3

THEORIES OF COVALENT BONDING AND SHAPES OF MOLECULES

After completing this lesson, you will be able to:

This is 12 days lesson
(period including homework)

- Describe the features of sigma and pi bonds.
- Describe the change in bond lengths of hetero-nuclear molecules due to difference in electronegativity values of bonded atoms.
- Describe the difference among molecular, network and metallic solids.
- Explain what is meant by the term ionic character of a covalent bond,
- Use VSEPR and VBT theories to describe the shapes of simple covalent molecules.
- Describe the shapes of some molecules using orbital hybridization.
- Predict the molecular polarity from the shapes of molecules.
- Determine the shapes of some molecules from the number of bonded pairs and lone pairs of electrons around the central atom.
- Define bond energies and explain how they can be used to compare bond strengths of different chemical bonds.
- Describe how knowledge of molecular polarity can be use to explain some physical and chemical properties of molecules.

INTRODUCTION

In this chapter we will discuss the shapes of molecules on the theoretical basis and some factors affecting their shapes and behaviours. We start by describing the VSEPR (valence shall electron pair repulsion) model, which allows us to connect two dimensional Lewis structures into three dimensional shapes.

You will see how molecular shape and bond polarity combine to create a polarity for the entire molecules and how molecular shape influences biological function. Then we consider two bonding theories based on quantum mechanics. Valence bond theory explains how the observed shape arises from the interactions of atomic orbitals. Molecular orbital theory proposes the existence of orbitals that extend over the whole molecule.

The Lewis concept of formation of covalent bond as a shared pair of electrons between two atoms does not explain shapes of molecules. Similarly, many other properties such as bond energy, relative strengths of bonds, and paramagnetism cannot be explained on the basis of this concept. However, modern theories of chemical bonding not only explain most of our experimental observations, but also allow us to predict the shapes and geometries of molecules. These theories can also be used to predict many physical and chemical properties of molecules.

3.1 SHAPES OF MOLECULES

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The shapes of molecules can be predicted by Valence Shell electron pair repulsion (VSEPR) theory.

This theory was suggested by Sidgwick and Powell (1940). According to this theory, the shapes or geometry of a molecule or ion depends on the number of shared pairs as well as the lone pairs of electrons around the central atom of the molecule or ion.

Gillespie and Nyholm in 1957 proposed that the arrangement of atoms in a molecule is mainly determined by the repulsive interactions among all electron pairs in the valence shell of central atom.

Postulates of VESPR Theory

The postulates of VSEPR theory are as follows:

1. The electron pairs present around the central polyvalent atom are arranged in space as far apart as possible so that, there is minimum repulsion between them.
2. A non-bonding pair or lone pair of electron occupies more space on the surface of an atom than a bonding pair.
3. Both the lone pairs as well as bond pairs determine the geometry of the molecules.
4. The magnitude of repulsion between the electron pairs in a given molecule decreases in the following order.
   Lone pair – Lone pair > Lone pair - Bond pair > Bond pair - Bond pair
   A Lone pair causes deviation from ideal bond angles, which in turn change regular geometry.
5. The two electron pairs of a double and three electron pairs of a triple bond contain a higher electron charge density. Therefore, they occupy more space than one electron pair of a single bond. However they behave like a single electron pair in determining the geometry of the molecules.

Applications of VSEPR Theory

The molecules and ions will be classified according to the number of electron pairs present in them, irrespective of the fact whether they are of bonding or nonbonding type. In order to illustrate this theory, consider hypothetical molecules having central atom "A" with more than one "B" type atoms bonded with it. Lone pair if present in the molecules is represented by "E".

(a) Shapes of molecules containing two electron pairs around a central atom. AB_2 Type

A molecule having two bond pairs of electrons but no lone pair around a central atom always has a linear geometry, because such an arrangement of atoms keeps the two pairs as far as possible. The bond angle will be 180°.

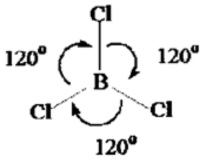
$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot \times Be \times \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \quad \text{or} \quad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\text{——}Be\text{——}\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

(b) Shapes of molecules containing three electron pairs around a central atom. AB_3, AB_2E Type

(i) AB_3 type with no lone pair

A molecule having three bond pairs of electrons but no lone pairs around a central atom always has a planar triangular geometry, because such an arrangement of atoms keeps the three pairs of electrons as far apart as possible. The bond angle will be 120°.

Example: (BCl_3)

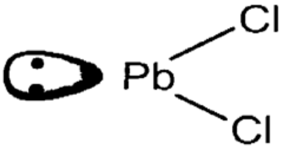


Boron trichloride (BCl_3) is a typical example of molecules, which contains three bond pairs of electrons. BCl_3 has trigonal planar shape. The bond angles will be 120° each. Other examples of this type are: $AlH_3, AlCl_3, GaH_3, InH_3$

(ii) AB_2E – type with one Lone pair and two bond pairs

Examples: $PbCl_2$ molecule

$SnCl_2$ molecule

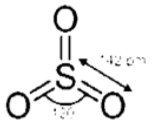


V. shaped $PbCl_2$ molecule

In case of $PbCl_2$ and $SnCl_2$ molecules, there are three electron pairs around the central atoms, one lone pair and two bond pairs. According to VSEPR concept the lone pair (non-bonding) of electron occupies more room and exerts a greater repulsion on the bond pairs resulting in the shortening of Cl-Pb-Cl angle. Thus, the shape of $PbCl_2$ molecule is distorted and becomes angular or V-shape with Cl-Pb-Cl bond angle less than 120°.

(iii) AB_3 type with multiple bonds

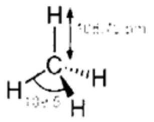
Examples: SO_3



In SO_3, all the three regions are occupied by S — O bonds. There is no lone pair hence the structure will be perfectly triangular having 120°.

(c) Shapes of molecules containing four electron pairs around a central atom AB_4, AB_3E & AB_2E_2 Type.

(i) AB_4 type with no lone pair

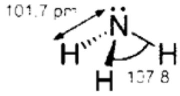


A molecule having four bond pairs of electrons but no lone pairs around a central atom always has regular tetrahedral geometry, because such an arrangement of atoms keeps the four pairs of electrons as far apart as possible. The bond angle will be 109.5°. The atoms are at the four corners of a regular tetrahedron.

Examples: CH_4 (Methane), CCl_4, SiF_4, $SnCl_4$ etc.

Methane is a typical example of this type.

(ii) AB_3E type with one lone pair and three bond pair



A molecule having three bond pairs and a lone pair around the central atom has triangular pyramidal geometry instead of tetrahedral. Due to repulsions between lone pair and bond pairs, the bond angles are reduced to 107.5° instead of 109.5°.

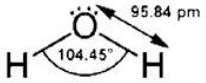
Example: NH_3 is a typical example.

Other examples: PH_3, AsH_3, SbH_3, etc.

(iii) AB_2E_2 type with two Lone pairs and two bond pairs

In this case, presence of two lone pairs, introduces three types of repulsions i.e. lone pair-lone pair, lone pair-bond pair and bond pair – bond pair.

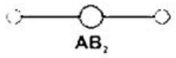
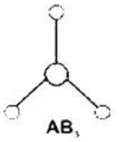
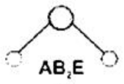
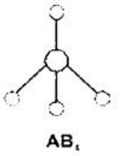
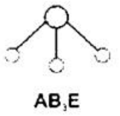
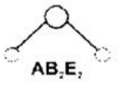
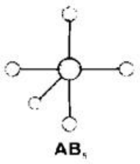
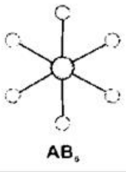
Example: H_2O, H_2S etc.



VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pair in addition to bond pairs in determining overall geometry of water molecule. Two of the corners of a tetrahedron are occupied by each of the two lone pairs and remaining by bond pairs. But due to spatial arrangement of lone pairs and their repulsion among themselves and with the bond pairs, the bond angle is further reduced to 104.5° and geometry becomes V shaped.

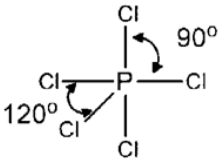
Table 3.1: Bonding and the shape of Molecules

Table 3.1: Bonding and the shape of Molecules

Number of Bond pairs	Number of Lone pairs	Total Number of Electron pairs	Molecular Shape	Examples	Ball-and-Stick Models
2	0	2	Linear	BeCl$_2$ HgCl$_2$ CO$_2$	
3	0	3	Triangular	BF$_3$ AlBr$_3$ CH$_2$O	
2	1	3	Bent	SO$_2$, O$_3$	
4	0	4	Tetrahedral	CH$_4$ CBr$_4$ SiCl$_4$	
3	1	4	Pyramidal	NH$_3$ PCl$_3$	
2	2	4	Bent	H$_2$O H$_2$S SCl$_2$	
5	0	5	Trigonal bipyramid	PCl$_5$	
6	0	6	Octahedral	SF$_6$	

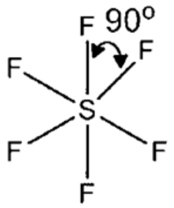
(d) Molecules containing five electron pairs AB_5 – type

With the increasing number of electron pairs, it becomes increasingly difficult to visualize the true shapes of the molecules. Thus a central atom containing five electron pairs presents a more complicated system. A trigonal bipyramid arrangement – represents a structure in which five electron pairs can have minimum repulsion. In PCl_5, there are five electron pairs in the valence shell of phosphorus atom. All of them are bonding pairs and thus PCl_5 molecule adopts trigonal bipyramidal structure.



(e) Molecules containing six electron pairs (AB_6 – type)

Molecules, in which the central atom has six electron pairs, adopt octahedral geometry. The examples of such molecules are SF_6, SeF_6, TeF_6.



Prediction of shape of molecules:

The following steps are generally required to predict geometrical shape by VSEPR-method.

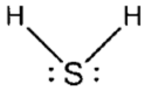
1. Draw dot diagram for the molecule.
2. Determine the number of valence electrons surrounding the central atom.
3. Determine the number of bond pairs and lone pairs of electrons.
4. Determine the geometrical distribution of electron pairs so that they are as far apart as possible.

Example:

Predict the shape of H_2S.

Solution:

Valence electrons of S-atom = 6
Electrons contributed by 2H-atoms = 2
Total no. of electrons around S-atom = 8
Electron pairs = 4
Bond pairs = 2
Lone pairs = 2



Thus H_2S is AB_2E_2 type molecule. It will possess V-shaped geometry

3.2 THEORIES OF COVALENT BONDING

There are two theories which are used to understand the nature of covalent bond.

