

# UNIT-1

## CHEMICAL BONDING AND MOLECULAR STRUCTURE

Bonds: Forces that hold groups of atoms together & make them function as a unit.

- Ionic Bonds: transfer of electrons
- Covalent Bonds: sharing of electrons

### Kassel Lewis approach to chemical bonding

- Lewis postulated that atoms achieve a stable octet when linked via chemical bonds.
- In case of bonds formed from  $H_2, F_2$ , etc. the bond is formed from sharing of electrons between the atoms. In this case, each atom attains a stable outer octet of electrons.
- Lewis symbols: In the formation of a molecule only outer electrons or group valence of the electrons take part in chemical bonding & hence are called valence electrons.

- 9 electrons of the s, p and f orbitals do not take part in chemical bonding. Only 'd' orbitals take part.

### Lewis Symbols

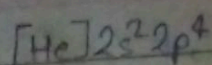
Lewis symbols only show the group valence or electrons that take part in chemical bonding & hence it is called valence electrons.

Significance of Lewis Symbols: The no. of dots around the symbol represents the no. of valence electrons. This no. common or group valence of the electrons. The group valence of the elements is generally either equal to the no. of dots in Lewis symbols or 8 minus the no. of dots or valence electrons.

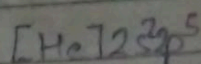
### Electron Dot Notation

<u>Element</u>	<u>Electron Conf.</u>	<u>Electron dot symbol</u>
Li	$[\text{He}]2s^1$	Li•
Be	$[\text{He}]2s^2$	•Be•
B	$[\text{He}]2s^22p^1$	•B•
C	$[\text{He}]2s^22p^2$	•C•
N	$[\text{He}]2s^22p^3$	•N•

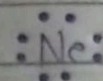
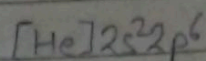
O



F



Ne

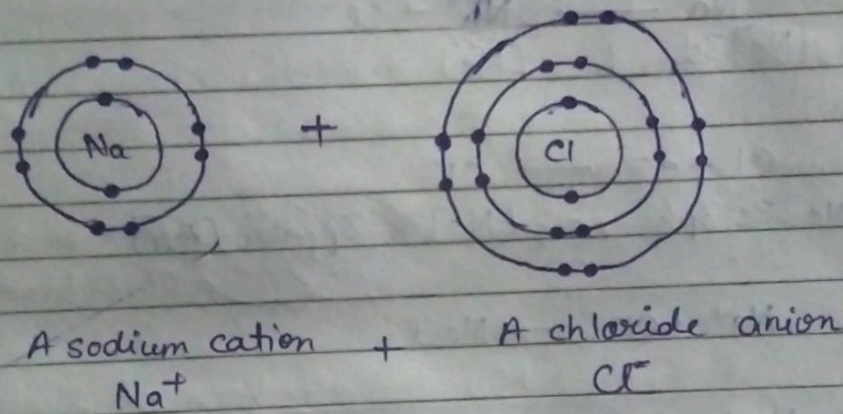
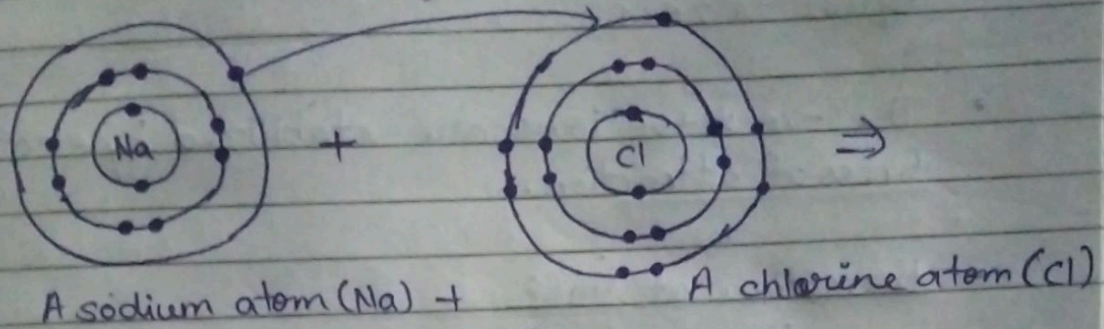


### Kossel's theories in terms of chemical bonding

- In the periodic table, the highly electronegative halogens & the highly electropositive alkali metals are separated by noble gases.
- The formation of a -ve ion from a halogen atom & a positive ion from an alkali metal atom is associated with the gain and loss of an  $e^-$  by the respective atoms.
- The -ve & +ve ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons  $n^2ns^2np^6$ .

## The Octet Rule - Ionic Compounds

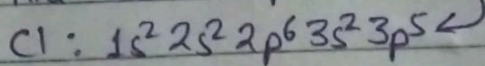
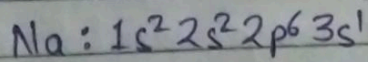
Ionic compounds tend to form so that each atom, by gaining or losing electrons, has an octet of electrons in its highest occupied energy level.



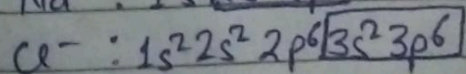
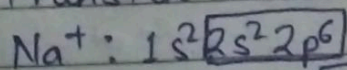
### Ionic Bonding:

#### The Formation of Sodium Chloride

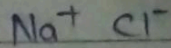
- Sodium has 1 valence  $e^-$
- Chlorine has 7 valence  $e^-$
- An  $e^-$  transferred gives each an octet



This transfer forms ions, each with an octet:



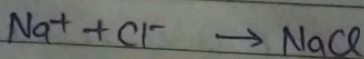
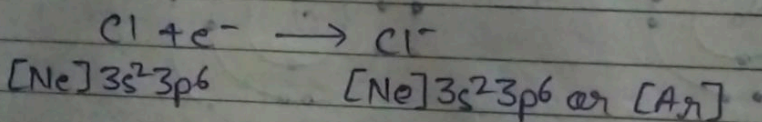
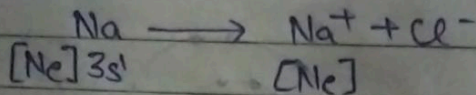
The resulting ions come together due to electrostatic attraction (opp. attraction);



The net charge on the compound must be equal to zero.

- The -ve & +ve ions are stabilized by electrostatic forces of attraction.

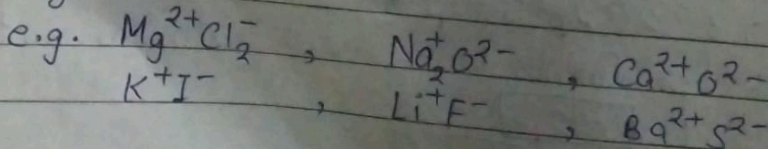
#### • Formation of NaCl



Similarly  $\text{CaF}_2$  molecule formation can take place as given in the text book.

#### Examples of Ionic Compounds

All salts, which are composed of metals bonded to nonmetals, are ionic compounds & form ionic crystals.



#### Electro

- The ions attract as the
- The e charge

Monoatomic Cations	Name
$H^+$	Hydrogen
$Li^+$	Lithium
$Na^+$	Sodium
$K^+$	Potassium
$Mg^{2+}$	Magnesium
$Ca^{2+}$	Calcium
$Ba^{2+}$	Barium
$Al^{3+}$	Aluminium

Monoatomic Anions	Name
$F^-$	Fluoride
$Cl^-$	Chloride
$Br^-$	Bromide
$I^-$	Iodide
$O^{2-}$	Oxide
$S^{2-}$	Sulphide
$N^{3-}$	Nitride
$P^{3-}$	Phosphide

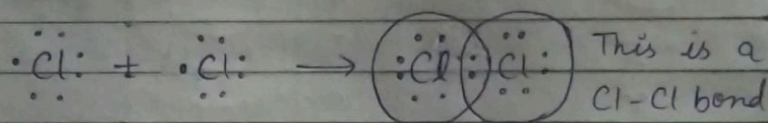
### Electro covalent bond & the octet rule

- The bond which is formed as a result of the electrostatic attraction between the +ve & the -ve ions is termed as the electro covalent bond.
- The electrovalence is thus equal to the no. of unit charge(s) present on the ion.

- Octet rule: According to the octet rule configuration, atoms can combine either by the transfer of valence electrons from one atom to the other or by sharing of valence electrons in order to have their octet in the valence shells. This is called the octet rule.

### Covalent bond

- Langmuir refined the Lewis postulates by introducing the term covalent bond.
- Covalent bond is formed by the sharing of electrons between two shells or sub shells.



### Types of bonding b/w the electrons of 2 atoms

- There are 3 types of bonding b/w the electrons of 2 atoms.
- These are single bond, double bond & triple bond.
- Single bond is the bond where 1 pair of electrons take part in chemical bonding that is 2 electrons.
- Double bond is the bond where 2 pairs of electrons take part in chemical bonding that is 4 electrons.

- Similarly triple bond is the bond where 3 pair of electrons take part in chemical bonding that is 6 electrons.

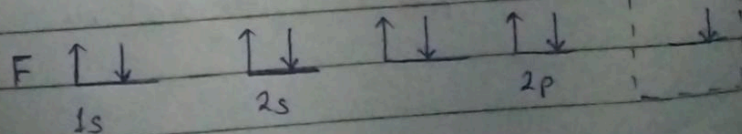
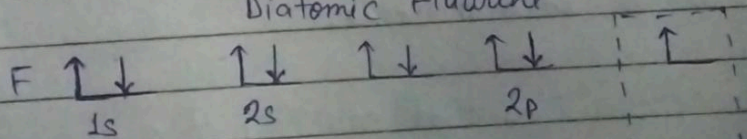
### Important Conditions of the Lewis Dot Structures

- Each bond is formed as a result of sharing of an electron pair between the atoms.
- Each combining atom contribute at least  $1e^-$  to the shared pair.
- The combining atoms attain the outer shell noble gas configuration as a result of the sharing of electrons.
- In many compounds, there are multiple bonds present b/w them.

### The Octet Rule - Covalent Compounds

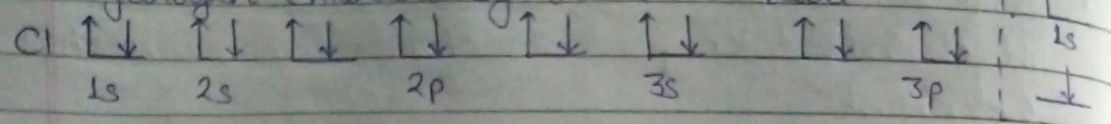
Covalent compounds tend to form so that each atom, by sharing electrons, has an octet of electrons in its highest occupied energy level.

#### Diatomic Fluorine

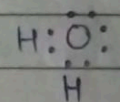
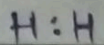
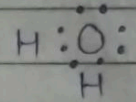
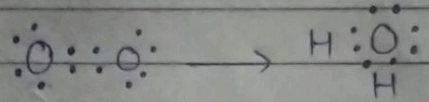
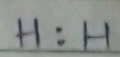
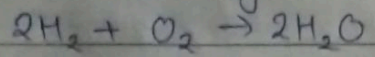




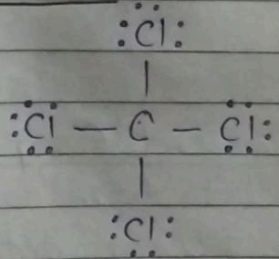
### Hydrogen Chloride by the Octet Rule



### Formation of Water by the Octet Rule



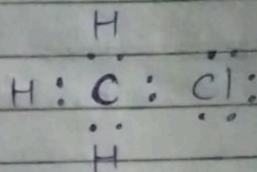
### Lewis Structures



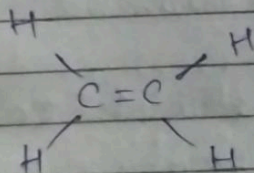
- Shows how valence electrons are arranged among atoms in a molecule.
- Reflects central idea that stability of a compound relates to the noble gas  $e^-$  configuration.

## Completing a Lewis Structure - CH<sub>3</sub>Cl

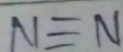
- Make carbon the central atom.
- Add up available valence electrons:  
C = 4, H = 3(3), Cl = 7    Total = 14
- Join peripheral atoms to the central atom with electron pairs
- Complete octets on atoms other than hydrogen with remaining electrons



Molecule & their covalent bond structures in terms of single, double & triple bonds  
Ethyne Molecule



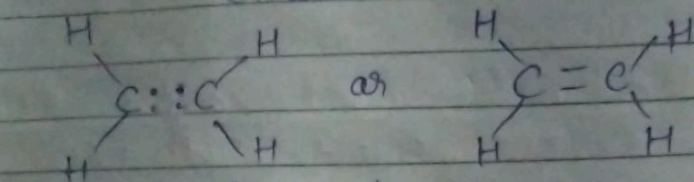
When combining atoms share 3 electron pairs as in the case of two nitrogen atoms in the N<sub>2</sub> molecule & the two carbon atoms in the ethyne molecule, a triple bond is formed.



