Chapter 4

Chemical Bonding and Molecular Structure

TYPES OF BONDS

1. Ionic Bond
2. Covalent Bond
3. Co-ordinate Bond
4. Hydrogen Bond

Ionic Bond

An ionic bond is formed by complete transfer of one or more electrons from the valency shell of one atom to the valency shell of another atom. In this way both the atoms acquire the stable electronic configurations of the noble gases. The atom losing the electrons becomes a positive ion and the atom which gains electron becomes negative ion.

FAJAN'S RULE

Covalent character in ionic bonds

When oppositely charged ions approach each other, there is not only the attraction between the positively charged cation and the negatively charged anion but also simultaneous repulsion between their nuclei. Thus there is distortion, or deformation or polarization of anions. The electronic charge of anion does not remain spherical but gets distorted.

No polarization Polarization of anion

(1) Polarizing power of cation increases with

  (i) High charge on cation

  (ii) Small size of cation

  (iii) Pseudo (18) electronic configuration in outermost shell of cation

(2) Tendency of an anion to get polarized increases with

   (i) High charge on anion

   (ii) Large size of anion

This polarization of ion results in a electric charge concentration between the two nuclei resulting in a covalent bond with a large degree of charge separation.

The extent of polarization depends upon

(1) Polarizing power of cations.

(2) Tendency of an anion to get polarized (polarizability)

FORMAL CHARGE

$$\text{FC} = \begin{bmatrix}\text{Total number of valence}\\ e^- \text{ in free atom (v)}\end{bmatrix} - \begin{bmatrix}\text{Total number of}\\ \text{non-bonding } e^- \text{ (u)}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{Total number of}\\ \text{bonding } e^- \text{ (s)}\end{bmatrix}$$

DIPOLE MOMENT (μ)

Dipole moment is product of the magnitude of charge developed on any one of the two atoms and the distance between the atoms. ($\mu = q \times d$), where q = charge developed and d = distance between two atoms. The unit of dipole moment is debye (D). 1 debye = 1×10^{-18} esu cm = 3.34×10^{-30} coulomb metre (Cm)

$1e^-$ charge = 4.8×10^{-10} esu = 1.6×10^{-19} coulomb

(a) Dipole moment is a vector quantity.

(b) Molecule with more than one bond will have more than one bond dipole moments. The resultant of bond dipole moments of the molecule containing two bonds is given as

$$\mu_{\text{res.}} = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

(c) Dipole moment predicts whether a molecule is polar or non-polar.

(d) Dipole moment is zero for symmetrical and planar species.

(e) Dipole moment helps to determine percentage ionic character and can be calculated as

$$\%\text{ ionic character} = \frac{\text{Observed dipole moment}}{\text{Calculated dipole moment assuming 100\% ionic bond}} \times 100$$

% ionic character = $16|X_A - X_B| + 3.5\,[X_A - X_B]^2$, where X_A and X_B are the electronegativity of A and B element.

VALENCE SHELL ELECTRON PAIR REPULSION THEORY (VSEPR)

(a) A number of physical and chemical properties of molecules are affected by the geometry and shape of molecules.

(b) VSEPR theory gives the information of shape of molecules.

(c) The arrangement of bond pair electron and lone pair electron is done to minimize the repulsion *i.e.*,

Lone pair – lone pair > lone pair – bond pair > bond pair – bond pair.

(d) These repulsion - effects result in deviations from idealized shape and alterations in bond angles in molecules.

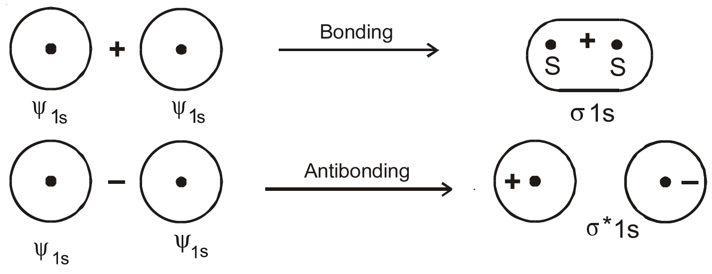
HYBRIDIZATION & SHAPES OF MOLECULES

S.No.	Type of hybridisation	No. of hybridised orbitals	Bond pair	Lone Pair	Geometry	Shape	Examples
1.	sp	2	2	–	Linear	Linear	CO_2, $BeCl_2$
2.	sp^2	3	3	–	Trigonal Planar	Trigonal Planar	BF_3
			2	1	Trigonal Planar	V-shape	SO_2
3.	sp^3	4	4	–	Tetrahedral	Tetrahedral	CH_4
			3	1	Tetrahedral	Pyramidal	NH_3
			2	2	Tetrahedral	V-shape	H_2O
4.	sp^3d	5	5	–	Trigonal bipyramidal	Trigonal bipyramidal	PCl_5
			4	1	Trigonal bipyramidal	See-saw	SF_4
			3	2	Trigonal bipyramidal	T-shape	ClF_3
			2	3	Trigonal bipyramidal	Linear	ICl_2^-
5.	sp^3d^2	6	6	–	Square bipyramidal	Square (octahedral) bipyramidal	SF_6
			5	1	Square bipyramidal	Square pyramidal	IF_5
			4	2	Square bipyramidal	Square Planar	XeF_4
6.	sp^3d^3	7	7	–	Pentagonal bipyramidal	Pentagonal bipyramidal	IF_7
			6	1	Pentagonal bipyramidal	Distorted octahedral	XeF_6

