

Chemical Bonding and Molecular Structure

Chemical Bond

It is defined as the attractive force which hold the various chemical constituents (atoms, ions, etc.) together in different chemical species. Bond forms to get the stability, with a release of energy.

Kossel-Lewis Approach to Chemical Bonding

According to this theory, atoms take part in the bond formation to complete their octet or to acquire the electronic configuration of the nearest inert gas atoms (octet rule). This can be achieved by gaining, losing or sharing the electrons.

Lewis Symbols

Valence electrons are reported by dots around the chemical symbol of element, e.g.

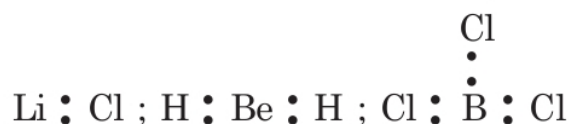


Octet Rule

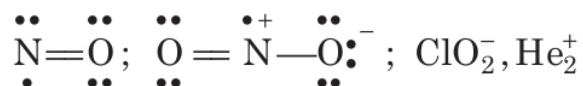
According to Octet rule during the formation of a covalent bond, the atoms attain an inert gas electronic configuration (valence shell contains $8e^-$ or shell is completely filled). An atom may attain this configuration by gaining, losing or sharing electrons with other atoms.

Exceptions to the Octet Rule

(i) Incomplete octet of the central atom, e.g. LiCl, BeH₂ and BCl₃



(ii) Odd-electron molecules

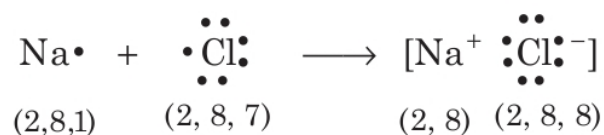


(iii) Expanded octet of central atoms



Ionic Bond

A chemical bond formed by complete transference of electrons from one atom (metal) to another (non-metal) and hence, each atom acquires the stable nearest noble gas configuration, is called ionic bond or **electrovalent bond**, e.g. formation of sodium chloride



Favourable factors for the formation of ionic bonds

- (i) Metal should have low ionisation enthalpy.
- (ii) Non-metal must have high electron gain enthalpy.
- (iii) The energy released during the formation of 1 mole of crystal lattice, i.e. lattice enthalpy must be high.

Some elements exhibit variable electrovalency. The reason for this is unstable configuration of penultimate orbit and inert pair effect.

Ions

Species carrying either positive or negative charge are termed as ions. Species carrying positive charge are called **cations** and those carrying negative charge are called **anions**. Metals usually form cation while non-metals (except H) usually form anions.

General Characteristics of Ionic Compounds

- (i) Ionic compounds are usually solid in nature.
- (ii) Ionic compounds have high melting and boiling points.

- (iii) Ionic compounds are soluble in polar solvents like water but insoluble in non-polar solvents like benzene, CCl_4 etc.
- (iv) Ionic compounds are good conductor in molten state and in aqueous solution.
- (v) Ionic compounds have crystal structure.

Method of Writing Formula of Ionic Compound

- (i) Write the symbol of cation at the left and anion at the right.
- (ii) Write their electrovalencies in figures on the top of each symbol as $A^x B^y$.
- (iii) Divide their valencies by HCF.
- (iv) Now apply criss-cross rule as $\begin{matrix} x & \searrow & y \\ & A & B \end{matrix}$, i.e. formula is $A_y B_x$.

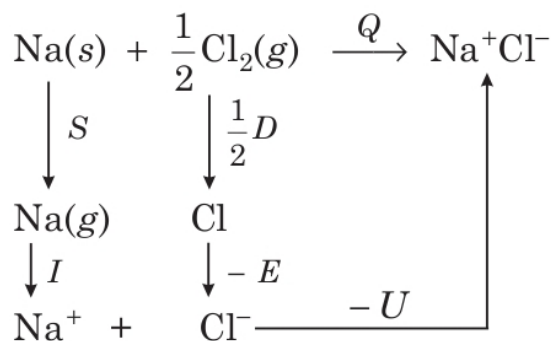
e.g. formula of aluminium sulphate $\begin{matrix} 3+ & \searrow & 2- \\ & \text{Al} & \text{SO}_4 \end{matrix}$ is $\text{Al}_2(\text{SO}_4)_3$.

