Chemical Bonding and Molecular Structure

Chemical bond:

Chemical bond is the attractive force, which holds various constituents (such as atoms, ions) together in different chemical species.

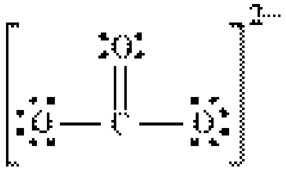
Octet rule:

Atoms tend to gain, lose, or share electrons so as to have eight electrons in their valence shells.

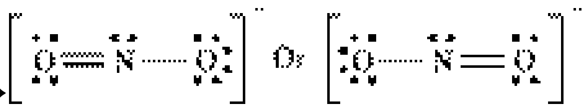
Lewis dot Structure:

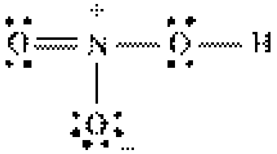
Representation of molecules and ions in terms of the shared pairs of electrons and the octet rule

CO_3^{2-}→

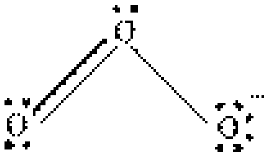


NO_2^-→



HNO_3 → 

Formal charge:

Lewis structure of O_3→ 

$$\begin{bmatrix}\text{Formal charge (F.C)}\\ \text{on an atom in a}\\ \text{Lewis structure}\end{bmatrix} = \begin{bmatrix}\text{Total number of}\\ \text{valence electrons}\\ \text{in the free atom}\end{bmatrix} - \begin{bmatrix}\text{Total number of}\\ \text{nonbonding (lone}\\ \text{pair electrons)}\end{bmatrix} - \frac{1}{2}\begin{bmatrix}\text{Total number of}\\ \text{bonding (shared}\\ \text{electrons)}\end{bmatrix}$$

F.C. on the $O^{-1} = 6 - 2 - \frac{1}{2}(6) = +1$

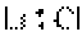
F.C. on the $O^{-2} = 6 - 4 - \frac{1}{2}(4) = 0$

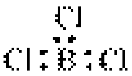
F.C. on the $O^{-3} = 6 - 6 - \frac{1}{2}(2) = -1$

Limitations of the octet rule:

- Incomplete octet of the central atom

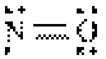
E.g. BeH_2, LiCl, BCl_3

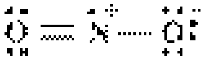




- Odd electron molecules

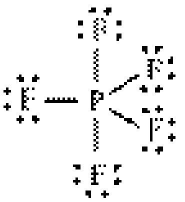
E.g. NO, NO_2

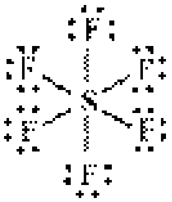


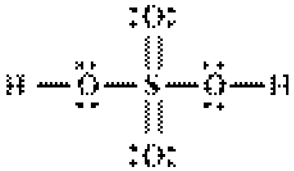


- Expanded octet

E.g. PF_5, SF_6, H_2SO_4







- Some other drawbacks:

1. It is based upon chemical inertness of noble gases. However, some noble gases can combine to form compounds such as XeF_2, KrF_2, $XeOF_2$, etc.
2. Does not account for the shape of molecules
3. Does not explain the relative stability of molecules

Conditions for Formation of Covalent Bond

- Presence of four or more electrons in the outermost shell of an atom (exception H, Be, B and Al)
- High electronegativity of both the atoms
- High electron affinity for both the atoms
- High ionisation energy of both the atoms
- Electronegativity difference between combining atoms should be zero or very low

Ionic or Electrovalent Bond: Formation of ionic compound depends upon ease of formation of positive and negative ions and also on arrangement of positive and negative ions.

Ionisation enthalpy ($\Delta_i H$) and electron gain enthalpy ($\Delta_{eg}H$):

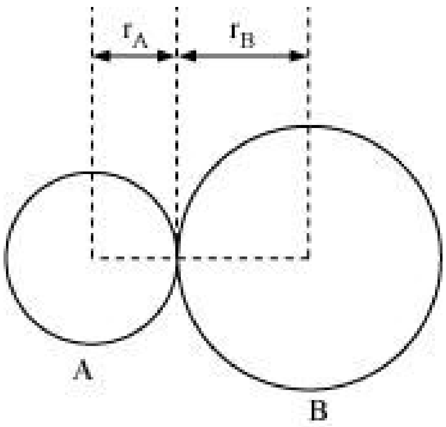
The ionisation enthalpy is the enthalpy change when a gas phase atom in its ground state loses an electron and the electron gain enthalpy is the enthalpy change when a gas phase atom in its ground state gains an electron.