## Multiple Covalent Bonds:

### Double Bonds

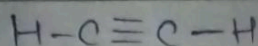
ethene



Two pairs of shared electrons

### Triple Bonds

ethyne (acetylene)



Three pairs of shared electrons

### Comments About the Octet Rule

- 2<sup>nd</sup> row elements C, N, O, F observe the octet rule.
- 2<sup>nd</sup> row elements B & Be often have fewer than 8 electrons around themselves - they are very reactive.
- 3<sup>rd</sup> row & heavier elements can exceed the octet rule using empty valence d orbitals.
- When writing Lewis structures, satisfy octets first, then place electrons around elements having available d orbitals.

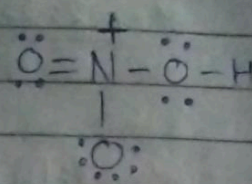
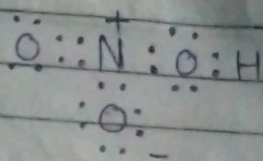
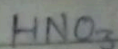
## Lewis Representation for simple molecules

- The total no. of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the  $\text{CH}_4$  molecule there are 8 valence electrons available for bonding (4 from carbon & 4 from the four hydrogen atoms).
- For anions, each -ve charge would mean addition of  $1e^-$ . For cations, each +ve charge would result in subtraction of one electron from the total no. of valence electrons. For example, for the  $\text{CO}_3^{2-}$  ion, the 2 -ve charges indicate that there are 2 additional electrons than those provided by the neutral atoms. For  $\text{NH}_4^+$  ion, one +ve charge indicates the loss of  $1e^-$  from the group of neutral atoms.
- Knowing the chemical symbols of the combining atoms & having knowledge of the skeletal structure of the compound, it is easy to distribute the total no. of electrons as bonding shared pairs b/w the atoms in proportion to the total bonds.
- In general the least electronegative atom occupies the central position in the molecule/ion. For example in the  $\text{NF}_3$  &  $\text{CO}_3^{2-}$ , nitrogen & carbon are the central atoms whereas fluorine & oxygen occupy the terminal positions.

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

### Lewis Structure for Some Molecules

<u>Molecule/Ion</u>	<u>Lewis Representation</u>	
$H_2$	$H:H$	$H-H$
$O_2$	$:\ddot{O}::\ddot{O}:$	$:\ddot{O}=\ddot{O}:$
$O_3$		
$NF_3$		
$CO_3^{2-}$		



### Examples on Lewis Structures

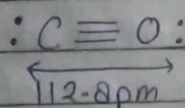
- Write the electron dot structure of CO molecule.

Solution:

Step 1: Count the total no. of valence electrons of carbon & oxygen atoms. The outer (valence) shell configurations of carbon & <sup>oxygen</sup>hydrogen are:  $2s^2 2p^2$  &  $2s^2 2p^4$  respectively. The valence electrons available are  $4 + 6 = 10$ .

Step 2: The skeletal structure of CO is written as:  
C O

Step 3: Draw a single bond (one shared e<sup>-</sup> pair) b/w C & O and complete the octet on O, the remaining two electrons are the lone pair on C.



- Write the Lewis structure of the nitrite ion NO<sub>2</sub><sup>-</sup>.

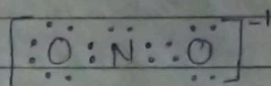
Solution:

Step 1: Count the total no. of valence electrons of the nitrogen atom, the oxygen atoms & the additional one -ve charge (equal to 1 e<sup>-</sup>).

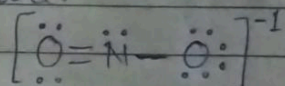
$$= \text{N}(2s^2 2p^3), \text{O}(2s^2 2p^4) = 5 + 2(6) + 1 = 18e^-$$

Step 2: The skeletal structure of  $\text{NO}_2^-$  is written as O N O

Step 3: Draw a single bond (one shared  $e^-$  pair) b/w the nitrogen & each of the oxygen atoms completing the octets on oxygen atoms. This however, doesn't complete the octet on nitrogen if the remaining two electrons constitute lone pair on it.



Hence we have to resort to multiple bonding b/w nitrogen & one of the oxygen atoms (in this case a double bond), this leads to following Lewis dot structure.

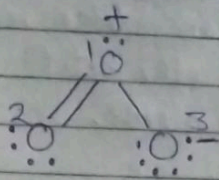


### Formal Charge

Formal charge can be defined as the difference b/w the valence electrons of that atom in an isolated or free state & the no. of electrons assigned to that atom in the Lewis structure.

- Formula of calculating formal charge is:  
Formal charge on the atom [F.C.] = [total no. of electrons in the free atom] - [total no. of non bonding (lone pair) electrons -  $\frac{1}{2}$  [total no. of bonding (shared pair) electrons]].

### Formal Charges on the ozone molecule:



The central atom marked as 1, on applying the formula we get,  $6 - 2 - \frac{1}{2}(6) = +1$

The end atom is marked as 2, on applying we get  $6 - 4 - \frac{1}{2}(4) = 0$

The end atom marked as 3, on applying the formula we get,  $6 - 6 - \frac{1}{2}(2) = -1$

Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electrons pairs are shared equally by neighbouring atoms.

### Limitations of the Octet Rule

- (i) The incomplete octet of the central atom  
In some compounds, the no. of electrons surrounding the central atom is less than 8. This is esp. in the case of elements having less than 4 valence electrons E.g.  $\text{LiCl}$ ,  $\text{BeH}_2$



(ii) The odd electron molecules: In molecules with an odd no. of electrons like nitric oxide, NO & nitrogen dioxide  $\text{NO}_2$ , the octet rule is not satisfied for all the atoms.

(iii) The expanded octet: Elements in & beyond the third period of the periodic table, apart from 3s & 3p orbitals, 3d orbitals are also available for bonding. In a no. of compounds of these elements there are more than 8 valence electrons around the central atom. This is termed as the expanded octet.

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

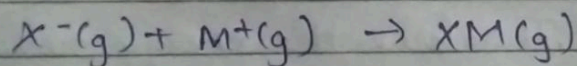
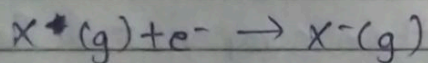
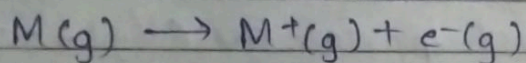
Other drawbacks of the octet rule:

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon & krypton) also combine with oxygen & fluorine to form a no. of compounds like  $\text{XeF}_2$ ,  $\text{KrF}_2$ ,  $\text{XeOF}_2$ , etc.
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

## Ionic or Electrovalent Bond

- From the Kossel & Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:
  - (i) The ease of formation of the +ve & -ve ions from the respective neutral atoms.
  - (ii) The arrangement of the +ve & -ve ions in the solid, that is lattice of the crystalline compound.

The formation of +ve ion involves ionisation i.e. removal of electron(s) from the neutral atom & that of the -ve ions involves the addition of electron(s) to the neutral atom.



The electron gain enthalpy,  $\Delta_{eg}H$ , is the energy change, when a gas phase atom in its ground state gains an  $e^-$  in electron gain process & the process may be exothermic or endothermic.

Ionic bonds will be formed more easily b/w elements with low ionisation enthalpies & elements with comparative high negative value of electron gain enthalpy.

Most ionic compounds have cations derived from metallic elements & anions from the non-metallic elements. The ammonium ion  $\text{NH}_4^+$  is an exception.  $\text{H}^+$  forms cation with a no. of ionic compounds.

In ionic solids, the sum of electron gain enthalpy & the ionization enthalpy may be +ve but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice.

For example:- the ionisation enthalpy for  $\text{Na}^+(\text{g})$  formation from  $\text{Na}(\text{g})$  is  $495.0 \text{ kJ mol}^{-1}$ ; while the electron gain enthalpy for the  $\text{Cl}(\text{g}) + e^- \rightarrow \text{Cl}^-(\text{g})$  is  $-348.7 \text{ kJ mol}^{-1}$  only. The sum of the two,  $147.1 \text{ kJ mol}^{-1}$  is more than compensated for by the enthalpy of lattice formation of  $\text{NaCl}(\text{s})$  ( $-788 \text{ kJ mol}^{-1}$ ). Therefore, the energy released in the process is more than the energy absorbed.

### Lattice Enthalpy

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

For example, the lattice enthalpy of  $\text{NaCl}$  is  $788 \text{ kJ mol}^{-1}$ . This means that  $788 \text{ kJ}$  of energy is required

to sep  
mole of  
infinite

### Bond

(i) Bond  
Bond  
distan  
a mole

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from  
of the  
The cr  
as the  
contact  
bonds  
The ca  
two si  
same

The v  
size  
shell

to separate one mole of solid (NaCl) into one mole of  $\text{Na}^+(\text{g})$  & one mole of  $\text{Cl}^-(\text{g})$  to an infinite distance.

### Bond Parameters

(i) Bond Length:

Bond length is defined as the equilibrium distance b/w the nuclei of two bonded atoms in a molecule.

In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom.

(g)

The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation.

The covalent radius is half of the distance b/w two similar atoms joined by a covalent bond in the same molecule.

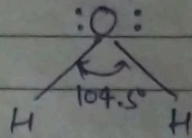
The van der Waals radius represents the overall size of the atom which includes its valence shell in a non bonded situation.

mol<sup>-1</sup>

## Bond Angle

It is defined as the angle b/w the orbitals containing bonding electron pairs around the central atom in a molecule / complex ion.

It gives some idea regarding the distribution of orbitals around the central atom in a molecule / complex ion & hence it helps us in determining its shape. For example H-O-H bond angle in water can be represented as under:



## Bond Enthalpy

It is the amount of energy required to break ~~some~~ one mole of bonds of a particular type between two atoms in the gaseous state. The unit of bond enthalpy is  $\text{KJ mol}^{-1}$ .

For every molecule same amount of energy or bond enthalpy is not needed to break that atom therefore different bond enthalpies are needed.

In polyatomic molecules, the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the no. of bonds broken.

## Bond Order

97 the Lewis description of covalent bond, the Bond Order is given by no. of bonds b/w the two atoms in a molecule. The bond order, for example in  $H_2$  (with a single shared electron pair), in  $O_2$  (with two shared electron pairs) and in  $N_2$  (with three shared electron pairs) as 1, 2, 3 resp.

Isoelectronic molecules & ions have identical bond orders; for example,  $F_2$  &  $O_2^{2-}$  have bond order 1.  $N_2$ ,  $CO$  &  $NO^+$  have bond order 3. A general correlation useful for understanding the stabilities of molecules is that: with increase in bond order, bond enthalpy increases & bond length decreases.

## Resonance Structures

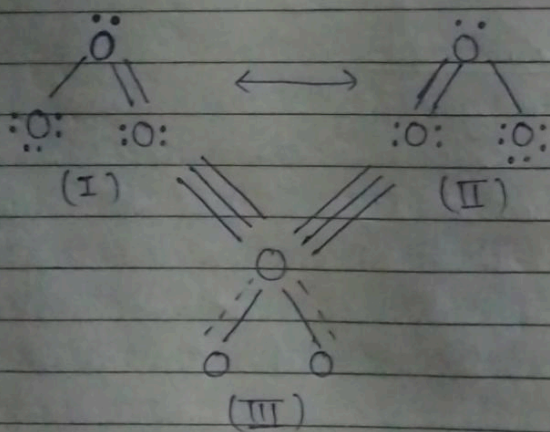
According to the concept of resonance, whenever a single Lewis structure can't describe a molecule accurately, a no. of structures with similar energy, positions of nuclei, bonding & non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

For  $O_3$ , the two structures shown above constitute the canonical structures or resonance structures & 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.

