Bond order : Number of shared pair of electrons or number of bonds between two molecules is known as bond order.
 Bond order

		Rona ore
Н:Н	$\mathbf{H} - \mathbf{H}$	1
0::0	0=0	2

	<u> </u>	2
N :: N	N = N	3

Isoelectronic molecules or ions have same bond order. *Example* : N_2 , CO, NO⁺ (14 electrons) have bond order = 3.

LEWIS STRUCTURE

- Lewis symbol of an atom is represented by the chemical symbol for the atom surrounded by a number of dots corresponding to the number of valence electrons.
- Lewis symbols :

Li. Be $B \leftarrow C \leftarrow N \leftarrow O \leftarrow F$

- Lewis structure for molecules
 - Write a symmetrical 'skeleton' for the molecules and polyatomic ions.
 - Calculate the number of electrons available in the valence shell of all the atoms (A).
 - Calculate the total number of electrons needed by all the atoms to achieve noble gas configuration (N).
 - > Calculate the total number of electrons shared, S = N - A.
 - Place the shared pair of electrons into the skeleton, using double and triple bonds only when necessary.

Illustration 3

Write the Lewis dot formula or dash formula for the CO_3^{2-} ion. Soln.: Step (i) : skeleton O C Φ^{2-}

Step (ii):
$$A = 1 \times 4$$
 (for C) + 3 × 6 (for O) + 2 (for negative charge)

= 4 + 18 + 2 = 24 electrons Step (iii) : N = 1 × 8 (for C) + 3 × 8 (for O) = 8 + 24 = 32 electrons

Step (iv) : S = N - A = 32 - 24 = 8 electrons shared (4 pair shared)

Step (v):
$$\begin{bmatrix} 0 : C :: 0 \end{bmatrix}^{2^{-}}$$

Step (vi): $\begin{bmatrix} \vdots \vdots : C :: \bullet \\ \vdots \vdots : \end{bmatrix}^{2^{-}}$ or $\begin{bmatrix} \vdots \vdots -C = \vdots \\ \vdots : 0 : \end{bmatrix}^{2^{-}}$

VALENCE BOND THEORY (VBT)

- The valence bond theory was put forward by Heitler and London in 1927, later it was developed by Pauling and Slater in 1931. The basic assumptions of this theory were –
 - A covalent bond is formed by overlapping of atomic orbitals of valence shell of the two atoms.
 - Only half-filled atomic orbitals, *i.e.*, orbitals singly occupied take part in overlapping process.
 - As the orbital of one atom overlaps the orbital of another, the electrons in the orbitals begin to move around both atoms.
 - > The strength of bonding depends on orbital overlap, orbitals other than s-orbitals form bonds only in given directions.
- Sigma (σ) bond : Bonding orbital which is symmetrical about the line joining the two nuclei is known as σ bond. A \bullet bond has a cylindrical shape around the bond axis.
 - Pi (π) bond : A π bond has an electron distribution above and below the bond axis.

Orbitals used in bond formation	Types of bond formed	Diagram showing overlap	Examples
s-orbital – s-orbital	σ		H ₂
s-orbital – p-orbital	6		H ₂ O, NH ₃ , HF, HCl
<i>p</i> -orbital – <i>p</i> -orbital (head-head overlap)	σ		$\overline{F_2, Cl_2, Br_2}$
p_{y} -orbital – p_{y} -orbital (sidewise overlap)	π	828	O ₂ , N ₂

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Hybridisation

 This is a hypothetical concept and has been introduced by Pauling and Slater. According to this concept any number of atomic orbitals of an atom which differ in energy slightly may mix with each other to form new orbitals called hybrid orbitals. The process of mixing or amalgamation of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridisation.

- > Only orbitals (atomic) of nearly same energy belonging to same atom or ion can take part in hybridisation.
- > Number of the hybrid orbitals formed is always equal to number of atomic orbitals which have taken part in the process of hybridisation.

