

Chapter- 4: Chemical Bonding and Molecular Structure

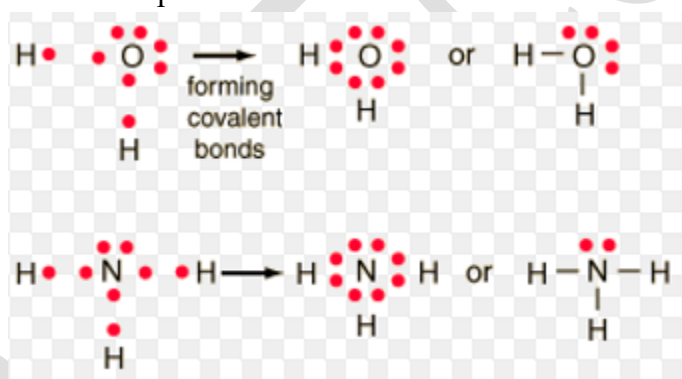
1. Octet Rule- Kossel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to attain their octet. This is known as octet rule.

2. Covalent Bonds- The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets or duplets.

3. Lewis dot structure: The structures are written as the **element** symbol surrounded by dots that represent the valence **electrons**.

Rules (step) for draw lewis structure:

- Count the total no. of valence electron of compound
- Count the total no. of lone pair electron
- Write the structure of compound and draw the lewis structure of compound

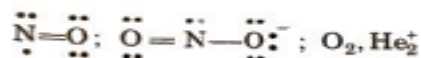


4. Limitations of octet rule

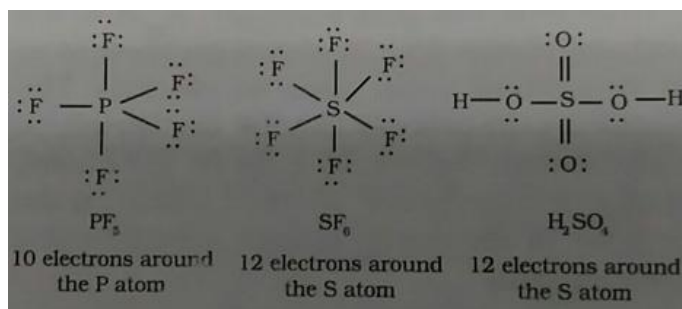
- Incomplete octet of the central atom:** In some compounds the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples- LiCl, BeH₂, BCl₃



- Odd-electron molecules:** Like nitric oxide (NO) and nitrogen dioxide.



- The expanded octet :** Elements in and beyond the third period of the periodic table having more than eight valence electrons around the central atom due to available d orbitals like

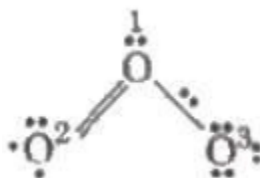


d) Pseudo inert gas configuration:

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

$$= \text{Valence } e^- - \text{lone pair } e^- - 1/2 * \text{bonding } e^-$$

$$= \text{Valence } e^- - \text{lone pair } e^- - \text{No. of bond line}$$

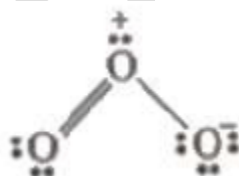


$$\text{F.C. on O atom marked 1} = 6 - 2 - 1/2 (6) = +1$$

$$\text{F.C. on O atom marked 2} = 6 - 4 - 1/2 (4) = 0$$

$$\text{F.C. on O atom marked 3} = 6 - 6 - 1/2 (2) = -1$$

Hence, O₃ along with the formal charges can be represented as follows



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



Favorable factors for the formation of ionic bonds:

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

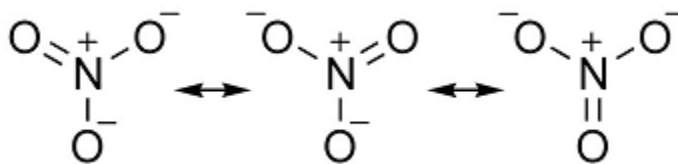
Properties of Ionic bond:

7. Difference b/w Properties of Ionic Compounds and Covalent Compounds:

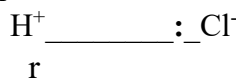
- Ionic compounds are usually solids (crystal structure) in nature while covalent compounds exist in the liquid or gaseous state at room temperature.
- Ionic compounds have high melting and boiling points while Covalent compounds have low melting and boiling points.
- Ionic compounds are soluble in polar solvents like water but insoluble in non-polar solvents like benzene etc while covalent compound are soluble in non-polar solvents but usually insoluble in water.
- Ionic compounds are good conductor in aqueous solution while covalent compounds are generally poor conductors of electricity because they do not contain free electrons or ions to conduct electricity.

8. Resonance: Resonance structures are multiple lewis structure that collectively describes a single molecule.

Conditions for Resonance: Require (: , σ , π) for resonance structure.



9. Dipole Moment (μ): It is defined as the product of the magnitude of the charge and the distance between the centers of positive and negative charge. It is a vector quantity and is represented by an arrow with its tail at the positive centre and head pointing towards a negative centre.



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

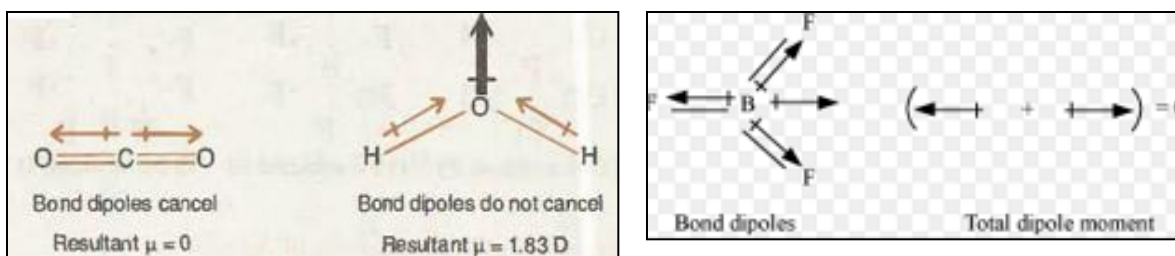
Dipole Moment is expressed in Debye (D)

1 D = 3.33564×10^{-30} C-m; where, C is coulomb and m is meter.

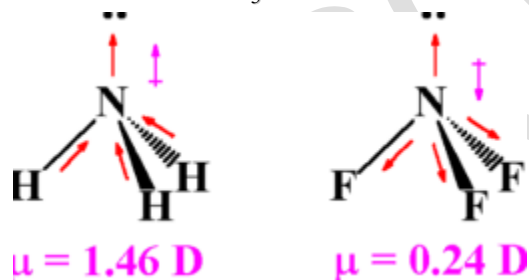
1 D = 10^{-18} e.s.u. cm

Significance of Dipole moment:

- It is helpful in predicting the geometry of the molecule and determining the polarity.
- If $\mu = 0$ Non polar due to planar structure (Example- H_2 , O_2 , F_2 , Cl_2 , BF_3 , CCl_4 , PCl_5 , CO_2 , CH_4 , Benzene, Naphthlene, Diphenyl etc).



- If $\mu \neq 0$ Polar (Example- NH_3 , HF , HCl)
- If electronegativity difference is more so polarity is more so μ is more, example $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$; $\text{H}_2\text{O} > \text{H}_2\text{S}$
- If molecule have angular structure than dipole moment is more, example $\text{CCl}_4 < \text{CHCl}_3 < \text{CH}_2\text{Cl}_2 < \text{CH}_3\text{Cl}$
- NH_3 has higher dipole moment than NF_3 like



10. Fajan's Rule: In ionic bonds also having partial covalent character which 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.

Cation Size \downarrow Covalent character in Ionic Bond \uparrow
 Anion Size \uparrow Covalent character in Ionic Bond \uparrow

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

11. Theory of Covalent bonding:

12.1. The Valence Shell Electron Pair Repulsion (VSEPR) Theory

12.2. Valence bond theory (VBT) and Hybridization

12.3. Molecular Orbital Theory (MOT) and Electron Delocalization

11.1. 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. 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.