Born Haber Cycle

This cycle is based upon the fact that the formation of an ionic compound may occur either by direct combination of the elements or by an alternate process in which :

- (i) The reactants (metal) are vaporised to convert into gaseous state.
- (ii) The gaseous atoms are converted into ion.
- (iii) The gaseous ions are combined to form ionic lattice of molecules.

e.g. formation of NaCl can be shown as

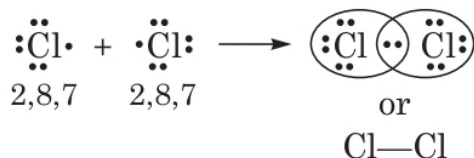


Thus, $Q = S + I + \frac{1}{2}D - E - U$

where, S = enthalpy of sublimation, I = ionisation enthalpy
 D = enthalpy of dissociation, E = electron gain enthalpy
 U = lattice enthalpy
 Q = total enthalpy change.

Covalent Bond

A chemical bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets or duplets, is known as **covalent bond** and the number of electrons contributed by each atom is known as **covalency**, e.g. formation of Cl_2 .



In covalent bonding, the shared pairs of electrons present between the atoms are called **bond pairs** while unshared or non-bonding electron pairs are known as **lone pairs**.

Types of Covalent Bonds

(a) Non-polar Covalent Bond

If the covalent bond is formed between two homonuclear atoms, i.e. between atoms of exactly equal electronegativity, e.g. H_2 , Cl_2 etc.

(b) Polar Covalent Bond

If a covalent bond is formed between the different atoms, the shared pair is displaced towards the more electronegative atom causing greater concentration of electron density around the more electronegative atom. Such a covalent bond develops some ionic character and is called **polar covalent bond**, (e.g. H—Cl).

Properties of Covalent Compounds

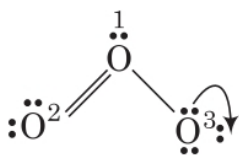
- (i) In general, covalent compounds exist in the liquid or gaseous state at room temperature due to magnitude of intermolecular forces.
- (ii) Covalent compounds have low melting and boiling points.
- (iii) Covalent compounds are generally poor conductors of electricity because they do not contain free electrons or ions to conduct electricity.
- (iv) They are soluble in non-polar solvents like benzene but usually insoluble in water.

Formal Charge on an Atom in a Molecule/Ion

Formal charge (F.C.) on an atom in a Lewis structure

$$\begin{aligned} &= [\text{total number of valence electrons in the free atom}] \\ &\quad - [\text{total number of non-bonding (lone pair) electrons}] \end{aligned}$$

$$-\frac{1}{2} [\text{total number of bonding (shared) electrons}]$$

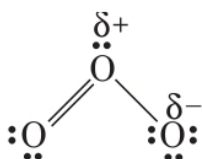


$$\text{F.C. on O}^2 = 6 - 2 - \frac{1}{2}(6) = +1$$

$$\text{F.C. on O}^2 = 6 - \left[4 + \frac{1}{2} \times 4 \right] = 6 - 6 = 0$$

$$\text{F.C. on O}^3 = 6 - \left[6 + \frac{1}{2} \times 2 \right] = 6 - 7 = -1$$

Hence, O_3 along with the formal charges can be represented as follows:



Bond Characteristics

Bond Length

In a covalently bonded molecule, distance between the nuclei of the two atoms is known as bond length. Bond length increases with increase in the size of bonded atoms and decreases with an increase in the number of bonds between bonded atoms.

Bond type	Covalent bond length (in pm)
C—H	107 pm
C—C	154 pm
C=C	133 pm
C≡C	120 pm

Bond length is determined by X-ray diffraction or electron diffraction methods.

Bond Angle

In a covalently bonded molecule having more than two atoms, the bonds form an angle with each other, which is known as bond angle. In general an increase in the size of central atom decreases the bond angle.

