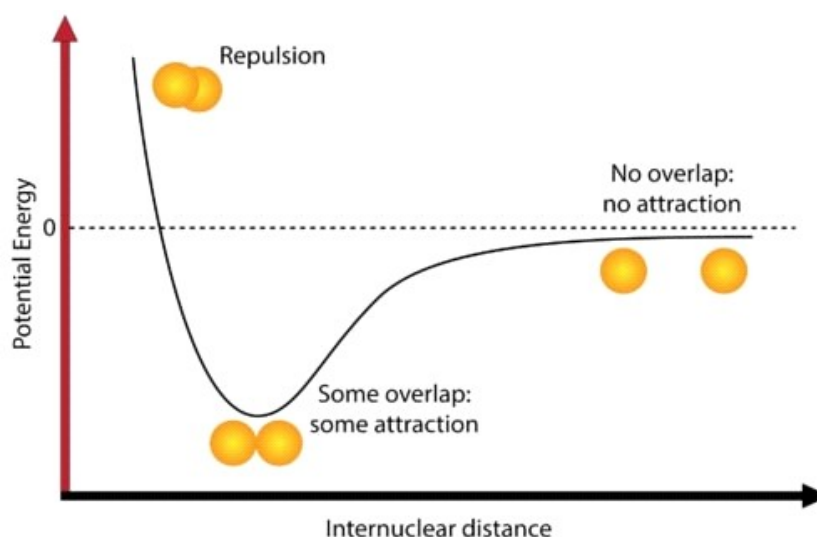
- (a) Atoms combine with each other to minimize their energy.  
 (b) Let us take the example of hydrogen molecule in which the bond between two hydrogen atoms is quite strong.  
 (c) During the formation of hydrogen molecule, when two hydrogen atoms approach each other, two types of interaction become operative as shown in figure.



The force of attraction between the molecules of one atom and electrons of the other atom. The force of repulsion between the nuclei of reacting atoms and electrons of the reacting atoms

(d) As the two hydrogen atoms approach each other from the infinite distance, they start interacting with each other *when the magnitude of attractive forces is more than that of repulsive forces a bond is developed between two atoms.*

(e) The decrease in potential energy taking place during formation of hydrogen molecule may be shown graphically



(f) The inter nuclear distance at the point O have minimum energy or maximum stability is called bond length.

(g) The amount of energy released (i.e., decrease in potential energy) is known as enthalpy of formation.

(h) From the curve it is apparent that greater the decrease in potential energy, stronger will be the bond formed and vice versa.

(i) It is to be noted that for dissociation of hydrogen molecule into atoms, equivalent amount of energy is to be supplied.

(j) Obviously in general, a stronger bond will require greater amount of energy for the separation of atoms. The energy required to cleave one mole of bonds of the same kind is known as the bond energy or bond dissociation energy.

This is also called as orbital overlap concept of covalent bond.

## (2) Overlapping

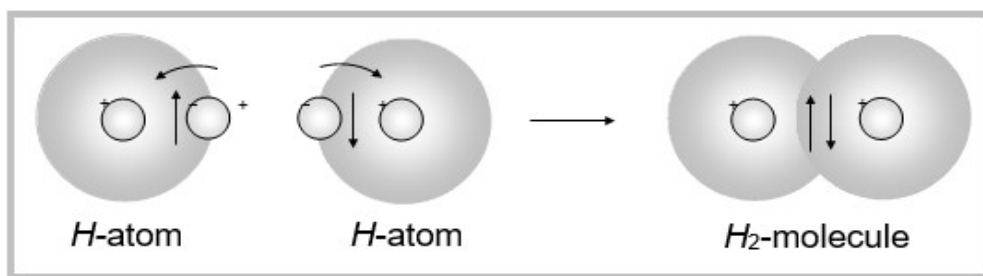
(i) According to this concept a covalent bond is formed by the partial overlapping of two half filled atomic orbitals containing one electron each with opposite spins then they merge to form a new orbital known as **molecular orbital**.

(ii) These two electrons have greater probability of their presence in the region of overlap and thus get stabilised i.e., during overlapping energy is released.

**Examples of overlapping are given below :**

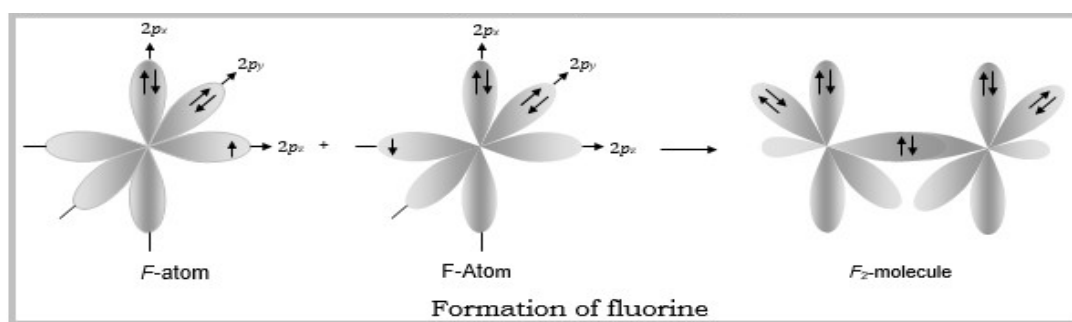
### Formation of hydrogen molecule :

Two hydrogen atoms having electrons with opposite spins come close to each other, their s-orbitals overlap with each other resulting in the union of two atoms to form a molecule.



