



Chemical Bonding-I

Chemical Bond: The attractive force which holds various constituents such as atoms, ions etc., together in different chemical species is called a chemical bond.

Covalent Bond :

A chemical bond formed by sharing of electrons between two elements is called as covalent bond.

$A-A$ (Single bond) : When 2 electrons are shared between the two combining elements.

$A=A$ (Double bond) : When 4 electrons are shared between the two combining elements.

$A\equiv A$ (Triple bond) : When 6 electrons are shared between the two combining elements.

To explain nature of chemical bond, different theories are given

(i) Octet rule

(ii) Valence bond theory

(iii) Valence shell electron pair repulsion theory

(iv) Molecular orbital theory.

Section (A) : Octet rule, Lewis dot structures

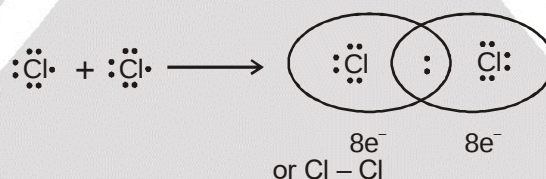
Octet rule : "Tendency of atoms to have eight electrons in their outermost shell is known as Lewis octet rule". To achieve inert gas configuration atoms lose, gain or share electrons.

- (i) It has been observed that atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements.
- (ii) It means that these atoms must have a stable electronic configuration.
- (iii) These elements (noble gases) have 8 electrons ($ns^2 np^6$) except helium which has 2 electrons ($1s^2$) in their outer most shell.

Element	Ne	Ar	Kr	Xe	Rn
Outer most shell configuration	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$

- (iv) It is therefore concluded that $ns^2 np^6$ configuration in the outer energy level constitutes a structure of maximum stability or minimum energy.

The **Octet rule** can be understood by considering the formation of the chlorine molecule, Cl_2 . The Cl atom with electronic configuration, $[Ne]^{10} 3s^2 3p^5$, is one electron short of the argon configuration. The formation of the Cl_2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both



Covalent bond between two Cl atoms

Figure

chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures.

Lewis Dot Structures :

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different.

To write the Lewis dot structure following steps are to be followed :

- (i) The total number of electrons are obtained by adding the valence electrons of combining atoms.
- (ii) For Anions, we need to add one electron for each negative charge.
- (iii) For cations, we need to subtract one electron for each positive charge.
- (iv) After then the central atom is decided.



To decide, Central atom, following steps are followed :

- (1) In general the **least electronegative atom** occupies the central position in the molecule/ion. For example in the NF_3 and CO_3^{2-} , nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions.
- (2) Generally the atom which is/are less in number acts as central atom.
- (3) Generally central atom is the atom which can form maximum number of bonds (which is generally equal to the number of electrons present in the valence shell of the atom).
- (4) Atom of highest atomic number or largest atom generally acts as central atom.

Hence fluorine and hydrogen can never act as central atoms.

After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons.

Lewis representations of a few molecules/ions are given in the following Table

Table

Molecule/ion	H_2	O_2	O_3	NF_3	CO_3^{2-}	HNO_3	CH_4	HCHO
Lewis Representation	$\text{H}-\text{H}$	$:\ddot{\text{O}}::\ddot{\text{O}}:$	$:\ddot{\text{O}}::\overset{+}{\text{O}}::\ddot{\text{O}}:$	$:\text{F}::\ddot{\text{N}}::\text{F}:$ $:\text{F}::$	$\left[\begin{array}{c} :\ddot{\text{O}}: \\ :\ddot{\text{O}}::\text{C}::\ddot{\text{O}}: \end{array} \right]^{2-}$	$\ddot{\text{O}}::\overset{+}{\text{N}}::\ddot{\text{O}}::\text{H}$ $:\ddot{\text{O}}::$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{H} \end{array}$

Each H-atom attains the configuration of helium (a duplet of electrons)

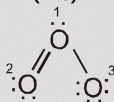
Section (B) : Formal charge & limitations of octet rule

Formal Charge : The formal charge of an atom in a molecule or ion is defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the lewis structure.