3.

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

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

Geometry of Molecules on the basis of VSEPR:

Types of Molecule	No. of bonding Atoms	No. of Lone pair	Shape	Example
AB ₂	2	0	Linear	BeCl ₂
AB ₃	3	0	Trigonal	BCl ₃
AB ₄	4	0	Tetrahedral	CH ₄
AB ₅	5	0	Trigonal bipyramid	PCl ₅
AB ₆	6	0	Octahedral	PCl ₆
AB ₂ L	2	1	Bent	SO ₂
AB ₃ L	3	1	Pyramidal	NH ₃
AB ₂ L ₂	2	2	V-Shape	H ₂ O
AB ₄ L	4	1	See-Saw	SF ₄
AB ₃ L ₂	3	2	T-Shape	ClF ₃
AB ₂ L ₃	2	3	Linear	XeF ₂
AB ₅ L	5	1	Square Pyramidal	ClF ₅ , IF ₅
AB ₄ L ₂	4	2	Square Planar	XeF ₄

11.2. Valence bond theory (VBT) and Hybridization: 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. The covalent bond may be classified in to two types according to the types of overlapping-

a) **Sigma Bond** (σ bond): Sigma bond should be form during result of following overlapping

(i) s-s overlapping: Example H_2

(ii) s-p overlapping: Example HF, HCl etc.

(iii) p-p head to head overlapping (axial): Example F_2 , Cl_2 etc.

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

b) **Pi Bond** (π bond): It is formed by the sidewise or lateral overlapping between p- atomic orbitals. π bond is a weaker bond than σ bond. Example O_2 etc.

Difference b/w Sigma and Pi Bonds

(a) It is formed by the end to end overlap of orbitals.	It is formed by the lateral overlap of orbitals.
(b) The orbitals involved in the overlapping are s-s, s-p, or p-p.	These bonds are formed by the overlap of p-p orbitals only.
(c) It is a strong bond.	It is weak bond.
(d) The electron cloud is symmetrical about the line joining the two nuclei.	The electron cloud is not symmetrical.
(e) It consists of one electron cloud, which is symmetrical about the internuclear axis.	There are two electron clouds lying above and below the plane of the atomic nuclei.
(f) Free rotation about σ bonds is possible.	Rotation is restricted in π bonds.

Limitations of VBT

1. Fails to explain, the magnetic properties of some molecules. It.
2. Bonding in electron deficient compounds.

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

Method for Finding the Hybridization: Apply the following formula to find the hybridization of central atom.

Z = 1/2 (No. of valence electron + No. of attached atoms + negative charge – positive charge)

Examples Hybridization of $\text{NH}_3 = 1 / 2[5 + 3 + 0 - 0] = 4 \Rightarrow \text{sp}^3$

Or

Hybridisation = No. of Lone pair + No. of Bond atoms

No. of Lone pair = No. of valence electron - No. of bond atoms + negative charge – positive charge

Value of Z	2	3	4	5	6	7
Hybridization	sp	sp ²	sp ³	sp ³ d	sp ³ d ²	sp ³ d ³

Salient Features of hybridization:

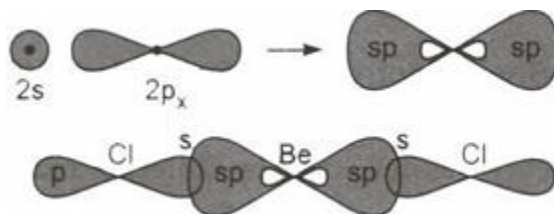
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridized orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals have minimum repulsion between electron pairs and thus a stable arrangement.

Types of Hybridization

1. **sp hybridization**- During mixing of one s and one p orbital of same atom, they will be form two equivalent sp hybrid orbitals like BeCl_2 .

Bond angle b/w sp hybrid orbitals is 180° and shape is linear.