### Formation of fluorine molecule :

In the formation of  $F_2$  molecule  $p$ -orbitals of each fluorine atom having electrons with opposite spins come close to each other, overlapping take place resulting in the union of two atoms.





## VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

In 1957 Gillespie and Nyholm gave this theory to predict and explain molecular shapes and bond angles more exactly. The theory was developed extensively by Gillespie as the Valence Shell Electron Pair Repulsion (VSEPR) theory.

### This may be summarized as:

1. The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.

2. A lone pair of electrons takes up more space round the central atom than a bond pair, since the lone pair is attracted to one nucleus whilst the bond pair is shared by two nuclei. It follows that repulsion between two lone pairs is greater than repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs. Thus the presence of lone pairs on the central atom causes slight distortion of the bond angles from the ideal shape. If the angle between a lone pair, the central atom and a bond pair is increased, it follows that the actual bond angles between the atoms must be decreased. The order of repulsion between lone pairs and bond pairs of electrons follows the order as:

**Lone pair - lone pair repulsion > lone pair - bond pair repulsion > bond pair - bond pair repulsion.**

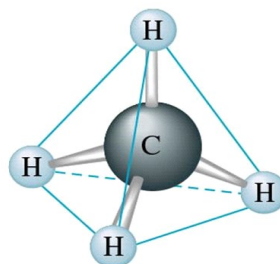
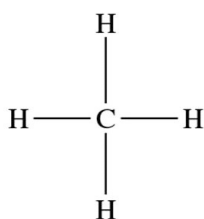
3. The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.

4. Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.

### Effect of Lone Pairs:

Molecules with four electron pairs in their outer shell are based on a tetrahedron. In  $\text{CH}_4$  there are four bonding pairs of electrons in the outer shell of the C atom, and the structure is a regular tetrahedron with bond angle  $\text{H} - \text{C} - \text{H}$  of  $109^\circ 28'$ .

#### Example: Methane

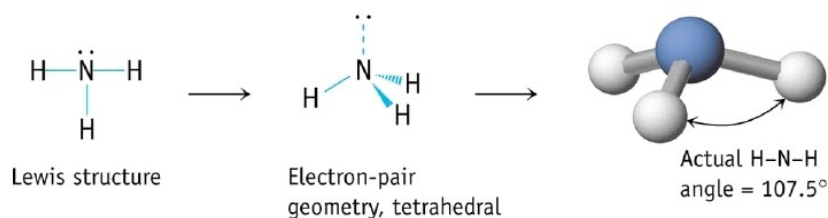


- 4 equivalent C-H covalent bonds
- VSEPR predicts a tetrahedral geometry

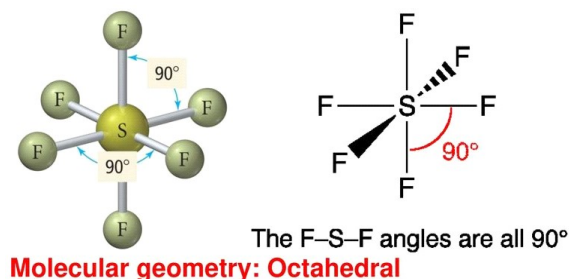
In  $\text{NH}_3$  and N atom has four electron pairs in the outer shell, made up of three bond pairs and one lone pair. Because of the lone pair, the bond angle  $\text{H} - \text{N} - \text{H}$  is reduced from the theoretical tetrahedral angle of  $109^\circ 28'$  to  $107^\circ 28'$ . In  $\text{H}_2\text{O}$  the O atom has four electron pairs in the outer shell. The shape of the  $\text{H}_2\text{O}$

molecule is based on a tetrahedron with two corners occupied by bond pairs and the other two corners occupied by lone pairs. The presence of two lone pairs reduces the bond angle further to  $104^{\circ}27'$ .

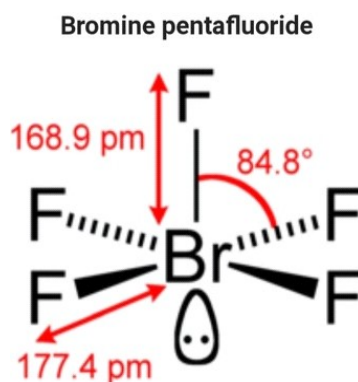
### Ammonia Molecule ( $\text{NH}_3$ )



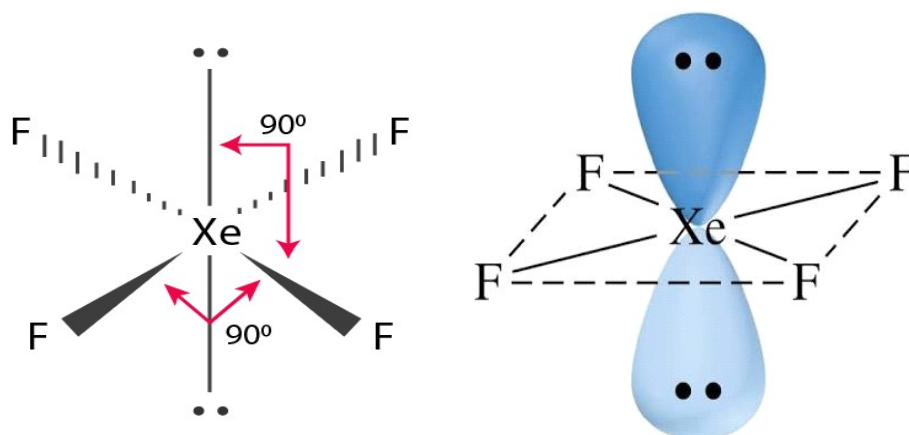
$\text{SF}_6$  has six bond pairs in the outer shell and is a regular octahedron with bond angles of exactly  $90^{\circ}$ .



