Chemical Bonding and Molecular Structure

1.1 Introduction

Matter is made up of one or more types of elements. Atoms of inert gases exist independently in nature, but under normal conditions the atoms of other element do not remain independent and so are obtained in combined form. The groups of atoms combine and exist as species having characteristic properties are known as molecules. There must be some attraction force which keeps the atoms present in the molecule combined with each other. Thus, **the attraction force that keeps the different components (atom/ion) combined together is called chemical bond.**

The chemical compounds that formed as a result of this chemical bond creates some problems viz. Why do atoms combine? Why do they combine in definite proportion? Why do certain atoms combine with each other and not with other atoms ? Why do molecules possess some definite shapes ? The answers to these problems can be given by the principles like **Kossel-Lewis approach, VSEPR principle, valence bond theory, molecular orbital theory.**

1.2 Kossel - Lewis Approach of Chemical Bonding

Many attempts have been made to explain existence of chemical bond in relation to electron but, in 1916, Scientists Kossel and Lewis gave satisfactory explanation.

Lewis proposed atom as positively charged Kernel. In this Kernel, nucleus and electrons in the inner orbit are present, while eight electrons can be accomodated in outer shell. Thus, one electron of sodium element in the outermost shell is on the corner of a cube while all the eight electrons of inert gases (except helium) are arranged on the eight corners of the cube.

Lewis noted that when atoms are combined by chemical bond, they attain stable structure of octet of eight electrons. The atom of sodium element loses one electron (Na^+) and attain stable octet structure. While atom of chlorine element receives one electron (Cl^-) and attains stable octet structure. Molecules such as Cl_2, O_2, F_2 etc. attain stable octet structures by sharing of valence electrons (Exception H_2).

Lewis Symbols : In the formation of molecules by chemical bond, the electrons in the outermost shell only take part, and the electrons in the inner shells do not take part in the formation of bond because they are protected. Lewis utilised the following type of symbols. e.g. The valence electrons of the elements of second period of periodic table can be shown as below by Lewis Symbols :

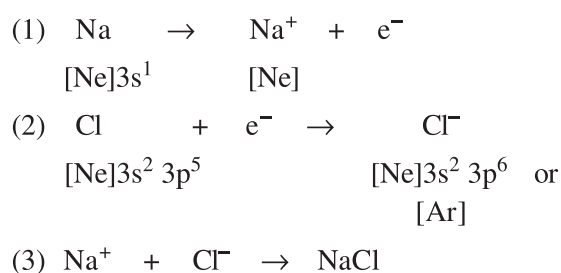Li   Be   •B•   •C•   •N•   •O•   •F•   •Ne•

The number of dots around the symbol of the elements are considered as valence electrons of that element. The number of this valence electrons is useful in calculation of valency of the group.

Approach of Kossel for Chemical Bonding :

- The strongly electronegative halogen elements and strongly electropositive alkali elements in the periodic table differ from inert gases.

- Halogen elements receive one electron and become negatively charged, while alkali elements lose one electron and become positively charged.

- The positively charged and negatively charged ions formed this way attain stable electronic structure like inert gases (Except Helium) whose general electronic structure can be given as $ns^2 np^6$ (octet).

- This positive ion and negative ion are stable due to electrostatic attraction.

- In the formation of ionic compound, the atoms having less ionisation enthalpy combine with atoms having more electronegativity and the bond formed by this combination is called **ionic bond.**

- The capacity of formation of ionic bond of an element is called **electrons lost or gained by element.**

The explanation of formation of ionic bond in sodium chloride compound is as follows :

(1)   Na $\rightarrow$ Na^+ + e^-
      $[Ne]3s^1$ $[Ne]$

(2)   Cl   + e^- $\rightarrow$ Cl^-
      $[Ne]3s^2 3p^5$ $[Ne]3s^2 3p^6$ or
                                         $[Ar]$
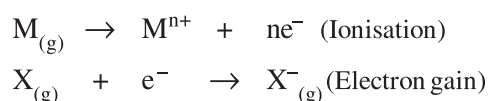
(3) Na^+ + Cl^- $\rightarrow$ NaCl

The bond formed by electrostatic attraction between positive ion and negative ion is called electrovalent bond. This approach of Kossel is not able to explain the formation of large number compounds.

1.3 Ionic Bond, Covalent Bond (including Lewis Structure), bond length, bond angle, bond energy, bond order, and their concept, Born-Haber Cycle

Ionic Bond : On the basis of approach of Kossel and Lewis, the formation of ionic bond depends on the following factors:

(1) Easy availability of positive ion and negative ion from neutral atoms.

(2) Arrangement of positive ion and negative ion in ionic bond.

The formation of positive ion from neutral atom or formation of negative ion from neutral atom depends on the values of ionisation enthalpy and electron gain enthalpy of atoms respectively.

$M_{(g)}$ $\rightarrow$ M^{n+} + ne^- (Ionisation)

$X_{(g)}$ + e^- $\rightarrow$ $X^-_{(g)}$ (Electron gain)

|		
CO_3^{2-}	[Lewis structure of carbonate]	[resonance structure of carbonate]
HNO_3	[Lewis structure of nitric acid]	[structure of nitric acid]
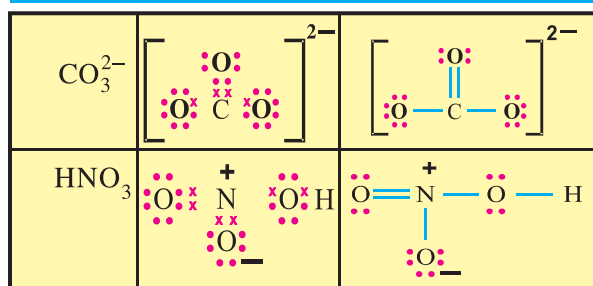
* Each H atom attains the configuration of Helium (only two electrons.)

With the help of the Lewis Approach, the shapes of molecule/ion cannot be known and also there are certain exceptions.

e.g. $BeCl_2$ [Lewis structure $:Cl \overset{x}{\cdot} Be \overset{x}{\cdot} Cl:$]

In the molecule of $BeCl_2$, the octet of the central Be atom is not completed; even then this compound is stable. Similarly, in certain examples like PCl_5, there are ten electrons around central phosphorus atom; even then the compound is stable.

[Lewis structure of PCl_5 with P surrounded by five Cl atoms]
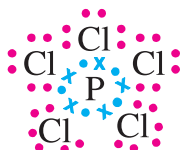
In certain cases, the stability decreases with increase in atomic size of central atom even though the octet structure is complete in the elements of the same group. e.g. $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. Electrons are shared in formation of covalent bond, but on the basis of the type of sharing and type of atom of combining element, it is divided into three parts :

(i) Polar Covalent Bond : In this type of covalent bond, atoms of element having different electropositivity or electronega-tivity takes part in the formation of covalent bond. As a result, the property of polarity is Induced in moecules.

e.g. HCl   [Lewis structure $H \overset{x}{\cdot} Cl:$]

(ii) Non-polar Covalent Bond : When a covalent bond is formed by sharing of elec-trons of atoms of the same element, the bond is called nonpolar covalent bond. Such compounds are nonpolar because the electropositivity or electro-negativity of their elemants is same.

e.g.   H:H   [Lewis structure of Cl_2]

(iii) Co-ordinate Covalent Bond : For the formation of bond of this type, the required electron pair is donated by the atom of only one from the two elements. As a result the covalent bond formed is called **co-ordinate covalent bond.** This bond is shown by the sign of arrow ($\rightarrow$) and the direction of the arrow is from the atom donating the electron pair to the atom receiving the electron pair.

[Lewis structure showing $BF_3 + NH_3 \longrightarrow F-B \leftarrow N-H$ coordinate bond formation]
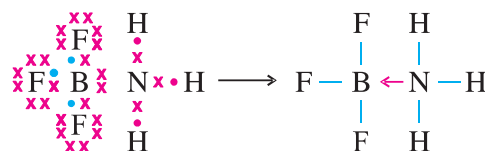
Bond Length : The equilibrium distance between the nuclei of two atoms conbined by bond in the molecule is called bond length. The bond length is measured by X-ray diffraction and spectroscopic methods. It is expressed in picometer ($pm = 10^{-12}m$)

The bond lengths of some common molecules are shown in Table 1.2.

**Table 1.2 Bond Lengths of some common molecules**

Molecule	Bond Length (pm)
H_2 (H – H)	74
F_2 (F – F)	144
Cl_2 (Cl – Cl)	199
Br_2 (Br – Br)	228
I_2 (I – I)	267
N_2 (N – N)	109
O_2 (O – O)	121
HF (H – F)	92
HCl (H – Cl)	127
HBr (H – Br)	141
HI (H – I)	160

The less values of bond length mention greater stability.

Bond Angle : The angle between the orbitals possessing bonding electron pairs around central atom of the molecule/ion is called bond angle. Bond angle is expressed in degrees which can be determined by spectroscopic methods. With the help of the bond angle, the preliminary information about shapes of molecules

can be obtained. e.g. The bond angle in molecule of water can be shown as below :
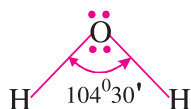

Bond Energy (Bond Enthalpy) : The energy required for breaking 1 mole bond in one mole gaseous substance is called bond energy or bond enthalpy. The unit of bond enthalpy is $kJmol^{-1}$. e.g. The bond enthalpy of H – H bond in hydrogen molecule is 435.8 $kJ\ mol^{-1}$.

$H_{2(g)} \rightarrow H_{(g)} + H_{(g)}$ Bond enthalpy = 435.8 $kJ\ mol^{-1}$. More the value of bond enthalpy higher will be the stability of molecule/ion.

Bond Order : The number of bonds between atoms present in molecule is called bond order. e.g. In H_2 molecule, there is sharing of one electron pair. As a result, the two hydrogen atoms present in hydrogen molecule are combined by single bond, H–H. Similary, in O_2 and N_2 there are sharing of two and three electron pairs respectively and so double bond and triple bonds are formed. $\ddot{O}=\ddot{O}$, $:N\equiv N:$ Single bond, double bonds and triple bonds are respectively shown as –, =, and ≡. With the increase in bond order, the values of bond enthalpy increase. As a result bond length decreases and so stability increases.

Born-Haber Cycle : The formation of ionic bond depends on lattice enthalpy. More the value of lattice enthalpy of the product easier will be the formation of ionic bond. The value of lattice energy will be more only when the attraction force between two atoms is more. Born-Haber first of all gave value of total enthalpy-lattice enthalpy by studying the enthalpies of different steps involved in the formation of ionic compounds by ionic bonds.

We shall try to explain Born-Haber Cycle by taking example of different enthalpy changes involved in the formation of NaCl crystalline compound from its components in standard state. Generally the simple equation for the formation of NaCl crystal can be written as follows:

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow NaCl_{(s)}$$
$$\Delta_f H = -411\ kJmol^{-1}$$
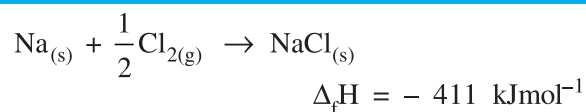
The different steps of formation of NaCl crystal are as follows :

(i) First of all, sodium element/atom which is in solid form at room temperature is sublimed and the value of sublimation enthalpy $(\Delta_s H)$ is 108 $kJmol^{-1}$.

$$Na_{(s)} \xrightarrow{\text{Sublimation enthalpy}} Na_{(g)}$$
$$\Delta_s H = +108\ kJmol^{-1}$$
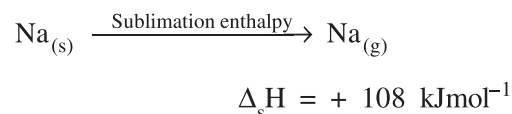
(ii) The value of ionisation enthalpy required to remove electron from one mole $Na_{(g)}$ atom to infinite distance is 496 $kJmol^{-1}$

$$Na_{(g)} \xrightarrow{\text{Ionization enthalpy}} Na^+_{(g)} + e^-$$
$$\Delta_i H = +496\ kJmol^{-1}$$
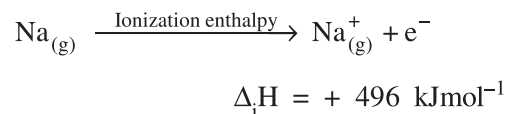
(iii) Gaseous chlorine element exists as diatomic molecule of room temperature. In one mole solid NaCl crystal structure formation only one chlorine atom is required. Hence decomposition of dichlorine molecule becomes essential. The enthalpy required for this is called decomposition enthalpy.

