Chapter # 03

Chemical Bonding

Major Concepts

- 3.1 Shapes of Molecules
- 3.2 Resonance
- 3.3 Theories of Covalent Bonding
- 3.4 Bonding Characteristics
- 3.5 Effects of Bonding on Physical and Chemical Properties

Learning Outcomes

The students will be able to:

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

Introduction

Why do two oxygen atoms combine and give an O_2 molecule while two neon a stay apart from each other and do not give a Ne_2 molecule? Why do some a combine while certain others do not? Certainly there must be some force w holds two oxygen atoms together. . forces of attraction which holds va elements (atoms or ions) together in different chemical compounds are called chemical bonds. [redacted]

It is the natural tendency of an element to be stabilized. If there are two or eight electrons in the outermost shell of an atom then this is called a stable one. Stable elements do not form chemical bonds e.g. Noble gases are the most stable elements and have a little tendency to form chemical bonds. The elements with incomplete outermost shells are tried to gain, lose or share their electrons with other elements to complete their valence (outermost) shells. In this way chemical reactions are occurred and chemical bonds are formed.

Chemical bonds between atoms are usually classified as either ionic or covalent.

Ionic bonds are formed between oppositely charged ions (cations and anions) by the transfer of electrons from one element to another e.g. the bonds in NaCl, KBr, and CaO are ionic. They generally result when a metal reacts with a non-metal. It is non-directional. The electronegativity (E.N) difference should be more than 1.7.

Covalent bonds are formed by the mutual sharing of electrons between two different or similar atoms. The bonds in N_2, H_2O, and CO_2 are covalent. The E.N difference for covalent bond should be less than 1.7. They generally occur between non-metal atoms. They are directional and are shown by signs (−, =, ≡).

If you know the type of bonds in a compound, you can predict many of its physical properties.

In this chapter we will discuss the geometries of molecules and we will also explore two theories of chemical bonding: valence bond theory and molecular orbital theory.

Society, Technology and Science

Straight and Curly Hair

Hairs are mainly made up of protein, called keratin. Keratin is also present in nails and skin. Keratin is composed of long chain of sulphur containing amino acids called cysteine. The cysteine of one keratin molecule forms a disulphide bond (a covalent bond formed between the sulphur atoms of two thiol groups) with the cysteine of the neighbouring keratin molecule. The greater the number of disulphide

Straight Hair Curly Hair Wavy Hair

bonds, the curlier the hair. The fewer the number of disulphide bonds, the straighter the hair. It depends upon the number of disulphide bonds between cysteine molecules of keratin whether your hair is curly, wavy or straight. A disulphide bonds imbalance causes the hair to appear straight in certain areas and curly in other areas. People with straight hair can change their hair to force it into curly state by using chemicals. They are chemically forcing the making of strong disulphide bonds. The waves do not stay for all time, because the new hair grows in, which is straight, and only the ends curly.

3.1 Shapes of Molecules

Why do molecules possess definite shapes? Why is the shape of CO_2 linear? Why is the shape of water angular? The answers of these and many more questions can b found in the VSEPR theory. Chemists are interested in the shapes of molecules. Th bond angle and molecular shape are very important concepts in chemistry. Th physical and chemical properties of substances such as melting point, boiling poin bond energy and density etc. are strongly influenced by the geometry (3- arrangement of atoms in space). The shapes of molecules can be best explained wit the help of "ball-and-stick" models. The ball represents the atom and the stic represents the bond pair.

3.1.1 Valence Shell Electron Pair Repulsion (VSEPR) Theory

In 1940, the Sidgwick and Powel pointed out that the shapes of molecules can be explained by the arrangement of electron pairs in the valence shell (outer most shell) of central atom. The atom in the center which is not present at the terminal in the polyatomic molecule is called central atom.

In 1957, Gillespie and Nylholm proposed VSEPR (pronounced as "vesper") theory. It explains shapes and bond angles of molecules and ions in terms of the electrostatic repulsion between electron pairs. The repulsion between the negative charges of electron pairs around the central atom determines the geometry of the molecule but we name the shape of molecules by the position of the atoms.