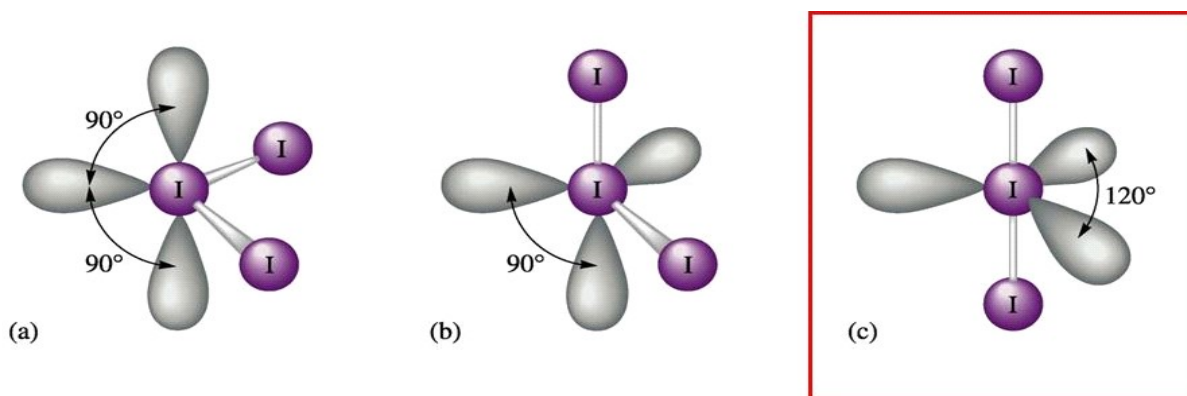
In a similar way, In  $\text{BrF}_5$ , the Br also has six outer pairs of electrons, made up of five bond pairs and one lone pair. The lone pair reduces the bond angles to  $84^{\circ}30'$ .



Whilst it might be expected that two lone pairs would distort the bond angles in an octahedral as in  $\text{XeF}_4$  but it is not so. Actual bond angle is  $90^{\circ}$ , reason being that the lone pairs are trans to each other in the octahedron, and hence the atoms have a regular square planar arrangement.



Molecules with five pairs of electrons are all based on a trigonal bipyramid. Lone pairs distort the structures as before. The lone pairs always occupy the equatorial positions (in an triangle), rather than the axial positions (up and down). Thus in  $I_3^-$  ion, the central I atom has five electron pairs in the outer shell, made of two bond pairs and three lone pairs. The lone pairs occupy all three equatorial positions and the three atoms occupy the top, middle, and bottom positions in the trigonal bipyramid, thus giving a linear arrangement with a bond angle of exactly  $180^\circ$ .



**Effect of Electronegativity:**  $NF_3$  and  $NH_3$  both have structures based on a tetrahedron with one corner occupied by a lone pair. The high electronegativity of F push the bonding electrons further away from N than in  $NH_3$ . Hence the lone pair in  $NF_3$  causes a greater distortion from tetrahedral and gives a  $F - N - F$  bond angle of  $102^\circ 30'$ , compared with  $107^\circ 48'$  in  $NH_3$ . The same effect is found in  $H_2O$  (bond angle  $104^\circ 27'$ ) and  $F_2O$  (bond angle  $102^\circ$ ).

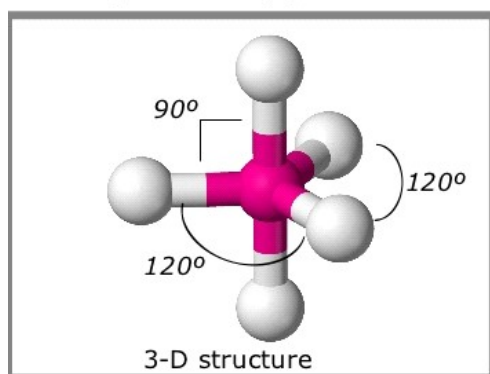
### Some more examples using the VSEPR Theory

#### Phosphorus pentachloride $PCl_5$ :

Gaseous  $PCl_5$  is covalent. (The electronic structure P is  $1s^2 2s^2 2p^6 3s^2 3p^3$ ). All five outer electrons are used to form bonds to the five Cl atoms. In the  $PCl_5$  molecule

the valence shell of the P atom contains five electron pairs: hence the structure is a trigonal bipyramid. There are no lone pairs, so the structure is not distorted. However, a trigonal bipyramid is not a completely regular structure, since some bond angles are  $90^\circ$  and others  $120^\circ$ . Symmetrical structures are usually more stable than asymmetrical ones.

### Trigonal bipyramidal



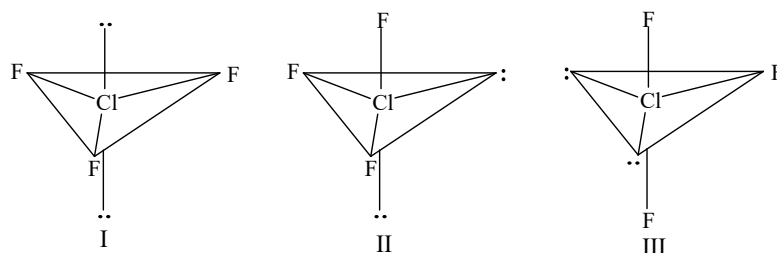
**Note:** Thus  $\text{PCl}_5$  is highly reactive, and in the solid state it splits into  $\text{PCl}_4^+$  and  $[\text{PCl}_6]^-$  ions, which have tetrahedral and octahedral structures respectively.