### Resonance of ozone molecule

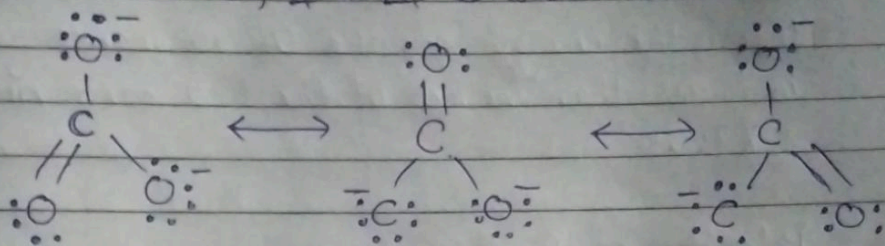
For example, the ozone,  $O_3$  molecule can be equally represented by the structures I & II bond & a  $O=O$  double bond. The normal  $O-O$  &  $O=O$  bond lengths are  $148\text{ pm}$  &  $121\text{ pm}$  respectively. Experimentally determined oxygen-oxygen ~~atoms~~ bond lengths in  $O_3$  molecule are same ( $128\text{ pm}$ ). Thus the oxygen-oxygen bonds in the  $O_3$  molecule are intermediate b/w a double & a single bond. Obviously, this can't be represented by either of the two Lewis structure shown above.



Draw the structure of Carbonate Ion

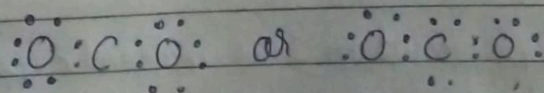
The single Lewis structure based on the presence of two single bonds & one double bond b/w carbon & oxygen atoms is inadequate to represent

the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in  $\text{CO}_3^{2-}$  are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II & III shown below.



Explain the resonance of  $\text{CO}_2$  molecule.

The experimentally determined carbon to oxygen bond length in  $\text{CO}_2$  is 115 pm. The lengths of a normal carbon to oxygen double bond ( $\text{C}=\text{O}$ ) & carbon to oxygen triple bond ( $\text{C}\equiv\text{O}$ ) are 121 pm & 110 pm resp. The carbon-oxygen bond-lengths in  $\text{CO}_2$  (115 pm) lie b/w the values for  $\text{C}=\text{O}$  &  $\text{C}\equiv\text{O}$ . Obviously, a single Lewis structure can't depict this position & it becomes necessary to write more than one Lewis structures & to consider that the structure of  $\text{CO}_2$  is best described as a hybrid of the canonical or resonance forms I, II & III.





### Points on Resonance

- Resonance stabilizes 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.

Thus the energy of the  $O_3$  resonance hybrid is lower than either of the two canonical forms I & II.

### Polarity of Bonds

When covalent bond is formed b/w two similar atoms, for example in  $H_2$ ,  $O_2$  or  $F_2$ , the shared pair of electrons is equally attracted by the two atoms. As a result electron pair is situated exactly b/w the two identical nuclei. The bond so formed is called non polar covalent bond.

The bond so formed contrary to this in case of a heteronuclear molecule like  $HF$ , the shared electron pair b/w the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond, formed is polar covalent bond.

As a result of polarisation, the molecule possesses the dipole moment which can be defined as the product

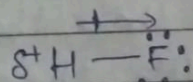
of the magnitude of the charge & the distance b/w the centres of +ve & -ve charge. It is usually designated by a Greek letter ' $\mu$ '. Mathematically, it is expressed as follows:

Dipole moment ( $\mu$ ) = charge ( $q$ )  $\times$  distance of separation ( $r$ )

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

Further dipole moment is a vector quantity & by convention it is depicted by a small arrow with tail on the -ve centre & head pointing towards the +ve centre. But in chemistry presence of dipole moment is represented by the crossed arrow ( $\rightarrow$ ) put on Lewis structure of the molecule. The cross is on positive end & arrow head is on -ve end.

For example the dipole moment of HF may be represented as:



The arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opp. to the conventional directional of dipole moment vector.

In case of polyatomic molecules, the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various

bonds in the molecule. In such case, the dipole moment. In such case the dipole moment of a molecule is the vector sum of dipole moments of various bonds.

In tetra-atomic molecule, for example in  $\text{BF}_3$ , the dipole moment is zero although the B-F bonds are oriented at an angle of  $120^\circ$  to one another, the three bond moments give a net sum of zero as the resultant of any two is equal & opp. to the third.

Let us study an interesting case of  $\text{NH}_3$  &  $\text{NF}_3$ . Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen atom. Although fluorine is more electronegative than nitrogen, the resultant dipole moment of  $\text{NH}_3$  ( $4.90 \times 10^{-30} \text{ C m}$ ) is greater than that of  $\text{NF}_3$ . This is because, in case of  $\text{NH}_3$  the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N-H bonds, whereas in  $\text{NF}_3$  the orbital dipole moment of the three N-F is in the direction opposite to the resultant dipole moment of the three N-F bonds. The 'orbital dipole' because of lone-pair decreases the effect of the resultant N-F bond moments, which results in the low dipole moment of  $\text{NF}_3$ .

### Fajans Rules:

Just as the all the covalent bonds have some partial ionic character; the ionic bonds also have partial covalent character. The partial covalent character was discussed by Fajans rules:

- (1) The smaller the size of the cation & the larger the size of the anion, the greater the covalent character of an ionic bond.
- (2) The greater the charge on the cation, the greater the covalent character of the ionic bond.
- (3) For cations of the same size & charge, the one, with electronic configuration  $(n-1)d^n ns^0$ , typical of transition elements, is more polarising than the one with a noble gas configuration,  $ns^2 np^6$  typical of alkali & alkaline earth metal cations.

### VSEPR THEORY

The main postulates of VSEPR theory are:

- The shape of a molecule depends upon the no. of valence shell  $e^-$  pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are  $-vely$  charged.

- These pairs of electrons tend to occupy such positions in space that minimise repulsion & thus maximise distance b/w them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at max. distance from one another.
- A multiple bond is treated as if it is a single electron pair & the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

The repulsive interaction of electron pair decrease in the order:

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

For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecule into two categories as:

- (i) molecules in which the central atom has no lone pair.

(ii) Molecules in which the central atom has one or more lone pairs.

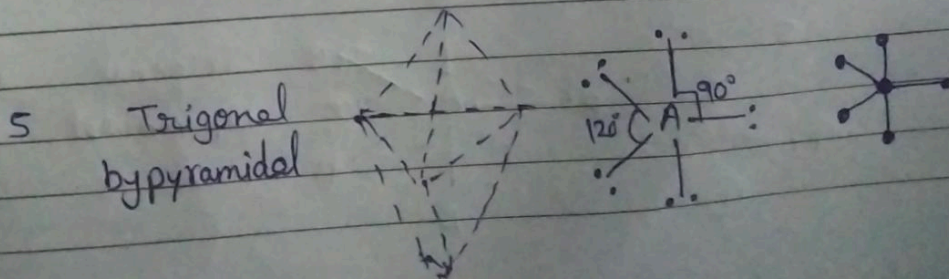
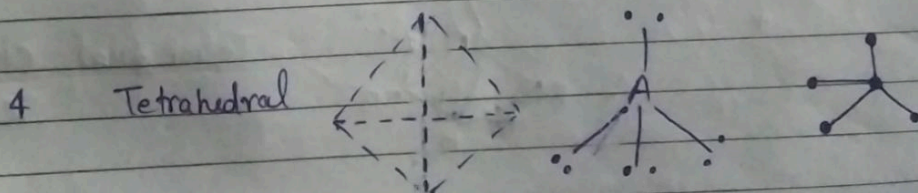
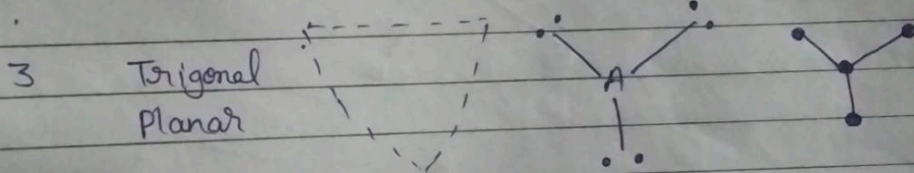
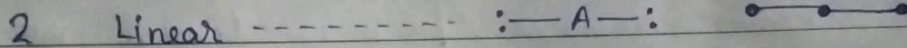
VSEPR theory is used to predict the shape of the atomic models.

There are different shapes such as tetrahedral, linear, trigonal planar, trigonal-bipyramidal, octahedral.

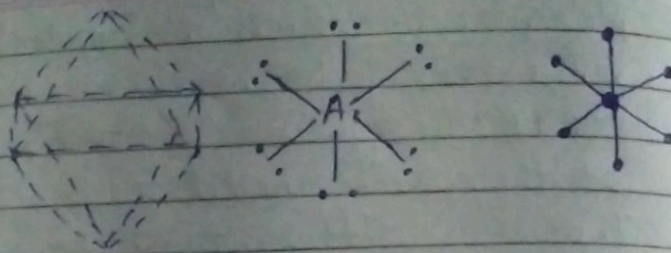
Arrangement of Electron Pairs Around an Atom

Yielding Minimum Repulsion

No. of e <sup>-</sup> pairs	Arrangement of Electron pairs	Example
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6 Octahedral



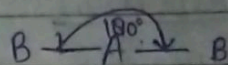
No. of shared  
e<sup>-</sup> pair around  
central atom

Geometry  
of the  
molecules

Shape of  
the  
molecule

Examples

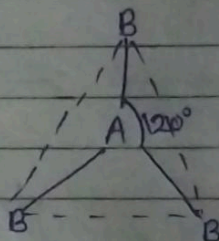
2



Linear

$\text{BeF}_2, \text{BeCl}_2$   
 $\text{MgF}_2, \text{MgCl}_2$

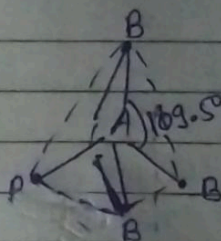
3



Trigonal  
Planar

$\text{BF}_3, \text{BCl}_3$   
 $\text{AlF}_3, \text{AlCl}_3$

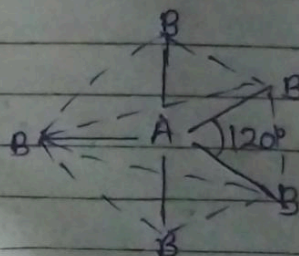
4



Tetrahedral

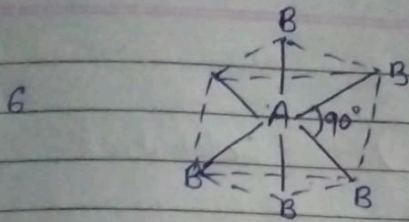
$\text{CH}_4, \text{CCl}_4,$   
 $\text{SiCl}_4$

5



Trigonal  
bipyramidal

$\text{PF}_5,$   
 $\text{PCl}_5,$   
 $\text{SbF}_5$



Octahedral

$SF_6, TeF_6$

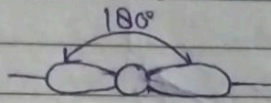
No. of  
electron  
Domains

Arrangement  
of Electric  
Domains

Electron  
Domain  
Geometry

Predicted  
Bond  
Angles

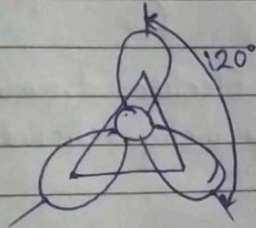
2



Linear

$180^\circ$

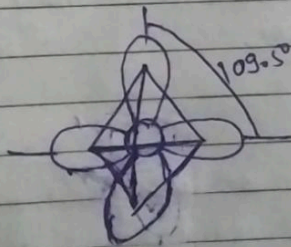
3



Trigonal  
Planar

$120^\circ$

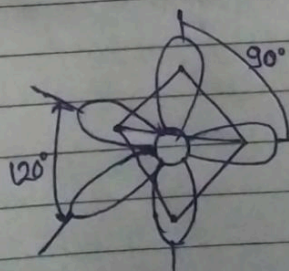
4



Tetrahedral

$109.5^\circ$

5

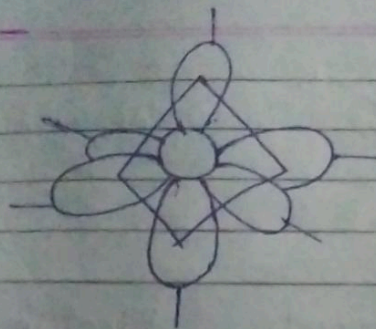


Trigonal  
bipyramidal

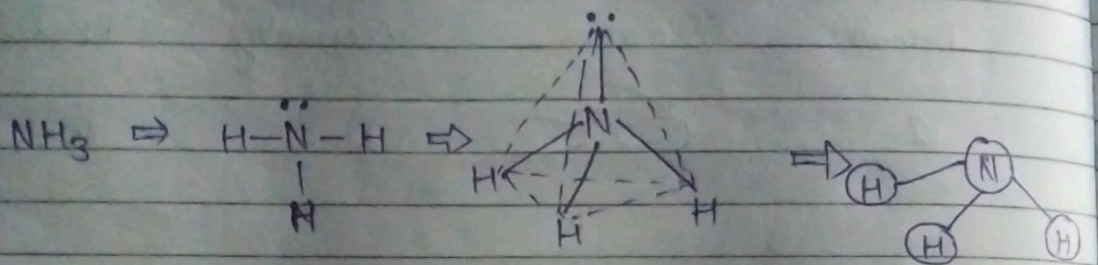
$120^\circ,$   
 $90^\circ$



6



Octahedral 90°

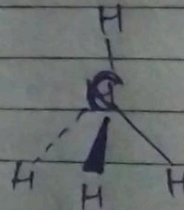
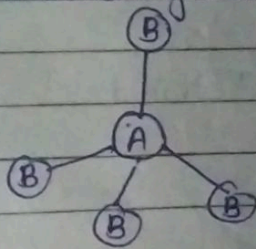


Lewis structure

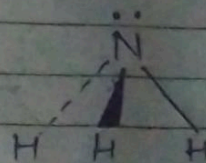
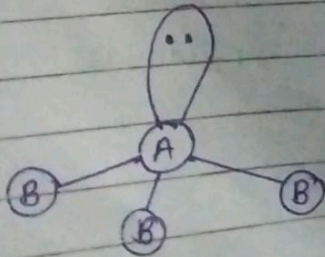
Electron-domain geometry-tetrahedral

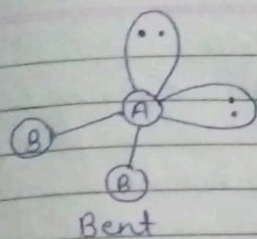
Molecular geometry (trigonal pyramidal)

Within each e- domain, there may be several molecular geometries.