(i) The Valence bond theory (VBT)
(ii) The Molecular orbital theory (MOT)

3.2.1 The Valence Bond Theory (VBT)

This theory was proposed by Heitler and London (1927) and later on developed by Pauling. This concept is based on wave – mechanical treatment of molecules and has been successful in explaining the bond energies, bond lengths and shapes of covalent molecules.

According to valence bond theory, a covalent bond between two atoms is formed when the atoms come so close that a partially filled atomic orbital of one atom overlaps with a partially filled atomic orbital of the other. The two overlapping atomic orbitals retain their identity. The term overlap means that the two orbitals share same common region in space.

Postulates of VBT:

1. A bond between two atoms is formed by the overlap of half filled atomic orbitals of two atoms. The two overlapping atomic orbitals retain their identity.
2. The two overlapping orbitals must have electrons of opposite spin.
3. The number of bonds formed by an atom is equal to the number of unpaired electrons present in the valence shell of the atom.
4. If only two orbitals overlap, a single bond is formed. If additional orbitals of atoms overlap then multiple bonds are formed.
5. In order to form a bond, the overlapping orbitals must have the same symmetry with respect to the bond axis.

   "A line joining the nuclei of two bonded atoms is called bond axis"
6. In overlapping of orbitals energy is released. The greater the overlap between the orbitals, the greater is the energy released and the stronger will be the bond formed.

Types of overlapping and nature of covalent bonds

There are two main types of covalent bonds which are obtained by overlapping. These are:

- Sigma bond (σ)
- Pi Bond (π)

Sigma bond (σ)

"Any first bond formed between two partially filled atomic orbitals by head on overlap is called sigma bond"

In a sigma bond, the region of highest electron density is symmetrically distributed around the bond axis. The probability of finding the electron is maximum in the region between the two nuclei. The first bond formed between any two atoms is the sigma bond. All single covalent bonds are sigma bonds (σ) and the electrons occupying a bond are called σ electrons.

A sigma bond is formed by the overlapping of the following types as shown in figure 3.1.

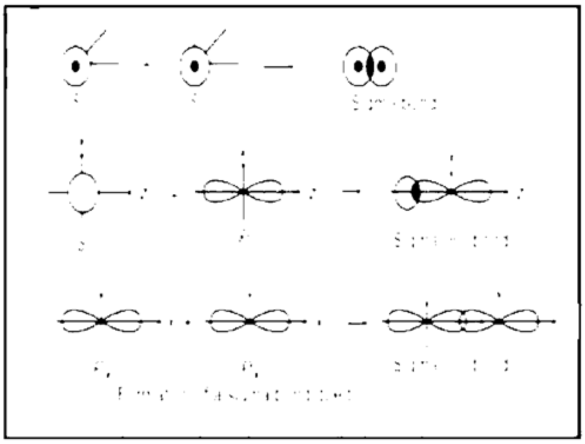


Figure 3.1: Formation of Sigma bonds

Pi (π) bond

"A bond formed between two already σ bonded atoms by the sidewise overlap of their two half filled p-atomic orbitals whose axes are parallel is called a Pi (π) bond.

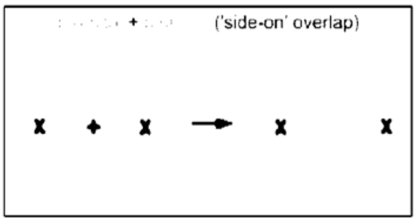


Figure 3.2: A Side wise view of overlap of p_y - p_y orbitals in formation of π bond

In the formation of pi bond, the two overlapping p-orbitals must be coplanar and their axes must be parallel. The electron density in this bond is unsymmetrical around the bond axis.

The probability of finding the electron is maximum in the region above and below the line joining the two nuclei. The overlap of p-orbitals in pi bond formation is not as good as in sigma bond. A pi bond is weaker than a sigma bond. One or two pi bonds can form between any two atoms already bonded covalently.

π bond is formed by side wise or lateral overlap between two p-orbitals which have their lobes perpendicular to the molecular axis. The side wise overlap is not too efficient, so result is a weak bond. **That's why sigma bond is always stronger than a pi bond.**

Remember:

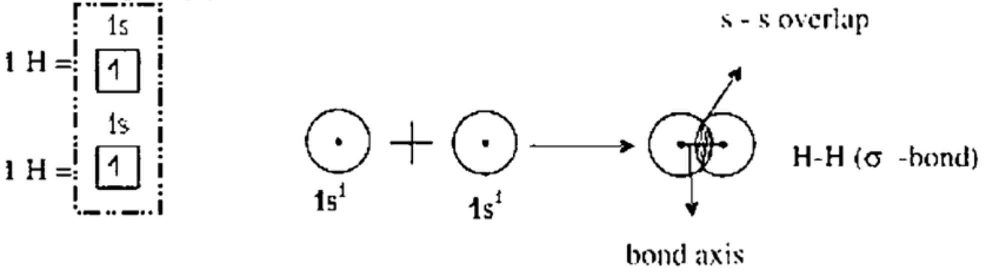
a) In case of pi bond formation which is over a covalent bond, the electron density is greatest above and below the line joining the two nuclei and this is also called nodal plane.
b) Only pure, parallel, co-planar, half filled p-orbitals on adjacent atoms can form a π bond.
c) Only one bond in any multiple bonds can be a sigma bond, the remaining bonds are pi bonds.
d) In case of hybridization, the overlapping of any hybrid-orbitals always produces a sigma (σ) bond.

Applications of Valence bond Theory

Single Bond Formation

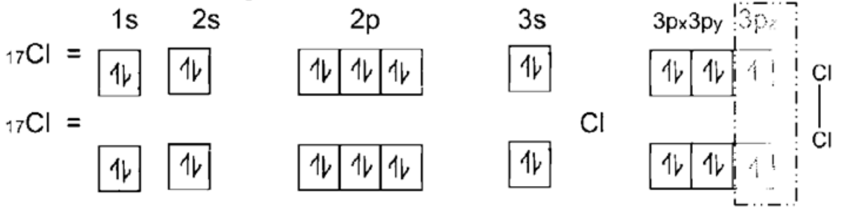
a) Formation of H_2 molecule

Each H atom has the electron configuration $1s^{\uparrow}$. As two hydrogen atoms approach each other, their half filled 1s orbitals overlap, giving H-H bond. The overlap of orbitals provides a means for sharing electrons, thereby allowing each 1s to complete its valence shell. The electron density is concentrated in the region along the line joining the two nuclei. The bond formed is a sigma (σ) bond.



b) Formation of Cl_2 molecule

The electronic configuration of chlorine is:



Each Chlorine atom has one half-filled $3p_z$ orbitals. On the basis of VBT, sigma bond is formed between two Cl atoms by head on overlap of half-filled $3p_z$ atomic orbital of each chlorine atom.

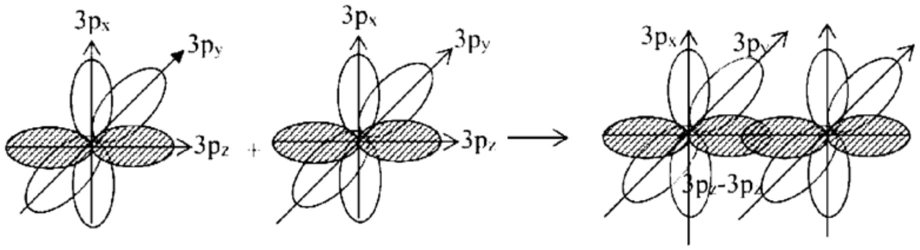


Figure 3.4: Orbital diagram of Cl_2

c) Formation of HF molecule

The electronic configurations of F and H atoms are:

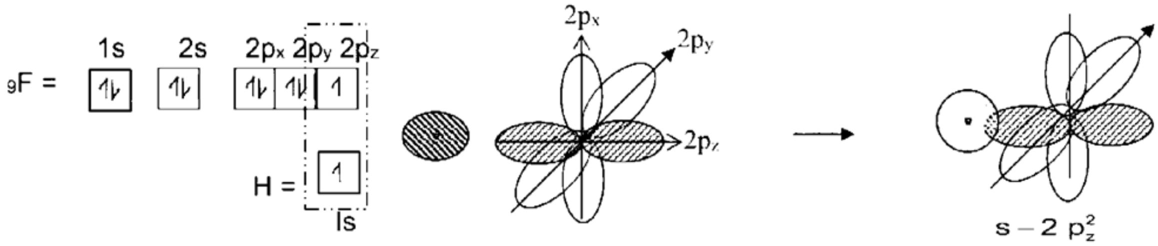


Figure 3.5: Orbital diagram of HF

In the formation of HF molecule, the half-filled 1s orbital of H atom overlaps with the half-filled $2p_z$ orbital of F to form σ bond.

Multiple bond formation

a) Formation of O_2 molecule

Oxygen molecule, O_2 is obtained by the combination of two oxygen atoms. Electronic configuration of an oxygen atom is:

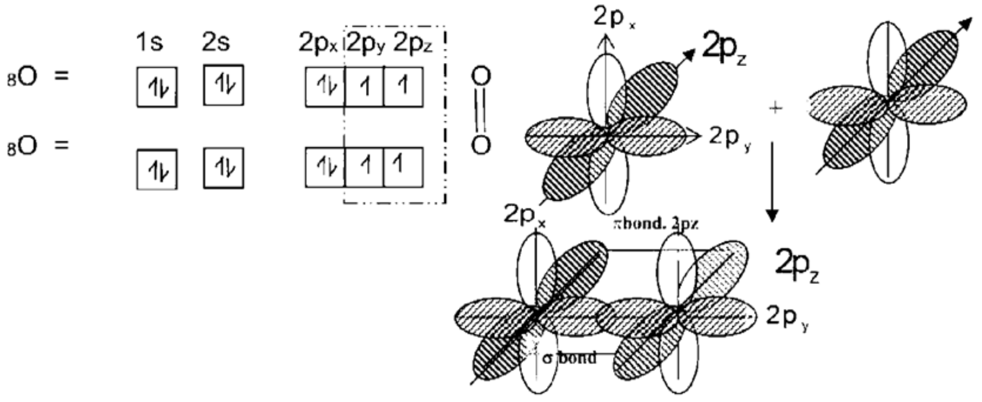
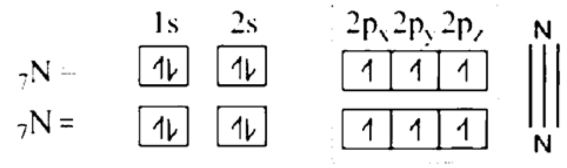