Keep in mind

The shared pair of electrons called *bond pair* while th unshared pair of electrons called *lone pair*. We can sa that the electrons that a involved in making bonds a called bond pairs and th electrons that are not involv in making bonds are call lone pairs.

Main Features (Postulates)

The main points of VSEPR theory are as follows:

i) Electron pair geometry of molecules depends upon the number of electron airs (both bond pairs and lone pairs) present in the outermost shell of central atom.

i) Geometry (shape) of molecules depends upon the number of bond pairs resent in the outermost shell of central atom.

ii) The electron pairs in the valence shell repel one another because they are egatively charged.

v) Electron pairs around central atom are located at maximum distances where epulsion is the minimum.

) A lone pair (lp) occupies more space than a bond pair (bp).

i) Repulsion between electron pairs in valence shell decreases in the following rder:

$$lp - lp \gg lp - bp > bp - bp$$

The repulsion between electron pairs in the valence shell may be called Van er Waals repulsion or exchange repulsion.

ii) A multiple bond (double or triple bond) occupies more space than a single ond. However these behave as a single electron pair bond for the purpose of SEPR theory.

iii) The shape of molecule will be regular, if a molecule has only bond pairs.

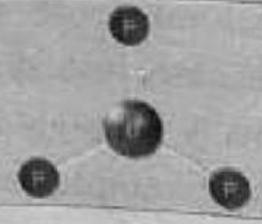
x) The shape of molecule will be irregular, if a molecule has some lone pairs of lectrons.

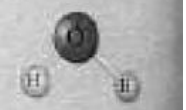
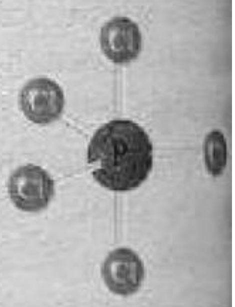
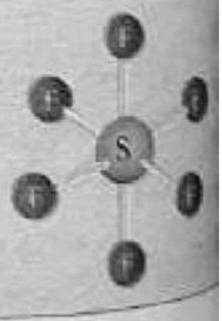
) The geometry around an atom is described by the general formula:

$$AB_mE_n$$

Where A is central atom, B is a bonded atom, E is a lone pair, m is the number f B atoms around the central atom A and n is the number of lone pairs around entral atom.

Table 3.1: Shapes of Molecules according to VSEPR Theory

umber f Electron Pairs	Number of Bond Pairs	Number of Lone Pairs	Electron Pair Geometry	Formula	Molecular Geometry	Example	Ball and Stick Model
1	1	0	Linear	AB	Linear	HF	
2	2	0	Linear	AB_2	Linear	CS_2	
3	3	0	Trigonal planar	AB_3	Trigonal planar	BF_3	

Number of Electron Pairs	Number of Bond Pairs	Number of Lone Pairs	Electron Pair Geometry	Formula	Molecular Geometry	Example	Ball and Stick Mod
3	2	1	Trigonal planar	AB_2E	Bent	SO_2	
4	4	0	Tetrahedral	AB_4	Tetrahedral	CH_4	
4	3	1	Tetrahedral	AB_3E	Trigonal pyramidal	NH_3	
4	2	2	Tetrahedral	AB_2E_2	Bent	H_2O	
5	5	0	Trigonal bipyramidal	AB_5	Trigonal bipyramidal	PCl_5	
6	6	0	Octahedral	AB_6	Octahedral	SF_6	

Applications of VSEPR Theory

The shapes of regular and irregular molecules are discussed below:

1) Shape of Molecules having one Electron Pair (AB type)

A diatomic molecule has only one bond pair and no bond angle. Because the geometric shape determined by two points is a straight line, all diatomic molecules are linear in shape. Examples are: HCl, CO, F_2, and N_2.

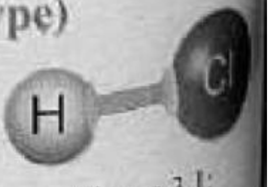


Figure 3.1: Linear Geometry

2) Shape of Molecules having two Electron Pairs (AB_2 type)

Molecules having two bond pairs and no lone pair give linear geometry. Their bond angle would be of 180°. Examples are: $BeCl_2$, $CdCl_2$, CO_2, CS_2, $HgCl_2$.