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

$$= \left[\begin{array}{c} \text{Total number of valence} \\ \text{electron in the free atom} \end{array} \right] - \left[\begin{array}{c} \text{Total number of non bonding} \\ \text{(lone pair) electrons} \end{array} \right] - \left(\frac{1}{2} \right) \left[\begin{array}{c} \text{Total number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

Let us consider the ozone molecule (O_3). The Lewis structure of O_3 , may be drawn as :



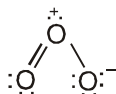
The atoms have been numbered as 1, 2 and 3. The formal charge on :

The central O atom marked 1 = $6 - 2 - \frac{1}{2}(6) = +1$

The terminal O atom marked 2 = $6 - 4 - \frac{1}{2}(4) = 0$

The terminal O atom marked 3 = $6 - 6 - \frac{1}{2}(2) = -1$

Hence, we represent O_3 along with the formal charges as follows :

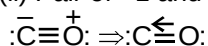


It should be kept in mind that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. **Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species.** Generally the lowest energy structure is the one with the smallest formal charges on the atoms.



Note : (i) The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms.

(ii) Pair of +1 and -1 formal charge on adjacent atoms is considered a coordinate bond.



(iii) Lewis dot structure with minimum formal charges is most stable.

Limitations of the Octet Rule :

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

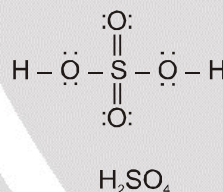
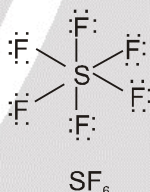
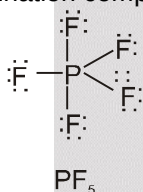
- The incomplete octet of the central atom :** In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are LiCl, BeH₂ and BCl₃.
BeF₂, BF₃, AlCl₃



- Odd-electron molecules :** In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide (NO₂), the octet rule is not satisfied for all the atoms.
e.g. NO, ClO₂, ClO₃

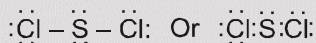


- The expanded octet :** Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.
Some of the examples of such compounds are: PF₅, SF₆, PCl₅, HNO₃, SO₃, SO₂, H₂SO₄ and a number of coordination compounds.



10 electrons around the P atom 12 electrons around the S atom 12 electrons around the S atom

- Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.



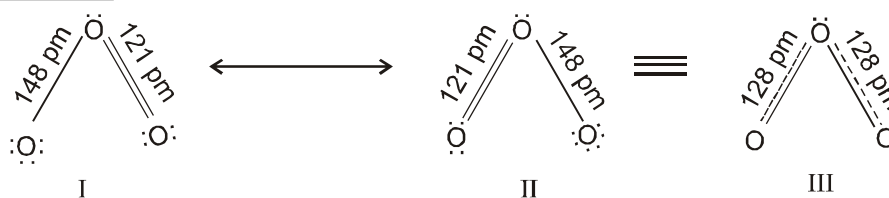
- Other drawbacks of the octet theory :**

(i) It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF₂, KrF₂, XeOF₂ etc.,
(ii) This theory does not account for the shape of molecules.
(iii) It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Section (C) : Resonance and bond order calculation

Resonance :

It is often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, O₃ molecule can be equally represented by the structures I and II shown below :

Resonance in the O_3 molecule

Structures I and II represent the two canonical forms.

The structure III is the resonance hybrid

In both structures we have a $O-O$ single bond and a $O=O$ double bond. The normal $O-O$ and $O=O$ bond lengths are 148 pm and 121 pm respectively.

Experimentally determined oxygen-oxygen bond lengths in the O_3 molecule are same (128 pm). Thus the oxygen-oxygen bonds in the O_3 molecule are intermediate between a double and a single bond.

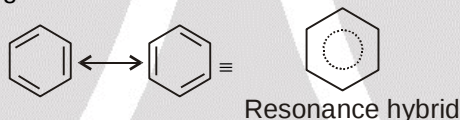
Obviously, this cannot be represented by either of the two Lewis structures shown above.