Figure 3.6: Orbital diagram of O_2

Each oxygen atom has two half-filled 2p orbitals in the valence shell. On the basis of VBT two covalent bonds can be formed between two O atoms. One bond is formed by the end-to-end overlap of half-filled $2p_x$ orbitals on each oxygen atom. This gives a σ bond. The second bond is formed by the side-to-side overlap of half-filled $2p_y$ orbitals on each oxygen atom. This gives a π bond. Thus a double bond is formed between two oxygen atoms. One is σ bond while the other is π-bond.

b) Formation of N_2 molecule:

Nitrogen molecule, N_2 is formed by the combination of two N atoms. The electronic configuration of N atom is:



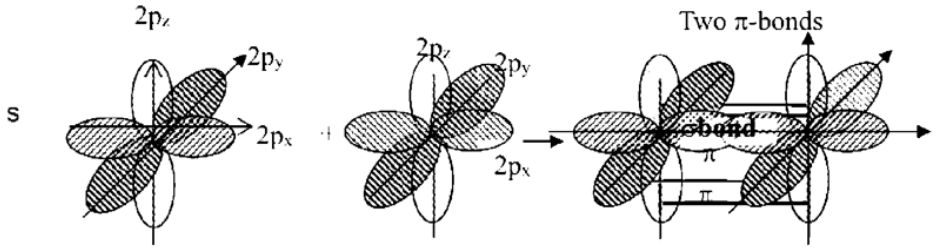


Figure 3.7: Orbital diagram of N_2

Each N atom has three half-filled p orbitals. On the basis of VBT, three covalent bonds can be formed between two nitrogen atoms. When the two nitrogen atoms approach each other, their $2p_x$ orbitals undergo end-to-end overlap, giving a σ bond. The end-to-end overlapping brings the two nitrogen atoms so close together that their parallel 2p orbitals undergo side-to-side overlap to produce two pi bonds. Note that each π bond is in two separate regions surrounding a σ bond. There are five distinct regions of electron charge density in the nitrogen molecule.

i. The σ electrons between the nuclei forming a σ bond.
ii. The π electrons above and below the σ electrons forming a π bond.
iii. The π electrons in front of and behind the σ electrons forming another π bond.

Thus a triple bond is formed between two nitrogen atoms; one is σ bond while the other two are π bonds.

Hybridization of Atomic Orbitals

Valence number shown by any element generally corresponds to the number of partially filled (half-filled) orbitals in an atom of that element. However this is not always the case because if only the unpaired electrons in an atom were permitted to form bond, e.g. beryllium whose electronic configuration is $1s^2\ 2s^2$ would be inert. Boron which has the electronic structure $1s^2\ 2s^2\ 2p_x^1$ would have a valency of one and carbon ($_6C$) with the electronic configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ would show a valency of two. In actual practice, beryllium shows a valency of two, boron has a valency of three and carbon has a valency of four.

Pauling and Slater resolved this discrepancy by introducing the concept of orbital hybridization which involves mixing of the pure s and p (one or more) orbitals of an atom to form new hybrid orbitals, before the bonding process takes place. The number of hybridized orbitals are equal to the number of atomic orbitals overlapped. A bonding process can then be considered as a process of overlapping the hybrid atomic orbital of one atom with a pure or hybrid atomic orbital of another.

As we know simple valence Bond theory does not explain the covalent bond formation of certain elements. So modification in this theory was made in the form of "hybridization concept".

So **a process of mixing atomic orbitals of different energy and shape to form set of new orbitals of the same energy and same shape is called hybridization and the orbitals so obtained are called "hybrid orbitals"**. According to this concept atomic orbitals differing slightly in energy intermix to form new orbitals of equal energies and are called hybrid orbitals which differ from the parent atomic orbitals in shape and energy and possess specific geometry. It also gives a satisfactory explanation for the valency of the elements. In this process, the electron belonging to the ground state structure are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

The atomic orbitals, undergo hybridization. The energy required for the excitation is compensated by the energy released during the process of bond formation with other atoms. Depending upon the nature of orbitals involved there are many types of hybridization.

For example, sp^3, sp^2, sp hybridization

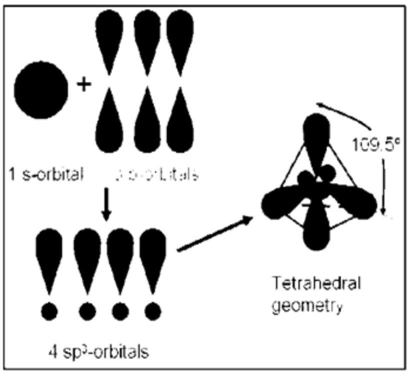


Figure 3.8: Structure of sp^3 hybridized orbitals

(i) sp^3 Hybridization

"The process of mixing one's orbital and three p orbitals to form four new equivalent sp^3 hybrid orbitals is called sp^3 hybridization"

Let us discuss the structure of methane, ammonia and water by understanding the sp^3 hybridization of carbon, nitrogen and oxygen atoms.

a) Structure of Methane

$_6C$ (Ground state) $= 1s^2, 2s^2\cdot 2p_x^1, 2p_y^1, 2p_z^o$

$_6C^*$ (Excited state) $= 1s^2, 2s^1\cdot 2p_x^1, 2p_y^1, 2p_z^1$

$_6C$ (Hybrid state) $= 1s^2$, $(sp^3)^1\cdot (sp^3)^1, (sp^3)^1, (sp^3)^1$

When carbon atom in a molecule is attached to four other atoms, then sp^3 hybridization occurs.

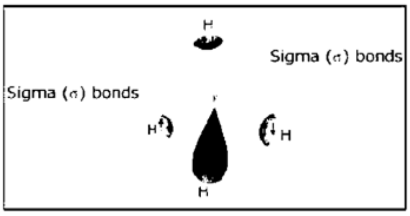


Figure 3.9: Structure of Methane (CH_4)

Each sp^3 hybrid orbital consist of two lobes, one larger and the other smaller. The energies of hybrid orbitals are lower than unhybridized orbitals. Further the ratio of s and p character in each sp^3 hybrid orbitals is 1:3 i.e. it contain 25% S-character and 75% P-character. The four new hybrid orbitals of equal energy have a **tetrahedral** geometry with carbon at the centre and are oriented in space in such a manner that the angle between them is **109.5°** as shown in the figure 3.9.

Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule of methane, thus formed possesses a tetrahedral geometry. The C-H bonds which result from sp^3-s overlaps are directed towards the corners of a regular tetrahedron. Each H-C-H bond angle is 109.5^0. The tetrahedral structure of CH_4 molecule has four faces and four corners.

b) Structure of Ammonia, NH_3

In NH_3 molecule, the central atom is nitrogen. It contains five electrons in its valence shell.

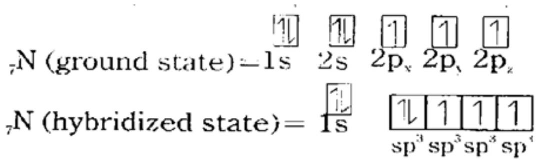


Figure 3.10: Structure of Ammonia (NH_3)

Hence one s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals. They are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled by a lone pair of electrons and the remaining three orbitals are half filled. The half filled sp^3 hybridized orbitals of nitrogen overlap with three 1s-orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners, whereas the lone pair of electron is at the fourth corner of the tetrahedron. This results in a **pyramidal** molecule, in which three hydrogen atoms form the base and the lone pair of electrons the apex as shown in the fig 3.10. The experimentally determined value of H-N-H bond angle in NH_3 molecule is **107.5^0** which is less than the normal tetrahedral value of 109.5^0. The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pair and bond pairs. The lone pair-bond pair repulsion is greater than bond pair-bond pair repulsion. As a result, the bond pairs move away from the lone pair and come closer to each other. Hence, the angle between bond pairs decreases.

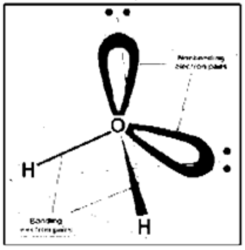


Figure 3.11: Structure of Water (H_2O)

c) Structure of Water H_2O

In H_2O molecule, the central atom is oxygen. It contains six electrons in the valence shell. Its electronic configuration is as follows,

$_8O$ (Ground state) = $1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$

$_8$O (Hybrid state) = 1s^2, (sp^3)^2, (sp^3)^2, (sp^3)^1, (sp^3)^1

One 2s and three 2p orbitals of O-atom intermix to produce four sp^3 hybrid orbitals. The four sp^3 hybrid orbitals are directed towards the four corners of a regular tetrahedron with oxygen atom at the centre. Two of the sp^3 hybrid orbitals contain two lone pairs of electrons, each and are completely filled. The remaining two sp^3 hybrid orbitals contain one electron each and are partially filled. Thus the two partially filled sp^3 hybrid orbitals now overlap with the two 1s orbitals of two hydrogen atoms to form two sigma bonds. Each sigma bond is formed by sp^3-s overlap. The two hydrogen atoms are located at two corners of a tetrahedron, whereas the two lone pairs at the remaining two corners of the tetrahedron. The result is a **V-shaped** molecule. The experimentally determined value of H-O-H bond angle in H_2O molecule is **104.5°**, which is lesser than the normal tetrahedral value (109.5°). The deviation from the tetrahedral angle is explained on the basis of repulsion between lone pairs and bond pairs. The repulsion of lone pair-lone pair > lone-pair-bond pair > bond pair-bond-pair. As a result, the bond pairs move away from the lone pairs and come closer to each other. Hence the angle between bond pairs decreases up to 104.5°.