$$\frac{1}{2}Cl_{2(g)} \xrightarrow{\text{decomposition}} Cl_{(g)}$$
$$\Delta_{\frac{D}{2}} H = +121\ kJmol^{-1}$$
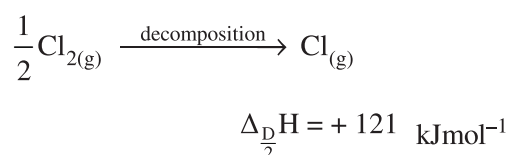
(iv) The gaseous atom of chlorine obtained this way accepts one electron and changes to chloride ion. The enthalpy released for this is called electron gain enthalpy $(\Delta_{eg} H)$

$$Cl_{(g)} + e^- \xrightarrow{\text{Electron gain enthalpy}} Cl^-_{(g)}$$
$$\Delta_{eg} H = -349\ kJmol^{-1}$$
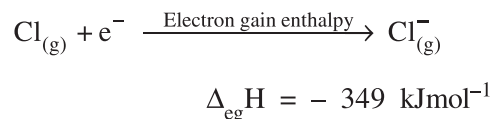
(v) One mole gaseous positive ion (Na^+) and one mole gaseous negative ion (Cl^-) combine with each other and form one mole of solid ionic crystal. The enthalpy released during this is called lattice enthalpy which is expressed as 'U'.

$$Na^+_{(g)} + Cl^-_{(g)} \xrightarrow{\text{Lattice enthalpy}} NaCl_{(s)}$$
$$\Delta_U H = -787\ kJmol^{-1}$$
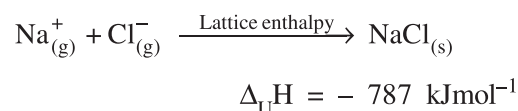
By the above method, the crystal structure of any ionic solid can be known by the study of each step of the different steps according to Born-Haber cycle, and the value of enthalpy of formation - lattice enthalpy can be obtained. The above different steps can be shown as below :

$$Na_{(s)} + \tfrac{1}{2}Cl_{2(g)} \xrightarrow[\Delta_f H]{\text{Formation enthalpy}} NaCl_{(s)}$$

(Born-Haber cycle diagram with steps: Sublimation enthalpy $\Delta_s H$, Delonposition enthalpy $\Delta_{D/2} H$, electron gain enthalpy $\Delta_{eg} H$, Ionisation enthalpy $\Delta_i H$, Lattice enthalpy $\Delta_U H$)

$$Cl_{(g)} + e^- \xrightarrow[\Delta_{eg} H]{\text{electron gain enthalpy}} Cl^-_{(g)}$$

$$Na_{(g)} \xrightarrow[\Delta_i H]{\text{Ionisation enthalpy}} Na^+_{(g)} + e^-$$
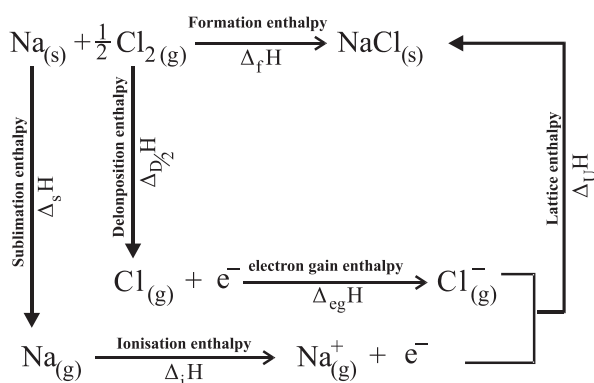
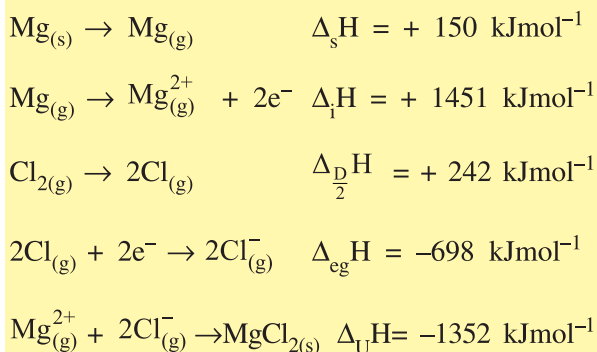All the above different steps can be written in the form of equation as follows :

$$\Delta_f H = \Delta_s H + \Delta_{\frac{D}{2}} H + \Delta_i H + \Delta_{eg} H + \Delta_U H \quad ....(1.1)$$

The enthalpy of formation of crystal of one mole NaCl can be obtained by adding up the different enthalpies as below :

$$\Delta_f H = 108 + 121 + 496 + (-349) + (-787)$$

$$= -411 \ kJmol^{-1}$$

Thus, the value of enthalpy of formation for one mole NaCl obtained is negative which indicates its stability.

Example 1.1 : Find the enthalpy of formation of $MgCl_2$ using the following values:

$Mg_{(s)} \to Mg_{(g)}$ $\Delta_s H = + 150 \ kJmol^{-1}$

$Mg_{(g)} \to Mg^{2+}_{(g)} + 2e^-$ $\Delta_i H = + 1451 \ kJmol^{-1}$

$Cl_{2(g)} \to 2Cl_{(g)}$ $\Delta_{\frac{D}{2}} H = + 242 \ kJmol^{-1}$

$2Cl_{(g)} + 2e^- \to 2Cl^-_{(g)}$ $\Delta_{eg} H = -698 \ kJmol^{-1}$

$Mg^{2+}_{(g)} + 2Cl^-_{(g)} \to MgCl_{2(s)}$ $\Delta_U H = -1352 \ kJmol^{-1}$

Solution :

$$\Delta_f H = \Delta_s H + \Delta_i H + \Delta_{\frac{D}{2}} H + \Delta_{eg} H + \Delta_U H$$

$$= 150 + 1451 + 242 + (-698) + (-1352)$$

$$= -207 \ kJmol^{-1}$$

1.4   Rasonance Structures

The experimentally observed properties of the molecules cannot be explained only by Lewis Structure. This is its limitation. This means that Lewis Structure is incomplete to explain the experimentally observed properties of molecules e.g. Ozone molecule can be explained by following two structures :
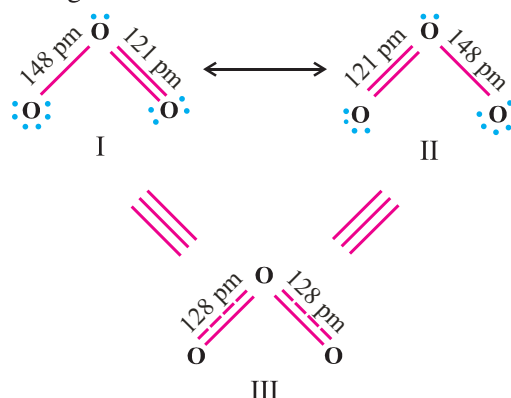

Fig. 1.1 The resonance structures of Ozone molecule

In both the structures, O – O single bond and O = O double bond are present. O – O single bond length is 148 pm (1 picometer (pm) = 10^{-12} meter) and O = O double bond length is 121 pm; but the bond length between any oxygen-oxygen in ozone molecule is same, and its value is 128 pm. Thus, the bond length between oxygen-oxygen in ozone molecule is in middle of single bond and double bond, which cannot be explained by any one of the structures I and II as shown in fig 1.1. Hence, the idea of resonance was presented to explain the real structures of molecules like ozone and others. You have studied about resonance structures of CO_2 molecule in Semester I. Thus, in resonance structure, same energy, same position of nucleus as well as bonding electron pairs and non bonding electron pairs are taken into consideration, the resonance structure which represents the molecule definitely. According to Fig 1.1, structures I and II, represent the resonance structures of structure III which is the real structure of ozone. Such structures are called hybrid resonance structures. Such similar examples like benzene; carbonate ion $\left(CO_3^{2-}\right)$ also can explain the resonance.

Resonance structures give stability to the molecule because the energy of resonance structure is less than those of structures shown separately. Thus decrease in energy is responsible for the stability of resonance structure.

1.5 Geometrical Structures of Molecules

Variety has been observed in geometric structures of molecules. The basis of diversity in geometrical structures of molecules in one type of molecules, the bonding and non-bonding electron pairs present in them as well as the magnitude of the attraction produced between them.

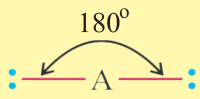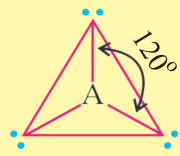**Table 1.3 Geometrical shapes of molecules in which central atoms of the molecule has no non-bonding electron pairs**
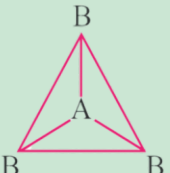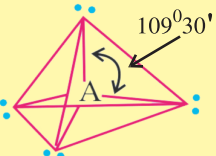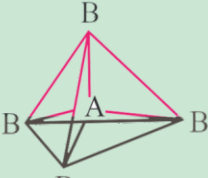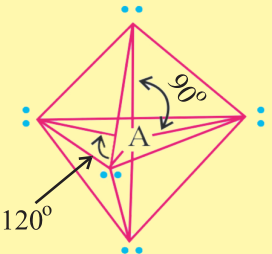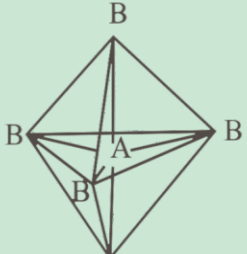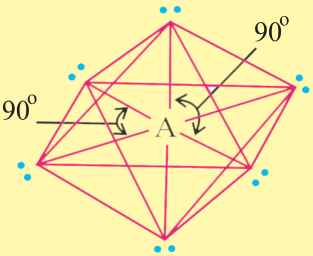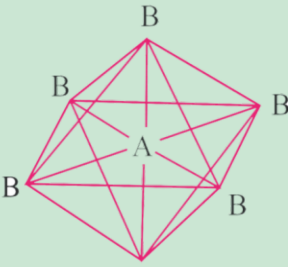
Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Hybridisation	Examples
2	Linear	B—A—B Linear	sp	BeH_2, $BeCl_2$ $HgCl_2$
3	Trigonal planar	Trigonal planar	sp^2	BF_3, BCl_3
4	Tetrahedral	Tetrahedral	sp^3	CH_4, NH_4^+ BF_4^-, CCl_4
5	Trigonal bipyramidal	Trigonal bipyramidal	sp^3d	PCl_5
6	Octahedral	Octahedral	sp^3d^2	SF_6

Table 1.4 Geometrial shapes of molecules in which the central atom of molecule has one or more non-bonding electron pairs
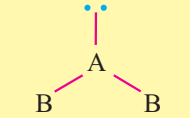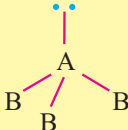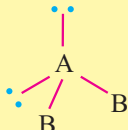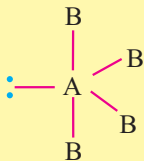
Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3 PCl_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O F_2O
AB_4E	4	1	 Trigonal bipyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bipyramidal	T- shape	ClF_3
AB_5E	5	1	 Octahedral	Square pyramidal.	BrF_5
AB_4E_2	4	2	 Octahedral	Square planar	XeF_4

Table 1.5 Geometrical shapes of molecules having bonding and non-bonding electron pairs

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Example
AB_2E	2	1		Bent	SO_2
AB_3E	3	1		Trigonal pyramidal	NH_3
AB_2E_2	2	2		Bent	H_2O
AB_4E	4	1	(a) (b) (More Stable)	See saw	SF_4