Factors affecting bond angle (i) Lone pair repulsion (ii) hybridisation of central atom. It is determined by X-rays diffraction method.

Bond Order

It is defined as the number of covalent bonds present in a molecule.

$$\text{Bond order} = \frac{1}{2} [\text{Number of electrons in bonding orbitals} \\ - \text{Number of electrons in anti-bonding orbitals}]$$

$$\text{Bond order} \propto \frac{1}{\text{bond length}}$$

If bond order comes out to be zero, the molecule does not exist.

Bond Enthalpy

It is the amount of energy released when one mole of covalent bonds is formed while the bond dissociation enthalpy is the amount of energy required to break one mole of bonds of the same kind so as to separate the bonded atoms in the gaseous state.

The bond enthalpy and bond dissociation enthalpy are equal in magnitude and opposite in sign.

┌ Bond dissociation enthalpy is determined by thermal or spectroscopic methods. └

As the bond order increases, bond enthalpy also increases and bond length decreases.

Factors affecting bond enthalpy

- (i) atomic size
- (ii) electronegativity
- (iii) extent of overlapping
- (iv) bond order

Fajan's Rule

The partial covalent character of ionic bonds was discussed by Fajan's in terms of following rules:

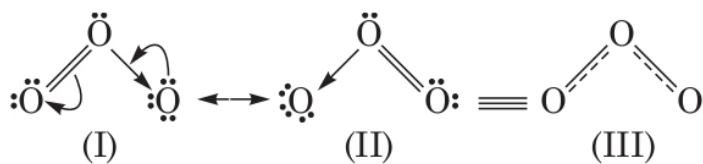
The smaller the size of cation and the larger the size of the anion, the greater the covalent character of an ionic bond.

The greater the charge on the cation or anion, the greater the covalent character of the ionic bond.

Resonance

According to the concept of resonance, a single Lewis structure cannot explain all the properties of the molecules. The molecule is then supposed to have many structures, each of which can explain most of the properties.

The actual structure lies in between of all these contributing structures and is called resonance hybrid and the different individual structures are called resonating structures or canonical structures. This phenomenon is known as resonance.



Resonance in ozone molecule

Resonance stabilises the molecule as the energy of the resonance hybrid is less than the energy of any single canonical structure.

Resonance averages the bond characteristics as a whole.

The difference in the energy of the resonance hybrid and the most stable contributing structure (having least energy) is called resonance energy. Greater the resonance energy, greater is the stability of the molecule.

Calculation of bond order for molecules showing resonance :

$$\text{Bond order} = \frac{\text{total number of bonds between two atoms in all the structures}}{\text{total number of resonating structures}}$$

Dipole Moment (μ)

It is defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charges.

$$\mu = \text{charge } (Q) \times \text{distance of separation } (r)$$

Dipole moment is expressed in Debye (D).

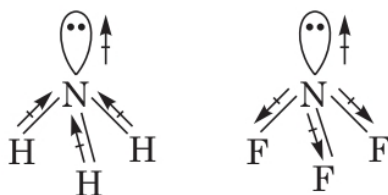
$$1 \text{ D} = 1 \times 10^{-18} \text{ esu-cm} = 3.33564 \times 10^{-30} \text{ C-m}$$

where, C is coulomb and m is meter.

(The shift in electron density is symbolised by broken arrow)

In chemistry, presence of dipole moment is represented by the crossed arrow (\rightarrow) put on Lewis structure of molecule. The cross is on positive end and arrow head is on negative end.

NH_3 has higher dipole moment than NF_3 .



Resultant dipole moment,

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta}$$

Applications of Dipole Moment

1. Dipole moment is helpful in predicting the geometry of the molecule.
2. Dipole moment helps in determining the polarity.

Hannay-Smith equation

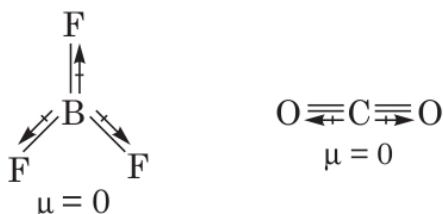
$$\text{Per cent ionic character} = 16 [X_A - X_B] + 3.5 [X_A - X_B]^2$$

where, X_A and X_B are the electronegativities of atoms.