According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

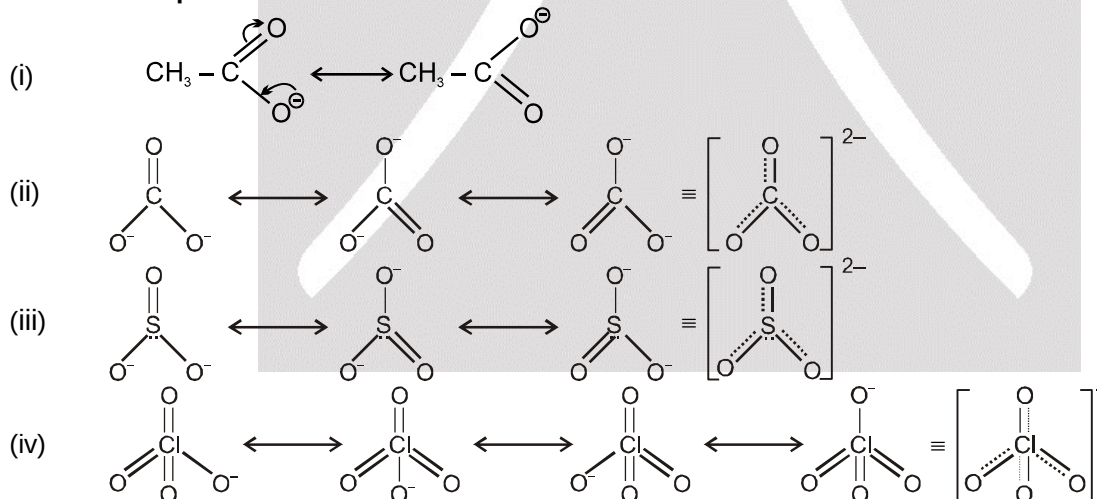
Thus for O_3 the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of O_3 , more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow.

Definition : Resonance may be defined as the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular compound

Resonance Hybrid : It is the actual structure of all different possible structures that can be written for the molecule without violating the rules of covalence maxima for the atoms.



Example :

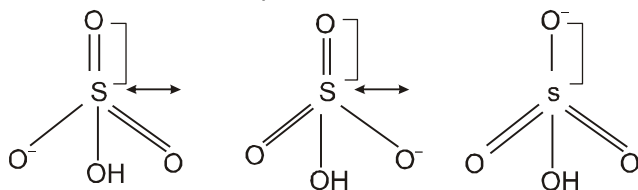


- Resonance energy = Actual bond energy – Energy of most stable resonating structure.
- Stability of molecule $\propto$ resonance energy.
- More is the number of covalent bonds in molecule more will be its resonance energy.
- Resonance energy $\propto$ number of resonating structures.



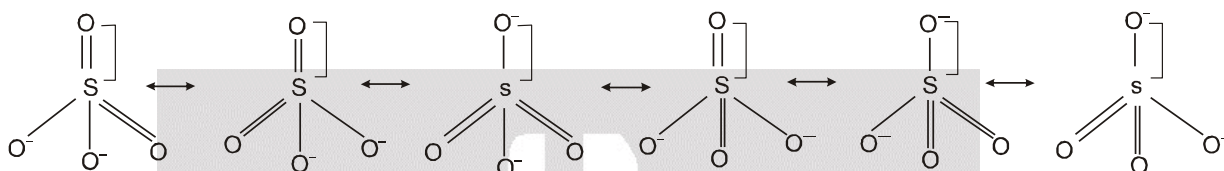
Bond order in oxoanions and corresponding acids :

Let's start with example of HSO_4^-



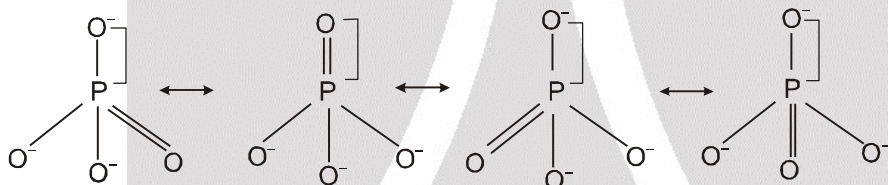
$$\text{Bond order} = \frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1}{3} = 5/3$$

Consider another example of SO_4^{2-} :



$$\text{Bond order} = \frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{2+2+1+2+1+1}{6} = 1.5$$

Consider another example of PO_4^{3-} :



$$\text{Bond order} = \frac{\text{Total No. of bonds formed between two atoms in all structures}}{\text{Total No. of resonating structures}} = \frac{1+2+1+1}{4} = 5/4$$

Section (D) : VBT, overlapping of orbitals

Modern Concept of Covalent Bond (VBT) :

(i) Introduced by Heitler and London.