AB_3E_2	3	2			T- shape	ClF_3
			(a)			
			(b)			
			(c)			
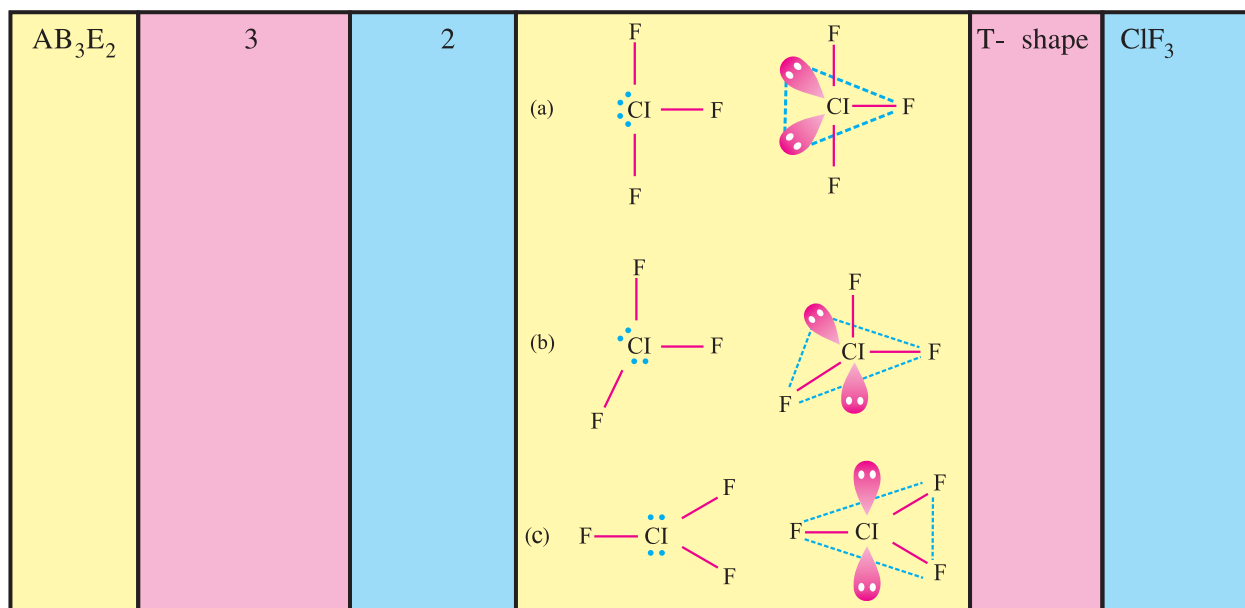
1.6 VSEPR Principle (Principle of Valence Shell Electron Pair Repulsion)

Lewis Aproach was incomplete to explain shapes of molecules. Only the hypotheses about the structures of molecules containing covalent bond can be made. First of all, in 1940, Sidgwick and Powell presented the theory of repulsion existing between electron pairs present in valence shells of atoms. In 1957, Nyholm and Gillespie presented this theory in the developed form. The main hypotheses of this theory are as follows :

- The shape of the molecule depends upon the number of electron pairs (bonding and non-bonding electron pairs) in valence shells around the central atom.
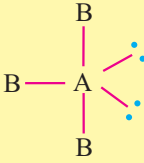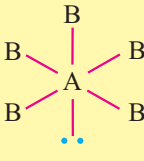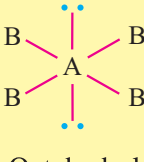
- The electron pairs present in valence shell being negatively charged, repel each other.

- These electron pairs possess the tendency of obtaining such an arrangement in the space that the repulsion between them is minimum and as a result there is maximum distance between them.

- If there are two or more than two resonance structures in the molecule, VSEPR principle can be applied to any of the structures.

- The magnitude of the repulsion produced between electron pair is as follows :

Thus, **VSEPR principle is helpful in determining geometrical shapes produced due to presence of electron pair in the molecule.** Especially, the geometric structures of compounds of elements of p-block can be explained by this principle.

The molecule of sulphur dioxide is angular and bond angle is 119.5^0 instead of 120^0. This is due to repulsion produced between bonding and non-bonding electron pairs. In the same way, in methane, ammonia and water molecules there is similar type of hybrid orbitals (sp^3), even then the repulsion forces are produced in different magnitudes due to different numbers of electron pairs and as a result different bond angles are obtained.

The electronic structure of central carbon atom in methane molecule in ground state is as follows :

$$_6C : 1s^2 \ 2s^2 \ 2p_x^1 \ 2p_y^1 \ 2p_z^0$$

| Repulsion produced between non-bonding and non-bonding pair of electron (Lp – Lp) | > | Repulsion produced between non-bonding pair of electron and bonding pair of electron (Lp – Bp) | > | Repulsion produced between bonding pairs of electrons (Bp – Bp) |
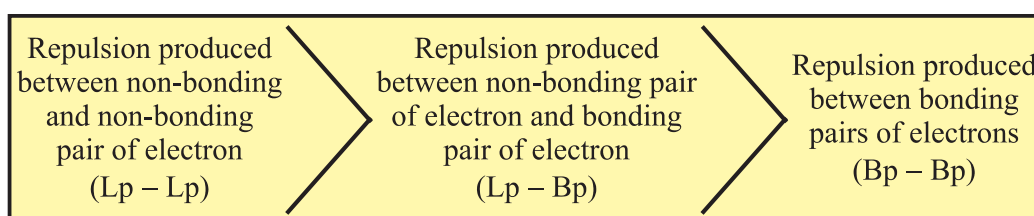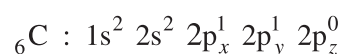
As four hydrogen atoms are combined with central carbon atom, four half filled orbitals will be requied. For this, writing the electron structure of carbon in excited state will be.

$$_6C^* \; : \; 1s^2 \; 2s^1 \; 2p_x^1 \; 2p_y^1 \; 2p_z^1$$
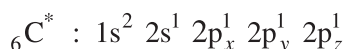
Thus, carbon atom in its excited state utilises sp^3 hybrid orbitals, combines with half filled $1s^1$ orbitals of hydrogen atom and forms four covalent bonds.
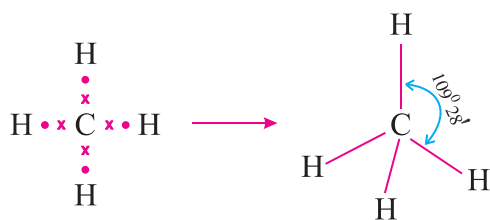
Thus, in methane molecule, there are four bonding electron pairs (Bp) between carbon and hydrogen atoms. According to Sidgwick-Powell rule, there is minimum repulsion between these four bonding electron pairs. As a result, tetrahedral structure corresponding to sp^3 hybridisation is observed in which the bond angle as in regular tetrahedral structure that is $109^0 28'$ is observed.

In the molecule of NH_3, nitrogen atom has five valence electrons, out of which three electrons combine with electrons of $1s$ orbital of three hydrogen atoms by sharing and form three covalent bonds. Even after that nitrogen atoms has two electrons or one electron pair which remains uncombined even after formation of bonds. Thus one non-bonding pair of electrons remains.

This non bonding electron pair of nitrogen atom repels the two bonding electron pairs around nitrogen according to Sidgwick-Powell rule. As a result, both these electron pairs are pushed inside. As a result the bond angle between them decreases or instead of regular tetrahedral bond angle $109^0 28'$ it is obtained as 107^0.

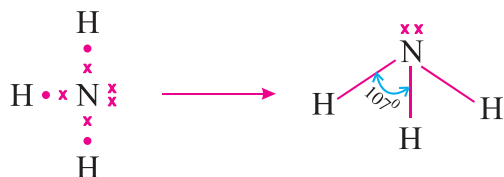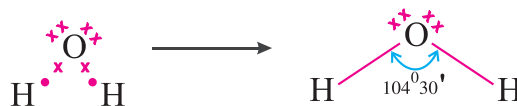In H_2O molecule, there are total six valence electrons around central oxygen atom, out of which, two valence electrons form covalent bond with $1s$ orbital electrons of two hydrogen atoms but remaining four electrons or two electron pairs become non bonding electron pairs.

According to Sidgwick-Powell rule there is maximum repusion force between these two non bonding electron pairs and as a result they remain away from each other. When it happens so, they go near the bonding electron pairs and repulsion is produced between them. Because of this, bonding electron pairs are pushed inside, in more proportion and there is noticeable decrease in the bond angle. In H_2O molecule, even though there is sp^3 hybridisation but bond angle formed is $104^0 \, 30'$ by decreasing from bond angle $109^0 28'$.

1.7 Polarity of Bond

Any chemical bond does not possess completely ionic or completely covalent nature. In the molecules like H_2, N_2, O_2, Cl_2 etc. the covalent bond is formed by sharing of electrons between its two atoms; but when the experimental values of bond lengths and bond enthalpies are studied, it is found that there is some contribution of ionic bond. Heteronuclear diatomic molecules like hydrogen fluoride (HF), the electron pair of covalent bond remains dragged more towards atom of fluorine element because the electronegativity of fluorine (in comparison to hydrogen atom) is more. As a result the partial negative charge ($-\delta$) is produced on atom of fluorine element and partial positive charge ($+\delta$) is produced on atom of hydrogen. Its real structural formula can be written as below :

Dipole Moment is found in the molecule due to this property of polarity. In the same way in the molecule of water, one oxygen atom and two hydrogen atoms combine to form two covalent bonds. The electronegativity of oxygen

element being more relative to that of atom of hydrogen element, the electron pairs remain dragged towards atom of oxygen. This produces partial positive charge $(+\delta)$ on hydrogen atom and partial negative charge $(-\delta)$ on oxygen atom. In addition due to the two non-bonding electron pairs on atom of oxygen element, property of polarity is as shown below :
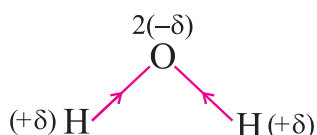
In linear molecule like beryllium flouride (BeF_2) polarity of the same magnitude exists between beryllium and each fluorine atom but in opposite directions. As a result, the resultant value of polarity becomes zero and the value of dipole moment becomes zero.
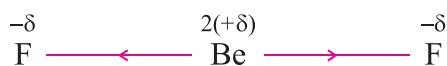
The value of dipole moment of ammonia (NH_3) is not zero, so it is not linear but the structure of the molecule is pyramidal.
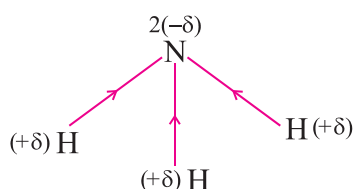
The electronegativity of flurine element being more than that of the electronegativity of hydrogen, the value of dipole moment of NH_3 molecule is more than the value of dipole moment of NF_3. In both these molecules, one non bonding electron pair is on central nitrogen atom. In the molecule of NH_3 the polarily of all the three N—H bonds is towards nitrogen atom. (The electronegativity of nitrogen is more than that of Hydrogen). Thus, the polarity of three bonds is concentrated on central nitrogen atom and so the resultant value of dipole moment increases while, in NF_3 molecule, the polarity of N—F bond is towards F atom (The electronegativity of fluorine is more than that of nitrogen). Thus in NF_3 three N—F bonds in different directions and so the resultant value of dipole moment is less in comparison to NH_3 molecule.
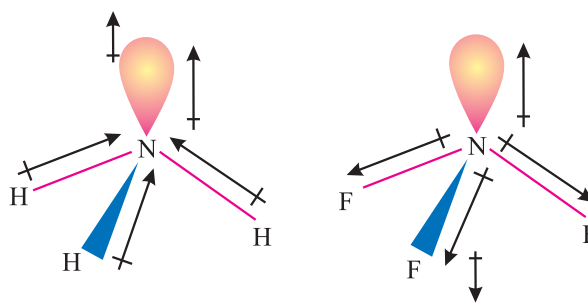
The values of dipole moments of some molecules and their geometrical shapes are shown in Table 1.6.

Table 1.6 Dipole moments of some selected compounds and their geometrical shapes

Type of molecule	Example	Dipole moment μ (D)	Geometrical shape
Molecule AB	HF	1.78	Linear
	HCl	1.07	Linear
	HBr	0.79	Linear
	HI	0.38	Linear
	H_2	0	Linear
Molecule AB_2	H_2O	1.85	Bent
	H_2S	0.95	Bent
	CO_2	0	Linear
Molecule AB_3	NH_3	1.47	Trigonal pyramidal
	NF_3	0.23	Trigonal pyramidal
	BF_3	0	Planar trigonal

Molecule AB_4	CH_4	0	Tetrahedaral
	$CHCl_3$	1.04	Tetrahedaral
	CCl_4	0	Tetrahedaral

1.8 Approach to Covalent Bond

The explanation of covalent bond can be given by Lewis Theory but the shapes of molecules and polarity of bonds cannot be explained by this theory. The modern theory of covalent bond formation is based on the quantum mechanics. For explanation of this, there are two major approaches-Valence Bond Theory and Molecular Orbital Theory.

Heitler and London had presented the theory of valence bond in 1927 which was later developed by scientist Pauling with some changes. According to this theory, the bond is formed by overlapping of valence orbitals of atoms. e.g. Dihydrogen molecule is formed by combination of two hydrogen atoms. Each hydrogen atom possesses one proton in the nucleus and one electron in its orbit. According to valence bond theory, one covalent bond between two hydrogen atoms H—H is formed by the overlapping of 1s orbital of each hydrogen atom. The directions of the spin of electron in 1s orbital of each hydrogen, which is overlapping are opposite to each other. In the formation of hydrogen molecule, the electron pair obtained by overlapping of two 1s orbitals, and having opposite spins remain in between nuclei of two hydrogen atoms and this bonding electron pair experiences similar attraction by both the nuclei.