Lattice enthalpy:

The energy required to separate completely one mole of a solid ionic compound into gaseous constituent ions is called the lattice enthalpy of the solid.

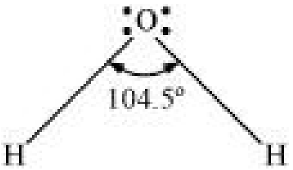
Bond parameters:

- Bond length → Equilibrium distance between the nuclei of two bonded atoms in a molecule



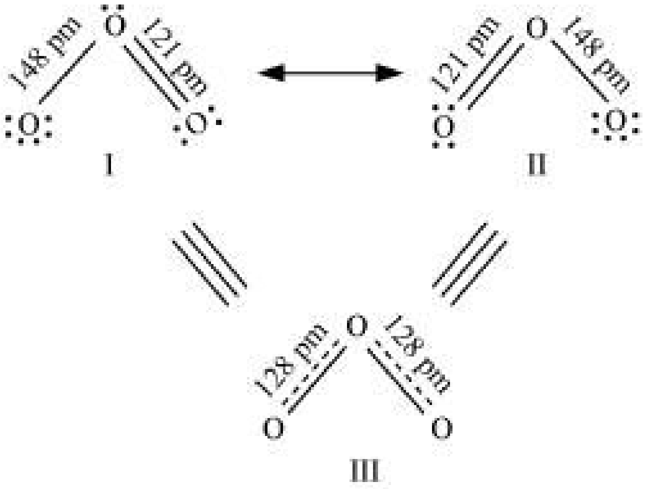
Bond length (R) = $r_A + r_B$

- Bond angle → Angle between the bonds around the central atom in a molecule/complex ion



- Bond enthalpy → Energy required to break one mole of a particular type of bond between two atoms in gaseous state
- Bond order → Number of bonds between two atoms in a molecule

- Resonance structures → Equivalent Lewis structures (example: ozone)



Here, I and II are resonance structures while III is the resonance hybrid.

- Polarity of bonds →

  Dipole moment (μ) = Charge (Q) × Distance of separation (*r*)

  Dipole moment is usually expressed in Debye units (D).

  $1\text{D} = 3.33564 \times 10^{-30}$ C m

VSEPR Theory:

The repulsive interaction of electron pairs decrease in the order:

Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

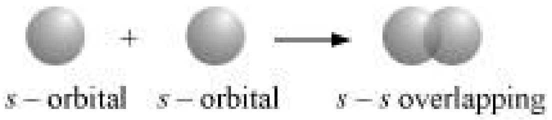
Valence bond theory:

It considers the formation of a chemical bond by the overlapping of atomic orbitals of the participating atoms.

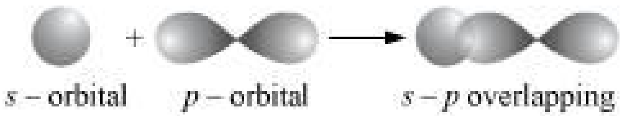
Types of overlapping and nature of covalent bonds:

There are two types of covalent bonds – Sigma $(\sigma)$and Pi (Π).

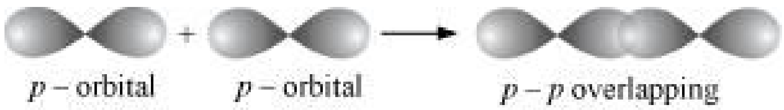
- Sigma (σ) bond (formed by head-on overlapping) *s*–*s* overlapping



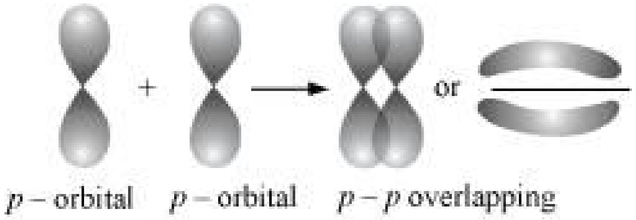
- *s*–*p* overlapping



- *p*–*p* overlapping



- Pi (Π) bond (formed by sidewise overlapping)