(ii) This theory is based on the knowledge of Atomic orbitals electronic configuration of electrons, the overlap criterion of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition.

Consider two hydrogen atoms A and B approaching each other having nuclei H_A and H_B and electrons present in them are represented by E_A and E_B . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.

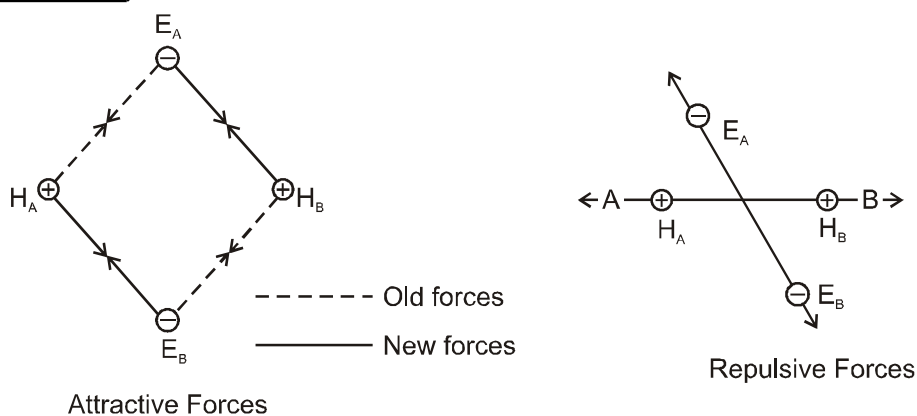
Attractive forces arise between :

- (i) nucleus of one atom and its own electron that is $H_A - E_A$ and $H_B - E_B$.
- (ii) nucleus of one atom and electron of other atom i.e., $H_A - E_B$, $H_B - E_A$.

Similarly repulsive forces arise between :

- (i) electrons of two atoms like $E_A - E_B$, (ii) nuclei of two atoms $H_A - H_B$.

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig.).

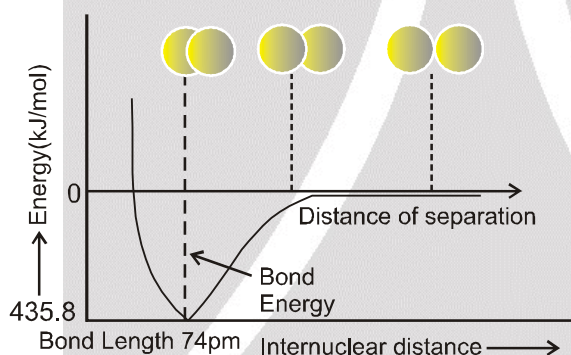
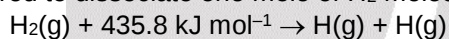


Attractive Forces

Figure : Forces of attraction and repulsion during the formation of H_2 molecule.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minima in the curve depicted in Fig. Conversely, 435.8 kJ of energy is required to dissociate one mole of H_2 molecule.

**Figure :** The potential energy curve for the formation of H_2 molecule as a function of internuclear distance of the H atoms. The minima in the curve corresponds to the most stable state of H_2 .

Orbital Overlap Concept

- In the formation of H_2 Molecule, In the minimum energy state when two H atoms are so near that their atomic orbitals undergoes partial interpenetration. This partial merging is called overlapping.
- Acc. to orbital overlap concept, The formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.
- The extent of overlap decides the strength of a covalent bond.
- Greater the overlap, stronger is the bond formed between two atoms.

Directional Properties of Bonds

The valence bond theory explains the formation and directional properties of bonds in polyatomic molecules like CH_4 , NH_3 and H_2O , etc. in terms of overlap and hybridisation of atomic orbitals.

Overlapping of Atomic Orbitals

When two atoms come close to each other there is overlapping of atomic orbitals. This overlap may be positive, negative or zero depending upon the properties of overlapping of atomic orbitals. The various arrangements of s and p orbitals resulting in positive, negative and zero overlap are depicted in the following figure.