1.9 Valence Bond Theory

In 1927, Heitler and London first of all presented the valence bond theory. Its detailed study and devlopment were carried out by scientists Linus Pauling and Slater. According to this theory, when half filled atomic orbitals come near to each other, then they get overlapped, and as a result the formation of covalent bond

is attained. Thus, one half filled orbital of one atom overlaps with half filled orbital of other atom and forms bond. Thus, the combining atoms share their valence electrons and form covalent bond. Sometimes, out of the two combining atoms, the orbital of one atom may be completely filled and the other orbital of the other atom may be vacant, even then they both overlap and form special type of covalent bond (which is called co-ordinate covalent bond).

Two atoms A and B of hydrogen element which possess nuclei N_A and N_B. Suppose, they go near to each other. The electrons in the two atoms are shown as e_A and e_B. When these two atoms are at very far distance, there is no interattractive force between them. When they come nearer to each other, the attractive and repulsive forces are produced between them.

The attractive forces are produced because of following factors :

(i) The attractive forces produced between nucleus of the atom itself and its own electron or $N_A - e_A$ and $N_B - e_B$.

(ii) The attractive force produced by nucleus of one atom and electron of other atom. $N_A - e_B$ and $N_B - e_A$.

In the same way, repulsive forces are produced because of the following factors :

(i) Repulsive force produced between electron-electron of two atoms $e_A - e_B$.

(ii) Repulsive force produced between nuclei of two atoms or $N_A - N_B$.

Attractive forces try to take both the atoms near to each other while repulsive forces try to push each other. This is shown in Fig 1.2.

Attractive Forces

- - - - - - - Old force

————— New force
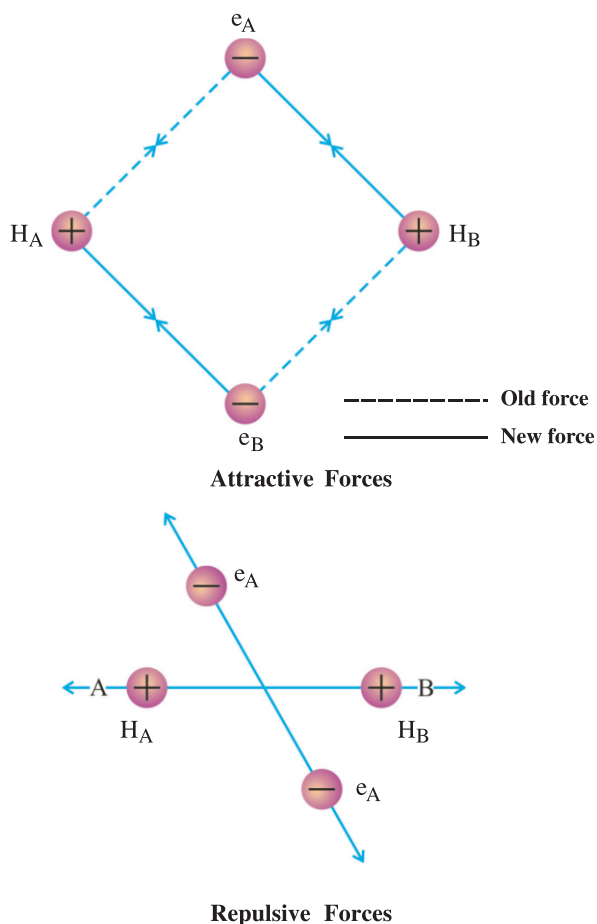
Repulsive Forces

Fig. 1.2 Forces of attraction and repulsion during the formation of H_2 molecule

It is proved from the experiments that the magnitude of attractive forces is more than that of repulsive forces. As a result both the atoms go near to each other and their potential energy decreases. Both the atoms go near to each other to such an extent that attractive forces are balanced by repulsive forces and the system attains minimum energy. At this stage, both hydrogen atoms combine with each other and remain at certain definite distance and forms stable hydrogen molecule. This distance or bond length is 74 pm.

Assumptions of Valence Bond Theory :
According to valence bond theory, the half filled atomic orbitals (and having same symmetry) having same energy overlap with each other and form covalent bond. As a result there is pairing of electrons in valence orbitals. The strength of covalent bond is directly proportional to the magnitude of overlapping of orbitals or if the overlapping of valence orbitals of atom is more, then stronger will be the covalent bond

The assumptions of valence bond theory can be given as follows :

(i) Generally there must not be much difference in energies of overlapping atomic orbitals.

(ii) The overlapping orbitals must be half filled and the spin of the electrons in them must be in opposite direction to each other.

(iii) There must be overlapping of atomic orbitals to proper extent, so that chemical bond formation can take place.

Overlapping of atomic orbitals : When two atoms come near to each other, there is overlapping of atomic orbitals. This overlapping can be positive, negative or zero wich depends upon the properties of the overlapping atomic orbitals. The different overlapping arrangements of s and p orbitals are shown in Fig. 1.3.
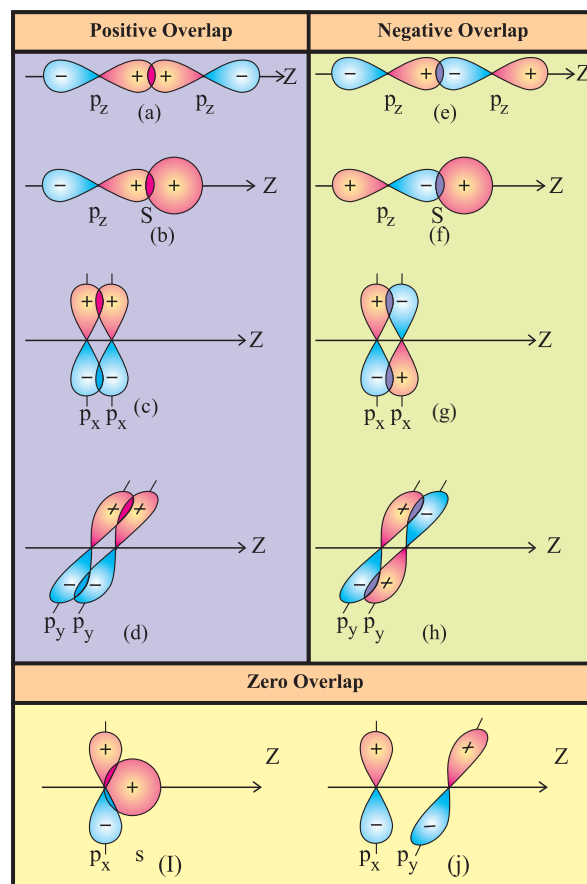
Fig. 1.3 Positive, negative and zero overlapping of s and p atomic orbitals

The assumptions of overlapping of atomic orbitals are applicable similarly to homonuclear, heteronuclear, diatomic and polyatomic molecules. The chemical bonding in molecules having

polynuclear atoms like CH_4, NH_3 and H_2O can be explained with the help of valence bond theory. Their shapes and bond angles can also be known. We know that the shapes of the molecules CH_4, NH_3 and H_2O are tetrahedral, pyramidal and bent respectively. These geometrical shapes can be explained with reference to overlapping of atomic orbitals.

The electronic structure of central atom carbon in CH_4 molecule, in its ground state is [He] $2s^2$ $2p_x^1$ $2p_y^1$ $2p_z^0$, and in excited state it is [He] $2s^1$ $2p_x^1$ $2p_y^1$ $2p_z^1$. Thus, four half filled orbitals of carbon atom overlap with 1s orbitals of four hydrogen atom, which are also half filled and form four $C - H$ bonds. Three p-orbitals of carbon atom are at 90^0 to one another and so three $C - H$ bonds are found at 90^0 to one another. But 2s orbital of hydrogen atom are symmetrically spherical, hence, they overlap with each other in any direction. Hence, the fourth $C - H$ bond is not determined clearly. But this assumption is not consistent with tetrahedral molecular structure in which bond angle is 109^028 . Hence, it can be said that the overlapping of atomic orbitals does not possess vector properties. In the similar way the shapes of molecules of NH_3 and H_2O and their bond angles can be explained.

Types of Overlapping and Nature of Covalent Bond : The covalent bond formed by overlapping of atomic orbitals can be divided in to two types.

(i) σ bond : This type of σ - covalent bond is obtained by end to end overlapping of the ends of two atomic orbital having internuclear axis. It is also called axial overlapping. This type of overlapping is obtained by overlapping of atomic orbitals as shown below :

Overlapping of s–s orbitals : In this type, overlapping of two half filled orbitals having one axis is observed.

s-Orbital   s-Orbital   s-s Overlapping
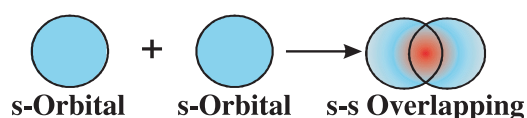
Overlapping of s–p orbitals : In this type, there is overlapping between half filled atomic s-orbital of one atom and half filled atomic p-orbital of other atom.

s-Orbital   p-Orbital   s-p Overlapping
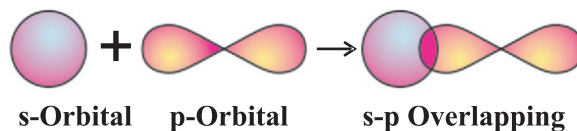
Overlapping of p–p orbitals : Here it is found that when the two atoms go near to each other the overlapping of p-p orbitals due to overlapping of half filled p-orbital of two atoms is observed.

p-Orbital   p-Orbital   p-p Overlapping
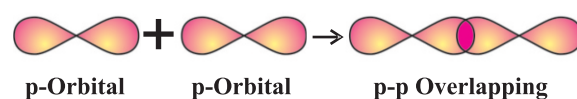
(ii) π– bond : In this type of π–covalent bond formation, the axes of atomic orbitals that are overlapping remains parallel to each other and it is perpendicular to internuclear axis.

p-Orbital p-Orbital   p-p Overlapping
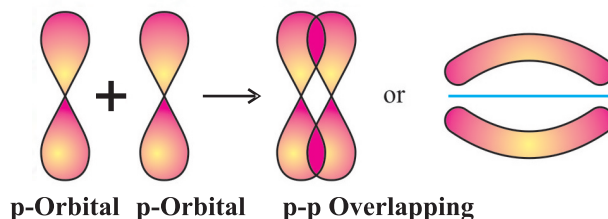
The strength of any type of σ or π bond is proportional to the magnitude of overlapping of atomic orbitals. In σ bond formation, overlapping of atomic orbitals is more and as a result σ– bond is strong. In π– bond formation the megnitude of overlapping is less because of overlapping of atomic orbitals is sidewise and as a result π– bond is weaker relative to σ– bond.

1.10 Molecular Orbital Theory

The molecular orbital theory was first of all presented by Mulliken and Hund in 1932. According to them, the description of molecular orbital is similar to that of atomic orbital. As electrons of atom are arranged in atomic orbitals (such as s,p,d...etc) in the same way the electrons of the molecule are arranged in molecular orbitals. The probability distribution of electrons around the nucleus of the atom can be shown by atomic orbitals. Similarly, the probability distribution of electrons around the nucleus of molecule can be shown by molecular orbitals is carried out obeying Auf bau principle, Pauli's Exclusion principle and Hund's rule of maximum multiplicity.

Important points of molecular orbital theory :

(i) As the electrons of the atom are arranged in different atomic orbitals, similarly electrons of the molecule are arranged in different molecular orbitals.

(ii) The atomic orbitals having similar energy and proper symmetry combine with each other in some definite way and forms molecular orbitals.

(iii) The electrons in the atomic orbital are under the effect of only one nucleus, while the electrons in the molecular orbitals are under the effect of two or more nuclei. It depends on how many atoms are there in the molecule. Thus atomic orbitals are monocentric, while molecular orbitals are polycentric.

(iv) The number of atomic orbitals that combine with each other is the same for molecular orbitals. Half the number these molecular orbitals are called Bonding Molecular Orbitals (BMO) and remaining half number of molecular orbitals are called Anti-bonding Molecular Orbitals (ABMO).

(v) The energy of the bonding molecular orbitals obtained by combination of respective atomic orbitals is less in comparison to the anti-bonding molecular orbitals.