Per cent ionic character can also be calculated by dipole moment as

$$\text{Per cent ionic character} = \frac{\text{observed dipole moment}}{\text{calculated dipole moment}} \times 100$$

3. Non-polar molecule has zero dipole moment like BF_3 , CCl_4 , etc.



4. *cis* and *trans* isomers can be distinguished by dipole moments usually *cis* isomer have higher dipole moment and hence, higher polarity.
5. Dipole moment is greatest for *ortho* isomer; zero for *para* isomer; and less than that of *ortho*, for *meta* isomer.

The Valence Shell Electron Pair Repulsion (VSEPR) Theory

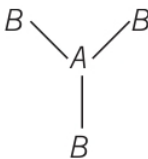
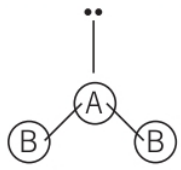
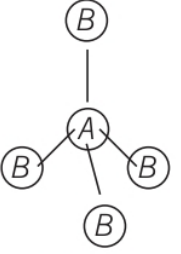
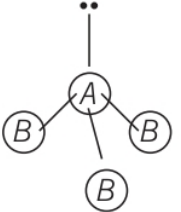
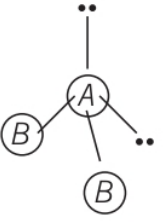
According to this theory,

1. The geometry of a molecule or ion depends on the number of electron pairs in the valence shell of its central atom.
2. To attain minimum repulsive state, electron pairs try to stay as far away as possible.
3. If the central atom is surrounded by only bonded electron pairs of similar atoms, the repulsive interactions are similar and the molecular geometry is regular.
4. If the central atom is surrounded by only bonded electron pairs of dissimilar atoms, the repulsive interactions are not equivalent and hence, the geometry of molecule will not be regular.

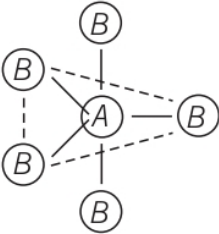
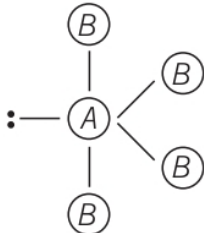
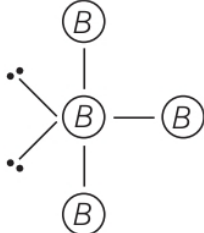
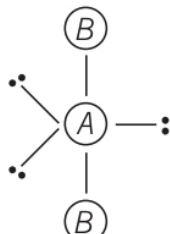
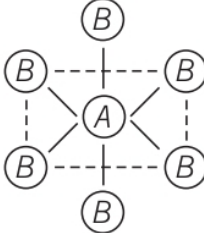
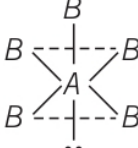
5. If the central atom is surrounded by both bonded pairs (*bp*) as well as lone pairs (*lp*) of electrons, repulsive interactions are not equivalent and hence, geometry of the molecule will be irregular. The repulsive interactions decrease in the order

$$lp - lp > lp - bp > bp - bp$$

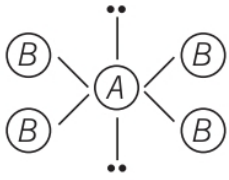
Shapes (Geometry) of Molecules Containing Bond Pairs Only or Bond Pairs and Lone Pairs

Total number of electron pairs	Number of bond pairs	Number of Lone pairs	Geometry (shape) of the molecule	Illustrative examples
2	2	0	$B-A-B$ Linear	BeF ₂ , CO ₂ , BeCl ₂
3	3	0	 Triangular planar	BF ₃ , AlCl ₃ , SO ₃
	2	1	 Bent (V-shape)	SO ₂ , O ₃ , NO ₂
4	4	0	 Tetrahedral	CH ₄ , SiF ₄ , NH ₄ ⁺
	3	1	 Trigonal pyramidal	NH ₃ , PCl ₃ , NCl ₃ , PH ₃
	2	2	 Bent	H ₂ O, H ₂ S

Contd....