(ii) sp^2 - Hybridization

"The mixing of one s and two p orbitals of the same atom to form three identical sp^2 hybrid orbitals is called sp^2-hybridization"

The hybrid orbitals are directed towards the three corners of an **equilateral triangle**. The angle between any two hybrid orbitals is **120°**. Each sp^2 hybrid orbital has 33.3% s-character and 66.7% p-character. The sp^2 hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

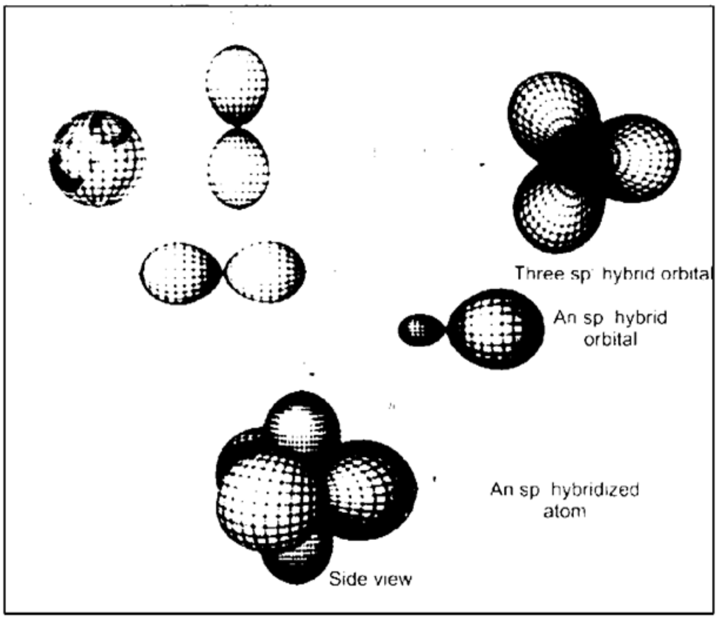


Figure 3.12: Structure of Hybridization (sp^2)

Examples: Boron trifluoride and Ethene

a) Structure of Boron trifluoride, BF_3:

Figure 3.13: Structure of BF_3

In BF_3 molecule, the central atom is boron. It contains three electrons in its valence shell. The electronic configuration of the valence shell of B-atom in the ground and excited states are as follow,

$_5B = 1s^2,\ 2s^2,\ 2p_x^1,\ 2p_y,\ 2p_z$ (ground state)

$_5B = 1s^2,\ 2s^1,\ 2p_x^1,\ 2p_y^1,\ 2p_z$ (excited state)

One 2s and two 2p orbitals of boron atom intermix to give three sp^2 hybridized orbitals. The three sp^2 hybrid orbitals lie in the same plane and are directed towards the corners of an equilateral triangle with boron atom at the centre.

Thus the angle between any two sp^2 orbitals is **120°**. The three sp^2 orbitals contain one electron in each and are thus partially filled. The partially filled 2p orbitals of three fluorine atoms overlap with each sp^2 hybrid orbitals of boron atom to form three **sp^2–p_z** sigma bonds. As a result, BF_3 molecule has **triangular planar** structure.

b) Structure of Ethene, $CH_2 = CH_2$

the electronic configuration of corban atom is:

$_6C\,(\text{Ground state}) = 1s^2, 2s^2\cdot 2p_x^1, 2p_y^1, 2p_z$

$_6C\,(\text{Excited state}) = 1s^2, 2s^1\cdot 2p_x^1, 2p_y^1, 2p_z^1$

$_6C\,(\text{Hybrid state}) = 1s^2, \left(sp^2\right)^{1\cdot}\left(sp^2\right)^1\left(sp^2\right)^1, 2p_z^1$

In $CH_2 = CH_2$ molecule, one s and two p orbitals of each C-atom intermix to form three hybrid sp^2 orbitals. The geometry of molecules depends upon the orientation of hybrid orbitals. Hybrid orbitals are **triangular planar** and oriented at the angle of **120°** to each.

Each atom is left with one half filled p-orbital perpendicular to the planar sp^2 hybrid orbitals. One sp^2 orbital of each C-atom overlaps linearly to form one C-C sigma bond. Remaining two sp^2 orbitals of each C-atom overlap linearly with 1s atomic orbital of H-atom to form two C-H single bonds.

A pi-bond is formed by the sideways overlap of two half-filled co-planar p-orbitals in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei.

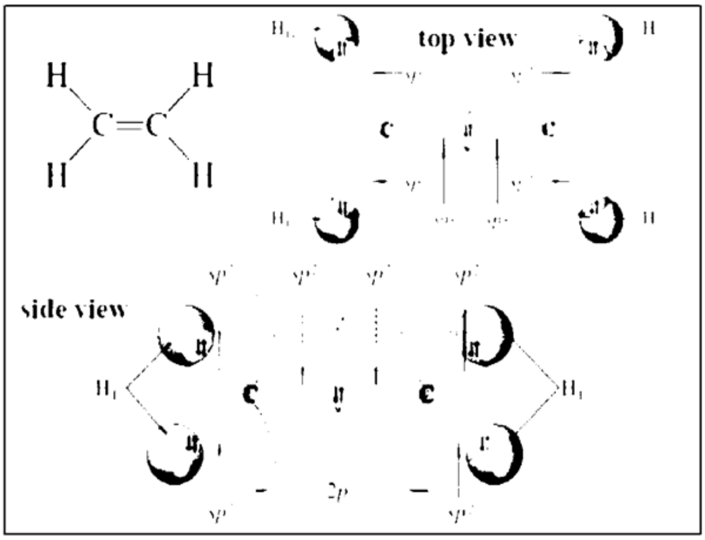


Figure 3.14: Structure of Ethene

(iii) Sp - Hybridization

"The mixing of one s-orbital and one p-orbital of an atom to form two equal energy hybrid orbitals is called sp hybridization"

The two sp hybrid orbitals are **linear** and angle between them is **180°**. Each sp-hybrid orbital has 50% s-character and 50% p-character. The sp-hybrid orbitals can form only sigma bonds by overlapping with other atomic orbitals.

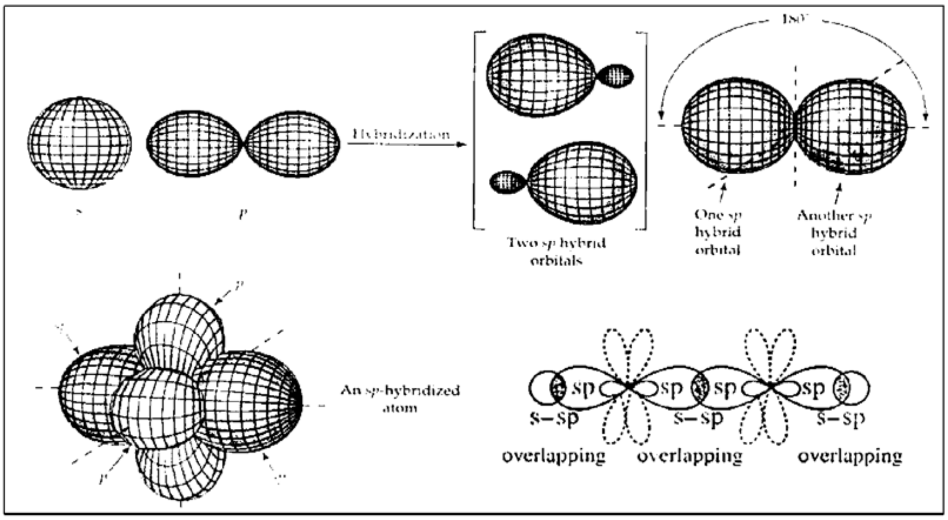


Figure 3.15: Structure of sp Hybridized orbitals

Examples:- $BeCl_2$, C_2H_2

a) Structure of $BeCl_2$ (Beryllium Chloride)

In $BeCl_2$ molecule, the central atom is beryllium atom. Beryllium atom contains two electrons in its valence shell. The electronic configuration of valence shell of beryllium atom in the ground state and excited state is as follow:

$_4Be = 1s^2, 2s^2, 2p_x, 2p_y, 2p_z$ (ground state)

$_4Be = 1s^2, 2s^1, 2p_x^1, 2p_y, 2p_z$ (excited state)

One 2s and one 2p orbitals of beryllium atom intermix to form two sp hybrid orbitals. Each sp hybrid orbital contains one electron. The two sp hybrid orbital lie in a straight line with beryllium atom at the centre. One sp orbital of Be overlaps linearly with p-orbital of other Cl to form Be-Cl sigma bond remaining sp hybrid orbital of Be overlaps linearly with 3Pz orbital of second Cl atom to form sigma bond. Thus $BeCl_2$ molecule is **linear**. The Cl-Be-Cl bond angle is **180°**.

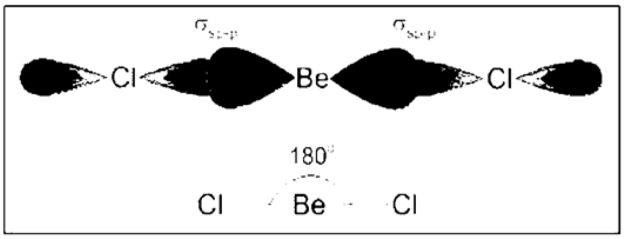


Figure 3.16: Structure of beryllium chloride

b) Structure of Ethyne, $CH \equiv CH$

The electronic configuration of carbon atom in the ground and excited states is as follow:

$_6C$ (Ground state) $= 1s^2, 2s^2\ 2p_x^1, 2p_y^1, 2p_z$

$_6C$ (Excited state) $= 1s^2, 2s^1\ 2p_x^1, 2p_y^1, 2p_z^1$

$_6C$ (Hybrid state) $= 1s^2, (sp)^1 (sp)^1, 2p_y^1, 2p_z^1$

One 2s and one 2p orbitals of carbon atom intermix to give two sp hybrid orbitals. The $2p_y$ and $2p_z$ orbitals remain unhybridized. Each sp hybrid orbitals contains one electron. The two sp hybrid orbitals are directed along a straight line at an angle of **180°** between them. The two unhybridized p orbitals which are perpendicular to each other are also perpendicular to the plane of the two sp hybrid orbitals. Thus each carbon atom possesses two sp hybrid orbitals and two pure p atomic orbitals. Each C-atom undergoes sp-s overlap with one H-atoms and sp-sp overlap with other carbon atom to form two σ-bonds.

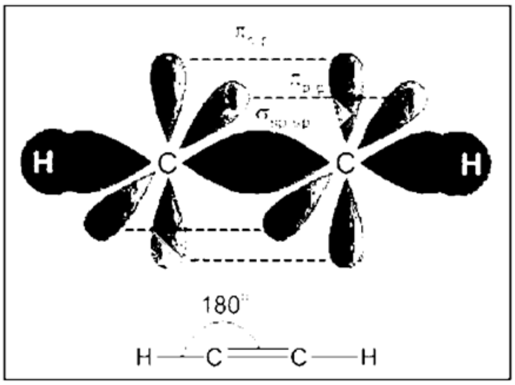


Fig. 3.17: Structure of ethyne molecule

The two half-filled p orbitals of two carbon atoms overlap sideways to form two π-bonds. Thus ethyne molecule contains one σ-bond and two π-bonds between two carbon atoms and two carbon-hydrogen σ-bonds. The electronic clouds of two π-bonds merge into each other to form cylindrical shaped π-electron cloud. The molecule is **linear** in shape.