Linear Combination of Atomic Orbitals (LCAO) and Formation of Molecular Orbitals : According to quantum mechanics, the formation of molecular orbitals between any two atoms is the linear combination of acceptable wave functions or Linear Combination of Atomic Orbitals. When two hydrogen atoms combine and H_2 molecule is formed, acceptable wave functions of each hydrogen atom $\Psi_{1s(1)}$ and $\Psi_{1s(2)}$ takes place by linear combination in two ways as follows : Hence two acceptable wave functions Ψ_{MO} and Ψ^*_{MO} are formed.

$$\Psi_{MO} = \Psi_{1s(1)} + \Psi_{1s(2)}$$
$$\Psi^*_{MO} = \Psi_{1s(1)} - \Psi_{1s(2)}$$

Here, (1) and (2) are the numbers used for two atoms of hydrogen. Two molecular wave functions formed here describe two molecular orbitals. The molecular orbital indicated by Ψ_{MO} is called bonding molecular orbital and by Ψ^*_{MO} is called antibonding molecular orbital.

When the molecular orbital is formed by complementary overlapping of two 1s orbital, it is spread over the nuclei of both the atoms. The total energy of this molecular orbital is less than the total energy of both the atomic orbitals. It is called bonding molecular orbital. When the molecular orbital formed by opposing overlapping of two 1s orbitals has total energy more than the total energy of both the atomic orbitals, is formed, it is called antibonding molecular orbital.
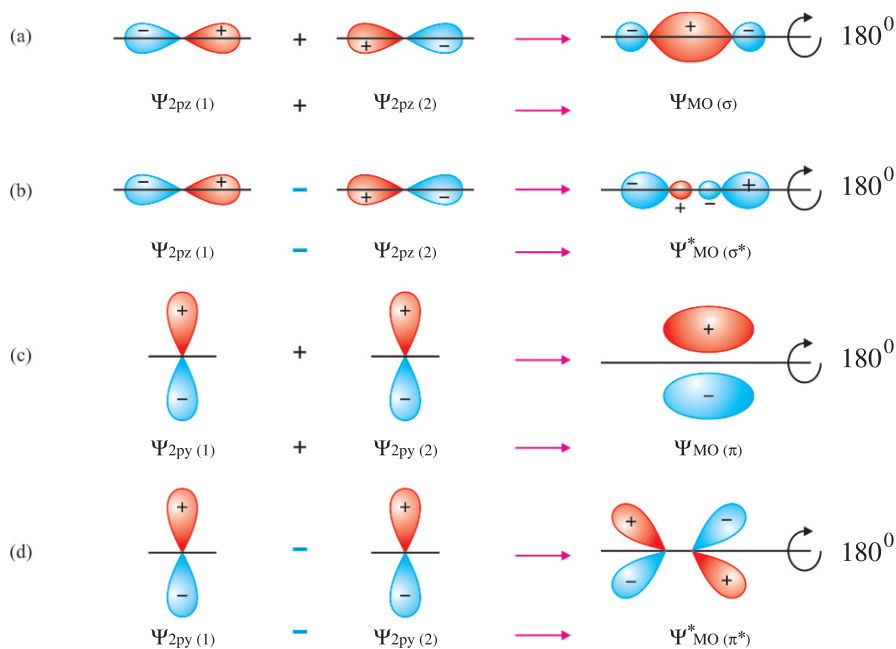

Fig. 1.4 Bonding and anti-bonding molecular orbitals

ney

ombini

energies

near as

The increasing order of molecular orbitals for molecules from H_2 to N_2 is as follows :

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

But the order is changed for molecules from O_2 to Ne_2, which is as follows :

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

1.13 Molecular Orbitals and their Relative Energies

The distribution of electrons in different molecular orbitals is called molecular electronic configuration. Some important information is obtained from electronic configuration of molecule.

Stability of Molecule : Suppose N_b is the number of electrons in bonding molecular orbital and N_a is the number of electrons in anti-bonding molecular orbitals, then :

(i) For $N_b > N_a$, molecule is more stable.

(ii) For $N_b < N_a$, molecule becomes unstable.

Bond Order and Stability : The stability of molecule is directly proportional to the value of bond order. The difference between total number of electrons in bonding molecular orbitals (N_b) and the number of electrons in anti-bonding molecular orbitals (N_a) when divided by two, the value of bond order is obtained i.e.

$$\text{Bond order} = \frac{1}{2}\left[N_b - N_a \right]$$

If the value of bond order is positive $(N_b > N_a)$ the molecule becomes stable but negative or zero value of bond order $(N_b < N_a$ or $N_b = N_a)$ indicates instability of molecule.

If unpaired electrons are there in electronic configuration of atomic orbitals, the molecule/ion becomes paramagnetic and if all the electrons are paired it becomes diamagnetic.

1.14 Energy Level Diagram Bond Order, Stability and Magnetic Properties of Homonuclear Diatomic Molecules Like He_2 to Ne_2

The energy level diagram of molecular orbitals of any homonuclear diatomic molecule can be drawn as shown in Fig 1.5 and the bond order can be calculated by arranging electrons in them. The energy level diagrams of molecular orbitals of H_2 molecule and O_2 molecule are shown as illustration in Fig 1.6 (a) and (b) respectively.

H_2
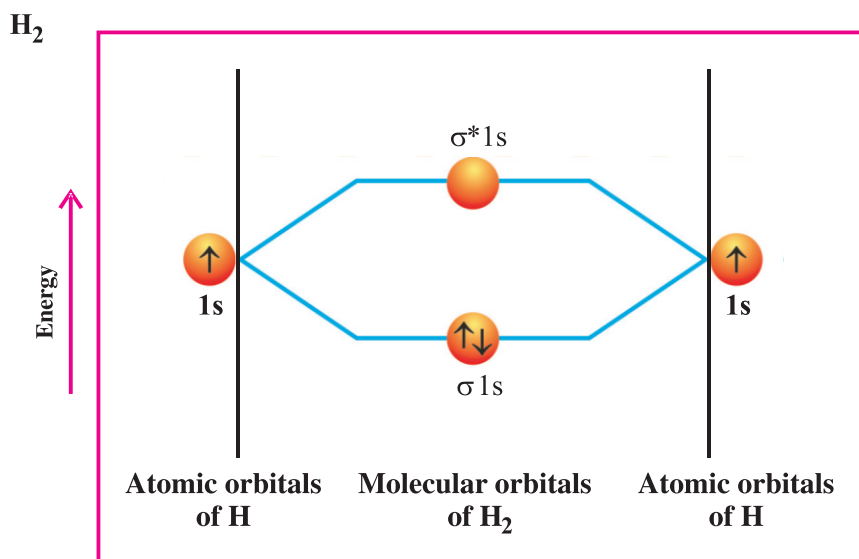
Fig. 1.6 (a) Energy level diagram of molecular orbital of H_2
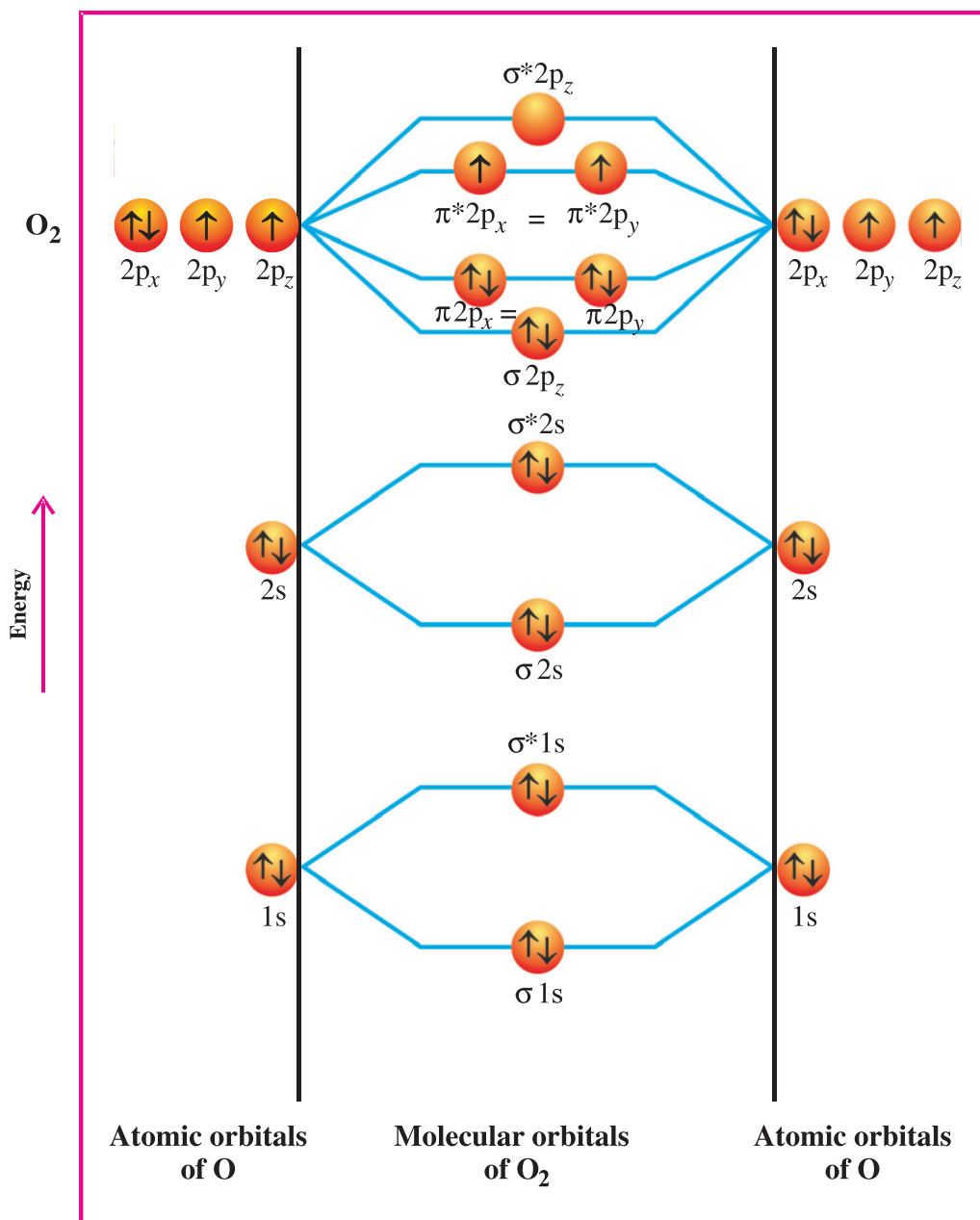
Fig. 1.6 (b) Energy level diagram of molecular orbitals of O_2

(1) H_2 molecule : The electronic configuration of H-atom is $1s^1$. Hence, there are two electrons in H_2 molecule. The molecular electronic configuration of these two electrons will be as follows :

$$H_2 = (\sigma 1s)^2$$
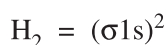
$$\text{Bond order} = \frac{1}{2} \left[N_b - N_a \right]$$

$$= \frac{1}{2} \left[2 - 0 \right]$$

$$= 1$$

Hence, H − H is in H_2.

(2) He_2 molecule: The electronic configuration of He atom is $1s^2$. Total four electrons are there in He_2 molecule, whose molecular electronic configuration can be shown as follows :

$$He_2 = (\sigma 1s)^2 (\sigma^* 1s)^2$$

$$\text{Bond order} = \frac{1}{2} \left[N_b - N_a \right]$$

$$= \frac{1}{2} \left[2 - 2 \right] = 0$$

Here, the value of bond order obtained is zero which indicates that He_2 molecule is unstable and so He_2 molecule is not possible.

(3) Li$_2$ molecule : The electronic configuration of Li atom is $1s^2\ 2s^1$. Thus, there are six electrons in Li$_2$ molecule whose arrangement in molecular orbitals can be made as follows :

$$Li_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [4 - 2] = 1$$

Hence, Li $-$ Li is there in Li$_2$.

(4) Be$_2$ molecule : The electronic configuration of Be atom is $1s^2\ 2s^2$. Thus, there are totally eight electrons in Be$_2$ molecule which will be arranged in molecule orbitals as follows :

$$Be_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [4 - 4] = 0$$

Thus, the value of bond order of Be$_2$ is zero which indicates unstable molecule.

(5) B$_2$ molecule : The electronic configuration of B atom is $1s^2\ 2s^2\ 2p^1$. Thus, in boron molecule there are ten electrons which will be arranged as follows in molecular orbitals.

$$B_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^1 = (\pi 2p_y)^1$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [6 - 4] = 1$$

Hence, B $-$ B is in B$_2$. Here, there are two unpaired electrons and so B$_2$ molecule is paramagnetic.