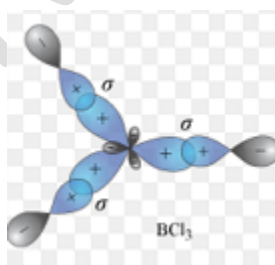
Be (4) Ground State	$\uparrow\downarrow$	$\uparrow\downarrow$			
	1s	2s	2p		
Be (4) Excited State	$\uparrow\downarrow$	\uparrow	\uparrow		
	1s	2s	2p		
Be (4) Hybridized State	$\uparrow\downarrow$	\uparrow	\uparrow		
		sp	sp		(Have equal energy)
Formation of BeCl₂ molecule	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$		
		Cl	Cl		



2. **sp² hybridization**- During mixing of one s and two p orbital of same atom, they will be form three equivalent sp² hybrid orbitals like BCl₃

Bond angle b/w sp² hybrid orbitals is 120* and shape is trigonal.

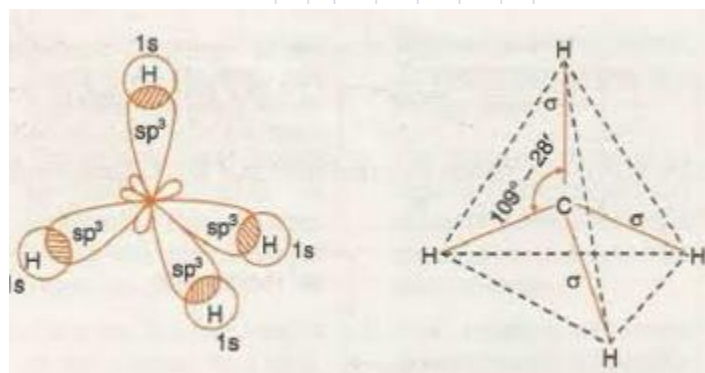
B (5) Ground State	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow		
	1s	2s	2p		
B (5) Excited State	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	
	1s	2s	2p		
B (5) Hybridized State	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	
		sp ²	sp ²	sp ²	(Have equal energy)
Formation of BCl₃ molecule	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	
		Cl	Cl	Cl	



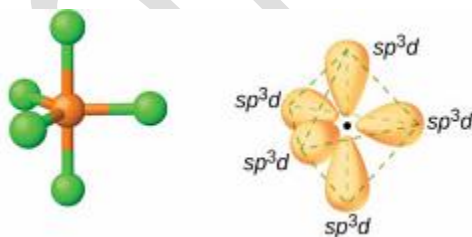
3. **sp³ hybridization**- During mixing of one s and three p orbital of same atom, they will be form four equivalent sp³ hybrid orbitals like CH₄

Bond angle b/w sp³ hybrid orbitals is 109.5* and shape is tetrahedral.

C (6) Ground State	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	
	1s	2s	2p		
C (6) Excited State	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow
	1s	2s	2p		
C (6) Hybridized State	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow
		(Have equal energy)			
		sp ³	sp ³	sp ³	sp ³
Formation of CH₄ molecule	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
		H	H	H	H

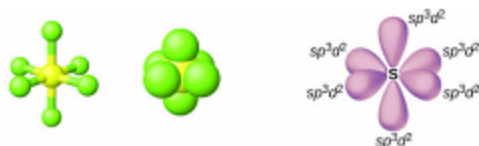


4. Sp³d hybridization: During mixing of one s, three p and one d orbital of same atom, they will be form five equivalent sp³d hybrid orbitals which arrange in shape as trigonal bipyramid.