### Chlorine trifluoride $\text{ClF}_3$ :

The chlorine atom is at the centre of the molecule and determines its shape. The electronic configuration of Cl is  $1s^2 2s^2 2p^6 3s^2 3p^5$ . Three electrons form bonds to F, and four electrons do not take part in bonding. Thus in  $\text{ClF}_3$ , the Cl atom has five electron pairs in the outer shell, hence the structure is a trigonal bipyramid. There are three bond pairs and two lone pairs.

It was noted previously that a trigonal bipyramid is not a regular shape since the bond angles are not all the same. It therefore follows that all the corners are not equivalent. Lone pair occupy two of the corners, and F atoms occupy the other three corners. Three different arrangements are theoretically possible, as shown in figure below.

The most stable structure will be the one of lowest energy, that is the one with the minimum repulsion between the five orbitals. The great repulsion occurs between two lone pairs. Lone pair bond pair repulsions are next strongest, and bond pair-bond pair repulsions are weakest. Groups at  $90^\circ$  repel each other strongly, whilst groups  $120^\circ$  apart repel each other much less.



Chlorine trifluoride molecule

Structure I is the most symmetrical, but has six  $90^\circ$  repulsions between lone pairs and atoms. Structure II has one  $90^\circ$  repulsion between two lone pairs, plus three  $90^\circ$  repulsions between lone pairs and atoms. These factors indicate that structure III is the most probable. The observed bond angles are  $80^\circ 40'$ , which is close to the theoretical  $90^\circ$ . This confirms that the correct structure is III, and the slight distortion from  $90^\circ$  is caused by the presence of the two lone pairs.

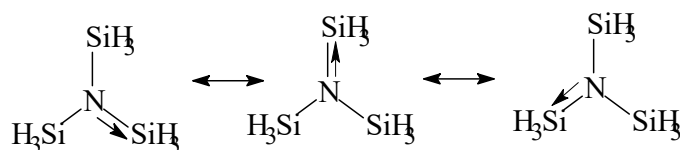
As a general rule, if lone pairs occur in a trigonal bipyramid they will be located in the equatorial position (round the middle) rather than the axial positions (top and bottom), since this arrangement minimizes repulsive forces.

### Back Bonding :

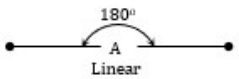
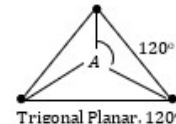
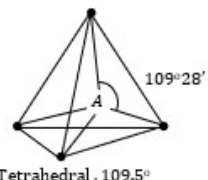
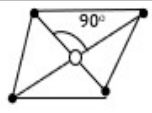
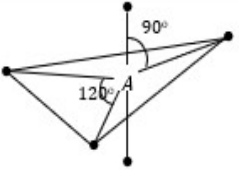
The interaction between an empty orbital and lone pair electron known as back bonding .

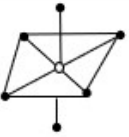
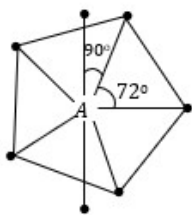
For example the nitrogen in trimethyl amine and trisilyl amine has a lone pair electron at nitrogen but nitrogen in trimethyl amine has pyramidal shape while in trisilyl amine nitrogen has planer shape because in trimethyl amine there is repulsion between lone pair and bond pair that's why the shape becomes pyramidal

In trisilyl amine, there is vacant d-orbital at silicon which overlaps with lone pair of nitrogen called  $p\pi - d\pi$  back bonding hence geometry becomes planer



## List of Examples with Molecular shapes and Bond angles

Geometry of molecules as per VSEPR theory	No. of bonded atoms	No. of lone pairs	Actual shape of molecules	Example
 Linear	2	0	Linear	$CO_2, HgCl_2, BeF_2, ZnCl_2,$ $MgCl_2, C_2H_2, HCN, BeH_2, C_2H_2, CS_2, N_2O, Hg_2Cl_2,$ $[Ag(NH_3)_2]^+$
 Trigonal Planar, $120^\circ$	3	0	Trigonal Planar	$BF_3, AlCl_3, SO_3^{2-}, C_2H_4, NO_3^-, CO_3^{2-}, HCHO$ $C_6H_6, CH_3^+, \text{graphite}, C_2Cl_4, C_2H_2Cl_2, [HgI_3]^-$ $[Cu(PMe_3)_3]^-, NO_2^-, SO_2, SnCl_2$
$< 120^\circ$	2	1	V-shape (bent)	
 Tetrahedral, $109.5^\circ$	4	0	Tetrahedra 1	$CH_4, SiH_4, SO_4^{2-}, SnCl_4, ClO_4^-, BF_4^-, NH_4^+, CCl_4,$ $SiF_4, H_2 - NH_2, [BeF_4]^{2-}, XeO_4,$ $[AlCl_4]^- , SnCl_4, PH_4^+, \text{Diamond, silica,}$ $N(CO)_4, Si(CH_3)_4, SiC, SF_2, [NiCl_4]^{2-}, [MnO_4]^{2-}, [VO_4]^{3-}$
$< 109.5^\circ$	3	1	Trigonal pyramidal	$NH_3, PCl_3, PH_3, AsH_3$ $ClO_3^-, POCl_3, H_3O^+, XeO_3$
$104.5^\circ$	2	2	V-shape (bent)	$H_2O, H_2S, PbCl_2, OF_2, NH_2^-, ClO_2$
 Square planar	4	0	Square planar	$[Cu(NH_3)_4]^{2+}, [Ni(CN)_4]^{2-}, [Pt(NH_3)_4]^{2+}$
 Trigonal bipyramidal	5	0	Trigonal bipyramidal	$PCl_5, SbCl_5, XeO_3, F_2, PF_5, AsF_5, PCl_4^+, PCl_6^-, [Cu(Cl)_5]^{2-}$ $[Ni(CN)_5]^{3-}, [Fe(CO)_5]$
Slightly less than $90^\circ$ and $120^\circ$	4	1	Irregular tetrahedral	$TeCl_4, SF_4$
$90^\circ$	3	2	T-shaped	$ClF_3, IF_3$
$180^\circ$	2	3	Linear	$I_3^-, XeF_2$