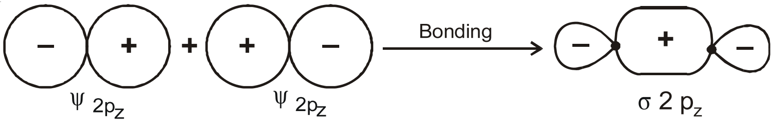
MOLECULAR ORBITAL THEORY

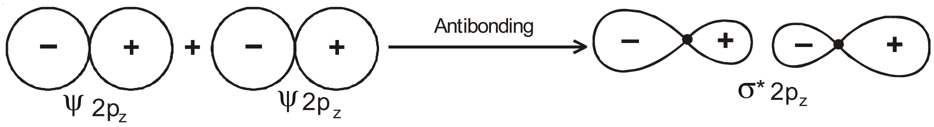
Types of Covalent Bond

***s – s overlap* (*Sigma Overlap*)**

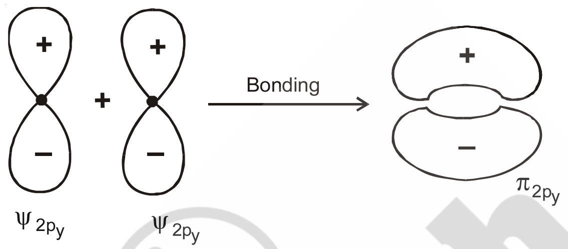


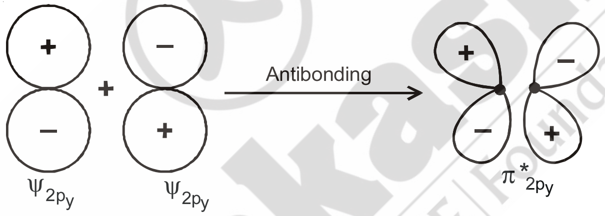
p – p overlap (Sigma Overlap)





p – p Overlap Lateral (π - overlap)





(a) Linear combination of atomic orbitals (LCAO) method is used for the formation of molecular orbitals.

(b) For two atomic orbitals A and B, whose wave function is given as ψ_A and ψ_B. Then molecular orbitals (MO) are given as $\psi_{MO} = \psi_A \pm \psi_B$.

(c) The molecular orbital σ formed by the addition of atomic orbitals is called **bonding molecular orbital**. And molecular orbital σ* formed by the subtraction of atomic orbitals is called **antibonding molecular orbital**.

(d) Molecular orbital configuration for diatomic molecules upto 14 electrons.

$\Rightarrow$ $\sigma 1s\ \sigma^*1s\ \sigma 2s\ \sigma^*2s\ \{\pi 2p_x = \pi 2p_y\}\ \sigma 2p_z\ \{\pi^*2p_x = \pi^*2p_y\}\ \sigma^*2p_z$

(Increasing order of energy)

(e) Molecular orbital configuration for diatomic molecules with more than 14 electrons.

$\Rightarrow$ $\sigma 1s\ \sigma^*2s\ \sigma 2s\ \sigma^*2s\ \sigma 2p_z\ \{\pi 2p_x = \pi 2p_y\}\ \{\pi^*2p_x = \pi^*2p_y\}\ \sigma^*2p_z$

(Increasing order of energy)

(f) Molecular orbitals are arranged with increasing order of energy level.

(g) $\pi 2p_x$ and $\pi 2p_y$ similarly π^*2p_x and π^*2p_y have same energy and follow Hund's rule.

(h) Bond order = $\frac{1}{2}$ [Bonding electrons – Antibonding electrons].

(i) Bond order $\propto$ Bond strength $\propto \dfrac{1}{\text{Bond length}}$.

e.g., N_2 = 14 electrons

$\therefore$ Molecular orbital configuration

$$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2.\ \sigma^* 2s^2\ \{\pi 2p_x^2, \pi 2p_y^2\}\ \sigma 2p_z^2\ \{\pi^* 2p_x, \pi^* 2p_y\}\ \sigma^* 2p_z$$

$$\text{B.O} = \frac{1}{2}\,[10 - 4] = 3$$

As no unpaired electron hence N_2 is diamagnetic.

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