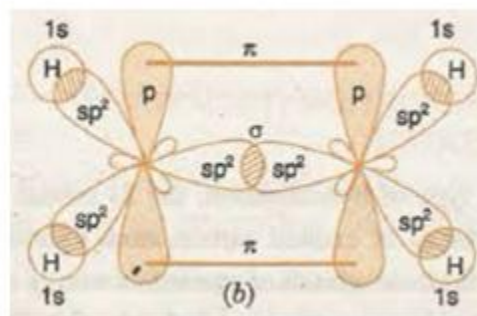
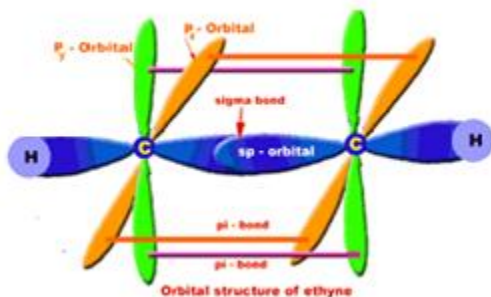
P (15) Ground State	$\uparrow\downarrow$		\uparrow	\uparrow	\uparrow				
	3s		3p			3d			
P (15) Excited State	\uparrow		\uparrow	\uparrow	\uparrow	\uparrow			
			3p			3d			
P (15) Hybridized State	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow				
	sp ³ d								
Formation of PCl₅ molecule	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$				
	Cl	Cl	Cl	Cl	Cl				

5. Sp³d² hybridization: During mixing of one s, three p and two d orbital of same atom, they will be form six equivalent sp³d² hybrid orbitals which arrange in shape of octahedral like SF₆



S (16) Ground State	↑↓		↑↓	↑	↑				
	3s		3p				3d		
S (16) Excited State	↑		↑	↑	↑		↑	↑	
	3s		3p				3d		
S (16) Hybridized State	↑	↑	↑	↑	↑	↑			
	sp3d2	sp3d2	sp3d2	sp3d2	sp3d2	sp3d2			
Formation of SF6 molecule	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓			
	Cl	Cl	Cl	Cl	Cl	Cl			

Other Examples: Structure of Ethyne and Ethene-



12.3. Molecular Orbital Theory (MOT) and Electron Delocalization: According to this theory, the atomic orbitals combine to form the molecular orbitals. Molecular orbitals are formed by linear combination of atomic orbitals. The number of molecular orbitals formed is equal to the number of atomic orbitals involved.

According to this theory-

(a) Molecular orbitals are represented by wave functions. A plus sign in an orbital indicates a positive wave function while a minus sign in an orbital represents a negative wave function.

(b) A molecular orbital that is formed by addition overlap (*i.e.*, when the lobes of atomic orbitals overlap with the same sign) of two atomic orbitals, which is known as *bonding molecular orbital*. It is represented as

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

Its energy is lower than the atomic orbitals from which it is formed. It favors bonding.

(c) A molecular orbital that is obtained by the subtraction overlap (*i.e.*, when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals, which is known as *anti-bonding molecular orbital*. It is represented as

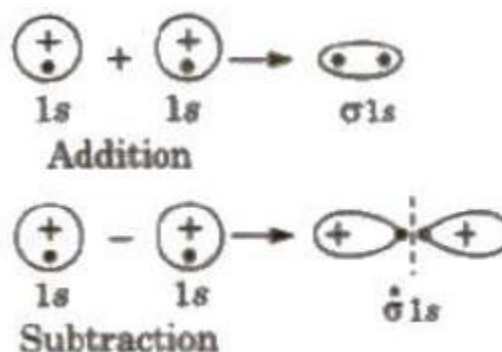
$$\Psi_{MO}^* = \Psi_A - \Psi_B$$

Its energy is higher than the atomic orbitals from which it is formed. It does not favour bonding.

(d) The shape is governed by the shape of atomic orbitals, e.g., s-s and p-p overlapping.

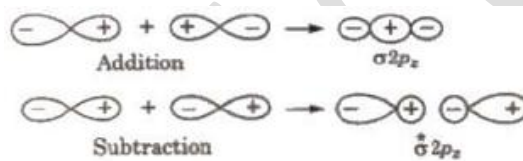
(i) Combination between 1s and 1s orbitals gives σ_{1s} and σ^*_{1s} orbitals.

(ii) It have one nodal plane.

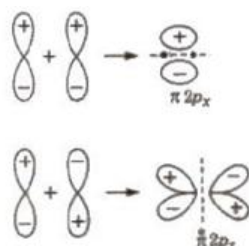


(ii) Combination between 2s and 2s orbitals gives σ_{2s} and σ^*_{2s} orbitals.