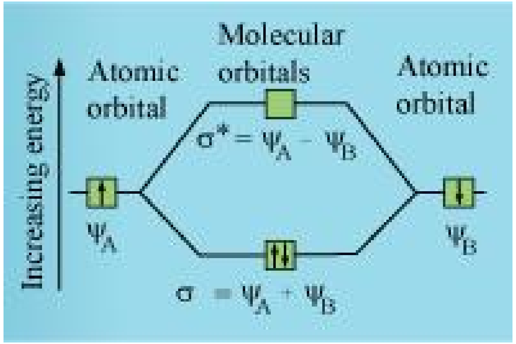
nd is stronger than Pi (Π) bond.

ı: Process of intermixing of the orbitals of slightly different energies

Hybridisation type	Shape of molecules/ions	Example
sp	Linear	$BeCl_2$
sp^2	Trigonal planar	BCl_3
sp^3	Tetrahedral	CH_4
dsp^2	Square planar	$[Ni(CN)_4]^{2-}$
sp^3d	Trigonal bipyramidal	PCl_5
sp^3d^2	Square pyramidal	BrF_5
d^2sp^3	Octahedral	SF_6

Molecular orbital theory

Linear combination of Atomic Orbitals (LCAO)



Energy levels for molecular orbitals -

- Increasing order of energies of various molecular orbitals for O_2 and F_2:

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

- Increasing order of energies of various molecular orbitals for Li_2, Be_2, B_2, C_2, and N_2:

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$

Where,

N_b= Number of electrons occupying bonding orbitals

N_a= Number of electrons occupying antibonding orbitals.

Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds respectively.

- The bond length decreases as bond order increases.
- If all the molecular orbitals in the molecule are doubly occupied, then the molecule is diamagnetic; and if one or more of the molecular orbitals are singly occupied, then the molecule is paramagnetic.

Hydrogen Molecule (H_2)

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

Helium Molecule (He_2)

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$$

Lithium Molecule (Li_2)

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$$

Beryllium Molecule (Be_2)

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{4-4}{2} = 0$$

Carbon Molecule (C_2)

$$\text{Bond order } = \frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$$

Oxygen Molecule (O_2)

$$\text{Bond order } \frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$$

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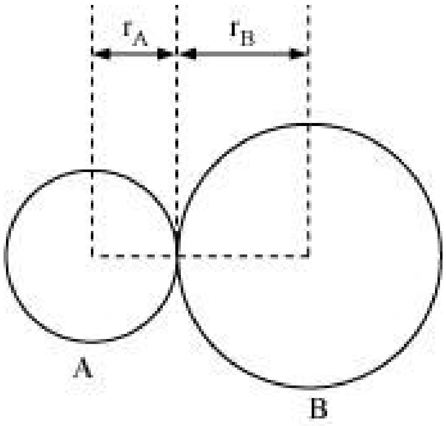

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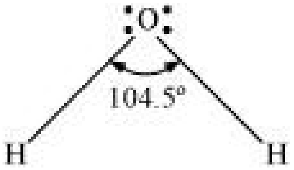

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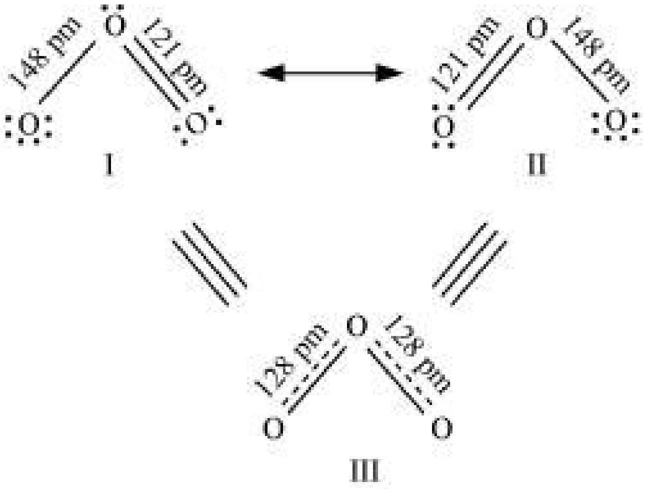

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