The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules.

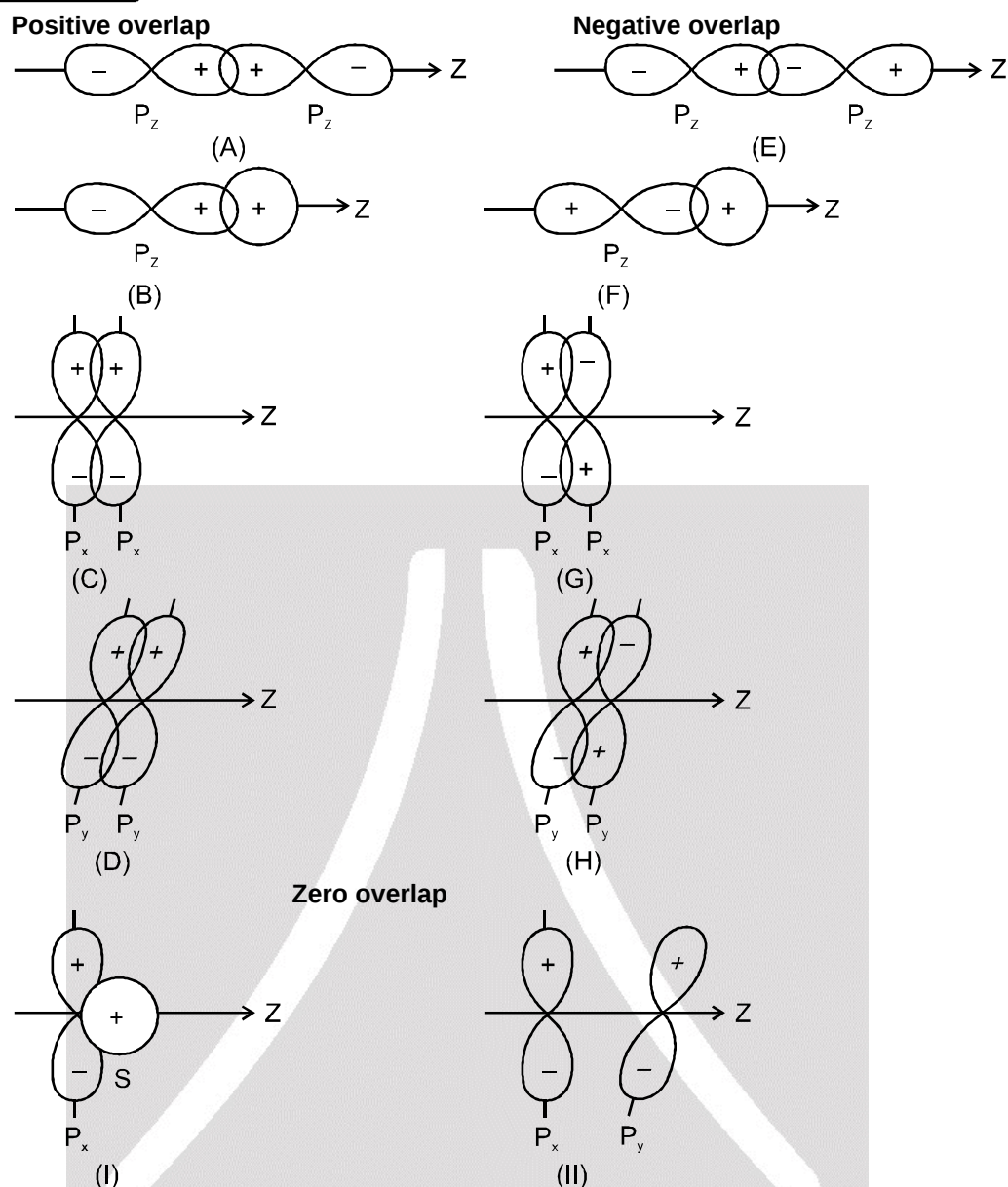


Figure : Positive, negative and zero overlaps of s and p atomic orbitals

Types of Overlapping and Nature of Covalent Bonds

The covalent bond may be classified into two types depending upon the types of overlapping :

(i) sigma(σ) bond, and (ii) pi (π) bond

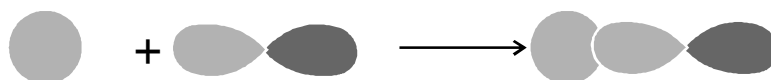
- (i) **Sigma (σ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

● **s-s overlapping** : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below :





- **s-p overlapping:** This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom.