 Octahedral	6	0	Octahedral	$SF_6, PF_6^-, SnCl_6^-, MoF_6,$ $(BaCl_6)^-, (PF_6)^-,$ $[Fe(CN)_6]^{4-}, [Fe(H_2O)_6]^{3+}$
90°	5	1	Square pyramidal	$ICl_5, BrF_5, IF_5, XeOF_4$
90°	4	2	Square planar	$XeF_4, ICl_4^-$
 Pentagonal bipyramidal	7	0	Pentagonal bipyramidal	$IF_7, [ZrF_7]^{3-}, [UF_7]^{3-}$ $[UO_2F_5]^{3-}$
90° and 72°	6	1	Distorted octahedral	$XeF_6$

### CDF POINTS

- Covalent bond is formed due to electrostatic attraction between nuclei and the accumulated electrons cloud and by attraction between spins of anti spin electrons.
- Greater is the overlapping, lesser will be the bond length, more will be attraction and more will be bond energy and the stability of bond will also be high.
- Between two sub shells of same energy level, the sub shell more directionally concentrated shows more overlapping. Bond energy :  
 $2s - 2s < 2s - 2p < 2p - 2p$
- s* -orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, *p* -orbitals are directionally concentrated and thus show either head on overlapping or lateral overlapping.
- A bond formed between two atoms by the overlap of singly occupied orbitals along their axes (end to end overlap) is called sigma ( $\sigma$ ) bond.
- “Bond orbital which is symmetrical about the line joining the two nuclei is known as sigma bond.” It is formed by head on or axial overlap.
- Sigma bonds are formed by three types of overlapping, they are s-s overlapping, s-p overlapping, p-p overlapping.

8.  $\pi$ -bonds are formed by the sidewise or lateral overlapping of p-orbitals.
9. The overlapping takes place at the side of two lobes and hence, the extent of overlapping is relatively smaller. Thus,  $\pi$ -bond is a weaker bond in comparison to sigma bond.
10. Single bond is equal to one ' $\sigma$ ' bond. Double bond is a combination of one ' $\sigma$ ' bond and one ' $\pi$ ' bond. Triple bond is a combination of one ' $\sigma$ ' bond and two ' $\pi$ ' bonds.
11. ' $\pi$ ' bond is formed only after the formation of ' $\sigma$ ' bond. Any type of orbitals can involve in ' $\sigma$ ' bond formation. Only 'p' or 'd' - orbitals can involve in ' $\pi$ ' bond information.
12.  $\sigma$  bond is stronger than ' $\pi$ ' bond. Strength of the bonds follows the order  

$$\sigma_{p-p} > \sigma_{s-p} > \sigma_{s-s} > \pi$$
 ' $\sigma$ ' bond between '1S' orbitals is exceptionally stronger .
13. Strength of the bonds follows the order : triple bond > double bond > single bond.
14. when the magnitude of attractive forces is more than that of repulsive forces a bond is developed between two atoms.
15. a stronger bond will require greater amount of energy for the separation of atoms. The energy required to cleave one mole of bonds of the same kind is known as the bond energy or bond dissociation energy.
16. According to this concept of overlap a covalent bond is formed by the partial overlapping of two half filled atomic orbitals containing one electron each with opposite spins then they merge to form a new orbital known as **molecular orbital**.
17. The shape of the molecule is determined by repulsions between all of the electron pairs present in the valence shell.
18. The order of repulsion between lone pairs and bond pairs of electrons follows the order as:  
 Lone pair - lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion.
19. The magnitude of repulsions between bonding pairs of electrons depends on the electronegativity difference between the central atom and the other atoms.
20. Double bonds cause more repulsion than single bonds, and triple bonds cause more repulsion than a double bond.
21. The interaction between an empty orbital and lone pair electron known as back bonding .

