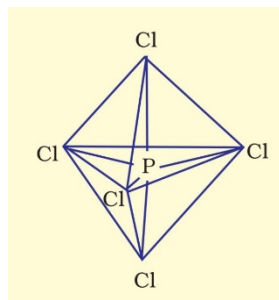


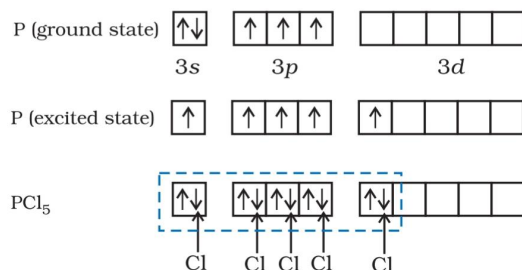
Case –V

The important hybridisation schemes Involving s, p and d orbitals are summarised below

- (i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outerelectronic configurations of phosphorus ($Z=15$) are represented



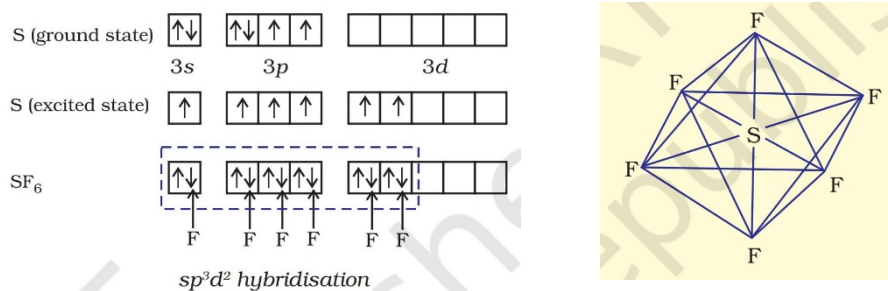
below.



Now the five orbitals (i.e., one s, three p and One d orbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a Trigonal bipyramidal. It should be noted that all the bond angles

in trigonal bipyramidal geometry are nonequivalent. In PCl_5 the five sp^3d orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bonds lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds—one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl_5 molecule more reactive.

(ii) Formation of SF₆ (sp³d² Hybridisation): In SF₆ The central sulphur atom has the Ground state outer electronic configuration 3s²3p⁴. In the excited state the available six Orbitals i.e., one s, three p and two d are singly Occupied by electrons. These orbitals hybridise To form six new sp³d² hybrid orbitals, which are projected towards the six corners of a Regular octahedron in SF₆. These six



sp³d² hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF₆ molecule has a regular octahedral geometry as shown in Figure.

MOLECULAR ORBITAL THEORY was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are :

- i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
 - ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
 - iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
 - (iv) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.
 - (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
 - (vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
 - (vii) The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.
- The formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wavefunctions of individual atomic orbitals as shown below :

$$\psi_{MO} = \psi_A \pm \psi_B$$

Therefore, the two molecular orbitals σ and σ^* are formed as :

$$\sigma = \psi_A + \psi_B$$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital σ^* formed by the subtraction of atomic orbital is called antibonding molecular orbital .

The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

1. The combining atomic orbitals must have the same or nearly the same energy.
2. The combining atomic orbitals must have the same symmetry about the molecular axis.
3. The combining atomic orbitals must overlap to the maximum extent.

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals . hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. There are two types of H-bonds.

- (1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H bond in case of HF molecule, alcohol or water molecules, etc.
- (2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.

[A] MCQ

1) Molecular orbital (MO) theory was developed by ...

- a) F. Hund and R.S. Mulliken
- b) Pauling and Lewis
- c) Nyholm and Gillespie
- d) Heitler and London

Ans- a) F. Hund and R.S. Mulliken

2) What is the hybridisation of PCl_5 ?

- a) sp^2d
- b) sp^3d
- c) sp^2
- d) sp^2d

Ans- b) sp^3d

3) The addition of atomic orbitals is called the ... molecular orbital

- a) Anti bonding
- b) non bonding
- c) bonding
- d) Extra bonding

Ans- c) Bonding

4) The ... of atomic orbitals is called the anti bonding molecular orbital.

- a) Division
- b) Multiplication
- c) Addition
- d) Subtraction

Ans- d) Subtraction

5) ... is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals .

- a) Bond angle
- b) Bond length
- c) Bond order
- d) Bond size

Ans- c) Bond order

[B]Short Answers

1) What are the two types of hydrogen bond ?

Ans- Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule. There are two types of H-bonds.

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.

2) What are bonding and anti bonding molecular orbitals ?

Ans- The formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

$$\psi_{\text{MO}} = \psi_{\text{A}} \pm \psi_{\text{B}}$$

Therefore, the two molecular orbitals σ and σ^* are formed as :

$$\sigma = \psi_{\text{A}} + \psi_{\text{B}}$$

$$\sigma^* = \psi_{\text{A}} - \psi_{\text{B}}$$

The molecular orbital σ formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital σ^* formed by the subtraction of atomic orbital is called antibonding molecular orbital .

3) What are the important conditions required for the linear combination of atomic orbitals to form molecular orbitals ?

Ans- The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

- 1.The combining atomic orbitals must have the same or nearly the same energy.
- 2.The combining atomic orbitals must have the same symmetry about the molecular axis.
- 3.The combining atomic orbitals must overlap to the maximum extent.

3) Explain the Formation of SF₆ (sp³d² Hybridisation).

Ans- In SF₆ The central sulphur atom has the Ground state outer electronic configuration 3s²3p⁴ . In the excited state the available six Orbitals i.e., one s, three p and two d are singly Occupied by electrons. These orbitals hybridise To form six new sp³d² hybrid orbitals, which are projected towards the six corners of a Regular octahedron in SF₆. These six sp³d² hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF₆ molecule has a regular octahedral geometry .

[C]Long Answers

1) State the salient features of molecular orbital theory .

Ans- MOLECULAR ORBITAL THEORY was developed by F. Hund and R.S.Mulliken in 1932. The salient features of this theory are :

- i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the

number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.

(iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.

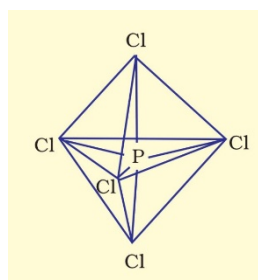
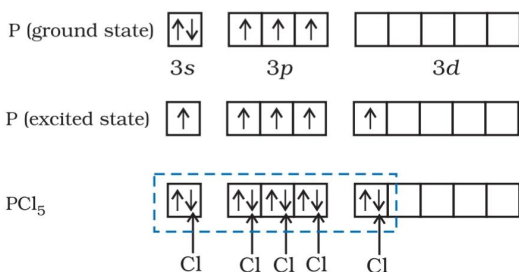
(v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.

2) Describe the formation of PCl_5 to explain hybridisation of Elements involving d Orbitals.

Ans-(i) Formation of PCl_5 (sp^3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus ($Z=15$) are represented below.



Now the five orbitals (i.e., one s, three p and One d orbitals) are available for hybridisation to yield a set of five sp^3d hybrid orbitals which are directed towards the five corners of a Trigonal bipyramidal. It should be noted that all the bond angles

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