(6) C$_2$ molecule : The electronic configuration of carbon atom is $1s^2\ 2s^2\ 2p^2$. Hence the total number of electronic configuration will be as follows :

$$C_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2$$

$$Bond\ order = \frac{1}{2}\ \Big[N_b - N_a\Big]$$

$$= \frac{1}{2}\ \Big[8 - 4\Big] = 2$$

Hence C $=$ C is in C$_2$. All the electrons are paired and so C$_2$ molecule is diamagntic.

(7) N$_2$ molecule : The electronic configuration of N atom is $1s^2\ 2s^2\ 2p^3$. Hence there are totally 14 electrons in N$_2$ molecular orbitals will be as follows :

$$N_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\sigma 2p_z)^2$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [10 - 4] = 3$$

Hence, N $\equiv$ N is in N$_2$ molecule. As all the electrons are paired, N$_2$ molecule is diamagnetic.

(8) O$_2$ molecule : The electronic configuration of O atom is $1s^2\ 2s^2\ 2p^4$. Hence, there are 16 electrons in O$_2$ molecule. The electronic configuration in molecular orbitals will be as follows :

$$O_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^* 2p_x)^1 = (\pi^* 2p_y)^1$$

$$Bond\ order = \frac{1}{2}\ [N_b - N_a]$$

$$= \frac{1}{2}\ [10 - 6] = 2$$

Hence, O $=$ O is in O$_2$ molecule. As two unpaired electrons are there in O$_2$ molecule, it is paramagnatic. This result expresses the importance of molecular orbital theory because O$_2$ molecule is diamagnetic according to valence bond theory.

(9) F$_2$ molecule : The electronic configuration of F atom is $1s^2\ 2s^2\ 2p^5$. Hence 18 electrons are there in F$_2$ molecule whose arrangement in molecular orbitals can be shown as follows.

$$F_2 = (\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2\ (\pi^* 2p_x)^2 = (\pi^* 2p_y)^2$$

Bond order $= \dfrac{1}{2} \left[N_b - N_a \right]$

$ = \dfrac{1}{2} \left[10 - 8 \right] = 1$

Hence F $-$ F is in F_2. As all the electrons in F_2 molecule are paired, the molecule will be diamagnetic.

(10) Ne_2 molecule : The electronic configuration of Ne is $1s^2\, 2s^2\, 2p^6$. Hence 20 electrons are there in Ne_2. The arrangement of it can be as follows :

$Ne_2 = (\sigma 1s)^2\, (\sigma^*1s)^2\, (\sigma 2s)^2\, (\sigma^*2s)^2\, (\sigma 2p_z)^2$

$\quad (\pi 2p_x)^2 = (\pi 2p_y)^2\, (\pi^*2p_x)^2 = (\pi^*2p_y)^2$

$\quad (\sigma^*2p_z)^2$
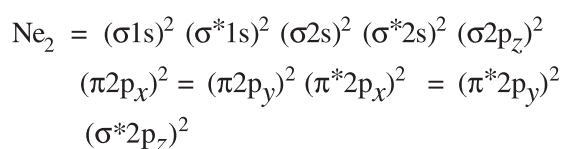
Bond order $= \dfrac{1}{2} \left[N_b - N_a \right]$

$ = \dfrac{1}{2} \left[10 - 10 \right] = 0$

Here, the value of bond order is zero. Hence, Ne_2 molecule is not possible.

1.15 The Energy Diagram, Bond Order, Stability and Magnetic Properties of Heteronuclear Diatomic Molecules like CO and NO

CO (carbon monoxide) molecule : CO is a heteronuclear diatomic molecule. Atoms of two different elements carbon and oxygen take part in its formation. There is difference in energy levels of atomic orbitals of carbon and oxygen atoms. As compared to carbon atom, the energy level of respective orbitals of oxygen atom is at lower level i.e. possess less energy. As a result it is more stable. Total fourteen electrons (six electrons of carbon atom and eight electrons of oxygen atom) are there in carbon monoxide molecule. These fourteen electrons are arranged in molecular orbitals obtained by combination of atomic orbitals of carbon and oxygen. It can be seen from the energy diagram of carbon monoxide that all the electrons in it are paired and so it is diamagnetic. The energy diagram of CO molecule is shown in Fig 1.7.
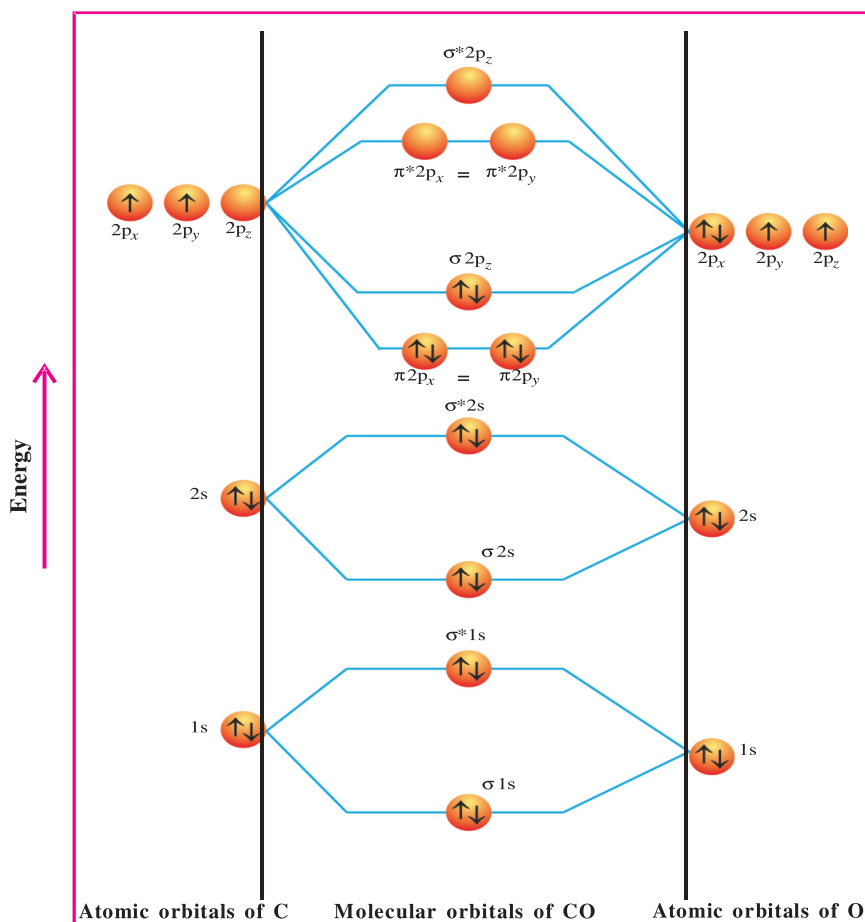
Fig. 1.7 Energy leval diagram of CO molecule

The arrangement of fourteen electrons present in carbon monoxide molecule, can be written in molecular orbitals as follows :

$$CO : (\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2 \ (\sigma 2p_z)^2$$

$$\text{Bond order} \ = \frac{1}{2} \left[N_b - N_a \right]$$

$$= \frac{1}{2} \left[10 - 4 \right]$$

$$= 3$$
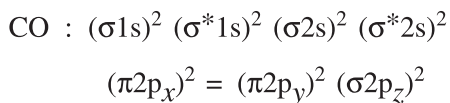
Hence, $C \equiv O$ will be in CO.

NO (Nitric oxide) molecule : NO is a heteronuclear diatomic molecule. Atoms of two different elements nitrogen and oxygen take part in its formation. There is difference in the energy of oxygen atom is less than corresponding to that of nitrogen atom.

There are total 15 electrons (seven electrons of nitrogen atom and eight electrons of oxygen atom). The arrangement of these 15 electrons can be made in molecular orbitals as shown in Fig 1.8.

The arrangement of electrons of NO molecule in molecular orbitals can be written as follows :

$$NO : (\sigma 1s)^2 \ (\sigma^* 1s)^2 \ (\sigma 2s)^2 \ (\sigma^* 2s)^2 \ (\sigma 2p_z)^2$$

$$(\pi 2p_x)^2 = (\pi 2p_y)^2 \ (\pi^* 2p_x)^1$$
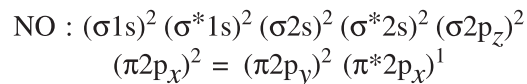
$$\text{Bond order} = \frac{1}{2} \left[N_b - N_a \right]$$

$$= \frac{1}{2} \left[10 - 5 \right] = 2.5$$

As there is one unpaired electron in NO molecule, it is paramagnetic and as the bond order is a fraction, NO molecule is unstable.

The electrons of 1s orbitals (inner shells) do not take part in formation of bond and so they are called non-bonding electrons.
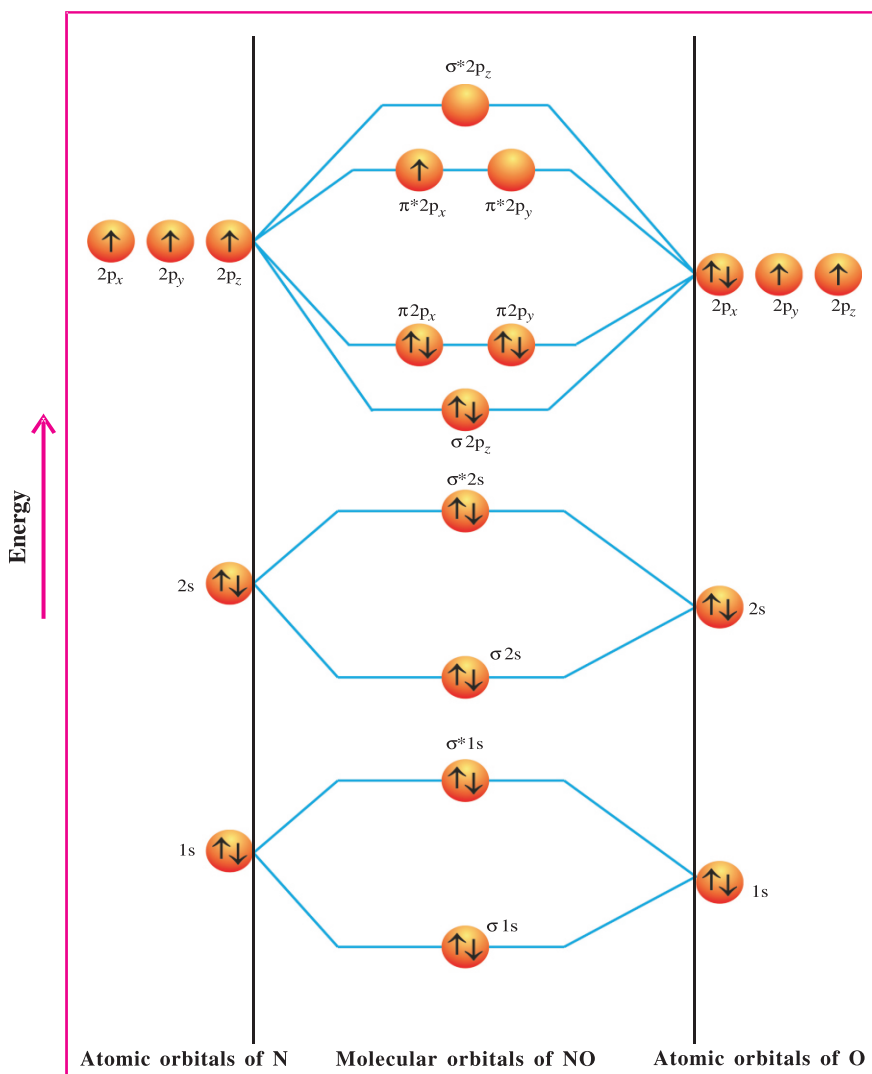
Fig. 1.8 Energy level diagram of NO molecule

1.16 Intermolecular Attraction Forces

Scientist van der Waals mentioned weak attraction force existing between molecule-molecule on the basis of the study of deviation from ideal behaviour of gas. The existence of this weak attraction force cannot be explained by any other chemical attraction force. It is called van der Waals attraction force. This phenomenon is universal. There is presence of van der Waals attraction force in components of ionic substances and also in components of covalent substances. As its dimension is very less about 42 kJ mole^{-1} in relation to other attraction force, it is mostly covered by other attraction forces. This attraction force prevails upto a very less distance about 4.5 $\overset{0}{A}$. The electrons on the surface of molecule experience attraction of nucleus of other molecule. Hence, van der Waals attraction force is produced. As the strength of this attraction force is different between molecules of different substances, the difference in melting points and boiling points of different substances is observed. The intermolecular forces depend upon the following factors :

(i) Shapes of molecules

(ii) Number of electrons in molecules

(iii) Contact surface of molecules

(iv) Average intermolecular distance

The study of these four factors can be understood from the molecule of nitrogen (N_2) and phosphorus (P_4) viz. At normal temperature, from amongst the elements of the same group nitrogen is in gaseous form while phosphorus is in solid form.