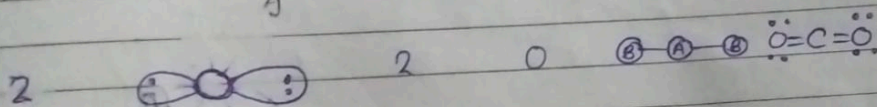


Tetrahedral





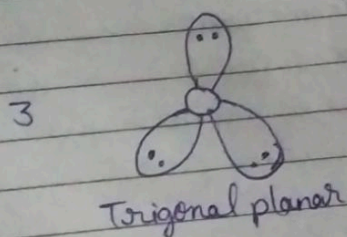
No. of Electron Domains	Electron Domain Geometry	Bonding Domain	Non-Bonding Domains	Molecular Geometry	Example
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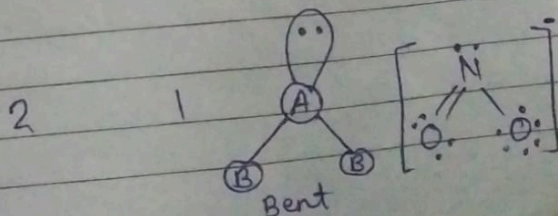
Linear

In this domain, there is only one molecular geometry: linear

NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

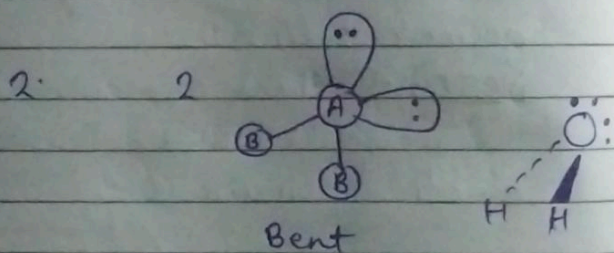
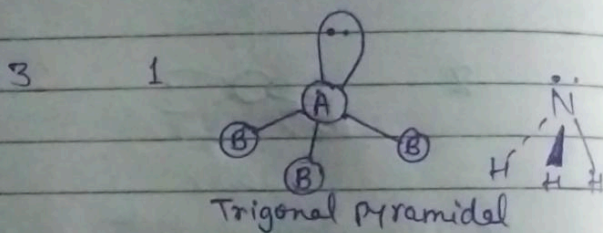
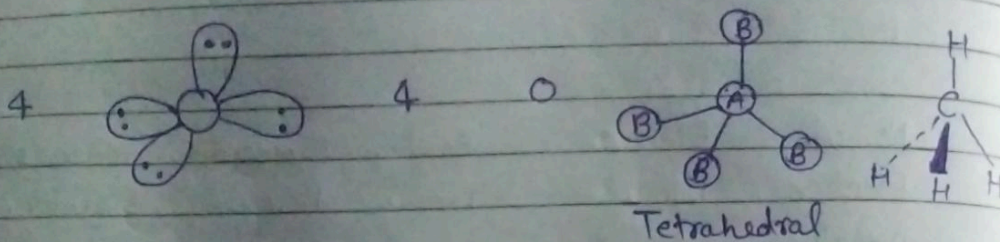


Trigonal planar



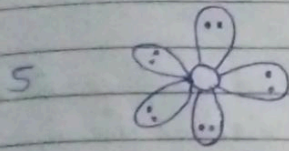
There are two molecular geometries:

- Trigonal planar, if all the electron domains are bonding
- Bent, if one of the domains is a nonbonding pair



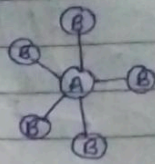
There are three molecular geometries:

- Tetrahedral, if all are bonding pairs
- Trigonal pyramidal, if one is a nonbonding pair
- Bent, if there are two nonbonding pairs



Trigonal  
bipyramidal

5 0

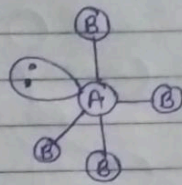


$PCl_5$

Trigonal  
bipyramidal

4

1

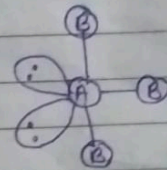


$SF_4$

See Saw

3

2

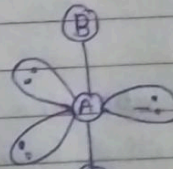


$ClF_3$

T-shape

2

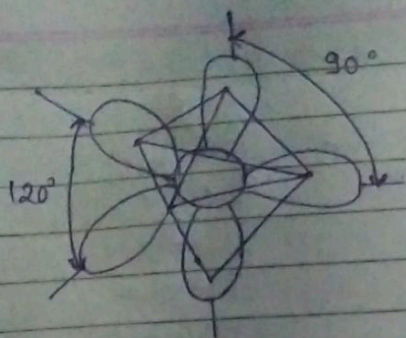
3



$XeF_2$

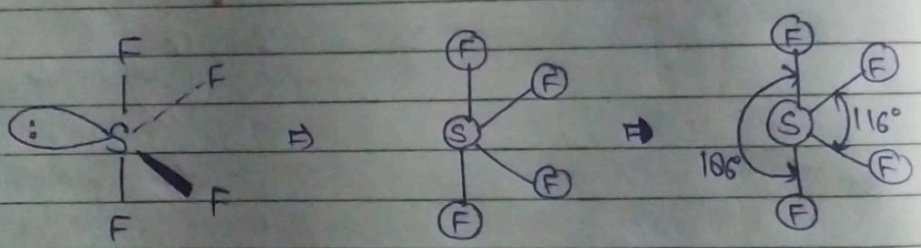
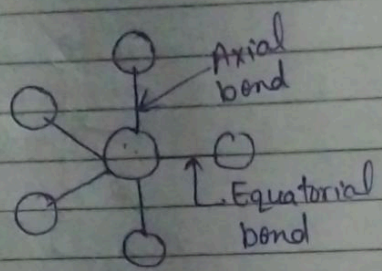
Linear

- There are four distinct molecular geometries:
- Trigonal bipyramidal
  - See Saw
  - T-shape
  - Linear

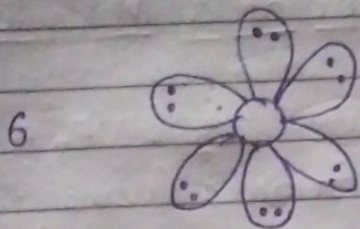


In the trigonal bipyramidal electron domain geometry, the electron domains have two distinct positions

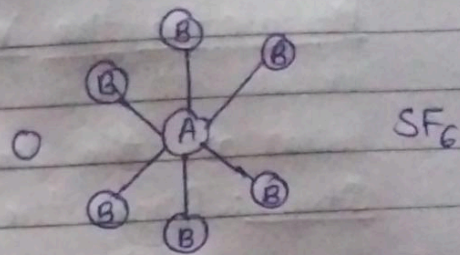
- Axial
- Equatorial



Nonbonding electron pairs occupy the equatorial, rather than axial positions in this geometry



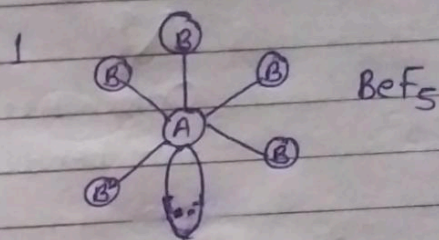
6



$SF_6$

Octahedral

5

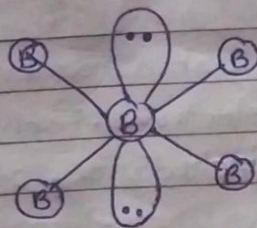


$BeF_5$

Square Pyramidal

4

2



$XeF_4$

All positions are equivalent in octahedral domain.

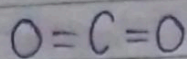
There are 3 molecular geometries:


- Octahedral
- Square pyramidal
- Square planar

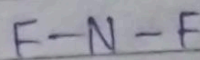
## Predicting the Molecular Shape of a Molecule:


What are the molecular shapes of  $\text{CO}_2$  &  $\text{NF}_3$ ?

Step 1: Draw the structural formula (using the outside atoms to determine the bonds).

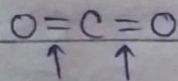



  
Oxygen needs  
two bonds

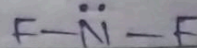


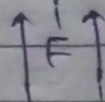
  
Fluorine needs  
one bond

Step 2: Add in lone pairs to the central atom (first determine how many valence electrons it has).



  
Carbon has 4 valence  
electrons. Each bond  
includes one of these  
valence electrons, so  
there are none left over.

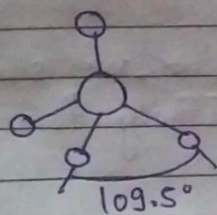


  
Nitrogen has 5 valence  
electrons. Each bond includes  
one of these valence electrons,  
so there are two left  
over (one lone pair).

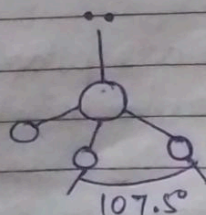
Step 3: Count the total no. of electron domains  
& the no. of lone pairs. Use this to determine  
the shape.

	Electron Domains	0 lone pair	1 lone pair	2 lone pairs
$O=C=O$ 2 electron domains, 0 lone pairs.	2	$X-A-X$		
$F-\ddot{N}-F$ $ $ $F$	3			
4 electron domains, 1 lone pair	4			
		Tetrahedral	Trigonal Pyramidal	

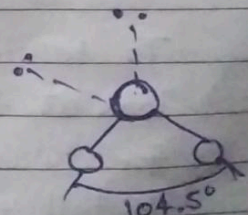
Nonbonding electron pairs (lone pairs) have a stronger repulsion than bonding electrons. This causes the actual bond  $\angle$ s to be slightly less than otherwise predicted.



CH<sub>4</sub>



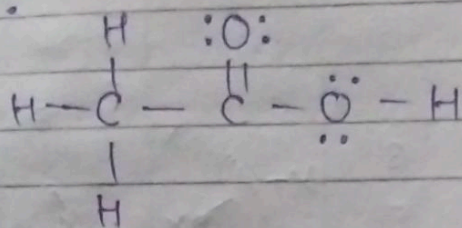
NH<sub>3</sub>



H<sub>2</sub>O



In larger molecules, it makes more sense to talk about the geometry about a individual atom rather than the geometry of the molecule as a whole.