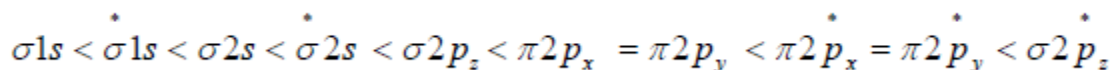
(iii) Combination between p-atomic orbitals gives σ_{2p_z} and $\sigma^*_{2p_z}$ orbitals.

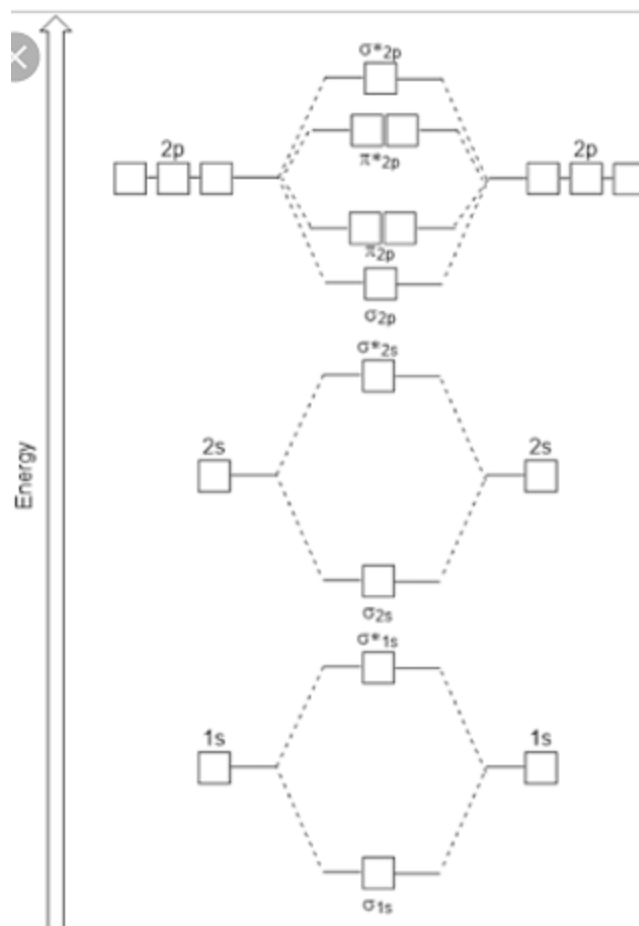


(iv) Combination between 2 p_x and 2 p_y atomic orbitals gives, it have one or two nodal planes.



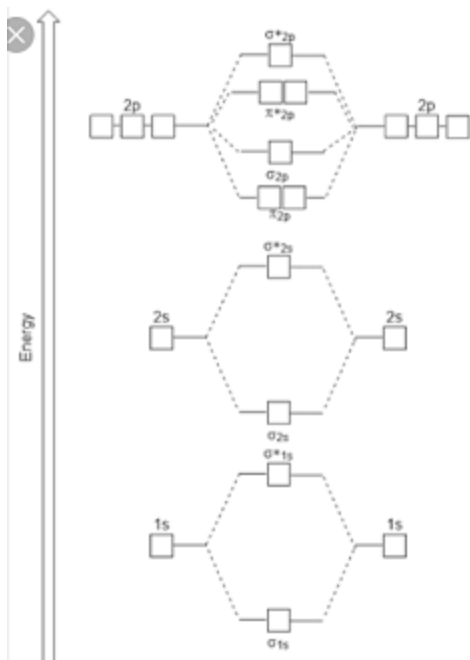
Energy level Diagrams and Electronic Configuration for Molecular Orbital: The order of energy of molecular orbitals has been determined experimentally by spectroscopy for the elements of the second period. The increasing order of energies of various molecular orbitals for O_2 and F_2 are as following





This sequence of energy levels of molecular orbitals is not correct for remaining molecules of second period like Li_2 , Be_2 , B_2 , C_2 , N_2 . For those, it has been observed experimentally the increasing order of energies is as following

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$$



Bond Order: It is defined as half of the difference between number of electrons in bonding N_b and anti-bonding orbitals N_a , *i.e.*,

$$\text{Bond Order} = \frac{1}{2} (N_b - N_a)$$

Relationship between electronic configuration and molecular behaviour: Bond order helps in estimating stability of atom.