 Actually the orbitals undergo hybridization and not the electrons.

Resonance

• Sometimes a molecule cannot be represented by a single Lewis structure to explain all its properties, then it is represented by more than one electronic arrangement, none of which can explain all the properties but can explain most of the properties. The actual structure of the compound is intermediate of the various electronic arrangements and is known as **resonance hybrid**. Various electronic arrangements are known as **resonating structures** or **canonical structures** or **contributing structures**.



Resonance hybrid

Type of Hybridisation	Orbitals used	Orientation of hybrid orbitals with bond	Sbape	Examples
sp	one s + one p	angle Linear, 180°	$\bigcirc \bigcirc \bigcirc \bigcirc \rightarrow$	BeF ₂ , BeCl ₂ , CO ₂ , CS ₂ , C ₂ H ₂ , etc.
sp ²	one s + two p	Trig●nal planar, 120°	X	BF ₃ , C_2H_4 , SO ₂ , SO ₃ , etc.
sp3	one s + three p	Tetrahedral, 109°28'	A +	CH ₄ , CCl ₄ , SiF ₄ , etc.
sp ³ d	one s + three p + one $d(d_{22})$	Trigonal bipyramidal, 120° and 90°		PCl ₅ , PF ₅ , etc.
sp ³ a ²	one s + three p + two $d(d_{x^2-y^2}, d_{z^2})$	Octahedral, 90°		SF ₆ , [СтF ₆] ^{3–} , ею
sp ³ d ³	one s + three p + three $d(d_{XY}, d_{YZ}, d_{XZ})$	Pentagonal bipyramidal, 72° and 90•		IF ₇ , XcF ₆ , etc.
dsp ²	One \mathcal{A} $(d_{\chi^2 - y^2})$ + one s + two p	square planar	\gg	$[Ni(CN)_4]^{2-},$ $[PtCl_4]^{2-},$ etc.

• Salient features of resonance

- > All the contributing structures have same position of atoms *i.e.*, same atomic arrangement.
- > All the contributing structures have same number of shared and unshared electrons.
- > Contributing structures have nearly equal energy.

Chemical Bonding and Molecular Structure

- > The contributing structures do not have real existence, but are all imaginary.
- Greater the number of resonating structures of comparable energy, greater is the stability of molecule.
- Resonance energy: It is defined as the difference in energy of resonance hybrid structure and most stable contributing structures (having least energy). Greater the resonance energy, greater is the stability of molecule.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- VSEPR theory was given by Sidgwick and Powell in 1940.
- In a molecule, the central atom is surrounded by shared pair of electrons (bond pairs) as well as non-bonding electrons (lone pairs).
- The electron pairs surrounding the central atom repel each other and move away from one another to occupy the most appropriate position in such a way that there are no further repulsions between them and molecule is in the state of minimum energy and maximum stability.
- The order of repulsion between electron pairs is as follows:
 lone pair-lone pair > lone pair-bond pair > bond pair-bond pair



MOLECULAR ORBITAL THEORY (MOT)

- Molecular orbital theory was proposed by Hund and Mulliken in 1932.
- According to this theory, in a molecule formation all atomic orbitals of participating atoms overlap or mix up to form equivalent number of new orbitals called molecular orbitals.
- Formation of molecular orbitals is explained on the basis of Linear Combination of Atomic orbitals (LCAO).

When atomic orbitals approach each other, their wave function (ψ) interact with each other in two different ways:

- > Constructive interference *i.e.*, when two waves are in phase and produce an additive effect to give rise to **bonding molecular orbital**.
- Destructive interference i.e., when two waves are out of phase and produce subtractive effect to give rise to antibonding molecular orbital.
- The atomic orbitals which do not take part in bond formation are known as **non-bonding orbitals**.
- The molecular orbitals are filled in increasing order of their energy *i.e.*, according to Aufbau principle.