Drawbacks of Valence Bond Theory

It fails to explain:

a) The formation of coordinate covalent bond.
b) The formation of odd electron molecules or ions.
c) The paramagnetic behaviour of oxygen molecule.

[illegible]

The method of molecular orbital theory was developed in 1927-1928 by Hurid and Mullikan and in 1929 by Lennard-Jones.

It is assumed that linear combination of atomic orbitals form new orbitals called molecular orbitals which are characteristics of the whole molecule. The molecular orbital surrounds two or more nuclei of the bonded atoms. Two atomic orbitals after combining linearly form two molecular orbital which differ in energy. One of them, having lower energy, is called **bonding molecular orbital (BMO)** while the other having high energy is called **anti-bonding molecular orbital (ABMO)**. The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital, while the anti-bonding molecular orbital is designated as σ*.

The filling of electrons into the molecular orbitals takes place according to

- Aufbau principle
- Pauli's exclusion principle
- Hund's Rule

The two electrons from each atom fill the low energy σ orbital or π orbital while the high energy σ^* orbital or π^*orbital may have electrons or remain empty.

The following diagram illustrates the formation of the molecular orbitals (lower energy and higher energy) and also the processing of filling of electrons according the rules mentioned above.

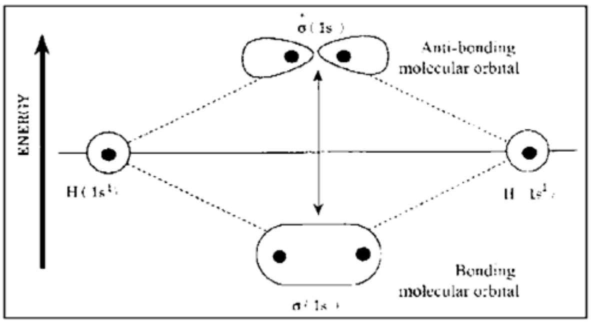


Figure 3.18: Energy diagram of bonding and anti-bonding molecular orbitals

In this type of diagram, the combining atomic orbitals are shown on two extremes and the resulting molecular orbitals (MO) are represented in the middle column.

Atomic orbitals of same energy are shown at the same level. The difference between the energies of atomic orbitals and the bonding MO's depend upon the extent of overlap of atomic orbitals. A large overlap results in greater lowering of the energy of bonding MO (and a corresponding large rise in energy in the anti-bonding MO). Larger the overlap, stronger will be the resulting bond. According to the above diagram, the sequence of energy levels in which they one filled up is,

$$\sigma1s < \sigma^*1s < \sigma2s < \sigma^*2s < \sigma2p_x < \pi2p_y = \pi2p_z < \pi^*2p_y = \pi^*2p_z < \sigma^*2p_x$$

There are two types of overlapping in molecular orbital theory

i. Head on approach (linear overlapping) or linear combination
ii. Sideways approach (parallel overlapping)

i. Head on approach (linear overlapping)

Head on approach can take place between s-s, s-p and p-p atomic orbitals.

When two s atomic orbital overlap, they form two molecular orbitals. Molecular orbital having low energy than atomic orbital is called σs. Molecular orbital which has high energy then atomic orbital is called σ^*s orbital as shown in the figure 3.18.

ii. Sideways approach or parallel overlapping

When the axes of two–p orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals.

The bonding molecular orbital $\pi(2p_y)$ or $\pi(2p_z)$ has zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane. On the other hand, $\pi^*(2p_y)$ or $\pi^*(2p_y)$ anti-bonding molecular orbital has the least electron density in the inter-nuclear region. Since the $2p_y$ and 2pz atomic orbitals are degenerate orbitals (having the same energy) the π molecular orbitals i.e., π $(2p_y)$ and π $(2p_z)$ are also degenerate. Similarly the π^* $(2p_y)$ and $\pi^*(2p_z)$ molecular orbitals are also degenerate.

Two sets of 2-p atomic orbitals forms six molecular orbitals (three bonding and three anti-bonding). The bond formed as a result of linear overlapping is σ bond while that formed as a result of sideways overlap is called a π (pi) bond. Thus p orbital overlaps can lead to the formation of three bonds. One sigma and two pi bonds.

Bond order (No. of bonds)

The number of bonds formed between two atoms after the atomic orbitals overlap is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons.

$$\text{Bond order} = \frac{\text{No. of electrons in BMOs - No. of electrons in ABMOs}}{2}$$

The number of bonds formed in hydrogen molecule may be calculated as follows.

No. of electrons in the bonding orbitals = 2

No. of electrons in the anti-bonding orbitals = 0

$$\text{Bond order} = \frac{2-0}{2} = 1$$

It is a common practice that only MOs formed from valence orbital are considered in bond order calculations. It should be noted that a bond between two atoms can be formed only, when the number of electrons in the bonding orbital must be greater than the number of electrons in the anti-bonding molecular orbitals.

Relative Energies of the Molecular Orbitals

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals are determined by spectroscopic measurements.

a) The molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions can be shown in the following increasing order of energy.

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

b) The diatomic molecule such as H_2, He_2, B_2, C_2, and N_2 (lighter molecules) show slightly different energy order.

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

Reason

We have seen in the energy order of lighter molecules like B_2, C_2, N_2, $\sigma 2p_x$ is higher in energy than $\pi 2p_y = \pi 2p_z$ molecular orbitals. This reversal is due to mixing of 2s and $2p_x$ atomic orbitals.

Actually, the energy difference of 2s and 2p atomic orbitals is small; there is a possibility of mixing of these orbitals (hybridization of A.O.). As a result $\sigma 2s$ and $\sigma^* 2s$ MO do not retain pure s- character.

Similarly, $\sigma 2p_x$ and $\sigma^* 2p_x$ MOs do not have pure p-character. All the four MOs acquire sp-character. Due to this mixing, their energies change in such a way that MOs $\sigma 2s$ and $\sigma^* 2s$ become more stable and are lowered in energy MOs as $\sigma 2p_x$ and $\sigma^* 2p_x$ become less stable and are raised in energy. Since, $\pi 2p_y = \pi 2p_z$ remains unchanged. $\sigma 2p_x$ is raised to such an extent that it becomes higher in energy than $\pi 2p_y$ and $\pi 2p_z$

But, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 kJ/mol and 2078 kJ/mole for O_2 and F_2 respectively. The values are 554 kJ/mol for Boron, 846 kJ/mol for carbon and 1195 kJ/mol for nitrogen and these energy differences have been calculated by spectroscopic techniques.

Applications of Molecular Orbital Theory for Homo Nuclear Diatomic Molecules

After having discussed the basic principles of molecular orbital theory, we are now able to take up the electronic structures and bonding properties of some homo-nuclear molecules.

(1). Hydrogen Molecule H_2

$H = 1s^1$

Hydrogen molecule is formed from the overlap of 1s atomic orbitals of two hydrogen atoms. They give rise to two molecular orbitals σ 1s and σ^*1s. The molecule has two electrons which occupy the lower energy σ 1s orbital as shown in the diagram. The electronic configuration of the molecule is represented by the equation.

$$2H\ (1s^1) \longrightarrow H_2\ [(\sigma\ 1s)^2]$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

Thus the two hydrogen atoms are bonded through only one bond in the molecule. We conclude that the H_2 molecule is stable. It has bond dissociation energy of 436 $KJmol^{-1}$ and is diamagnetic in nature i.e (atoms, ions or molecules in which electrons are all paired in their molecular electronic configuration are diamagnetic). They are repelled by both poles of magnet.

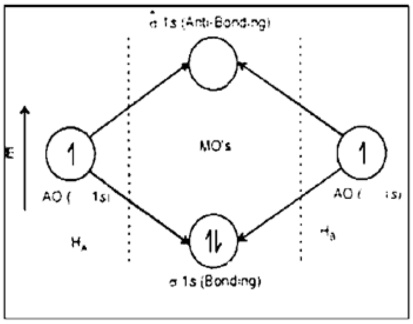


Figure 3.19: Molecular orbitals energy level diagram of H_2

(2). Helium Molecule (Hypothetical) He_2

$He = 1s^2$

The energy level diagram for He_2 is similar to that of H_2 except that it has two more electrons which occupy the anti-bonding σ^*1s orbital shown in the diagram.

$$2He\ (1s^2) \longrightarrow He_2\left[(\sigma 1s)^2(\sigma^* 1s)^2\right]$$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

Thus its bond order is zero and we conclude that the molecule is not stable. Infect, He_2 is not known, helium exist only as mono-atomic molecules.

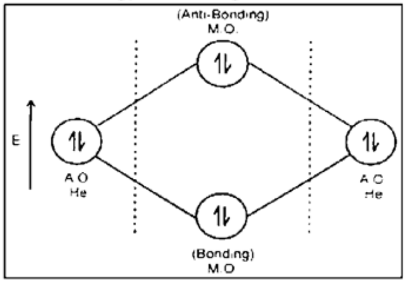


Figure 3.20: Molecular orbitals energy level diagram of He_2

(3) Lithium Molecule Li_2

$Li = 1s^2\ 2s^1$

The electronic configuration for Li_2 has a total of six electrons, two each in σ 1s, σ^*1s and σ2s molecular orbitals. In short hand notation this can be represented as $\sigma\ 1s^2$, σ^*1s^2 and $\sigma\ 2s^2$. There are two more electrons in the bonding orbitals than in anti-bonding orbitals and the bond order is one. We conclude that the molecule is stable and diamagnetic it is indeed to exist in the vapour phase. It possesses bond energy of 110 kJ mol^{-1} which is less than H_2 molecule.