Total number of electron pairs	Number of bond pairs	Number of Lone pairs	Geometry (shape) of the molecule	Illustrative examples
5	5	0	 <p>Trigonal bipyramidal</p>	PCl ₅
	4	1	 <p>See saw</p>	SF ₄
	3	2	 <p>T-shaped</p>	ClF ₃ , BrF ₃
	2	3	 <p>Linear</p>	XeF ₂ , I ₃ ⁻ , ICl ₂ ⁻
6	6	0	 <p>Octahedral</p>	SF ₆
	5	1	 <p>Square pyramidal</p>	BrF ₅ , ClF ₅

Contd....

Total number of electron pairs	Number of bond pairs	Number of Lone pairs	Geometry (shape) of the molecule	Illustrative examples
	4	2	 <p>Square planar</p>	XeF ₄

Valence Bond Theory of Covalent Bond

According to this theory, a covalent bond is formed by the overlapping of two half-filled atomic orbitals having electrons with opposite spins. It is based on wave nature of electron.

(i) Sigma Bond (σ bond)

This type of covalent bond is formed by head-on overlap, i.e. end to end overlap along the internuclear axis. Sigma bond can be formed by any one of the following types of combinations of atomic orbitals :

(a) *s-s* overlapping (b) *s-p* overlapping (c) *p-p* overlapping (axial)

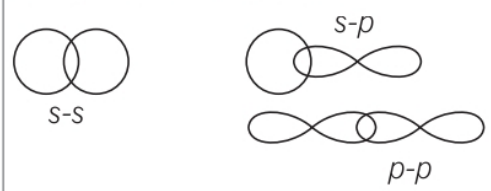
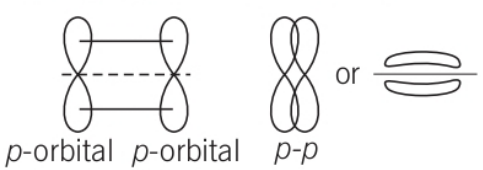
The strength of σ bond depends upon the extent of overlapping between atomic orbitals. The greater the extent of overlapping, the stronger is the σ bond.

(ii) Pi Bond (π bond)

It is formed by the sidewise or lateral overlapping between *p*-atomic orbitals [*p-p* side by side or lateral overlapping]

π bond is a weaker bond than σ bond.

Comparison of Sigma and Pi Bonds

	Sigma bond	Pi bond
1.	<p>This bond is formed by overlapping of orbitals along their internuclear axis.</p> 	<p>This bond is formed by sideway overlapping of atomic orbitals.</p> 
2.	Free rotation along a σ bond is possible.	Free rotation about a π bond is not possible.
3.	Sigma bond consist of only one electron cloud symmetrical about the internuclear axis.	Pi (π) bond consists of two electron clouds, one above the plane of atomic nuclei and the other below it.

Limitations of VBT

It fails to explain

1. The magnetic properties of some molecules.
2. Bonding in electron deficient compounds.

Hybridisation

It is defined as the mixing of the atomic orbitals belonging to the same atom but having slightly different energies so that a redistribution of energy takes place between them resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbitals and are more stable.

Method for Finding the Hybridisation

Apply the following formula to find the hybridisation of central atom.

$$Z = \frac{1}{2} \left(\begin{array}{l} \text{number of valence electrons of central atom} \\ + \text{number of monovalent atoms attached to it} \\ + \text{negative charge if any} - \text{positive charge if any} \end{array} \right)$$


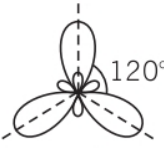
Value of Z	2	3	4	5	6	7
Hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