- If N_b is greater than N_a , the molecule is stable.
- The molecule is unstable if N_a is greater than N_b .
- The molecule is also unstable if N_a is equal to N_b because anti-bonding effect is stronger than bonding effect.
- Molecular species having unpaired electrons are paramagnetic (attracted by magnetic field), while if all the electrons in the orbitals are paired then the molecule is diamagnetic (repelled by magnetic field).

Magnetic moment (μ) = $n(n+2)$ BM (Bohr magneton), Here, n = No. of unpaired electron

Bonding in homonuclear diatomic molecules:

Molecule	Bond Order $(N_b - N_a)/2$	Stability	Unpaired electron	Magnetic Property
H ₂	$2 - 0 / 2 = 1$	Stable	Nil	Diamagnetic
He ₂	$2 - 2 / 2 = 0$	Unstable	~	~
Li ₂	$4 - 2 / 2 = 1$	Stable	Nil	Diamagnetic
C ₂	$8 - 4 / 2 = 2$	Stable	Nil	Diamagnetic
O ₂	$10 - 6 / 2 = 2$	Stable	2	Paramagnetic

Important relation: Bond order \propto Bond energy \propto Stability \propto 1/ Bond length \propto 1/ Reactivity
 (NOTE: First find out bond order by tricky then solve others. Magnetic properties also solve by tricks)

13. Bond Parameters:

13.1. Bond Length: Distance between the nuclei of the two atoms is known as bond length. It depends mainly on electronegativities of constituents atoms.

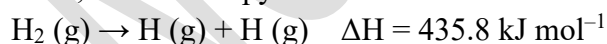
Factor affected bond length:

- **Size of side atoms:**
Bond length \propto Size of side atoms, example $RF < RCl < RBr < RI$
- **Lone pair:**
Bond length \propto Lone pair, example $N_2 < O_2 < F_2$
- **% s character (Multiplicity or bond order):**
Bond length $\propto 1 / \% s$ character (Multiplicity), example $N_2 < O = O < H - H < F - F$

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

- **Electronegativity:**
Bond length $\propto 1 /$ Difference of Electronegativity, example $HF < HCl < HBr < HI$; $H_2O < H_2S$
- **Resonance:** Bond length affected due to Resonance, It is b/w single and double bond.

13.2. Bond energy: It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1} . For ex in hydrogen molecule, bond enthalpy is $435.8 \text{ kJ mol}^{-1}$.



Factor affected bond energy:

Bond energy $\propto 1 /$ Bond length

13.3. Bond Angle: It is defined as the angle between the orbital containing bonding electron pairs around the central atom in a molecule/complex ion.

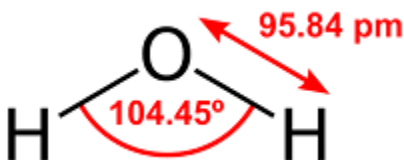
Factor affected bond angle:

- **Hybridization (/ % s character):**
 $sp (180) > sp^2 (120) > sp^3 (109.28)$
- **Lone pair repulsion:**
If hybridization same then lone pair different so Bond angle $\propto 1 /$ Lone pair, Example $CH_4 > NH_3 > H_2O$
- **Electronegativity of central atom:**
Central atom different but side atoms are same then Bond angle \propto Electronegativity of central atom, Example $NH_3 > PH_3 > AsH_3$, $NCl_3 > PCl_3 > AsCl_3$

- **Size of side atom:**

Side atom different but central atoms are same then Bond angle \propto Size of side atom

Bond angle \propto Size of side atom, Example $\text{OBr}_2 > \text{OCl}_2 > \text{OH}_2 > \text{OF}_2$