### CONCEPTUAL UNDERSTANDING QUESTIONS (CUQ's)





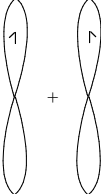
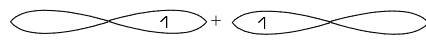
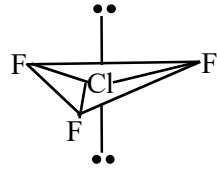
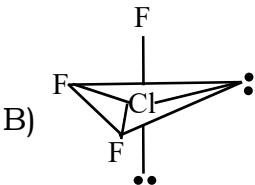
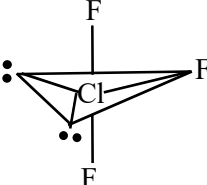
1. Which statement is not correct ?
  - A) Double bond is shorter than a single bond
  - B) Sigma bond is weaker than pi-bond
  - C) Double bond is stronger than a sigma bond
  - D) Covalent bond is stronger than hydrogen bond



2. Formation of  $\pi$  - bond  
 A) Increases bond length                      B) Decreases bond length  
 C) Distorts the geometry of molecule  
 D) Make homoatomic molecules more reactive
3. A covalent bond is formed between the atoms by the overlapping of orbitals containing  
 A) Single electron                              B) Paired electron  
 C) Single electron with parallel spin  
 D) Single electron with opposite spin
4. The strength of bonds formed by  $2s-2s$ ,  $2p-2p$  and  $2p-2s$  overlap has the following order  
 A)  $s-s > p-p > p-s$                       B)  $s-s > p-s > p-p$   
 C)  $p-p > p-s > s-s$                       D)  $p-p > s-s > p-s$
5. How many  $\sigma$  and  $\pi$  bonds are there in the molecule of
- $\begin{array}{l} X \\ \diagdown \\ C=O \\ \diagup \\ X \end{array} \quad [X = Cl, Br \text{ or } I]$
- A) One  $\sigma$  and one  $\pi$  bond                      B) Two  $\sigma$  and two  $\pi$  bond  
 C) Three  $\sigma$  and three  $\pi$  bond                      D) Three  $\sigma$  and one  $\pi$  bond
6. Which of the following phenomenon will occur when two atoms of the elements having same spin of electron approach for bonding?  
 A) Orbital overlap will not occur                      B) Bonding will not occur  
 C) Both (A) & (B) are correct                      D) None of the above are correct
7. Which of the following is not true about sigma bond?  
 A) It involves axial overlap  
 B) It is non-directional  
 C) Electron cloud is cylindrically symmetrical about internuclear axis  
 D) It is formed by hybrid orbitals as well as pure atomic orbitals
8. The shape of which of the following molecules will not be distorted?  
 A)  $BrF_3$                       B)  $ClF_3$                       C)  $XeF_4$                       D)  $XeF_6$
9. Which of the following species will have the lone pair effects cancelled?  
 A)  $ICl_2^-$                       B)  $ClF_3$                       C)  $PCl_3$                       D)  $BrF_5$
10. Shape of  $NH_3$  is very similar to –  
 A)  $CH_4$                       B)  $CH_3^-$                       C)  $BH_3$                       D)  $CH_3^+$

**JEE MAIN LEVEL QUESTIONS**

1. In  $XeF_2$ ,  $XeF_4$  and  $XeF_6$  the number of lone pairs on Xe is respectively  
 A) 2, 3, 1                      B) 1, 2, 3                      C) 4, 1, 2                      D) 3, 2, 1

2. Which of the following has the regular tetrahedral structure?  
 A)  $\text{XeF}_4$                       B)  $\text{SF}_4$                       C)  $\text{BF}_4^-$                       D)  $[\text{Ni}(\text{CN})_4]^{2-}$
3. The structure of  $\text{IF}_7$  is:  
 A) trigonal bipyramid                      B) octahedral  
 C) pentagonal bipyramid                      D) square pyramid
4. In which of the following pairs the two species are not isostructural?  
 A)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$                       B)  $\text{PCl}_4^+$  and  $\text{SiCl}_4$                       C)  $\text{PF}_5$  and  $\text{BrF}_5$                       D)  $\text{AlF}_6^{3-}$  and  $\text{SF}_6$
5. Which statements are correct  
 a) a pi bond is weaker than sigma bond  
 b) a sigma bond is weaker than pi bond  
 c) a double bond stronger than single bond  
 d) a covalent bond is stronger than ionic Bond  
 A) a,c                      B) b,c                      C) b,d                      D) a,c,d
6. In which of the following cases covalent bond does not takes place  
 a)  +                       b)  +   
 c)                       d)   
 A) a,c,d                      B) b,c,d                      C) a,b,c                      D) a,b,c,d
7. Which of the following possess two lone pair of electrons on the central atom and square planar in shape?  
 A)  $\text{SF}_4$                       B)  $\text{XeO}_4$                       C)  $\text{XeF}_4$                       D)  $\text{XeF}_6$
8. The expected bond angle in  $\text{H}_2\text{O}$  and  $\text{F}_2\text{O}$  are respectively.  
 A)  $104^\circ 30'$  &  $103^\circ$                       B)  $104^\circ 30'$  &  $120^\circ$                       C)  $120^\circ$  &  $104^\circ 30'$                       D)  $104^\circ 30'$  &  $107^\circ$
9. Among the following the correct representation of  $\text{ClF}_3$ .  
 A)                       B)                       C)                       D) All the above
10. The shapes of  $\text{PCl}_4^+$ ,  $\text{PCl}_4^-$  and  $\text{AsCl}_5$  are respectively  
 a) square planar, tetrahedral and see-saw  
 b) tetrahedral, see-saw and trigonal bipyramidal  
 c) tetrahedral, square planar and pentagonal bipyramidal  
 d) Trigonal bipyramidal, tetrahedral and square pyramidal