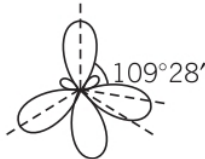
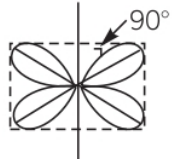
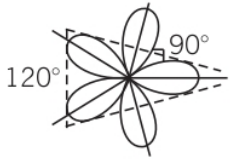
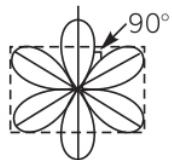
Examples

$$\text{Hybridisation of N in NH}_3 = \frac{1}{2} [5 + 3 + 0 - 0] = 4 \Rightarrow sp^3$$

$$\text{Hybridisation of S in SO}_4^{2-} = \frac{1}{2} [6 + 0 + 2 - 0] = 4 \Rightarrow sp^3$$

Some Common Types of Hybridisation with Shapes and Examples

Types of hybridisation	Atomic orbitals involved	Representing directions of hybrid orbitals formed alongwith bond angles	Examples
sp	one s + one p	 180° Linear	BeCl_2 , BeH_2 , C_2H_2
sp^2	one s + two p	 120° Triangular planar	BF_3 , BCl_3 , C_2H_4 , CO_3^{2-}

Types of hybridisation	Atomic orbitals involved	Representing directions of hybrid orbitals formed alongwith bond angles	Examples
sp^3	one s + three p	 Tetrahedral	CH_4 , CCl_4 , $SnCl_4$, NH_4^+
dsp^2	one d + one s + two p	 Square planar	XeF_4
sp^3d	one s + three p + one d	 Trigonal bipyramidal	PCl_5 , PF_5
sp^3d^2	one s + three p + two d	 Octahedral	SF_6 , $[CrF_6]^{3-}$

Coordinate or Dative Bond

It is a type of covalent bond in which the electron pair (lone pair) is donated by one atom but shared by both the atoms so as to complete their octets, e.g.



Molecular Orbital Theory

According to this theory, the atomic orbitals combine to form the molecular orbitals. The number of molecular orbitals formed is equal to the number of atomic orbitals involved. Molecular orbital of lower energy is known as **bonding molecular orbital** and that of higher energy is known as **anti-bonding molecular orbital**. Aufbau rule, Pauli's exclusion principle and Hund's rule are all applicable for molecular orbitals.

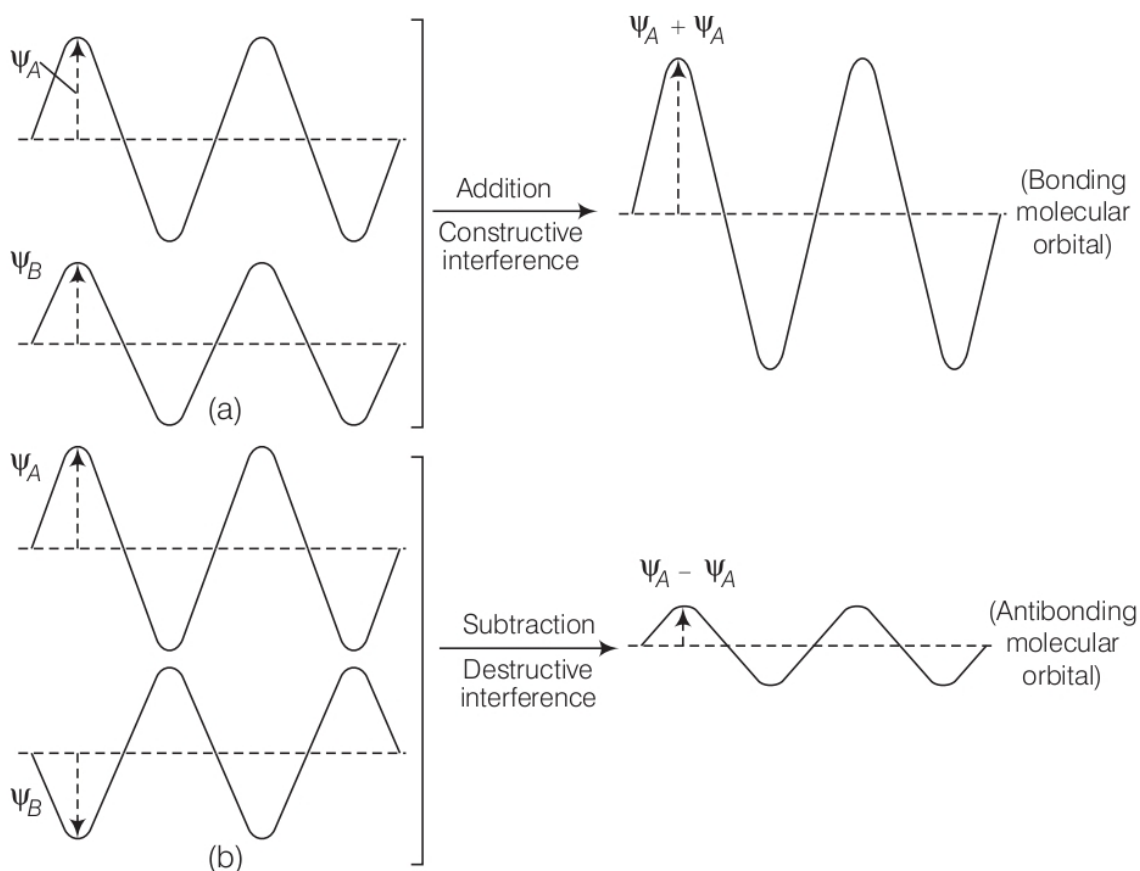
Formation of Molecular Orbitals : Linear Combination of Atomic Orbitals (LCAO)