Hydrogen Bond : Nitrogen, oxygen and fluorine are strong electronegative elements. When such elements combine with hydrogen atom through covalent bond, the electrons combined by sharing in covalent bond remains dragged towards more electronegative element. Thus, partial positively charged hydrogen atom of one hydride forms strong attraction bond with more electronegative element of the other hydride which is called hydrogen bond (H-bond). Hydrogen bond is weaker than covalent bond. Thus, **the attraction force produced between electronegative elements having non-bonding electron pair with positively charged hydrogen atom is called hydrogen bond.**

Hydrogen bond is shown by dotted (.........) line. e.g. In molecule of HF, hydrogen atom of one molecule and fluorine atom of other molecule has formed H—bond shown as below :

$$\cdots\cdots \overset{\delta+}{H} \rule{1cm}{0.4pt} \overset{\delta-}{F} \cdots\cdots \overset{\delta+}{H} \rule{1cm}{0.4pt} \overset{\delta-}{F} \cdots\cdots$$

Here, hydrogen bond works as a bridge between two atoms in which it forms covalent bond with one atom and forms hydrogen bond with other atom. The hydrogen bonds in NH_3, H_2O and HF molecule can be shown as in Fig. 1.9

H-Bond in liquid NH$_3$

H-Bond in H$_2$O liquid

H-Bond in liquid HF
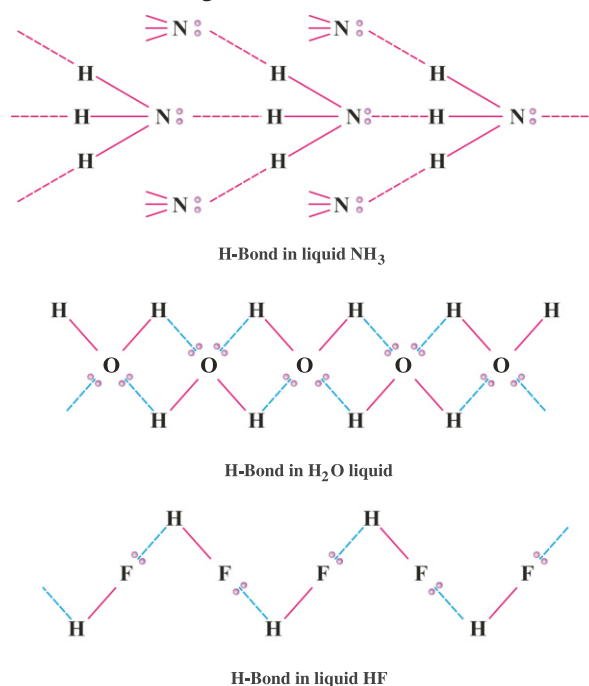
Fig. 1.9 Hydrogen bond

NH_3, H_2O and HF in their liquid states possess strong hydrogen bond. Hence their boiling points and melting points are very high in expectation to those of hydrides of other elements of the same group viz. the higher melting points and boiling points of hydrides of first elements of group 15, 16 and 17 (NH_3, H_2O, HF) support presence of hydrogen bond in them. The energy of hydrogen bond is about 40 kJmol^{-1}, which is higher than the van der Waals' forces.

The density of water is maximum at 277 K In the temperature interval of 273 K to 277 K the density of water being more than that of ice, ice floats on water. Ice is a solid crystal of water having hydrogen bond. The magnitude of hydrogen bond is maximum in solid state of a substance and is minimum in gaseous state of a

substance. The effect of hydrogen bond is observed on the structures and the properties of the compounds.

Importance of Hydrogen Bond :

(i) As hydrogen bond is formed in water, its evaporation is slow at normal temperature. Hence, water on the surface of the earth is retained in large proportion.

(ii) The storage of water in animal and vegetative cell is due to hydrogen bond.

(iii) Molecules of water forms hydrogen bond with components of the soil. Hence, the moisture is retained in the soil.

(iv) Hydrogen bond is formed in protein molecules in the muscles of living ones through amide (−CONH−) group. Hence, certain functions of muscles are due to hydrogen bond.

(v) The effectiveness of medicines increases and becomes faster due to hydrogen bond.

(vi) Hydrogen bond plays an important role in living cells of biochemical molecules in nucleic acid, DNA, RNA etc.

(vii) The clothes of synthetic fibres (nylon, terrylene etc) dry faster than cotton clothes because of hydrogen bond formation by water with cellulose of cotton clothes.
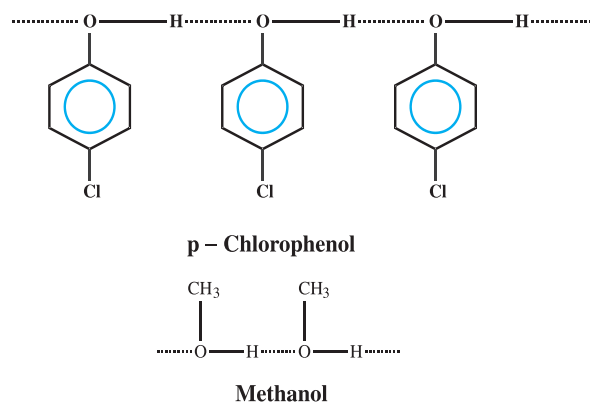
Types of Hydrogen Bonds :

Hydrogen bond is mainly of two types :

(i) Intramolecular Hydrogen Bond

(ii) Intermolecular Hydrogen Bond

If hydrogen bond is formed between atoms of same molecule, then that type of hydrogen bond is called intramolecular hydrogen bond. e.g.

o-Chlorophenol

Ethanediol
Ethane 1,2-diol
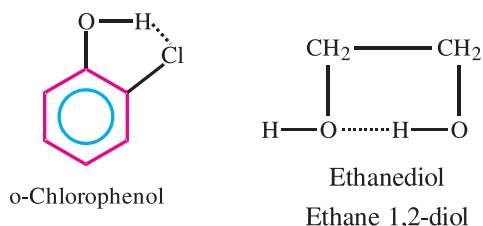
The hydrogen bond formed between two or more different molecules of the same compound is called intermolecular hydrogen bond. e.g.

p − Chlorophenol

Methanol

As the intermolecular hydrogen bond is formed with more than one molecules of the same compound, the number of such hydrogen bonds is more. As a result, the melting points and boiling points of such compounds are comparatively higher.

The intramoleaclar hydrogen bond is formed internally between atoms of the same molecule. As a result, the number of such hydrogen bonds is limited. Hence, the melting points and boiling points of the compounds having intramolecular hydrogen bond are relatively lower.

E.g. The boiling point of p-chlorophenol is higher than that of o-chlorophenol because intramolecular hydrogen bond is present in o-chlorophenol and intermolecular hydrogen bond is present in p-chlorophenol.

1.17 Concept of Metallic Bond

The less ionisation energy of metal indicates that metal atom has less attraction for valence electron. Also, it has less number of valence electrons (generally 1, 2 or 3) to form covalent bond. Hence, covalent bond between two atoms of metal is not formed. As a result, the directional property is not observed in metals. The valence electrons of atoms of metal are considered not specific for any nucleus but same for the whole crystal. These electrons are called delocalized electrons. The delocalized electrons can change their positively charged kernel (positively charged part of the atom with the nucleus except valence orbit). This can be described as positively charged sphere in the delocalized electron cloud. According to Laws of Electrostatics, the atomic kernel being positively charged, there must be repulsion between each other. Even then, the atomic kernel arranged very near to each other. The attraction between

atomic kernel and the delocalized electrons keep the atomic kernels together. The attraction between positively charged atomic kernel and the delocalised electrons arranged around it is the metallic bond. It makes the arrangement in such a way that atomic kernel can be accommodated in least possible space and also keeps parallel distance between each pair of spherical atomic kernel of any two nearby kernels.

The explanation of metallic bond can be given with the help of Electron Sea Model. According to this model, the metal crystal is considered as sea of delocalised valence electrons. The positively charged kernel is imagined to be floating in it. They are arranged near to each other. Because of the presence of delocalised electrons between such positively charged kernels, these delocalised electrons possess very strong attraction forces with positively charged kernels. Such an attraction force is called metallic bond. All the electrons which are delocalised, have attraction between electron sea and positively charged kernel.
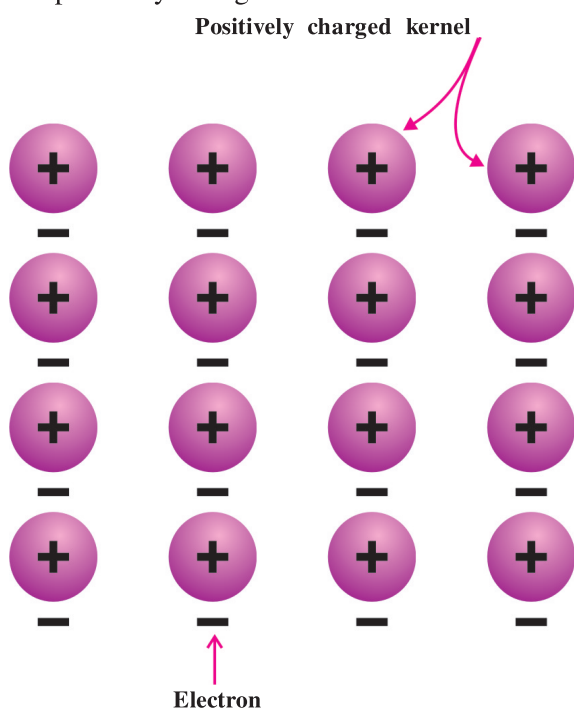
Positively charged kernel

Electron

Fig.1.10 Electron - Sea model of metallic bond.

1.18 Co-ordinate Covalent Bond

Co-ordinate covalent bond is one type of covalent bond. In the formation of covalent bond,

the atoms combining with bond give same number of electrons for sharing. e.g. H_2 molecule. But sometimes the electron pair required for sharing in the formation of molecule/ion, one of the atoms from the combining atoms donates the electron pair and bond is formed. The sharing of the electrons in this type of bond formation is called covalent bond. But the electron pair required for sharing are donated by atom of only one element, special type of covalent bond is formed which is called **co-ordinate covalent bond.** This bonding is expressed by the sign of arrow $(\rightarrow)$ and the direction of arrow is from the atom donating the electron pair towards the atom receiving the electron pair.

Generally, the molecules having one or more non-bonding electron pairs form this type of bond by donating electron pair. Thus, this type of bond is formed between completely vacant orbitals of the atom of the element and atoms possessing non-bonding electron pairs by sharing the electrons easily.

(1) e.g. In NH_4^+ ion, there are three covalent and one co-ordinate covalent bonds.

$$NH_3 + H^+ \longrightarrow NH_4^+$$

$$NH_4^+$$
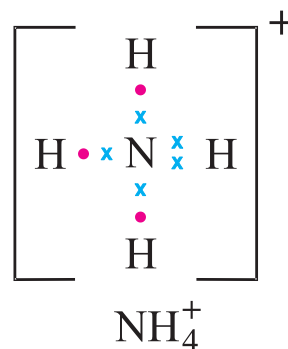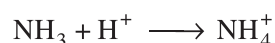
1.19 Hybridisation in BeH_2, BCl_3, CH_4, PCl_5, SF_6, by s, p and d Orbitals

The information of hybridisation in BeH_2, BCl_3, CH_4, PCl_5, SF_6 etc. through s, p and d orbitals is included in the table 1.3.

molecule ... ncepts like ... orbital theory ... orbitals around the ... think ab... ... the atom ... Als... ... stab... ...ioned ... called ... their ... e bond ... The b... ...edral. Y... covalent ...rds th... ...tom an... on elec... ...re s... electron... wo... than... te cova... com... ...tro... in ato... co... bond... he stab...ty a... ...red to... y may... ...rmation order... ...nav... and... the e... ...d in... ...es of... eaction ...f... Na... po... led...

by Nyholm and Gillespie and they proposed certain assumptions. In this it is important to note that when non-bonding electron pairs are there, then they show deviation in geometrical structure and bond angle due to repulsion between electron pairs. e.g. Molecule of water has sp^3 hybridisation and so its bond angle must be $109^0 28'$ but it becomes $104^0 30'$ due to repulsion by two non-bonding electron pairs. Hence, it is called distored tetrachedral. The polarity of bond is a vector quantity. Hence, if a polar bond is formed due to difference in electronegativities but another bond of the same type is formed in its opposite direction, then polar bond will be formed but the resultant polarity of the molecules becomes zero and molecule will be non-polar.

e.g   F ⟵₊ Be ₊⟶ F   or
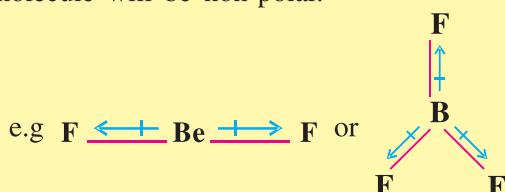
The dipole momentes of polar substances can be calculated for which both the charges $+\delta$ and $-\delta$ and the distance between them is to be utilised. More the value of dipole moment, more will be the polar bond and more will be the ionic bond. One important aspect is that polar substances dissolve only in polar solvents and non-polar substances dissolve in nonpolar solvents. e.g. NaCl will dissolve in water. Napthalene will dissolve in benzene. New hypotheses have been presented affter taking into consideration the limitations of the principles for the approach of covalent bond. Two are main from them : (1) Valence Bond Theory and (2) Molecular Orbital Theory. These concepts are based on quantum mechanics. Heitler and London first of all gave the idea of valence bond theory and it was developed by Pauling and Slater.