11. The correct statement about sulphur hexa fluoride include
- There are 12 F – S – F  $90^\circ$  bond angles
  - S in  $SF_6$  has an expanded octet
  - With  $H_2O$ ,  $SF_6$  can accept lone pair of electron with empty 3d atomic orbital and gets hydrolysed
  - $SF_6$  has a distorted octahedral geometry
- A) a,b,d      B) a,b      C) b,c      D) b,c,d
12. The geometrical arrangement of orbitals and shape of  $IF_3$  are respectively:
- trigonal bipyramidal geometry, linear shape.
  - hexagonal geometry, T-shape.
  - triangular planar geometry, triangular shape.
  - tetrahedral geometry, pyramidal shape.
13. Molecular shapes of  $SF_4$ ,  $CF_4$  and  $XeF_4$  are:
- the same with 2, 0 and 1 lone pair of electrons respectively.
  - the same, with 1,1 and 1 lone pair of electrons, respectively.
  - different, with 0, 1 and 2 lone pair of electrons, respectively.
  - different, with 1, 0 and 2 lone pair of electrons, respectively.
14. The molecule exhibiting maximum number of non-bonding electron pairs (l.p.) around the central atom is:
- (A)  $XeOF_4$                       B)  $XeO_2F_2$                       C)  $XeF_3^-$                       D)  $XeO_3$
15. The shapes of  $XeF_4$ ,  $XeF_5^-$  and  $SnCl_2$  are
- octahedral, trigonal bipyramidal and bent.
  - square pyramidal, pentagonal planar and linear.
  - square planar, pentagonal planar and angular.
  - see-saw, T-shaped and linear
16. A molecule  $XY_2$  contains two  $\sigma$ , two  $\pi$ - bonds and lone pair of electron in the valence shell of X. The arrangement of lone pair as well as bond pairs is:
- square pyramidal      B) linear      C) trigonal planar      D) unpredictable.
17. Which of the following has 4 bond pairs and 1 lone pair?
- (A)  $XeF_4$                       B)  $SF_4$                       C)  $BF_4^-$                       D)  $[Ni(CN)_4]^{2-}$
18. Which of the following set contains species having same angle around the central atom?
- A)  $SF_4, CH_4, NH_3$                       B)  $NF_3, BCl_3, NH_3$                       C)  $BF_3, NF_3, AlCl_3$                       D)  $BF_3, BCl_3, BBr_3$
19. The bond angles of  $NH_3$ ,  $NH_4^+$  and  $NH_2^-$  are in the order
- $NH_2^- > NH_3 > NH_4^+$                       B)  $NH_4^+ > NH_3 > NH_2^-$                       C)  $NH_3 > NH_2^- > NH_4^+$                       D)  $NH_3 > NH_4^+ > NH_2^-$
20. Which one of the following compounds has bond angle as nearly  $90^\circ$
- A)  $NH_3$                       B)  $H_2S$                       C)  $H_2O$                       D)  $CH_4$

## ADVANCED LEVEL QUESTIONS

### MULTIPLE CORRECT ANSWER TYPE

- Assuming pure 2s and 2p orbitals of carbon are used in forming  $\text{CH}_4$  molecule, which of the following statement/s are true ?
  - Three C–H bonds will be at right angle.
  - one C–H bond will be weaker than other three C–H bonds
  - the shape of molecule will be tetrahedral
  - The angle of C–H bond formed by S–S over lapping will be uncertain w.r.to other three bonds.
- $\text{CO}_2$  molecule is isostructural with
  - $\text{HgCl}_2$
  - $\text{SnCl}_2$
  - $\text{C}_2\text{H}_2$
  - $\text{NO}_2$
- Mark out the incorrect match of shape.
  - $\text{XeOF}_2$  — Trigonal planar
  - $\text{ICl}_4^-$  — Square Planar
  - $[\text{SbF}_5]^{2-}$  — Square pyramidal
  - $\text{NH}_2^-$  — Pyramidal
- Which of the following species are correctly matched with their geometries according to the VSEPR theory?
  - $\text{BrF}_6^+$  —> Octahedral
  - $\text{SnCl}_5^-$  —> trigonal bipyramidal.
  - $\text{SnCl}_5^-$  —> linear
  - $\text{IF}_4^+$  —> see – saw .

### STATEMENT TYPE

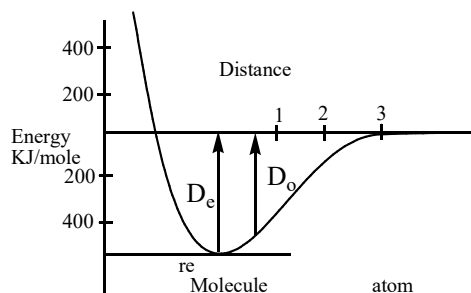
- Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
  - Statement-1 is True, Statement-2 is True; Statement-2 NOT a correct explanation for Statement-1.
  - Statement-1 is True, Statement-2 is False
  - Statement -1 is False, Statement-2 is True.
- STATEMENT – 1:**  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  ion both are triangular planar.  
**STATEMENT – 2:** Central atom in both  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  has same number of lone pairs
  - STATEMENT – 1:** pi bonds are weaker than sigma bonds.  
**STATEMENT – 2:** pi bonds are formed by the overlapping of p-p orbitals along their axis.