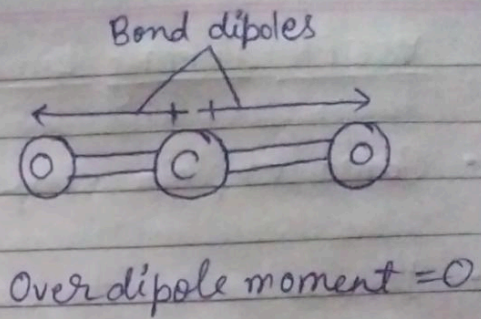
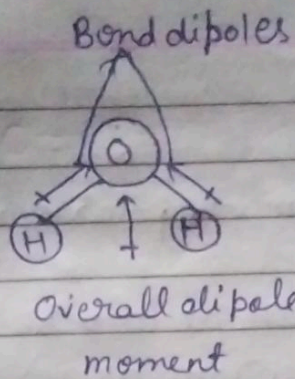


	$  \begin{array}{c}  \text{H} \\    \\  \text{H}-\text{C} \\    \\  \text{H}  \end{array}  $	$  \begin{array}{c}  \text{:O:} \\     \\  \text{C}  \end{array}  $	$  \begin{array}{c}  \ddot{\text{O}} \\    \\  \text{H}  \end{array}  $
No. of Electron Domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal Planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°

This approach makes sense, esp. because larger molecules tend to react at a particular site in the molecule.

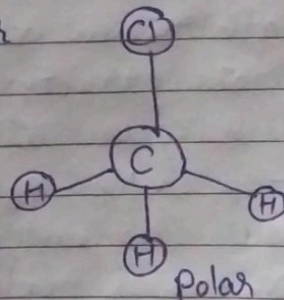
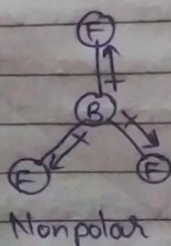
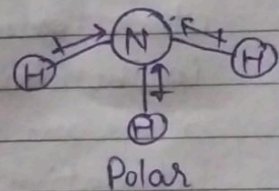
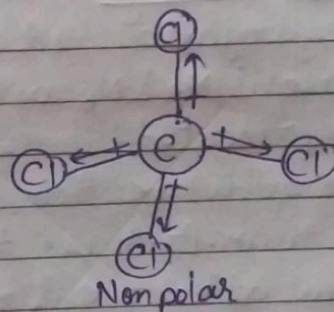
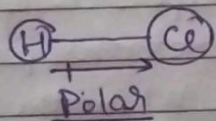
To tell if bonds are polar or nonpolar, we simply look at the difference in electronegativity for the two atoms.

To tell if a molecule is polar or nonpolar, we need to know its shape.



Nonpolar molecules have a symmetrical distribution of charge (even if the bonds themselves are polar).

Polar molecules have an asymmetrical distribution of charge (even if the bonds themselves are nonpolar).



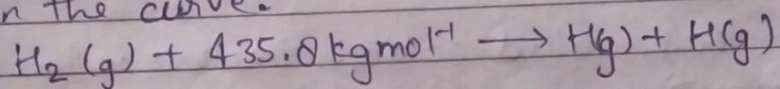
## VSEPR Theory Limitations

- Can't explain shape of very much polar compounds.
- Is also unable to explain the shape of very much polar in which delocalized  $p$  electrons are very much.
- VSEPR theory doesn't explain the shapes of molecules having inert electron pairs.

## Valence Bond Theory

- Consider two hydrogen atoms A & B approaching each other having nuclei  $N_A$  &  $N_B$  and electrons presented in them are represented by  $e_A$  &  $e_B$ . When the two atoms are at large distance from each other, there is no interaction b/w them. As these two atoms approach each other, new attractive & repulsive forces begin to operate. Attractive forces arise between:
  - nucleus of one atom & its own electrons that is  $N_A - e_A$  &  $N_B - e_B$ .
  - nucleus of one atom & electron of the other atom i.e.  $N_A - e_B$  & nucleus of the other atom & the electron of the other atom  $N_B - e_A$ .
- 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 & potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion & system acquired 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 b/w two hydrogen atom, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called bond enthalpy, which is corresponding to minimum in the curve.



- The valence bond theory explains the directional properties of bond as a consequence of inter electronic repulsion.
- The attractive & repulsive interactions oppose each other. When the attractive interactions are stronger than the repulsive interactions, certain amount of energy is released. Due to the lowering of energy the molecule becomes stable.

The first quantum mechanical model to explain the nature & stability of a covalent bond was formulated by Heitler & London 1927. This theory was then modified by Pauling & Slater in 1931. This theory is commonly known as Valence Bond Theory.

The main postulates of the VBT are:

- (i) A covalent bond is formed due to the overlap of the outermost half-filled orbitals of the combining atoms. The strength of the bond is determined by the extent of overlap.
- (ii) The two half-filled orbitals involved in the covalent bond formation should contain electron with opp. spins. The two electrons then move under the influence of both the nuclei.
- (iii) The completely filled orbitals (orbitals containing 2 paired electrons) do not take part in the bond formation.
- (iv) An s-orbital does not show any preference for direction. The non-spherical orbitals such as p- & d-orbitals tend to form bonds in the direction of the max. overlap; along the orbital axis.
- (v) B/w the two orbitals of the same energy, the orbital which is non-spherical e.g. p- & d-orbitals

forms stronger bonds than the orbital which is spherically symmetrical, eg - s-orbitals.

(vi) The valence of an element is equal to the no. of half filled orbitals in it.

### Orbital Overlap Concept

In the formation of hydrogen molecule, there is a min. energy state when two hydrogen atoms are so near that their atomic orbitals undergo interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed b/w two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond b/w 2 atoms results by pairing of electrons present in the valence shell having opp. spin.

### Types of Orbital Overlaps

1. Positive Overlap: If the symmetry of both the atomic orbitals is the same then it is called positive overlap i.e. if the symmetry of the overlapping orbitals is either +ve or -ve, then it is a type of +ve overlap.
2. Negative Overlap: If the symmetry of the atomic orbitals is not the same, i.e. one is +ve & the other -ve, then it is a type of -ve overlap.

3. Zero Overlap: If overlap of orbitals present in 2 different planes takes place, then it is called as zero overlap. e.g.  $P_x$  overlaps with  $P_y$  (in real situation, overlapping does not take place).

#### Directional properties of bonds

- As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of  $1s$ -orbitals of two  $H$ -atoms.
- The valence bond theory explains the shape, the formation & directional properties of bonds in polyatomic molecules like  $CH_4$ ,  $NH_3$  &  $H_2O$ , etc. in terms of overlap & hybridisation of atomic orbitals.

#### Overlapping of Atomic Orbitals

- When orbitals of two atoms come close to form bond, their overlap may be +ve, -ve or zero depending upon the sign (phase) & direction of orientation of amplitude of orbital wave function in space.
- The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules & polyatomic molecules. We know that <sup>the shapes</sup> of  $CH_4$ ,  $NH_3$  &  $H_2O$  molecules are tetrahedral, pyramidal & bent resp. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

• Let us first consider the  $\text{CH}_4$  (methane) molecule, The electronic configuration of carbon in its ground state is  $[\text{He}]2s^2 2p^2$  which is in the excited state becomes  $[\text{He}]2s^1 2p_x^1 2p_y^1 2p_z^1$ . The energy required for this excitation is compensated by the release of energy due to overlap b/w the orbitals of carbon & the hydrogen. The 4 atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the 4 H atoms which are also singly occupied. This will result in the formation of 4 C-H bonds. It will however be observed that while the 3 p orbitals of carbon are at  $90^\circ$  to one another, the HCH angle for these will also be  $90^\circ$ . That is 3 C-H bonds will be oriented at  $90^\circ$  to one another.

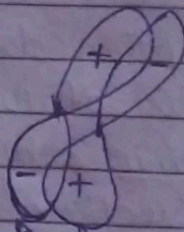
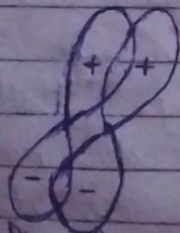
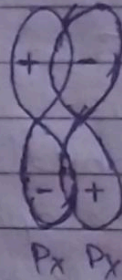
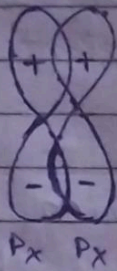
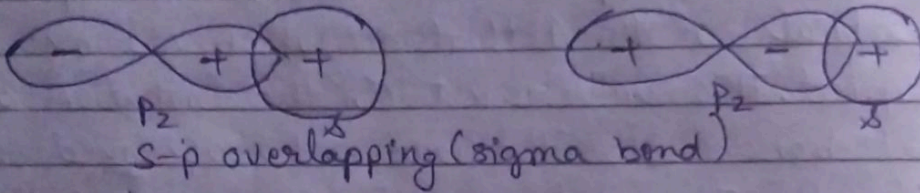
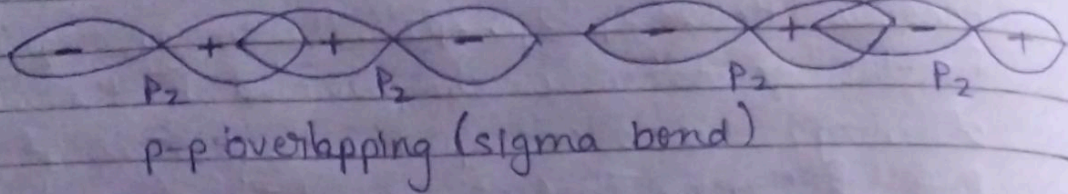
• The 2s orbital of carbon & the 1s orbital of H are spherically symmetrical & they can overlap in any direction. Therefore the direction of the 4th C-H bond can't be ascertained. This description does not fit in with the tetrahedral HCH angles of  $109.5^\circ$ . Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in  $\text{CH}_4$ .



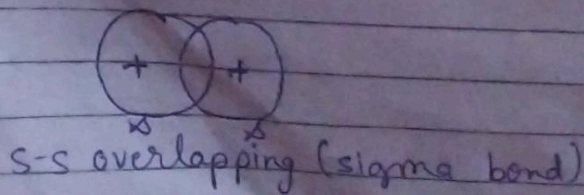
# Types of Overlapping

## Positive overlap

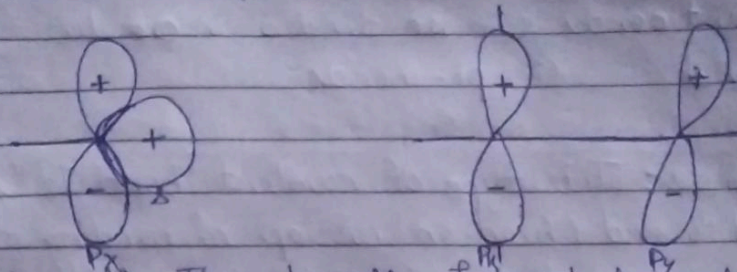
## Negative overlap



p-p overlapping (pi bond)

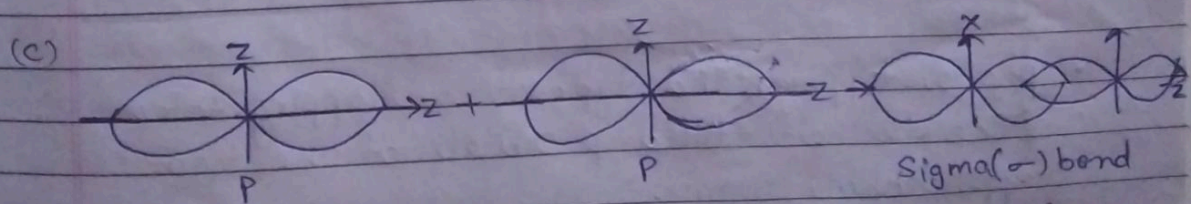
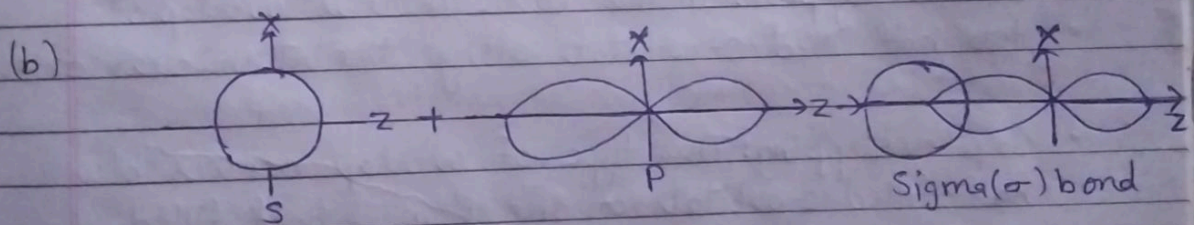
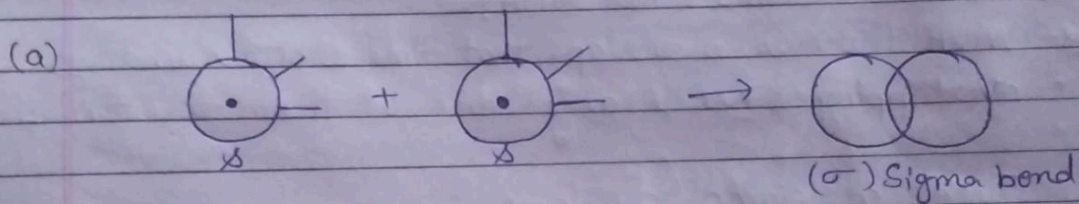


## Zero Overlap



Strength: The strength of bond depends upon the extent of overlap. So sigma bond has more strength than pi bond.