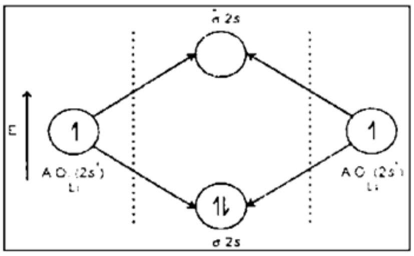


Figure 3.21: Molecular orbitals energy level diagram of Li_2

$$2Li\ (1s^2,\ 2s^1) \longrightarrow Li_2\left[KK(\sigma 2s)^2\right]$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

(4) Beryllium Molecule Be_2

$Be = 1s^2\,2s^2$

The situation for the Be_2 molecule is similar to that for He. Bonding and anti-bonding orbitals are equally populated and the bond order is zero. The electronic configuration is $\sigma\ 1s^2$, σ^*1s^2, $\sigma\ 2s^2$ σ^*2s^2. The Be_2 molecule is known but is very unstable.

$$2Be\ (1s^2\,2s^2) \xrightarrow{\qquad} Be_2\,[KK\,(\sigma\ 2s)^2\,(\sigma^*2s)^2\,]$$

$$\text{Bond order} = \frac{2-2}{2} = 0$$

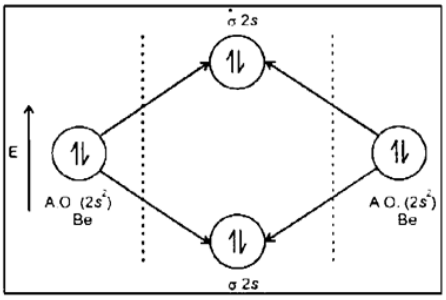


Figure 3.22: Molecular orbitals energy level diagram of Be_2

(5) Boron Molecule, B_2

$B = 1s^2\,2s^2 2p^1$

The boron atom has the configuration of $1s^2$, $2s^2$, $2p^1$ and is the first element with five electrons to participate in bonding.

Spectroscopic study has suggested that for B_2, C_2 and N_2 molecules $\pi 2p$ orbitals are lower in energy than $\sigma 2p$ orbital. Thus the electronic configuration of B_2 is:

$$2B\ (1s^2\,2s^2\,2p^1) \xrightarrow{\qquad} B_2\,[KK\,(\sigma\ 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_y)^1\,(\pi 2p_z)^1]$$

$$\text{Bond order} = \frac{2-0}{2} = 1$$

Thus the two B–atoms are bonded through only one bond in the molecule. The experiments verify not only that the molecule exists in vapour phase but that it is paramagnetic (atoms, ions or molecules) with two unpaired electrons. The bond energy is 270 kJ mol^{-1}. Molecules which have one or more unpaired electrons in their molecular electronic configuration are paramagnetic. They are attracted to magnetic field.

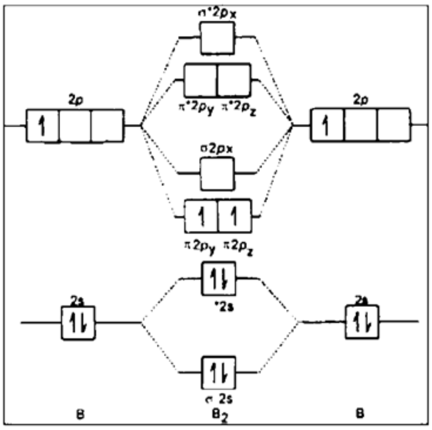


Figure 3.23: Molecular orbitals energy level diagram of B_2

(6) Nitrogen Molecule N_2

$N = 1s^2\,2s^2\,2\overset{\uparrow}{p_x}\,2\overset{\uparrow}{p_y}\,2\overset{\uparrow}{p_z}$

Looking at, the electronic configuration, only 2s and three 2p electrons from each N atom are to be considered in the bond formation.

Thus the electronic configuration of N_2 molecule is:

$$2N\left(1s^2 2\,s^2 2p_x^1 2p_y^1 2p_z^1\right) \xrightarrow{\qquad} N_2[KK\ (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_y)^2(\pi 2p_z)^2(\sigma 2p_x)^2]$$

$$\text{Bond order} = \frac{6-0}{2} = 3$$

It is obvious that the two N-atoms are bonded through triple bond. N_2 molecule is very stable molecule and has a very high bond energy 946 kJ mol^{-1}, which is consistent with MOT. It is diamagnetic in nature and possesses a very short bond length.

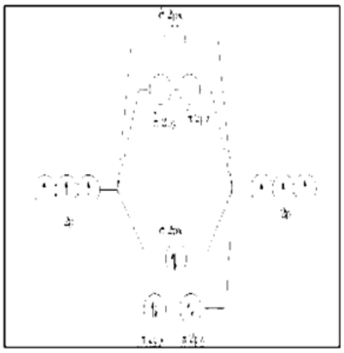


Figure 3.24: Molecular orbitals energy level diagram of N_2

(7) Oxygen Molecule O_2

$O = 1s^2 2s^2 2\overset{\uparrow\downarrow}{p_x} 2\overset{\uparrow}{p_y} 2\overset{\uparrow}{p_z}$

The valence bond theory predicts that O_2 would be diamagnetic. However experiments show that it is paramagnetic having two unpaired electrons. A structure consistent with this observation is predicted by MOT. Spectroscopic evidence indicates that for O_2, the σ2p orbital is lower in energy than π2p orbitals. The electronic configuration of O_2 molecule is:

$$2O\left(1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1\right) \longrightarrow O_2[KK\ (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p_x)^2 (\pi 2p_y)^2 (\pi 2p_z)^2 (\pi^* 2p_y)^1 (\pi 2p_z)^1]$$

$$\text{Bond Order} = \frac{6-2}{2} = 2$$

It is obvious that the two oxygen atoms are bonded through a double bond. The two unpaired electrons reside in the degenerate anti-bonding orbitals π^*2p_y and π^*2p_z, hence it is paramagnetic in nature. So we conclude that the molecule should be very stable as it possesses high bond energy i.e. 498 kJ mol^{-1} with bond length 1.21 Å.

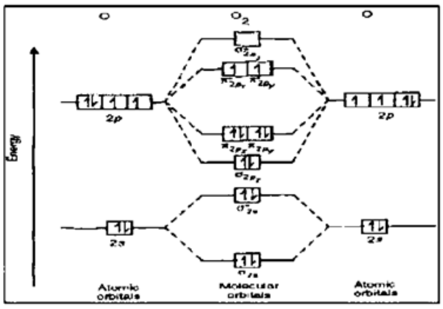


Figure 3.25: Molecular orbitals energy level diagram of O2

(8) Fluorine Molecule F_2:

$F = 9 = 1s^2 2s^2 2p^5$

Each F-atom has the $1s^2\ 2s^2\ 2p^5$ configuration. The participating electronic configuration of F_2 molecule is:

$F_2 = KK\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p_x)^2\ (\pi 2p_y)^2\ (\pi 2p_z)^2\ (\pi^* 2p_y)^2\ (\pi^* 2p_z)^2$

$$\text{Bond Order} = \frac{6-4}{2} = 1$$

It is obvious that two F-atoms are bonded through a single bond. The F-F bond distance is longer (1.43⁰A) than the bond distance for O_2(1.21⁰A) and N_2(1.09 ⁰A) molecules. The bond energy of F_2 molecule is quite low (159kJ mol^{-1}). It is diamagnetic in nature.

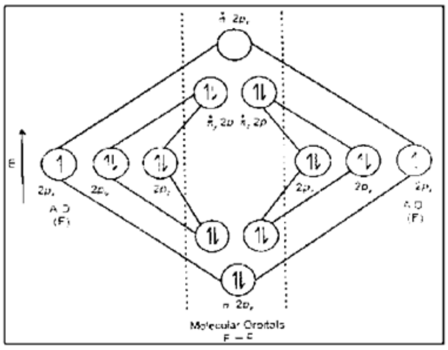


Figure 3.26: Molecular orbitals energy level diagram of F2

Comparison of Valence Bond and Molecular Orbital Theories:

Similarities:

The common features of the two theories are:

a) Both the theories explain the formation of covalent bond.
b) In both the theories, a covalent bond is formed by the overlapping of atomic orbitals having appropriate symmetry about the molecular axis.
c) According to both, the electronic charge resides in the region between the atomic nuclei.
d) Both the methods lead to the formation of two types of bonds σ and π bonds.
e) In both the methods, the atomic and molecular orbitals are filled up according to the same principles.

Differences:

Valence Bond Theory	Molecular Orbital Theory
1. According to this theory only valence electrons are involved in bond formation	1. According to this theory, all the electrons of interacting atoms are involved in bond formation
2. In VBT the two concerned atomic orbitals do not lose their individual identity	2. In MOT, the two atomic orbitals lose their individual identity
3. It does not explain the paramagnetic behaviour of molecules like O_2 molecule	3. In explains the paramagnetic behaviour i.e., electrical properties.
4. It does not give idea about the bond order	4. It give idea about bond order by which we can determine that whether the bond is single, double or triple
5. It does not explain the non-existence of He_2 molecule.	5. It explains the non-existence of He_2 molecule.

3.3 BOND ENERGY (BOND ENTHALPY)

When a bond is formed between two atoms, energy is released (exothermic process), the same amount of energy is absorbed (endothermic process) when the bond is broken to form neutral atoms. So the **bond energy is the amount of energy required to break all bonds of particular type in one mole of the substance**. The strength of a bond is measured by its bond energy. The higher the bond energy, the stronger is the bond. It is determined experimentally by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is measure of enthalpy change at 298K. **The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization.**

Units

It is expressed in kilojoules per mole ($kJmol^{-1}$). It is the energy required to break up an Avogadro number (6.02×10^{23}) of bonds i.e. one mole of bond. It is found that energies of multiple bonds are greater than those of single bonds. But a double bond is not twice as a strong as a single bond or a triple bond is not thrice as strong as a single bond. It means that a σ bond is stronger than a π bond. Also, a polar covalent bond is stronger than a non-polar covalent bond.

Examples

(i) The bond energy of H-H in H_2 molecule at 25°C (298K) is 436kJ/mole. The bond energy of Cl-Cl bond in Cl_2 molecule at 25°C is 242kJ/mole.

(ii) The bond energy of H-Cl bond in HCl molecule at 25°C is 431 kJ/mole.

Ionic character and Bond energy:

Bond energy is a measure of bond strength. Higher the bond energy, the stronger is the bond. The strength of a bond depends upon the following factors.

(i) Electronegativity
(ii) Size of the bonded atoms
(iii) Bond length
(iv) Bond order (number of bonds)

"Greater the difference in electronegativity between the bonded atoms, the greater is the bond energy and stronger is the bond"

Examples

Bond type H-X	**H-F**	**H-Cl**	**H-Br**	**H-I**
Bond energy ($kJmol^{-1}$)	567	431	366	299
ΔEN	1.9	0.9	0.7	0.4

From the above data it is observed that HF molecule has higher bond energy (567 $KJmol^{-1}$) due to greater electronegativity difference i.e. 1.9.

The smaller the size of the bonded atoms, the greater is the bond energy and stronger is the bond. The bond energy of H-H bond is 436$kJmol^{-1}$ and that Cl-Cl is 242$kJmol^{-1}$. It is due to the shorter bond length in H_2 molecule and greater bond length in Cl_2 molecule (larger size of Cl atom than H atom).