### COMPREHENSION TYPE

#### COMPREHENSION - I (Energy changes in bond formation)

Consider the formation of an  $\text{H}_2$  molecule when two H atoms come together. As the atoms approach the each other and a bond forms, they are subjected to an

attractive force. This force results from the fact that when they are close together the two atoms have lower energy than when they are far apart. It is as if the atoms were connected by a spring that pulled them together toward a region of lower potential energy. Quantum mechanical methods allow us to calculate this energy as a function of the distance between the two nuclei. The following figure shows this energy for a pair of H - atoms forming an  $H_2$  molecule. (Per 1 mole)



The most stable configuration of the  $H_2$  molecule would correspond to the bottom of the energy curve. Its equilibrium bond energy would be given by the value called 'De' and the equilibrium bond distance of the  $H_2$  molecule given by 're'. However no real  $H_2$  molecules can sit at the bottom of its energy curve. According to one of the principles of quantum mechanics, all molecules vibrate back and forth at least a little bit. The lowest possible energy for real  $H_2$  molecules shown by average bond energy is given by 'Do'

7. Bond formation is
  - A) always exothermic
  - B) always endothermic
  - C) may be exothermic or endothermic
  - D) neither exothermic nor endothermic
8. As attraction forces between constituent atoms increases during formation of molecule, potential energy
  - A) decreases
  - B) increases
  - C) remains constant
  - D) increases and remains constant
9. According to VBT, in  $H_2$  molecule the two electrons possess the following spin
  - A)  $\uparrow\uparrow$
  - B)  $\downarrow\downarrow$
  - C)  $\uparrow\downarrow$
  - D) Any of these
10. According to VBT, the bond formed in  $H_2$  is
  - A)  $\sigma 1s-1s$
  - B)  $\sigma 1s-2s$
  - C)  $\pi 2p-2p$
  - D)  $\sigma 2s-2p$

### Comprehension -II (VBT-VSEPR Theory)

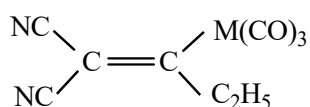
During chemical bond formation the potential energy of the bonding atoms decreases. According to VBT bond strength depends on extent of overlap. Shapes and bond angles of the molecules were explained by VSEPR theory. This theory explains the Geometry of the molecules based on the repulsions among the valence shell electron pairs. As number of lone pairs increases repulsions

increases and the shape is altered accordingly.

11. Molecule, which involves p-p overlapping, is  
A)  $H_2$                       B)  $HCl$                       C)  $Cl_2$                       D)  $NH_3$
12. Which of the following is correct with respect to  $SO_2$  molecule  
A)  $AB_2E_2$  type, trigonal planar shape    B)  $AB_2E$  type, Bent shape  
C)  $AB_3$  type, bent shape                      D)  $AB_3E$  type, square planar
13.  $AB_4E_2$  type of molecule with square planar shape is  
A)  $ClF_3$                       B)  $SF_4$                       C)  $H_2O$                       D)  $XeF_4$
14. Ratio of lone pairs and bond pair electrons in  $H_2O$  respectively  
A) 2:3                      B) 1:1                      C) 1:3                      D) 1:2
15. Which of the following shows maximum bond angle  
A)  $CH_4$                       B)  $NH_3$                       C)  $H_2O$                       D)  $BeF_2$
16. Orientation of electron pairs in  $ClF_3$  molecule is like  
A) T - Shaped                      B) Trigonal bi pyramidal  
C) Tetrahedral                      D) Octahedral

### INTEGER TYPE

- 17 The total number of sigma and  $p_i$  bonds present in the following structure are  $6x$ . Then what is 'x' ?



- 18 The molecule  $ML_x$  is planar with 7 pairs of electrons around M in the valence shell. What is the value of x?
19. Amongst the molecular species  $ClO_3^-$ ,  $XeF_4$ ,  $SF_4$  and  $I_3^-$ , what is the highest number of lonepairs present on any one of the central atoms ?
20. Amongst  $NO_3^-$ ,  $AsO_3^{3-}$ ,  $CO_3^{2-}$ ,  $ClO_3^-$ ,  $SO_3^{2-}$  and  $BO_3^{3-}$ , how many number of non-planar species are there?
21. What is the sum of lone pairs present on all central atoms of  $SF_4$ ,  $CF_4$  and  $XeF_4$  molecules ?

### MATRIX MATCHING TYPE

22. Match List-I (Species) with List - II (structures) and select the correct answer using the codes given below the lists :

#### List - I

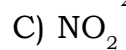
- A)  $ClF_3$
- B)  $PF_3$
- C)  $BF_3$
- D)  $SF_6$

#### List - II

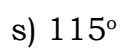
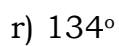
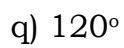
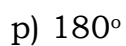
- p) Trigonal planar
- q) T-shaped (planar)
- r) Pyramidal
- s) Octahedral

23. Match List-I (Species) with List - II (structures) and select the correct answer using the codes given below the lists :

**List - I**  
(Species)



**List - II**  
(Bond angle)



**KEY****CUQ'S**

1	2	3	4	5	6	7	8	9	10
B	B	D	C	D	C	B	C	A	B

**MAIN LEVEL**

1	2	3	4	5	6	7	8	9	10
D	C	C	C	A	B	C	A	C	B
11	12	13	14	15	16	17	18	19	20
B	A	D	C	C	C	B	D	B	B

**ADVANCED LEVEL**

1	2	3	4	5	6	7	8	9	10
ABC	AC	AD	ABCD	B	A	A	A	C	A
11	12	13	14	15	16	17	18	19	20
C	B	D	B	D	B	5	5	3	3

**MATCHING**

**21- A - Q; B - R; C - P; D - S**

**22 A - Q; B - P; C - R; D - S**