## Types of Overlap Resulting in Sigma Bond Formation



Formation of sigma bond due to (a) the s-s overlap, (b) s-p overlap & (c) p-p overlap

## Types of Covalent Bonds

The covalent bonds can be divided into two types:-

- (i) Sigma bond                      (ii) pi-bonds

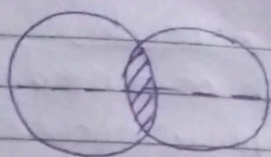
Sigma Bonds: This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.

Q) When do sigma bonds form?

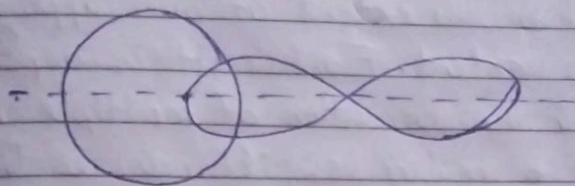
Ans- When there is a overlap, that time orbitals undergo overlapping & hence any one of them are formed.

### Types of sigma overlaps

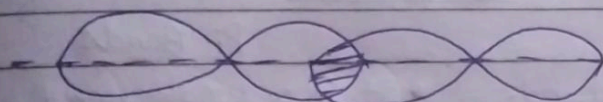
- s-s overlapping: In this case, there is overlap of two half filled s-orbitals along the internuclear axis.
- s-p overlapping: This type of overlap occurs b/w half-filled s-orbitals of one atom & half filled p-orbitals of another atom.
- p-p overlapping: This type of overlapping takes place b/w half-filled p-orbitals of the two approaching atoms.



s-s overlap

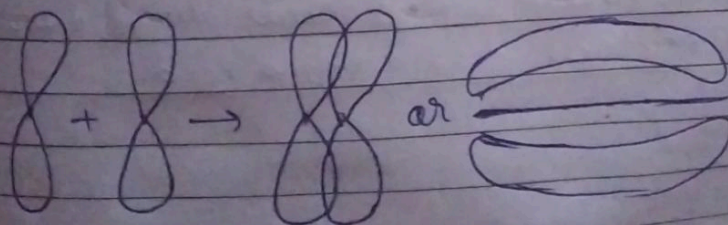


s-p overlap



p-p overlap

$\pi$  ( $\pi$ ) bonds: In the formation of  $\pi$  bond the atomic orbitals overlap in such a way <sup>such</sup> that their axes remain parallel to each other &  $\perp$  to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above & below the plane of the participating atoms. Due to lateral/sideways overlap of p-p orbitals present in same plane,  $\pi$  bond is formed.



### Strength of sigma & $\pi$ bonds

Basically, the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals take place to a larger extent. Hence, it is stronger as compared to pi-bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds b/w the two atoms of a molecule, pi(bonds) is formed in addition to a sigma bond.

### Comparison

#### Sigma Bonds

- It is a strong bond.
- Electron cloud is symmetrical along the internuclear-axis.
- There can be free rotations of atoms around this bond.
- These are less reactive.
- Shape of the molecule is determined by these bonds.
- Sigma bonds have independent existence.

#### Pi Bonds

- It is a weak bond.
- Electron cloud is asymmetrical.
- Free rotation is not possible around this bond.
- These are more reactive.
- These bonds do not affect the shape of the molecule.
- Pi bonds always exists with a sigma bond.

## Hybridisation

Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies so as to form a new set of orbitals of equivalent energies & shape.

For example, when one  $2s$  & three  $2p$ -orbitals of carbon hybridise, there is the formation of four new  $sp^3$  hybrid orbitals.

### Salient Features of Hybridisation:

- The no. of hybrid orbitals is equal to the no. of atomic orbitals that get hybridised.
- The hybrid orbitals are always equivalent in energy & shape but different from participating atomic orbitals.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- The hybrid orbitals are directed in space in some preferred direction to have min. repulsion b/w electron pairs & thus a stable arrangement.
- A hybrid orbital, like atomic orbitals, can't have more than 2 electrons. The 2 electrons should have their spins paired.

Therefore, the type of hybridisation indicates the geometry of the molecules.

### Important Conditions for Hybridisation

- The orbitals present in the valence shell of the atom are hybridised.
- The orbitals undergoing hybridisation should have almost equal energy.
- Promotion of electron is not essential condition prior to hybridisation.
- It is not necessary that only half-filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

The hybrid orbitals are designated according to the type & no. of atomic orbitals merging together.

For example,

Mixing Orbitals	Hybrid Orbital	Hybridisation
1s & 3p	4 $sp^3$ orbitals	$sp^3$ hybridisation
1s & 2p	3 $sp^2$ orbitals	$sp^2$ hybridisation
1s & 1p	2 sp orbitals	sp hybridisation

### Conditions Necessary for Hybridisation

Atomic orbitals undergo hybridisation only if the following conditions are satisfied:

- (i) Atomic orbitals of the same atom participate in hybridisation. Electrons present in these atomic orbitals do not participate in the hybridisation, and occupy the hybrid orbitals as usual.
- (ii) The atomic orbitals participating in hybridisation should have nearly same energy.

### Types of Hybridisation

Depending upon the nature of the orbitals involved in hybridisation, different types of hybridisation become possible. The type of hybridisation shown by an atom depends upon the requirements of the reaction.

#### (I) $sp$ hybridisation:

This type of hybridisation involves the mixing of  $1s$  &  $1p$  orbital resulting in the formation of two equivalent  $sp$  hybrid orbitals resulting in the formation of two equivalent  $sp$  hybrid orbitals.

The suitable orbitals for  $sp$  hybridisation are  $s$  &  $p_z$ , if the hybrid orbitals are to lie along the  $z$ -axis. Each  $sp$  hybrid orbitals has 50%  $s$ -character & 50%  $p$ -character. Such a molecule in which the central atom is  $sp$ -hybridised & linked



directly to two other central atoms. possesses linear geometry. This type of hybridisation is also known as diatomic hybridisation.

### (II) $sp^2$ hybridisation:

In this hybridisation, there is involvement of 1 s & 2 p orbitals in order to form three equivalent  $sp^2$  hybridised orbitals.

The 3  $sp^2$  hybrid orbitals are oriented in a plane along the 3 corners of an equilateral triangle. i.e. they are inclined to each other at an angle of  $120^\circ$ .

Each hybrid orbital has 33.3% s-character & 66.7% p-character. Formation of  $sp^2$  hybrid orbitals from one s & two p orbitals.

### (III) $sp^3$ hybridisation:

This type of hybridisation can be explained by taking the example of  $CH_4$  molecule in which there is mixing of one s-orbital & three p-orbitals of valence shell to form four  $sp^3$  hybrid orbitals of equivalent energies & shape. There is 25% s-character & 75% p-character in each  $sp^3$  hybrid orbital. The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbitals is  $109.5^\circ$ .

## Molecular Orbital Theory

### Salient features on MOT:

- (i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- (ii) The atomic orbitals of comparable energies & proper symmetry combine to form molecular orbitals.
- (iii) While an  $e^-$  in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the no. of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
- (iv) The no. of molecular orbital formed is equal to the no. of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.
- (v) The bonding molecular orbital has lower energy & hence greater stability than the corresponding antibonding molecular orbital.

(vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.

(vii) The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle & Hund's rule.

### Formation of Molecular Orbitals

#### Linear Combination of Atomic Orbitals (LCAO)

Consider the hydrogen molecule consisting of two atoms A & B. Each hydrogen atom in the ground state has one  $e^-$  in  $1s$  orbital. The atomic orbitals of these atoms may be represented by the wave functions  $\psi_A$  &  $\psi_B$ .

Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition & by subtraction of wave functions of individual atomic orbitals as shown below-

$$\psi_{AB} = \psi_A \pm \psi_B$$

Therefore, the 2 molecular orbitals  $\sigma$  &  $\sigma^*$  are formed

as:  $\sigma = \psi_A + \psi_B$

$$\sigma^* = \psi_A - \psi_B$$

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called bonding molecular orbital while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called antibonding molecular orbital.

### Conditions for the Combination of Atomic Orbitals

- (i) The combining atomic orbitals must have the same or nearly the same energy.
- (ii) The combining atomic orbitals must have the same symmetry about the molecular axis.
- (iii) The combining atomic orbitals must overlap to the max. extent.

### Types of Molecular Orbitals

- Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta), etc.
- In this nomenclature, the sigma ( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis while pi ( $\pi$ ) molecular orbitals are not symmetrical.
- If internuclear axis is taken to be in z-direction, it can be seen that a linear combination of  $2p_z$ -orbitals of 2 atoms also produces 2 sigma molecular orbitals designated as  $\sigma_{2p_z}$  &  $\sigma^*_{2p_z}$ .

## Energy Level Diagram for Molecular Orbitals

- 1s atomic orbitals on two atoms form two molecular orbitals designated as  $\sigma 1s$  &  $\sigma^* 1s$ .
- 2s & 2p atomic orbitals (8 atomic orbitals on two atoms) give rise to the following eight molecular orbitals.

Antibonding MOs:  $\sigma^* 2s$ ,  $\sigma^* 2p_z$ ,  $\pi^* 2p_x$ ,  $\pi^* 2p_y$

Bonding MOs:  $\sigma 2s$ ,  $\sigma 2p_z$ ,  $\pi 2p_x$ ,  $\pi 2p_y$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of energies of various molecular orbitals for  $O_2, F_2$  is  $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$ .

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules  $Li_2, B_2, C_2, N_2$ .

For instance, it has been observed experimentally that for molecules such as  $B_2, C_2, N_2$ , etc. the increasing order of energies of various molecular orbitals is

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

The imp. characteristic feature of this order is that the energy of  $\sigma 2p_z$  molecular orbital is higher than that of  $\pi 2p_x$  &  $\pi 2p_y$  molecular orbitals.

## Electronic Behaviour & Molecular Orbital

- The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get imp. information about the molecule as discussed below:
- Stability of Molecules: If  $N_b$  is the no. of electrons occupying bonding orbitals &  $N_a$  the no. occupying the antibonding orbital, then
  - (i) the molecule is stable if  $N_b$  is greater than  $N_a$ .
  - (ii) the molecule is unstable if  $N_b$  is less than  $N_a$ .

## Bond Order according to Molecular Orbitals

- Bond Order: Bond order (b.o.) is defined as one half the difference b/w the no. of electrons present in the bonding & the antibonding orbitals.
$$B.O = \frac{1}{2}(N_b - N_a)$$
- A +ve bond order (i.e.  $N_b > N_a$ ) means a stable molecule while a -ve (i.e.  $N_b < N_a$ ) or zero (i.e.  $N_b = N_a$ ) bond order means an unstable bond.
- Nature of bond: Integral bond order values of 1, 2 or 3 correspond to single, double or triple bonds resp.
- Bond Length: The bond order b/w 2 atoms in a molecule may be taken as an approximate measure of the bond length. The bond length increases as bond order decreases.

- Magnetic Nature: If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However, if one or more orbitals are singly occupied it is paramagnetic (attracted by magnetic field) e.g.,  $O_2$  molecule.

### Bonding in Some Homonuclear Diatomic Molecules

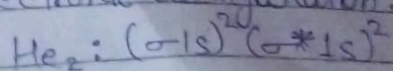
$H_2$  Molecule: It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in  $1s$  orbital. Therefore, in all there are 2 electrons in hydrogen molecule which are present in  $\sigma-1s$  molecular orbital. So electronic configuration of hydrogen molecule is  $\Rightarrow H_2: (\sigma-1s)^2$

The bond order of  $H_2$  molecule can be calculated as given below:  $B.O = \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$

This means that the 2 hydrogen atoms are bonded together by a single covalent bond.

Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

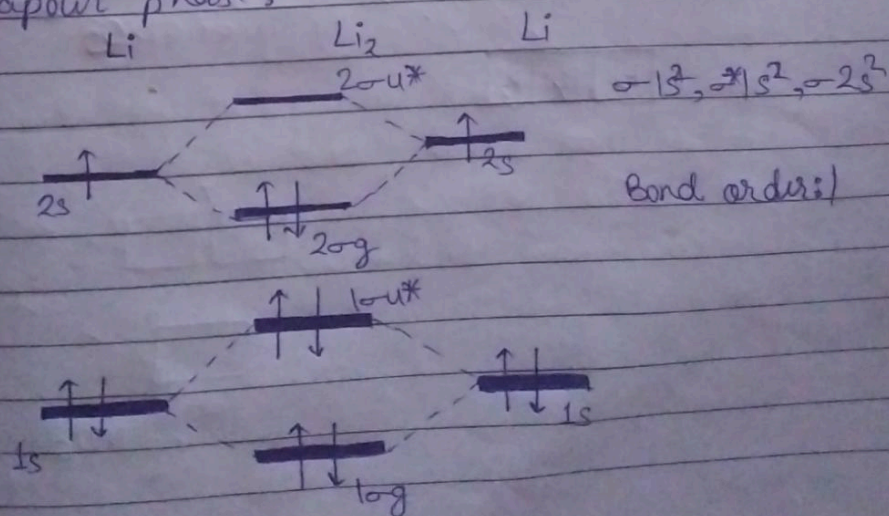
He molecule ( $He_2$ ): The electronic configuration of helium atom is  $1s^2$ . Each helium atom contains 2 electrons, therefore, in  $He_2$  molecule there would be 4 electrons. These electrons will be accommodated in  $\sigma-1s$  &  $\sigma^*-1s$  molecular orbitals leading to electronic configuration:



Bond order of  $He_2 = \frac{1}{2}(2-2) = 0$

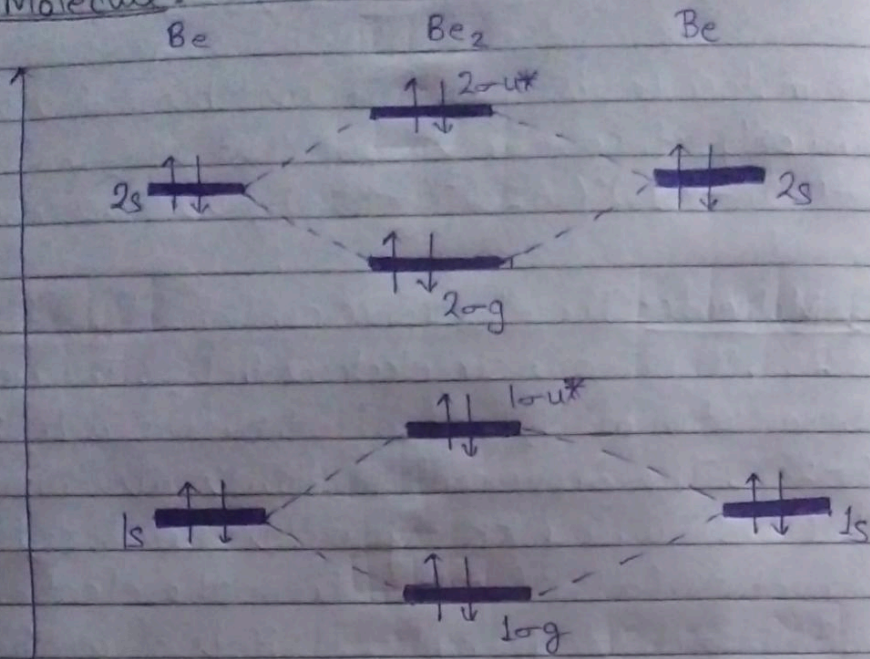
$He_2$  molecule is therefore unstable & does not exist. Similarly, it can be shown that  $Be_2$  molecule  $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2$  also does not exist.

$Li_2$  Molecule: The electronic configuration of lithium is  $1s^2 2s^1$ . There are six electrons in  $Li_2$ . The electronic configuration of  $Li_2$  molecule, therefore, is  $Li_2: (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$ . The above configuration is also written as  $KK(\sigma 2s)^2$  where  $KK$  represents the closed K shell structure  $(\sigma 1s)^2(\sigma^* 1s)^2$ . From the electronic configuration of  $Li_2$  molecule it is clear that there are four electrons present in bonding molecular orbital & 2 electrons present in antibonding molecular orbitals. Its bond order, therefore, is  $\frac{1}{2}(4-2) = 1$ . It means that  $Li_2$  molecule is stable & since it has no unpaired electrons it should be diamagnetic. Indeed diamagnetic  $Li_2$  molecules are known to exist in vapour phase.



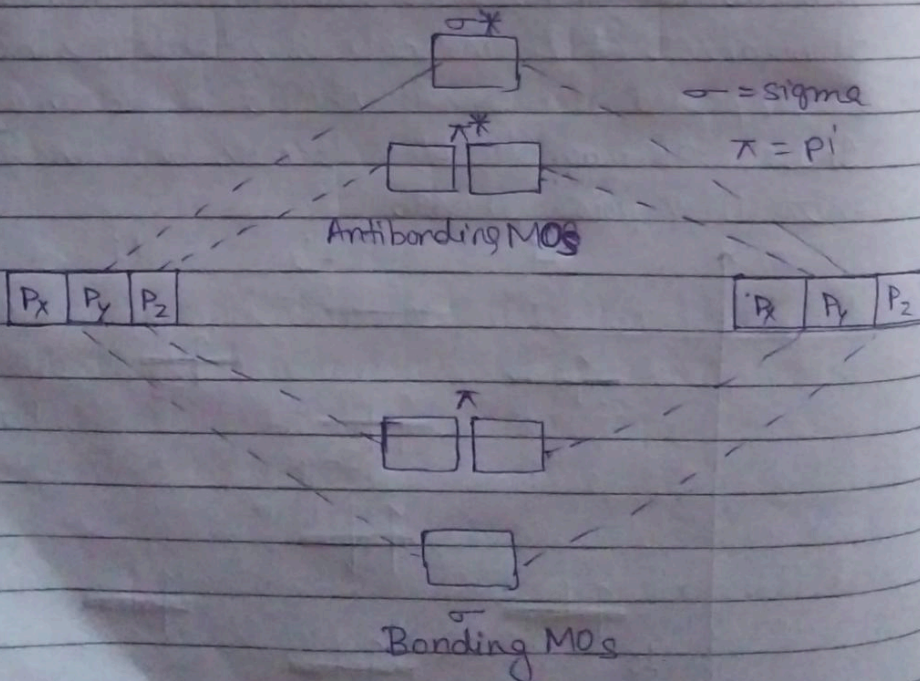


Be<sub>2</sub> Molecule:

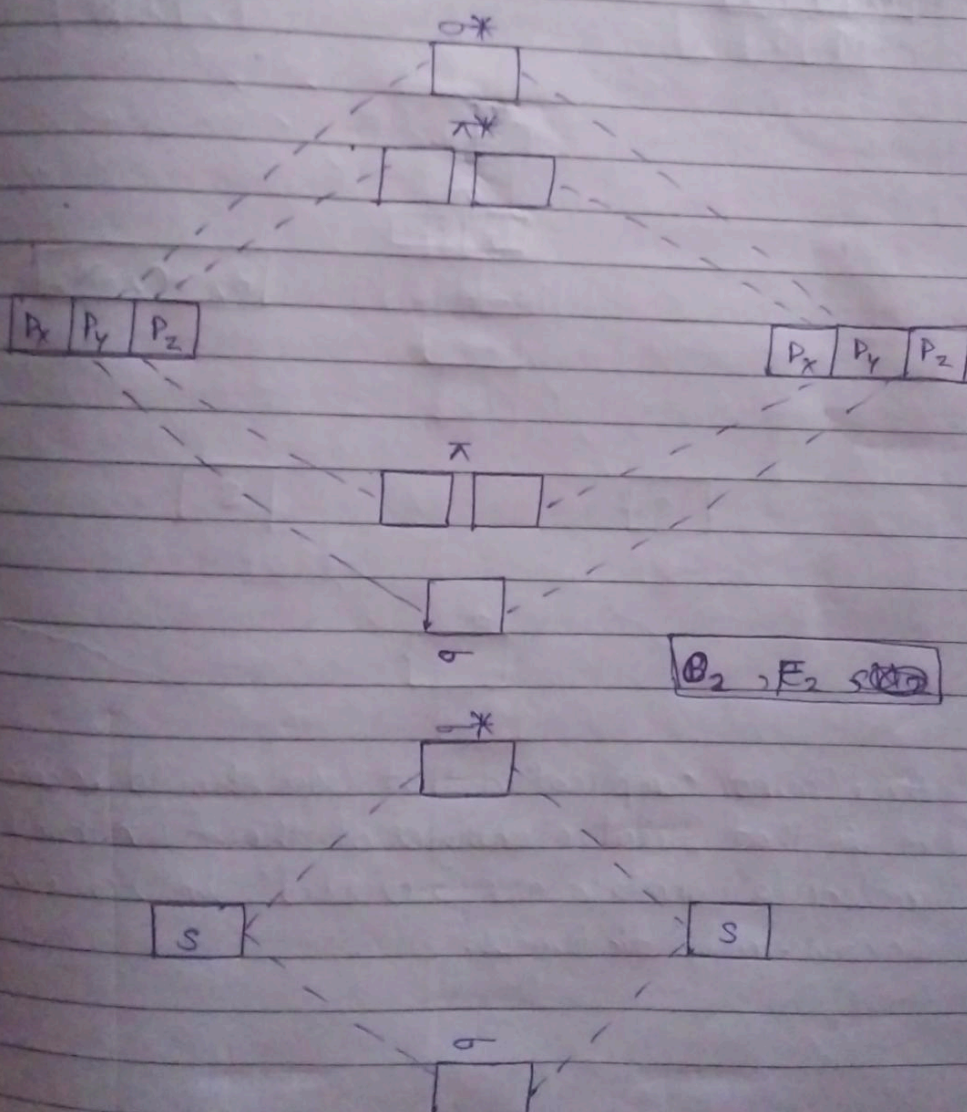


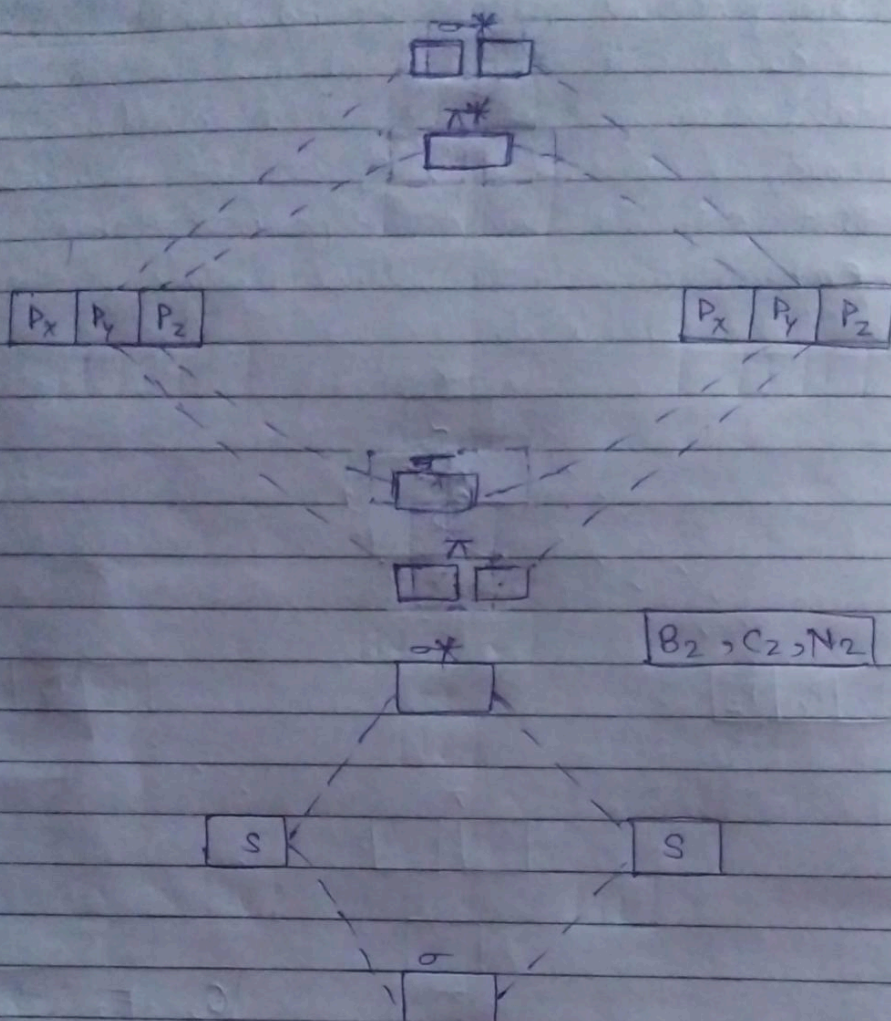
$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$