- The molecular orbitals are formed by LCAO (Linear combination of atomic orbitals) method, i.e. by addition or subtraction of wave functions of individual atoms, thus

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

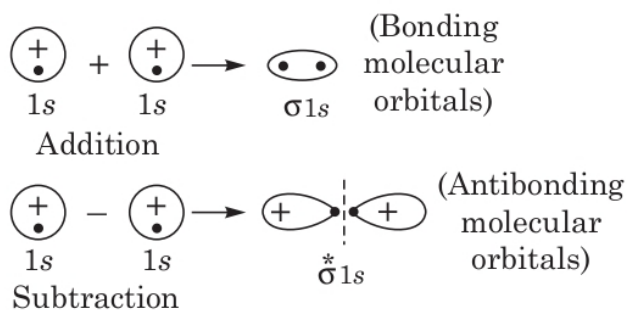
$$\Psi_b = \Psi_A + \Psi_B \quad [\text{constructive interference}]$$

$$\Psi_a = \Psi_A - \Psi_B \quad [\text{destructive interference}]$$



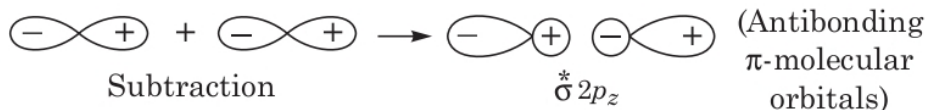
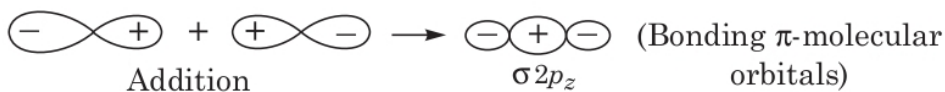
- The shape of molecular orbitals is governed by the shape of atomic orbitals, e.g. *s-s* and *p-p* overlapping.

- Combination between 1s and 1s atomic orbitals gives σ_{1s} and σ_{1s}^* orbitals.

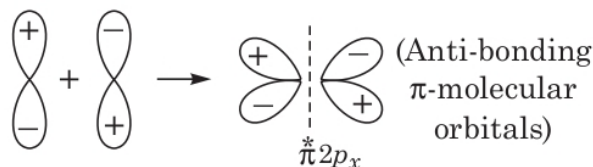
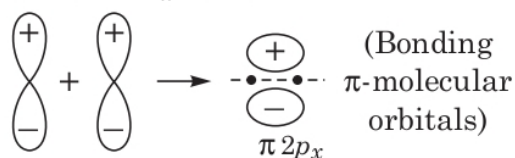


(ii) Combination between $2s$ and $2s$ orbitals gives $\sigma 2s$ and $\sigma^* 2s$ orbitals.