In the assumptions of valence bond theory the attraction - repulsion forces between positively charged nuclei of two atoms and the electrons arranged in the orbits around them. According to Coulomb's Law if attractive forces are more than repulsive forces then the bond will be formed and molecule will be formed. In this theory, on the basis of the overlapping of valence orbitals different overlaps can be formed. In this type of overlapping the excitation of electrons in valence orbitals can be shown and then formation of molecule by covalent bond with other atoms. viz. In carbon, the electrons of valence orbital $1s^2 2s^2 2p^2$ will be excited to give $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$ containing four orbitals with one electron in each and four hydrogen atoms, and hence will give stable molecule like CH_4. The geometrical structure, and bond angle can be expressed from the hybridisation associated with it. In such valence bonds, two types of bonds–σ and π are also observed. σ bond is a covalent bond; it attains axial overlap of internuclear axis. The stability of this bond is more than that of π bond. In the π–bond the axis of the atomic orbitals undergoing overlapping remains parallel to each other and is perpendicular to internuclear axis. $\pi-$ bonds are less stable in comparison to σ–bonds or they are weaker. Valence bond theory is based on overlapping of valence orbitals. It explains properties like the geometrical shapes, the bond angle etc. very simply but cannot explain magnetic properties.

Scientists Mulliken and Hund suggested molecular orbitals like atomic orbitals and proposed molecular orbital theory. Amongst its important points, the idea that atomic orbitals can also form molecular orbitals was taken into consideration. As many atomic orbitals take part in the formation, same number of molecular orbitals, their energy, symmetry etc. were taken into consideration. The formation of these types of atomic orbitals can be shown in the formation of homonuclear molecules like H_2, Be_2, F_2 etc. and heteronuclear molecules like CO, NO etc. Molecular orbitals are formed by linear combination of atomic orbitals–LCAO principle. On the basis of these types of combination

two types of molecular orbitals are formed which are known as Bonding Molecular Orbitals (BMO) and Anti-Bonding Molecular Orbitals (ABMO). In the formation of rules these types of BMO and ABMO the principles like Hund's rule of maximum spin, Pauli's exclusion principle, Aufbau principle etc. which are applicable in formation of atomic orbital are also obeyed and maintained. In the unit the molecular orbital diagrams of construction of molecular orbitals from the atomic orbitals for formation of homonuclear molecules from H_2 to Ne_2 elements as well as for formation of heteronuclear molecules like CO, and NO are shown. From these diagrams, important property like bond order can be calculated. Bond order

$= \dfrac{1}{2}$ {electron in bonding molecular orbitals − electrons in anti−bonding orbital} viz. for N_2

molecule bond order $= \dfrac{1}{2} (10-4) = 3$ i.e. there will be triple bond $N \equiv N$. In the same

way, in NO molecule bond order will be $= \dfrac{1}{2} [10 - 5] = 2.5$. Here, we will note that if the value of bond order becomes zero, the bond will not be formed e.g. He_2. If the value of bond order is integer, the bond will be formed and according to the integer 1, 2, or 3, there will be single (−), double (=) or triple (≡) bonds respectively. If the value of **bond order is fraction, then molecule will attain unstable structure.** The molecular orbital theory can explain the magnetic properties e.g. In O_2 molecule two unpaired electrons are there and so it is paramagnetic and in N_2 molecule, all the electrons are paired and so it is diamagnetic. Thus molecular orbital theory is superior to valence bond theory in this matter.

Above this, one important phenomenon is hydrogen bond. The first element of 15, 16, and 17, groups N, O, F being higer electronegative than the other elements of the group it can form covalent molecules like NH_3, H_2O and HF with hydrogen. Afterwards the molecule like H————F ············· H————F combines with each other H − F molecule through hydrogen bond H————F ············· H————F where H .... (dotted line) indicates hydrogen bond formation. HF, NH_3, H_2O possess hydrogen bonds and so their properties are different from those of other elements in the group. Hydrogen bond is of two types (1) Intermolecular and (2) Intramolecular hydrogen bonds. When hydrogen bond is formed between two molecules it is called intermoleculer hydrogen bond e.g. p-chlororphenol and between two groups in the same molecule, it is called intramoleculer hydrogen bond e.g. o-chlorophenol. Intermolecular hydrogen bond is stronger than intramolecular hydrogen bond. The presence of hydrogen bond is the reason for specific properties of the compounds. Viz the retaining of water in the soil, drying of terrylene clothes is faster than that of cotton clothes.

After knowing about ionic bond, covalent bond, co-ordinate covalent bond, we shall study the special type of bond present in metals which is called metallic bond. As there are 1, 2 or 3 electrons in the outermost orbit of the metals, they are not able to form covalent bonds. Their ionisation energy is less and attraction of electron towards the nucleus is less. One, two or three electrons are arranged around the nucleus of the atom. Hence, the positively charged nucleus or kernel is there. The electrons around it have attraction towards other nuclei of the atoms in the lattice. Thus, the electron instead of being localised for any one atom, remains delocalised in the whole metal crystal. For this theory Electron Sea model was proposed. In this, the atomic kernel is imagined as floating in the sea, delocalised electrons are arranged around kernel possessing positive charge. Because of this type of metallic bonds, the specific properties of metals, like density, ductility, malleability etc. are different.

Co-ordinate covalent bond is a type of covalent bond as seen earlier. The characteristic in it is that from the two atoms undergoing sharing of electrons, only one of the atoms provides a pair of electrons, and is shared by both the atoms. Hence, it is called co-ordinate covalent bond. e.g. In BF_3, three F atoms were bonded with B-atom through three covalent bonds but the octet of B is not complete. Similary in NH_3 molecule, three H atoms are bonded with N through three covalent bonds. But N has one non-bonding pair of electrons, which it gives to BF_3 molecule and is shared by both the molecules. Hence $F_3B \leftarrow NH_3$ Co-ordinate covalent bond is formed. In this, the molecule which gives pair of electrons is shown by arrow $(\rightarrow)$ from the molecule which donates it towards the molecule or atom which accepts and shares gained electron pair. You will study more about co-ordinate covalent bond in the unit of complex salts in Standard-12.

EXERCISE

1.   **Select the proper choice from the given multiple choices :**

(1)   Mention the relationship between bond order and stability of a compound ?

(A) Directly proportional   (B) Inversely proportional

(C) Equal   (D) Opposite.

(2)   Which type of the bond from the following is obtained by combination of the ions of strongly electropositive and strongly electronegative elements ?

(A) Ionic   (B) Covalent

(C) Co-ordinate covalent   (D) Metallic

(3)   In which of the following compounds the rule of octet is not obeyed ?

(A) CH_4 (B) PCl_5 (C) NH_3 (D) H_2O

(4)   Which from the following is the magnetic property of oxygen molecule on the basis of valence bond theory ?

(A) Diamagnetic   (B) Paramagnetic

(C) Ferromagnetic   (D) Antiferromagnetic

(5)   Which from the following is the magnetic property of oxygen molecule on the basis of molecular orbital theory ?

(A) Diamagnetic   (B) Paramagnetic

(C) Ferromagnetic   (D) Antiferromagnetic

(6)   Who presented the valence bond theory ?

(A) Linus Pauling   (B) van der Waals

(C) Mulliken   (D) Heitler and London

(7)   Who presented the molecular orbital theory ?

(A) Linus Pauling   (B) van der Waals

(C) Lewis   (D) Mulliken

(8)   The water on the surface of the earth is mostly retained, the reason for which is

(A) Density of water is 1.0 gml^{-1} (B) Hydrogen bond is present in water

(C) Water is neutral   (D) Water is used in large proportion

(9)   Which type of bond is observed in p-chlorophenol ?

    (A) Intermoleculer hydrogen   (B) Intramoleculer hydrogen

    (C) van der Waals   (D) Metallic

(10) Which of the following molecular orbitals possess minimum energy ?

    (A) $\sigma 2p_z$ (B) $\sigma 1s$ (C) $\sigma 2s^*$ (D) $\pi 2p_x$

2.   Answer the following questions in brief :

(1)   Write Lewis structures of following molecules/ions :

    BeF_2, PH_4^+

(2)   Write the rule of Octet.

(3)   Write resonance structures of NO_3^- ion

(4)   Mention types of hydrogen bond.

(5)   Give the values of bond angles of molecules of CH_4 and NH_3.

(6)   What is the value of bond order in H_2 molecule ?

(7)   On what depends the strength of hydrogen bond ?

(8)   Metals are good conductors of heat and electricity. On which type of bond does this property of metals depend ?

3.   Answer the following questions :

(1)   Explain with suitable example, the formation of polar and non-polar covalent bonds.

(2)   Explain co-ordinate covalent bond.

(3)   Give definitions : Lattice enthalpy, Enthalpy of formation.

(4)   Give Lewis structures of PCl_5, NH_4^+ , SF_6, H_2SO_4.

(5)   Give explanation of σ and π bonds. Mention by overlapping of which orbitals are σ and π bonds formed ?

(6)   Mention the condition for linear combination of atomic orbitals

(7)   Write the relative order of moleculer orbitals for homonuclear diatomic molecules H_2 to N_2 and O_2 to Ne_2 .

(8)   Explain the calculation of bond order in Be_2 molecule on the basis of molecular orbital theory.

(9)   Explain the factors affecting the intermolecular attraction forces.

(10) Mention importance of hydrogen bond.

4.   Answer the following questions :

(1)   Write a note on Kossel-Lewis approach for chemical bonding.

(2)   Explain bond angles of CH_4, NH_3, and H_2O molecules on the basis of VSEPR principle.

(3)   Explain polarity of bonds in NH_3 and NF_3 molecules.

(4)   Give explanation of LCAO with example.

(5)   Give explanation of bond order and magnetic property of O_2 molecule by drawing its energy level diagram according to M. O. theory.

(6) Give explanation ... and order ... drawing its molecul... rbital en...

(7) Write short note o... ...ermolecu...

(8) Give brief account ... metallic b...

(9) Justify the followin... statements

(i) The clothes of ... ...h dry fa...

(ii) The b... ...nt of ...chlorophenol is ... ...p-chlorophenol...

(iii) Amongst ... ...H$_2$S... ...only H$_2$O is obtained in ...

(iv) O$_2$ molec... ...par... ...c.

(v) σ−bond is ... ...er ... ...bond.

Do you know ... ...ulla... ...ndra Ray

...la ...ndra Ray was born on A... in the ...lace Rada... of East Bengal. He ob... educat... ...n the p...imary school of his vill... life sketc... ...ome scientists, New... Fra...lin, durin... ...s young age. He... ...t... England ... 1882 and s... ...Edin...urgh University. Af... in 1887 he obtained the D... ...ic Chemist... He work... ...ed to

1888 ... ...ined the Calc... ...ide... ...e studied ...r...poun...s. He was award... ...prestigious hon... ...te' by Prof. ...r...g because of his research work on nitrite compounds. In ...11, he became ...p... After some years be retired from the post of professor ... ...inued ... ...k. As a result ...f this he prepared an unstable su... ...oratory. The ... scientists of the world were ast... ...ote a book ... ...story of Indian Chemistry' with a pur... ...ay be aware of ... ...ent Indian chemistry. This book was ... After fifteen years, he published the second part of thi... given important ... ntribution in the devlopment of ch... Dr. Ray was ... ...covery of mercury nitrate and pr... above he ... ...d a series of compounds of m... ...chlori... ...ry in 19...