Bond Order: 0



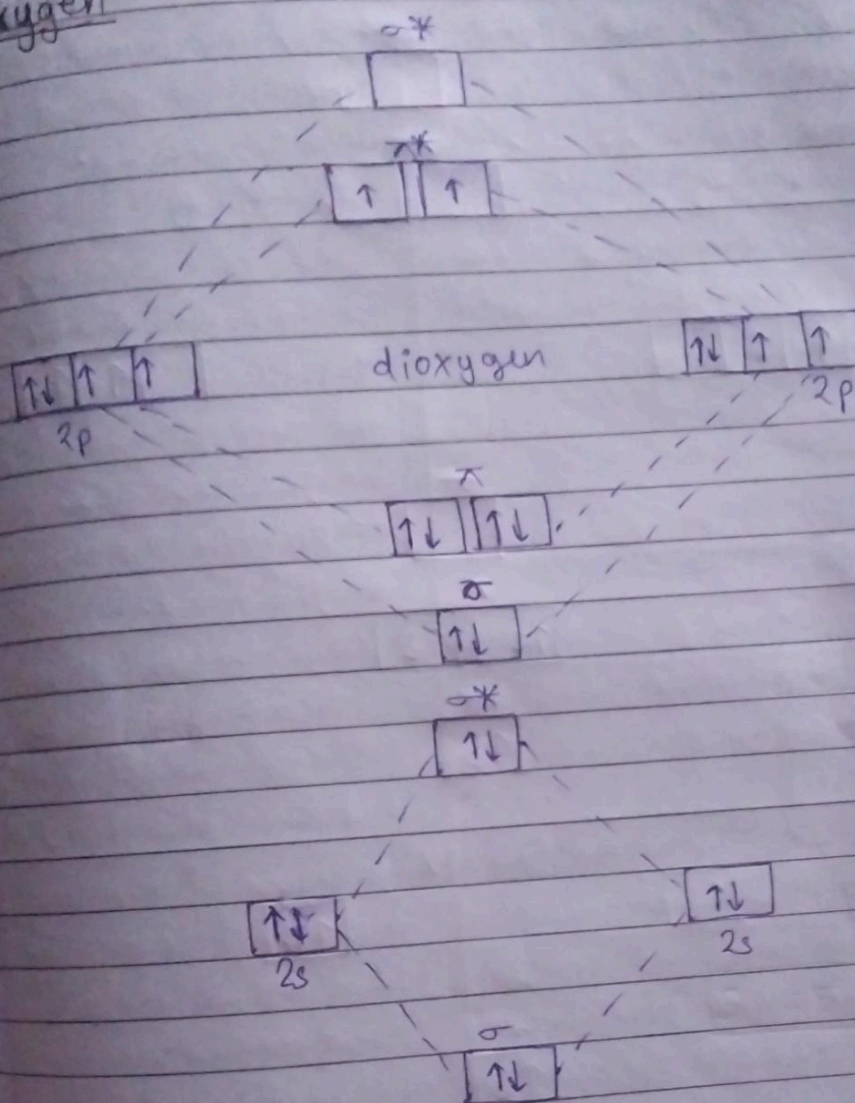
Splitting patterns for the second row Diatomic  
 If we combine the splitting schemes for the 2s & 2p  
 orbitals, we can predict bond order in all of the  
 diatomic molecules & ions composed of elements in  
 the first complete row of the periodic table.  
 Remember, that only the valence orbitals of the atoms  
 need to be considered.



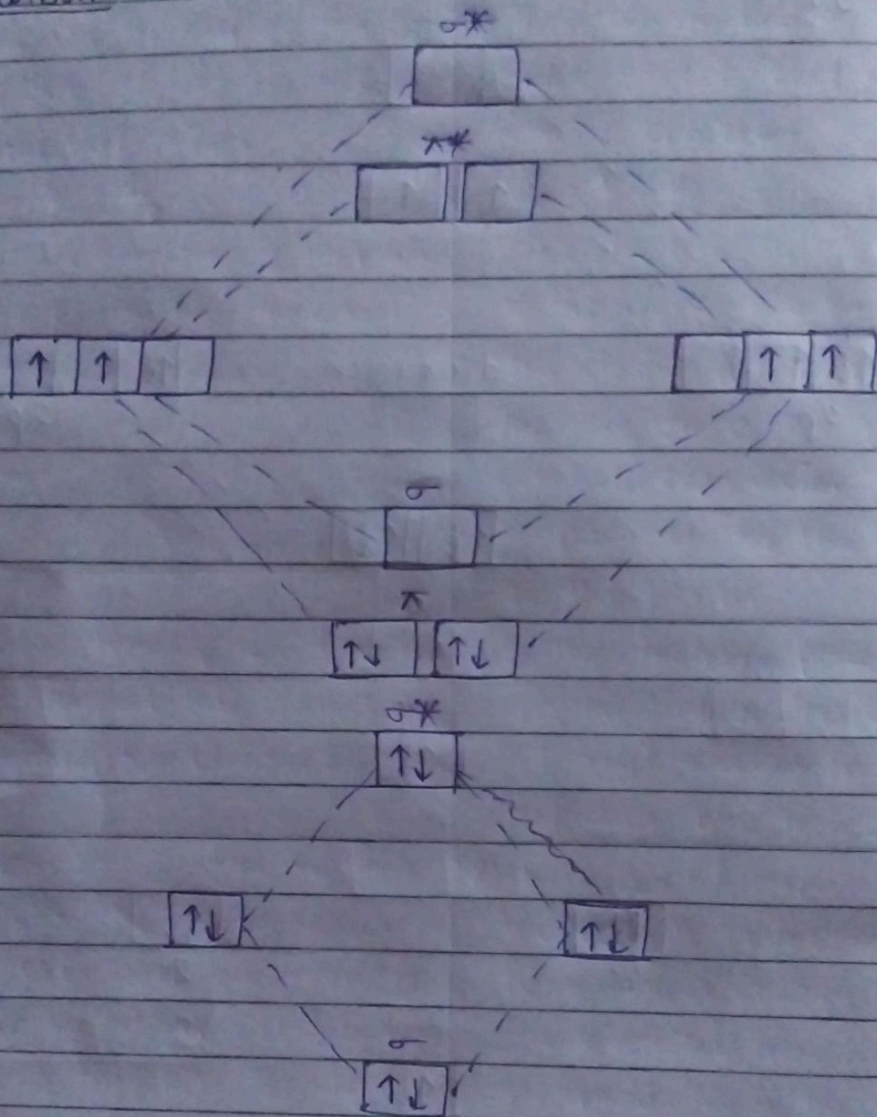


One minor complication that you should be aware of is that relative energies of the  $\sigma$  &  $\pi$  bonding molecular orbitals are reversed in some of the second-row diatomics.

# Dioxygen



Dicarbon



Atomic Orbitals	Molecular Orbitals
1. Their electron clouds extend around the nucleus of a single atom, i.e. atomic orbital is mono centric.	1. Their electron clouds extend around all the nuclei of bonded atoms in a molecule, i.e. a molecular orbital is polycentric. They are obtained by combining atomic orbitals of comparable energy.
2. They are less stable.	2. They are more stable.
3. They have simple shapes.	3. They have complex shapes.
4. They are represented by $s, p, d, f$ , etc.	4. They are represented by $\sigma, \sigma^*, \pi, \pi^*$ , etc. They may be bonding or antibonding.

$\sigma$ -Molecular orbital	$\pi$ -Molecular Orbital
1. It is formed by the overlap of atomic orbitals along the internuclear axis.	1. It is formed by the sideways overlapping of the atomic orbitals.
2. Due to head on overlap, the overlapping is maximum.	2. Due to sideways overlap, overlapping is less.
3. It consists of one electron cloud.	3. It consists of two electron clouds, one lying above & the other lying below a plane passing through the nuclei.
4. Its electron cloud is symmetrical about the internuclear axis.	4. Its electron cloud is not symmetrical about the internuclear axis.

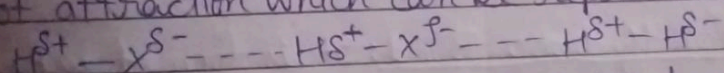
	Bonding Molecular Orbitals	Antibonding Molecular Orbitals
(i)-	They are formed by the additive effect of the atomic orbitals. $\phi_b = \psi_1 + \psi_2$	(i) They are formed by the subtractive effect of the atomic orbitals. $\phi_b = \psi_1 - \psi_2$
(ii)-	The electron density increases in the region b/w the nuclei of bonded atoms.	(ii) The electron density decreases in the region b/w the nuclei of the atoms & it increases in the region away from internuclear axis. This is responsible for the instability of the bond.
(iii)-	The electrons present in the bonding orbitals result in an attraction b/w the 2 atoms.	(iii) The electrons present in the antibonding molecular orbital (if any) results in the repulsion b/w the 2 atoms.
(iv)-	Because of attractive forces involved, these molecular orbitals have lower energy than the atomic orbitals from which they are formed. This is the cause of their greater stability.	(iv) Because of repulsive forces involved, these molecular orbitals have higher energy than the atomic orbitals from which they are formed. This is the cause of their lower stability i.e. it does not favour bond formation & that is why the name antibonding.
(v)-	They are formed when the lobes of the combining orbitals have the same sign.	(v) They are formed when the lobes of the combining orbitals are of opp sign.
(vi)-	These molecular orbitals are represented by $\sigma$ & $\pi$ .	(vi) These molecular orbitals are represented by $\pi^*$ & $\sigma^*$ .

## Hydrogen bonding

Hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

## Cause of Formation of Hydrogen Bond

When hydrogen is bonded to strongly electronegative element 'X', the electron pair shared b/w the two atoms moves far away from hydrogen atom. As a result the hydrogen atom becomes highly electropositive with respect to the other atom 'X'. Since there is displacement of electrons towards X, the hydrogen acquires fractional +ve charge ( $\delta^+$ ) while 'X' attain fractional -ve charge ( $\delta^-$ ). This results in the formation of a polar molecule having electrostatic force of attraction which can be represented as:



Hydrogen bond isn't a covalent bond as the 1s orbital of hydrogen is already completed, & the 2s level is high up in its energy.

## Conditions Necessary For the Formation of Hydrogen Bond

Hydrogen bond is formed only when the following conditions are satisfied:

- (i) Only the molecules in which hydrogen atoms is linked to an atom of highly electro-negative element, are capable of forming hydrogen bonds.



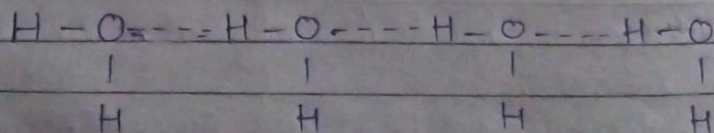
(ii)- The atom of the highly electronegative element should be small.

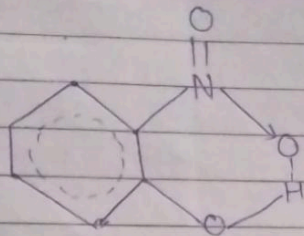
These conditions are met by fluorine, oxygen & nitrogen atoms. As a result, all compounds containing hydrogen atom linked to an atom of either N, O or F exhibit hydrogen bonding.

Examples of compounds showing hydrogen bonding:-  
Hydrogen Fluoride (HF), water ( $H_2O$ ), Ice ( $H_2O(s)$ ).

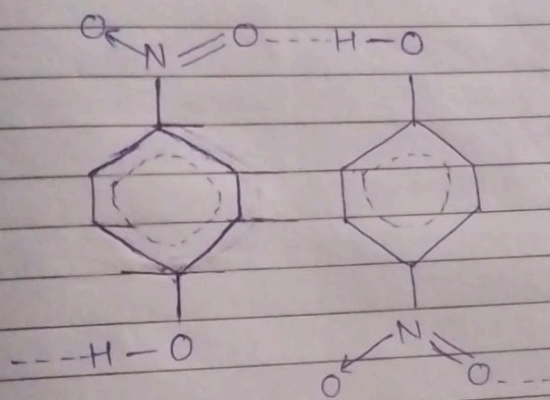
### Types of H-Bonds

- Intermolecular Hydrogen Bond: It is formed b/w two different molecules of the same or different compounds. For example, H-bond in case of HF molecules, alcohol or water molecules, etc.
- Intramolecular Hydrogen Bond: It is formed when hydrogen atom is in b/w the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is b/w the two oxygen atoms.





Intramolecular hydrogen bonding in o-nitrophenol molecule



Intermolecular hydrogen bonding in p-nitrophenol