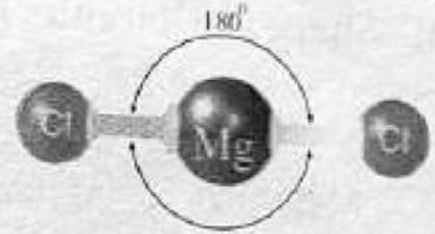


Figure 3.2: Linear Geometry

$MgCl_2$ has two bond pairs and minimize it's repulsion by arranging bond pairs at an angle of 180° and thus assume linear geometry.

3) Shape of Molecules having Three Electron Pairs

Such molecules are further divided into two types:

i) Molecules having three bond pairs and no lone pair (AB_3 type) give planar triangular geometry. Their bond angles are of 120°.

Examples are: BCl_3, $AlCl_3$, SO_3, hydrides of group IIIA.

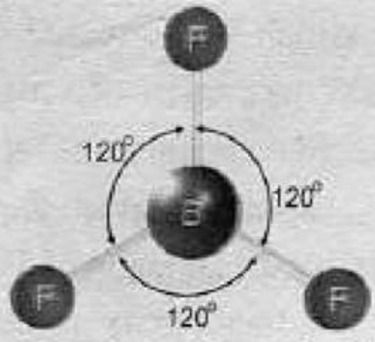


Figure 3.3: Planar Triangular Shape

The molecular shape of BF_3 is triangular planar because the triangle of boron atom and the fluorine atoms all lie in the same plane.

ii) Molecules having two bond pairs and one lone pair (AB_2E type) give distorted triangular shapes. Their bond angles are less than 120°. Examples are: $SnCl_2$, $PbCl_2$, SO_2.

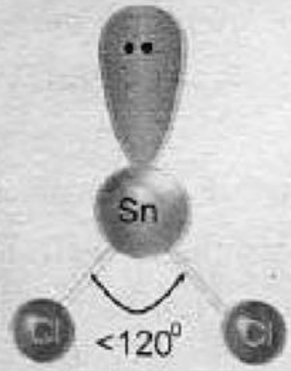


Figure 3.4: Distorted Triangular Shape

As we know that the lone pair occupies more space than a bond pair, hence it pushes the bond pair closer to each other and cause compression of angle between two bond pairs.

Conceptual Check Point:

The molecules which have two bond pairs but no lone pair show linear shapes while those which have two bond pairs and one lone pair show distorted triangular shapes. What will be your answer?

4) Shape of Molecules having Four Electron Pairs:

Such molecules are further divided into three types:

i) Molecules having four bond pairs and no lone pair(AB_4 type) give tetrahedral geometry with an angle of 109.5°. Examples are: SiH_4, CCl_4, CH_4.

The methane molecule has four bond pairs which are directed from the center towards the corners of a regular tetrahedron. These four bond pairs should be placed 109.5° apart to give them a tetrahedral geometry. At an angle of 109.5° the distance between bond pairs is the maximum and repulsion is minimum.

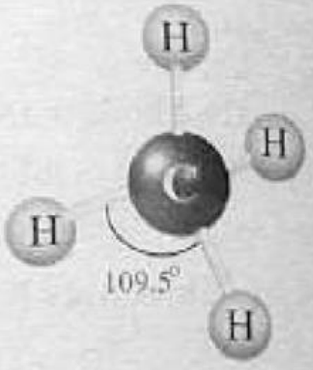
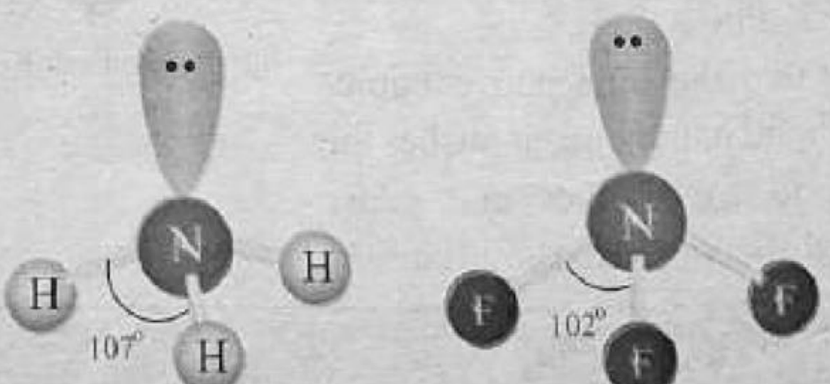