(iii) Combination between $2p_z$ and $2p_z$ atomic orbitals gives $\sigma 2p_z$ and $\sigma^* 2p_z$ orbitals



(iv) Combination between $2p_x$ and $2p_x$ atomic orbitals gives $\pi 2p_x$ and $\pi^* 2p_x$ orbitals.



$2p_y$ atomic orbitals will also overlap in the same way and thus, resulting molecular orbitals are $\pi 2p_y$ and $\pi^* 2p_y$.

If molecular orbital has symmetry with respect to centre, it is called **gerade (g)** otherwise **ungerade (u)**. All σ bonding and π^* anti-bonding MO are *g* while all π bonding and σ^* anti-bonding MO are *u*.

Electronic Configuration and Bond Order (BO) of Molecules

The order of energy of molecular orbitals has been determined experimentally by spectroscopy for the elements of the second period. The increasing order of energies of the molecular orbitals in homonuclear diatomic molecules is

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

[For O_2, F_2, Ne_2 more than 14 electrons]

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

[For B_2, C_2, N_2 upto 14 electrons]

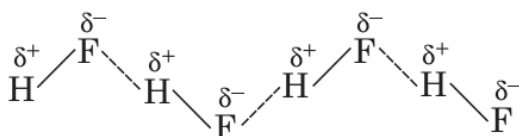
$$\text{Bond order (BO)} = \frac{N_b - N_a^*}{2}$$

A positive bond order, (i.e. $N_b > N_a^*$) means a stable molecule while a negative (i.e. $N_b < N_a^*$) or zero, (i.e. $N_b = N_a^*$) bond order means unstable molecule.

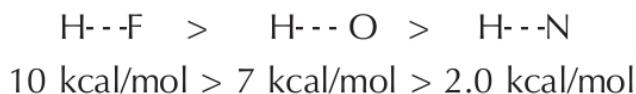
┌ Molecular species having unpaired electrons are paramagnetic, while if all the electrons in the orbitals are paired then the molecule is diamagnetic. ┐

Hydrogen Bond

It is defined as the force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines. The chains possess a **zig-zag** structure.



┌ Hydrogen bond is purely electrostatic and a weak bond. The strength of the strongest hydrogen bond is about 5-10 kcal per mol. The more the electronegativity of atom involved in H-bonding, the more is the bond strength, e.g.



Types of hydrogen bonds are:

Intermolecular H-bonding

H-bonding involving two or more different molecules. e.g. *o*-nitrophenol.

Intramolecular H-bonding

H-bonding within a same molecule. e.g., *p*-nitrophenol

Applications of Intermolecular H-bonding

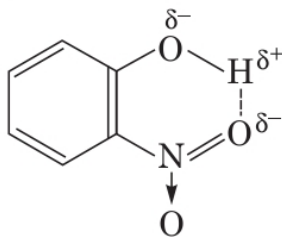
- (i) **Melting point and boiling point of water** Water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boiling points. It is due to intermolecular H-bonding in H_2O .
- (ii) **Ice has less density than water** In crystal structure of ice, every water molecule is associated with four other water molecules by H-bonding in a cage like tetrahedral structure. On melting the ice, H-bonds are broken and space between water

molecules decreases and density of water increases up to 4°C. Above 4°C, more H-bonds are broken, the water molecules get apart from each other and the density again decreases. Thus, water has maximum density at 4°C.

- (iii) **Melting point and boiling point of alcohols** The marked difference between the melting and boiling points of alcohols is also due to H-bonding.

Applications of Intramolecular H-bonding

Volatile character of nitrophenols *o*-nitrophenol is more volatile (b.p. 214°C) as compared to *meta* (b.p. 290°C) and *para* (b.p. 279°C). It is due to chelation (ring like structure).



In *meta* and *para* isomer, chelation is not possible due to the formation of desired size of ring.

Metallic Bond

The attractive force that binds the metal ions to the mobile electrons is called metallic bond. The positive metal ions are called positive cores or kernels and mobile electrons are electron pool or electron gas. **Electron-sea theory of metallic bond** explains number of the properties of the metal.

Strength of bonds

Ionic bond > covalent bond > metallic bond > H-bond