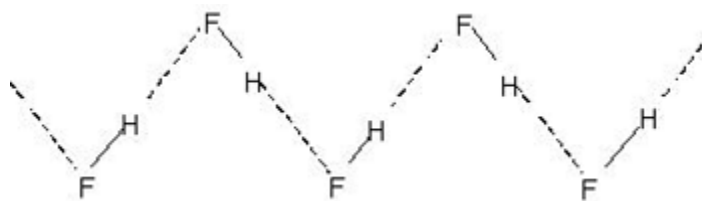


13.4. Bond Order: It is defined as the number of bonds between the two atoms in a molecule. E.g.: Bond Order of O_2 is 2, N_2 is 3. With increase in bond order, bond enthalpy increases and bond length decreases.

Bond order \propto Bond energy \propto Stability \propto 1/ Bond length \propto 1/ Reactivity

Bond order can be calculated by tricky as

14. 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.

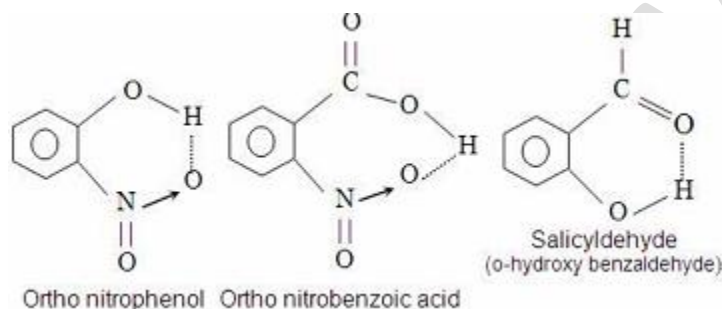


Hydrogen bond is purely electrostatic and a weak bond. The strength of the strongest hydrogen bond is about 5-10 kcal per mol. The more the electronegativity of atom involved in H-bonding, the more is the bond strength, e.g.,



Types of hydrogen bonds are

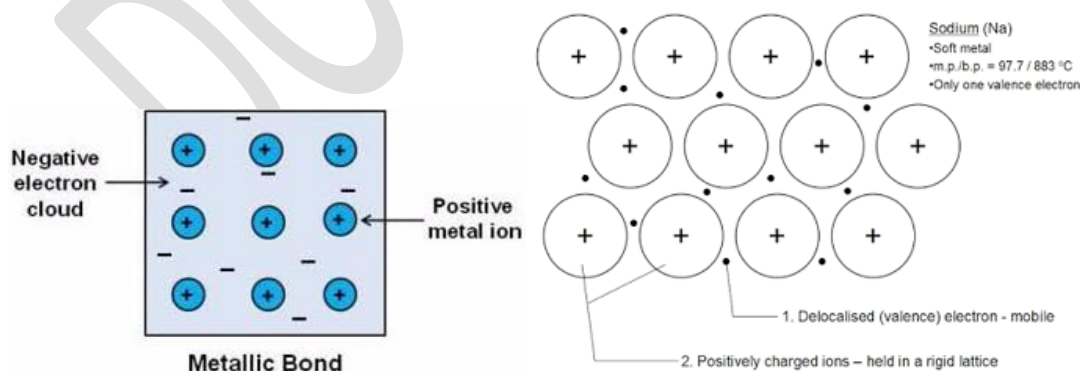
- (i) Intermolecular H-bonding : H-bonding involving two or more molecules.
- (ii) Intramolecular H-bonding : H-bonding within a molecule for example



Effect of H- bond on physical properties:

- a) Solubility
- b) M.P. and B.P.
- c) Viscosity
- d) Surface tension
- e) Molecular weight
- f) Physical state

15. Metallic Bond: Metallic bond is the force of attraction between a metal ion to a number of electrons within its sphere of influence. Electron-sea theory of metallic bond explains number of the properties of the metal



Strength of different bonds: Ionic bond > covalent bond > metallic bond > H-bond

16. Solubility of ionic compounds:

17. Thermal stability (Heating effect):

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