• The order of energy for diatomic molecules

For diatomic homonuclear molecules such as Li_2 , Be_2 , B_2 , C_2 , N_2 , is

$$\frac{\sigma_{ls} \bullet * ls}{\sigma_{ls} \bullet * ls} \bullet \frac{\sigma_{2s}}{\sigma_{2s}}, \frac{\sigma_{2p_x}}{\sigma_{2p_y}}, \frac{\sigma_{2p_z}}{\sigma_{2p_z}}, \frac{\sigma_{2p_x}}{\sigma_{2p_y}}, \frac{\sigma_{2p_z}}{\sigma_{2p_y}}, \frac{\sigma_{2p_z}}{\sigma_{2p_y}}$$

For homonuclear diatomic molecules such as \bullet_2 , F_2 , Ne₂, the energy diagram is

$$\sigma ls, \sigma^* ls, \sigma 2s, \sigma^* 2s, \sigma 2p_z, \frac{\pi 2p_x}{\pi 2p_y}, \frac{\pi^* 2p_x}{\pi^* 2p_y}, \sigma^* 2p_z$$

Energy increases

The difference in sequence of $\sigma 2p$ and $\pi 2p$ orbitals in two energy level diagrams is because of the interaction of 2s and $2p_z$ orbitals. In the molecules Li₂, Be₂, C₂ and N₂ the difference in energy level of 2s and $2p_z$ orbitals is small. As a result of that $\bullet 2s$ and $\sigma 2p_z$ are so close that the repulsive forces present between them raise the energy of $\sigma 2p_z$ and it becomes greater than that of $\pi 2p$ orbitals, whereas in O₂, F₂ and Ne₂ the energy difference of 2s and $2p_z$ atomic orbitals is large enough so that there is no interaction between $\sigma 2s$ and $\sigma 2p_z$ molecular orbitals.

HYDROGEN BOND

 Hydrogen bonding is a special type of dipole - dipole interaction. When H-atom is covalently bonded to a highly electronegative atom, there exists a weak electrostatic force of attraction between H-atom of one molecule and electronegative atom of another molecule. Hydrogen-bond is represented by dotted lines. For example, HF.

δ+	δ–	δ+	δ	δ+	δ-	- δ+	δ-
Н —	- F	H	· F	H	F	H —	· F

Hydrogen bond is not a true chemical bond.

- Types of hydrogen bonding : Generally hydrogen bonding is of two types :
 - Intermolecular hydrogen bonding : It is the hydrogen bonding taking place between different molecules of either same or different compounds. For example: HF, H₂O, *R*OH.



Hydrogen bonding in ammonia (NH₃)



Hydrogen bonding in formic acid (HCOOH) (dimerisation)

Intramolecular hydrogen bonding : This type of hydrogen - bonding takes place between two atoms of the same molecule. It is commonly known as chelation and frequently occurs in organic compounds.

Example : *o*-chlorophenol, *o*-nitrophenol, salicylic acid, 2,6-dihydroxy benzoic acid, etc.



• Consequences of hydrogen bonding : Hydrogen bonding has a great influence on physical properties of the compounds.

 Boiling point : The compounds having hydrogen bonding possess high melting point and boiling point.

e.g. HF - 292.4 K (higher than other halogen acids). H_2O has the highest boiling point among hydrides of other group 16 elements (H_2S , H_2Se , H_2Te) because of the association by virtue of hydrogen bonding.

- Solubility : A substance is soluble if it forms hydrogen bonds with covalent solvent molecules.
 For example, lower alcohols, carboxylic acids, ammonia are soluble in water.
- Volatility : The compounds possessing intermolecular H - bonds have higher boiling point and thus are less volatile.
- Lower density of ice than water : In solid ice, hydrogen bonding gives rise to an open cage like structure in which each water molecule is linked tetrahedrally to four water molecules. Thus molecules no longer remain closely packed and mass per unit volume *i.e.*, density decreases. When ice melts, the cage like structure collapses and molecules come closer to each other and thus density of liquid water increases.