Multiple bonds also affect the bond energy, **greater the no. of bonds greater will be the bond energy.**

Table 3.1: Average Bond energies ($kJmol^{-1}$) of single bonds.

Bond	**Bond Energy ($kJmol^{-1}$)**	**Bond**	**Bond Energy ($kJmol^{-1}$)**	**Bond**	**Bond Energy ($kJmol^{-1}$)**	**Bond**	**Bond Energy ($kJmol^{-1}$)**	**Bond**	**Bond Energy ($kJmol^{-1}$)**
C-H	413	Si-H	323	H-H	436	S-H	339	Cl-F	253
C-C	348	Si-Si	226	H-F	567	S-F	327	Cl-Cl	242
C-N	293	Si-C	301	H-Cl	431	S-Cl	253	Br-F	237
C-O	358	Si-O	368	H-Br	366	S-Br	218	Br-Cl	218
C-F	485	N-N	163	H-I	299	S-S	266	Br-Br	193
C-Cl	328	N-O	201	H-O	463	O-O	146	I-Cl	208
C-Br	476	N-F	272	H-F	155	O-F	190	I-Br	175
C-I	240	N-Cl	200	H-N	391	O-Cl	203	I-I	151
C-S	259	N-Br	243			O-I	234		

Table 3.2: Average Bond energies of multiple bonds ($kJmol^{-1}$)

Bond	**Bond Energy ($kJmol^{-1}$)**	**Bond**	**Bond Energy ($kJmol^{-1}$)**
C = C	614	N = N	418
C ≡ C	839	N ≡ N	941
C = N	891	O = O	495
C = O	799	S = O	523
C ≡ O	1072	S = S	418

[illegible]

Polar bonds are stronger than non-polar bonds and greater amount of energy is required to break these bonds. Due to ionic character, the strength of bond increases. Increase in strength of H-Cl bond or ionic character in H-Cl bond can be observed from the experimentally determined values of H-H, Cl-Cl and H-Cl bond and theoretically calculated bond energy value of H-Cl bond. It involves the following steps:

Step (i) Calculation of bond energy contribution of one H atom.

Bond energy of 1 mole of H-H bonds = 436 kJ
or Bond energy of 6.02×10^{23} H-H bonds = 436 kJ
or Bond energy of one H-H bond = $\frac{436}{6.02\times10^{23}}$ kJ
= 72.42×10^{-23}kJ
Bond energy contribution of one H atom = $\frac{72.42\times10^{23}}{2}$
= 36.21×10^{-23} kJ

Step (ii) Calculation of bond energy contribution of one Cl atom.

Bond energy of 1 mole of Cl-Cl bonds = 242 KJ
or Bond energy of 6.02×10^{23} Cl-Cl bonds = $\frac{242}{6.02\times10^{23}}$ kJ
Bond energy of one Cl-Cl bond = 40.19×10^{-23} kJ
Bond energy contribution of one Cl atom = $\frac{40.19\times10^{-23}}{2}$ kJ
= 20.09×10^{-23} kJ

Step (iii) Calculation of bond energy of 1 mole of H-Cl bonds.

This calculation is based on the assumption that H-Cl bond is non polar.

Bond energy of one H-Cl bond = Bond energy of H-atom + Bond energy of Cl atom.
= $(36.21\text{x } 10^{-23} + 20.09\text{x } 10^{-23})$ kJ
= $56.3\text{x}10^{-23}$ kJ
Bond energy of $6.02\text{x}10^{23}$ H-Cl bonds = $56.3\text{x}10^{-23}$ x $6.02\text{x}10^{23}$
= 338.93kJ

Bond energy of one mole of H-Cl bonds= 338.93 kJ/mole

The relation between bond energy and electronegativity can be seen from theoretically calculated and experimentally determined values of HCl bond.

Theoretically calculated bond energy of H-Cl bond = 338.93kJmol^{-1}.

Experimentally determined energy of H-Cl bond = 431kJmol^{-1}.

The experimentally determined bond energy is significantly greater than the calculated value, which means a more stable H-Cl bond. This stability is due to the ionic character present in the bond. The amount of additional bond energy depends on the electronegativity of the two bonded atoms. **Greater the difference of electro-negativity between the two bonded atoms, the greater is the ionic character and stronger is the bond.**

Table 3.3: Comparison of experimental and theoretical bond energies

Bond	**Bond energies kJmol^{-1}.**			
	X=F	X=Cl	X=Br	X=I
X-X	155	242	193	151
H-X(Calculated)	293	338	311	291
H-X (observed)	567	431	366	299
Difference	274	95	55	08

This data clearly indicate the part played by electronegativity in the strength of a bond. Electrons are not equally shared between hydrogen and halogen atoms in HX. Since halogen atom is more electronegative, the bonded electron pair is more attracted towards halogen atom. This develops polarity in H-X molecules which produces an additional attractive binding force.

Bond Length

Bond length may be defined as the distance between the nuclei of atoms joined by covalent bond. This distance between the bonded atoms is not constant, because the bonded atoms are always vibrating with respect to each other. Therefore, average of minimum inter nuclear distance is considered as bond length or bond distance. Thus bond length may also be defined as the internuclear distance when the maximum possible overlap of concerned atomic orbitals occurs. It is measured by techniques such as X-ray diffraction, neutron diffraction and microwave spectroscopy.

Measuring units

It is measured in Å or picometer: I pm = 10^{-12}m, 100 pm = I Å = 10^{-10}m.

It is observed that its measurements may vary in accuracy but still similar bonds have fairly constant lengths in different molecules, variation generally being less than 1%. In most of the compounds, the C-C single bond length is very close to 1.54 Å. For example in ethane molecule the C-C bond length is 1.54 Å and in ethyl chloride (C_2H_5Cl) the C-C bond length is 1.55 Å.

One half of the bond length between nuclei of two similar atoms join by single covalent bond is called the covalent radius of that atom. For example, the covalent radius of Carbon is 0.77 Å i.e. half of the C-C bond length which is 1.54 Å. The covalent-radii of other atoms are given in the following table:

Table 3.4: Covalent-radii of various atoms

Atom	Covalent-radiusÅ	Atom	Covalent-radius Å
H	0.28	F	0.72
C	0.77	Cl	0.99
N	0.75	Br	1.14
O	0.74	I	1.33

The covalent-radii can be used to calculate the bond length between two unlike atoms, which in some cases, is equal to the sum of the covalent radii of the two bonded atoms. For example, the C-Cl bond length in CH_3Cl is 1.76 Å, which is exactly the sum of the covalent radii of carbon (0.77 Å) and chlorine is (0.99 Å). However, in most cases, the length of a bond between two unlike atoms is markedly shorter than the sum of the two covalent radii. For example, the covalent radii of C and N add up to 1.52 Å where as the observed C-N bond length in methylamine (CH_3NH_2) is 1.47 Å. Similarly, the observed C-O bond length is ethanol (C_2H_5OH) is 1.42 Å, although the sum of the covalent radii of carbon and oxygen is 1.51 Å. In general, the shrinkage in bond length becomes more and more marked as the difference in electronegativity of the two bonded atoms increases.

Average single bond lengths of some of the important covalent bonds are given in the following table:

Table 3.5: Bond lengths of some Covalent Bonds

Covalent Bond	Bond Length A°	Covalent Bond	Bond Length A°
C-H	1.07	C-Br	1.93
C-C	1.54	C-I	2.14
C-O	1.42	C-Cl	1.76
C-N	1.47	O-H	0.96
C-F	1.38	N-H	1.01

Bond length is also affected by the nature of hybridization of the bonded atoms as shown in the following table:

Table 3.6: Effect of Hybridization on the Bond Length

Hybridization of Carbon	Bond Length (A°)		
	C-H	**C-O**	**C-N**
sp^3	1.11 (methane)	1.41 (ethanol)	1.47 (methylamine)
sp^2	1.10 (ethylene)	1.34 (formic acid)	1.36 (formamide)
sp	1.08 (acetylene)		

It can be noticed that the bonds are shortened by increasing “s” character. This is because the hybrid orbital with increased “s” character is held more tightly by the nucleus. A double bond between two atoms is shorter than a single bond between the same two atoms and a triple bond is shorter than the double bond as shown in the following table:

Table 3.7: Single, Double and Triple Bond Lengths.

Bonded atoms	Bond Length (Å)		
	Single bond	**Double bond**	**Triple bond**
C,C	1.54	1.38	1.19
C,N	1.47	1.28	1.16
C,O	1.42	1.20	---

This shrinkage of the multiple bonds is due to the presence of extra π electrons (two in the case of a double bond and four in the case of triple bond) between the two nuclei, which exert additional attraction on both the nuclei bringing them closer to each other.

Dipole Moment

(Determination of degree of polarity of molecules)

The degree of polarity of a molecule can be expressed in terms of dipole moment. **It is the product of the magnitude of the charge (positive or negative) and the distance between them.** If q is the charge at each end of dipole and r is the distance between the positive and negative centers, then dipole moment represented as μ is given by $\mu = q \times r$

Units: Its **SI** unit is Coulombs meter (C.m) but most common units used is Debye (D)

1 Debye (D) = 3.336×10^{-30} C.m

Application of dipole moment

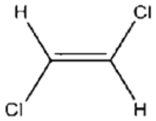
(i) Determination of polarity of molecule

Molecules which have zero dipole moment are non-polar, Whereas molecules which have dipole moment are polar.

For example benzene has zero dipole moment, so it is non polar. But Cholobenzene has dipole moment of 1.2D, so it is polar.

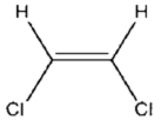
(ii) Prediction of Isomers

The study of dipole moment also finds applications in stereochemistry. For example, dipole moments of isomer 1, 2 – dichloroethene have been calculated are given below:



Trans

$\mu = 0$ D



Cis

$\mu = 1.89$D

Thus knowing the dipole moment of the given sample of 1, 2 – dichloroethene, one can predict whether it is Cis or trans isomer.

(ii) Calculation of %age ionic character in a bond.

The dipole moment helps to calculate the percentage ionic character in a bond.

Example

The observed dipole moment of HF is 1.90D. Find the percentage ionic character in HF bond. The distance between the charges is 0.917×10^{-10}m.