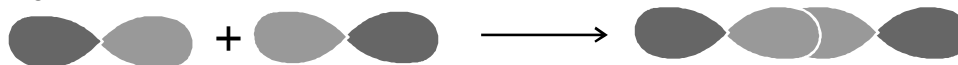


s-orbital

p-orbital

s-p orbital

- **p-p overlapping :** This type of overlap takes place between half filled p-orbitals of the two approaching atoms.

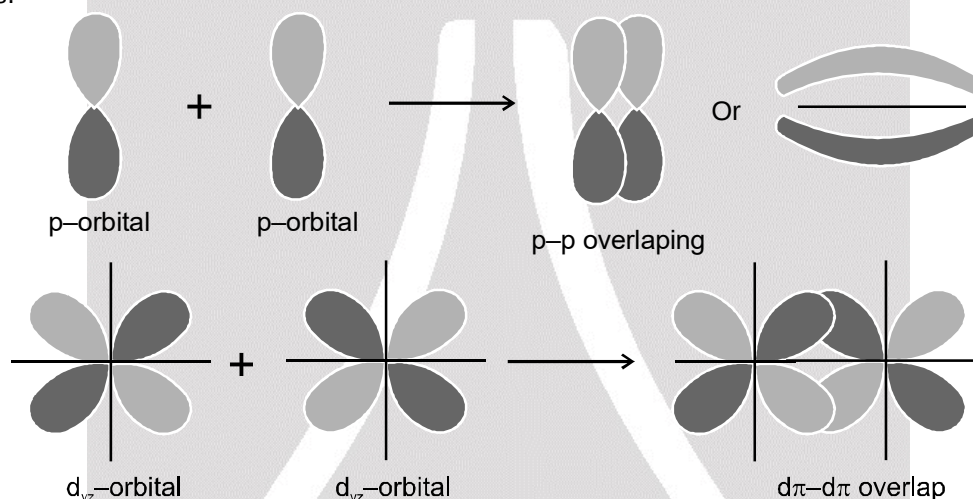


p-orbital

p-orbital

p-p overlapping

- (ii) **$\pi(\pi)$ bond :** In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.

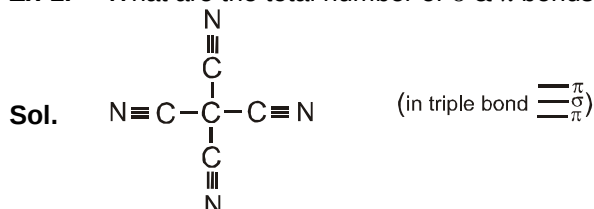


Strength of Sigma and pi Bonds :

Basically the strength of a bond depends upon the extent of overlapping- In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that pi bond between two atoms is formed in addition to a sigma bond. It is always present in the molecules containing multiple bond (double or triple bonds).

Solved Examples

Ex-1. What are the total number of σ & π bonds in tetracyanomethane.



From the structure it is clear that it has 8 σ and 8 π bonds.

**MISCELLANEOUS SOLVED PROBLEMS (MSPS)**

Ex-1. Classify the following bonds as ionic, polar covalent or covalent and give your reasons :

- (a) SiSi bond in $\text{Cl}_3\text{SiSiCl}_3$ (b) SiCl bond in $\text{Cl}_3\text{SiSiCl}_3$
(c) CaF bond in CaF_2 (d) NH bond in NH_3

Sol. (a) Covalent, due to identical electronegativity.
(b) Polar covalent, due to less electronegativity difference.
(c) Ionic, due to more electronegativity difference.
(d) Polar covalent, due to different electronegativity.

Ex-2. Why is anhydrous HCl predominantly covalent in the gaseous state but is ionic in aqueous solution?

Sol. It exists as HCl (bond formed by equal sharing of electrons) but in aqueous solution ionises as H^+ (or H_3O^+) and Cl^- due to polarity of HCl.