(Unit positive change = 1.6022×10^{-19}C)

Solution:

Let us suppose that HF molecule is 100% ionic. It means that H has full positive charge and F has full negative charge. To calculate their dipole moments multiply the bond length with full charges of electron or proton i.e. 1.6022×10^{-19}. This dipole moment is called $\mu_{\text{ionic.}}$

So, $\mu_{\text{ionic}} = q \times r$

$= (1.6022 \times 10^{-19}\text{C})\ (0.917 \times 10^{-10}\text{m})$

$= 1.469 \times 10^{-29}$ C.m

Since 1D = 3.336×10^{-30} C.m

$$\text{So, } \mu_{\text{ionic}} = \frac{1.469 \times 10^{-29}\,\text{C.m}}{3.336 \times 10^{-30}\,\text{C.m}} = 4.4 \text{ D}$$

The actual dipole moment as it is observed.

$\mu_{\text{observed}} = 1.90$ D

$$\%\text{ ionic character} = \frac{1.90\text{D} \times 100}{4.4\text{D}} = 43.2\%$$

Hence HF bond is 43% ionic and 57% covalent. The bond is predominantly covalent.

3.4 EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

The properties of substances are characterized by the type of bond present in them.

We shall consider the effects of the types of bond on physical and chemical properties of compounds.

Properties of Compounds:

Solubility

(a) Solubility of Ionic Compounds:

Most ionic compounds are soluble in water but insoluble in non-aqueous solvents.

Reason: When a crystal of ionic compound is placed in water, the polar water molecules detach the cation and anion from the crystal lattice by their electrostatic attraction. The ions are freed from the crystal lattice by hydration. This happens when the hydration energy is equal to or greater than the lattice energy. The energy released in hydration is used to overcome the lattice energy. Thus the ions are freed from their positions in the crystal.

Many ionic compounds do not dissolve in water because the attraction of water molecules cannot overcome the attraction between the ions. Their lattice energy dominates over their hydration energy. For the same reasons, the non-polar solvents benzene and hexane do not dissolve in ionic compounds.

(b) Solubility of Covalent Compounds:

Covalent compounds dissolve in non-polar organic solvents such as benzene, ether. Most covalent compounds are insoluble in water. However, some of them dissolve in water.

Reason: The attractive forces of solvent molecules in non-polar solvents are enough for overcoming the intermolecular forces of attraction in covalent compounds. Hence covalent compounds dissolve easily in non-polar organic solvents.

The solubility of covalent compounds in water depends on their ability to form hydrogen bonds with water molecules. Many organic compounds containing oxygen or nitrogen like carbohydrates, alcohols and amines are soluble in water due to hydrogen bonding.

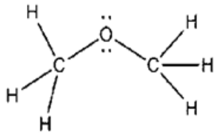
(c) Non-directional nature of ionic compounds:

Ionic bonds are non-directional and rigid in nature. They do not show the phenomenon of isomerism.

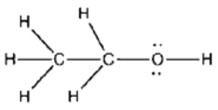
(d) Directional Nature of covalent compounds

Covalent bonds are non-rigid and directional. They show the phenomenon of isomerism.

Reason: Due to non-rigid and directional nature of the covalent bond, covalent compounds have different orientation of atoms in space. Hence many covalent compounds show the phenomenon of isomerism. For example C_2H_6O show structural isomerism.



Dimethyl Ether



Ethyl alcohol

3. Reaction Kinetics

(a) Speed of reaction of ionic compounds

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occurs rapidly. The reaction is so rapid because no bond is to be broken, only a new bond is formed. The ionic bonds have already been broken during the formation of solution.

For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously.

The oppositely charged ions combine at once to give the product. This is because no force is required to break the bonds of reacting compounds.

(b) Speed of reaction of covalent compounds.

Since there is no strong electrical force to speed up a chemical reaction, like in ionic reaction the covalent bonds are generally much slower to react as they involve both breaking and making of bonds. The molecules undergo a chemical change as a whole. It is because high energy is required to break the covalent bonds. Covalent compounds react in a variety of ways. The reactivity of covalent compounds depends upon the way a reaction proceeds and the kind of product-obtained at the end of a reaction.

4. Density:

The electrostatic force of attraction existing between the cations and anions in an ionic crystal brings these ions very close to one another. This decreases the volume of the crystal and consequently the ionic crystals have high density.

5. Types of Solids:

A solid is a structural unit of atoms, molecules or ions, which are held together strongly enough to give a rigid structure.

Four types of solids exist namely

(a) Molecular solids:

Consists of atoms or molecules held together by inter-molecular forces. Solid water (ice) and solid CO_2 (dry ice) are common examples.

(b) Metallic Solids:

Consists of atoms held together by metallic bonding, examples silver, copper and gold.

(c) Ionic Solids:

Consists of cations and anions held together by virtue of electrostatic attraction of the opposite charges. Examples are NaCl and $CaCl_2$.

(d) Covalent Network Solids:

Consists of atoms held together in large network or chains by covalent bonds. Diamond and graphite are typical examples.

Diference between metallic Solids and Molecular Network Solids *Metallic Solids*

Metallic Solids

Metallic solids consist of infinite arrays of bonded atoms; each cation in a metal has a high co-ordination number sometimes four or six, but more often eight or twelve they are good conductors of electricity.

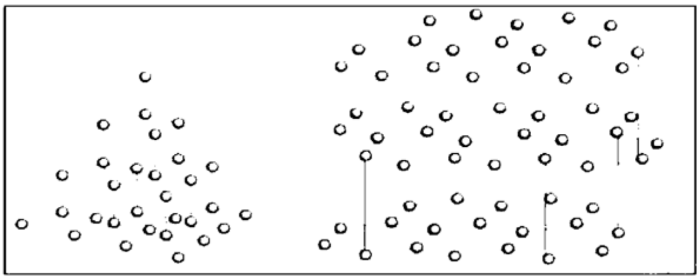
Covalent Network Solids

They consist of infinite arrays of bonded atoms; no individual molecules can be distinguished. Thus any given piece of network solid may be considered a giant, covalently bonded molecule. Network solids generally are poor conductor of heat and electricity. Strong covalent bonds among neighbouring atoms throughout the structure give these solids, strength and high melting temperature. Some of the hardest substances known are covalent network solids.

Diamond, the hardest allotrope of carbon, has the covalent network structure shown in the diagram. Diamond sublimes at 3500^0C and above.

Graphite, a softer allotrope of carbon has three layered structure shown in the diagram.

One feature that distinguishes covalent network solids from metals is the lower co-ordination number of atoms in network structures. For example; Co-ordination number of C in diamond is four, silicon (Si) is four and that of oxygen in quartz is two.



Diamond Graphite

Figure 3.27: Allotropic forms of carbon

References for additional information

- John C. Kotz, Paul M. Triechel and Gabriela C. Weaver, Chemistry and Chemical reactivity.
- Asim and K. Das, Fundamental concepts of chemistry.
- David E. Goldberg, Fundamentals of Chemistry.
- Graham Hill and John Holman, Chemistry in context.

[illegible]

1. **Choose the correct answer (MCQ).**

(i) The bond energies of F_2, Cl_2, Br_2, and I_2 are 37, 58, 46 and 36k Cals, respectively. The strongest bond formed is in;

(a) F_2 (b) Cl_2 (c) I_2 (d) Br_2

(ii) The percentage of ionic character of bond between two atoms is calculated from their;

(a) Dipole moment (b) Electronegativities

(c) Electron affinities (d) Ionization energies

(iii) The geometry of PF_5 molecules is;

(a) Planar (b) Square planar

(c) Trigonal bipyramidal (d) Tetrahedral

(iv) Sp^3 hybridization is not important in describing the bonding in;

(a) NH_4^+ (b) CCl_4 (c) H_2O (d) AgCl

(v) Greater the dipole moment

(a) Greater is the ionic nature (b) Lesser is the polarity

(c) Smaller is the ionic nature (d) None

(vi) A diatomic molecule has a dipole moment of 1.2 D. If its bond distance is 1.0 A°, what fraction of electric charge 'e' exist on each atom?

(a) 12% e (b) 18% of e (c) 25% e (d) 30% of e

(vii) H – O – H bond angle in H_2O is 104.5° and not 109.5° because of;
   (a) High electronegativity of oxygen (b) Bond pair – bond pair repulsion
   (c) Lone pair – lone pair repulsion (d) Lone pair – bond pair repulsion

(viii) Which is not characteristic of π bond?
   (a) π bond is formed when a sigma bond already exist
   (b) π bond are formed from hybrid sp arbitals
   (c) π bond may be formed by the parallel overlapping of p-orbitals
   (d) π bond results from lateral overlap of atomic orbitals.

(ix) In the formulation of N_2^+ from N_2, the electron is removed from;
   (a) σ_{2px} orbital (b) σ^{*}_{2px} orbital (c) π_{2py} orbital (d) π^{*}_{2py} orbital

(x) According to VESPR theory, the most probable shape of the molecule having 4 electron pairs around the central atom is;
   (a) Hexagonal (b) Tetrahedral (c) Octahedral (d) Linear

2 Read the given table below and answer the following questions.

Bond	**Bond energies in kJmol^{-1}**	
X- X	X = Cl	X= I
	242	151
H – X (Calculated)	336	291
H – X (Observed)	431	299
Difference	95	08

(a) Give reason for the difference in calculated values and observed values.
(b) Effect of high bond energy on bond length with reason.
(c) Ionic character on the basis of bond energies, with reason.

3. Energies of orbitals can be explained by molecular orbital theory. It has been observed that in case of Nitrogen molecule $\sigma 2p_x$ is higher in energy than $\pi 2p_y$ and $\pi 2p_z$
   (a) Draw molecular orbital energy diagram for nitrogen molecule.
   (b) Give reason why the $\sigma 2p_x$ energy is greater than $\pi\ 2p_y$ and $\pi\ 2p_z$.

4. Carbon can make a bond with hydrogen to form ethyne. Bond energy of C–H is same although 2s and 2p orbitals are involved which have difference in energies. Explain the formation of ethyne molecule on the basis of hybridization with the help of diagram.

5. Molecular orbital theory can explain the magnetic character of O_2, O_2^{2+} and O_2^{2-} species Evaluate it.

6. The melting points, boiling points, heat of vaporization and heats of sublimation of electrovalent (ionic) compounds are higher as compared to those of covalent-compounds. Argue.

7. The dipole moment of HCl is 1.03D and the distance between atoms is 127pm calculate the percentage of ionic character of the HCl bond. (**Ans.** 16.9%)

8. Differentiate between a sigma bond and a pi bond.

9. A double bond is stronger than a single bond and a triple bond is stronger than a double bond.