Figure 3.5: Tetrahedral Shape

ii) Molecules in which central atom has three bond pairs and one lone pair (AB type) give trigonal pyramidal shapes instead of tetrahedral shapes. Their bon angles are less than 109.5°. Examples are: NH_3 and NF_3.

In ammonia, the lone pair occupies more space than bond pairs. Therefo three N–H bond pairs are pushed closer and the bond angle decreases from 109.5° 107°.

In NF_3, fluorine is the most electronegative element. So N-F bond more polar than N–H. Therefore, lone pair exerts more repulsion on bondi pairs in NF_3. Hence, bond angle further reduces to 102°.



Ammonia

Nitrogen Trifluoride

Figure 3.6: Pyramidal Shape

Other examples are: PCl_3, PH_3, AsH_3.

iii) The Molecules in which central atoms have two bond pairs and two lone pairs (AB_2E_2 type) give angular or bent shape. Their bond angles are 104.5° instead of 109.5°. Examples are: H_2O, H_2S, SCl_2, $SeCl_2$.

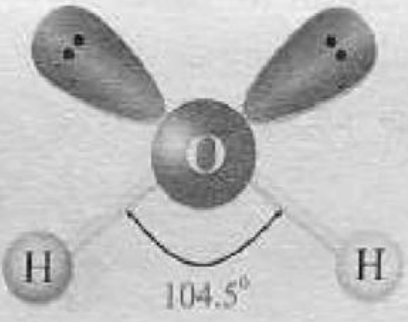


Figure 3.7: Angular Shape

In water molecule, the two lone pairs occupy more space than two bond pairs. As lone pair – lone pair repulsion is greater than lone pair – bond pair which in turn is greater than bond pair – bond pair. Hence, this forces the bond pairs closer together and reduces the bond angles to 104.5°. Therefore, the shape of water molecule is bent or angular or V–shaped.

Conceptual Check Point:

Why the shape of HCN is linear and that of H_2O is angular, although both of the molecules are triatomic?

) Shape of Molecules having Five Electron Pairs (AB_5 type)

Molecules having five bond pairs and no lone pair give triangular bipyramidal geometry. The equatorial bond angles are 120° and axial bonds are at right angles (90°) to the plane. Examples are: PF_5, PCl_5, $SbCl_5$, $SeCl_5$.

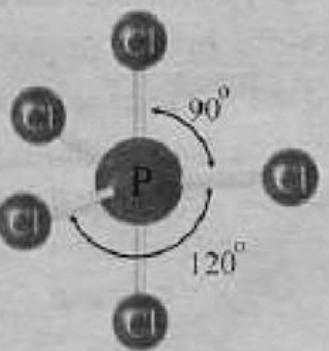


Figure 3.8: Triangular bi-pyramidal Geometry

Keep in mind

The atoms lie at the corner of an equilateral triangle are called equatorial atoms while the atoms above and below the plane of the triangle are called axial atoms. The bonds of equatorial atoms are called equatorial bonds while the bonds of axial atoms are called axial bonds.

[redacted]

6) Shape of Molecules having Six Electron Pairs (AB_6 Type)

Molecules having six bond pairs give octahedral geometry with bond angle equa 90°. Examples are: SF_6, TeF_6.

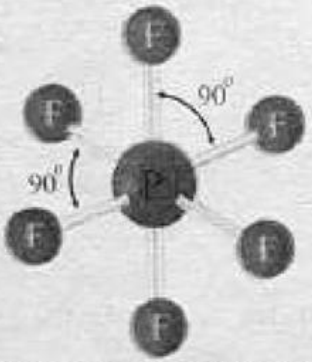


Figure 3.9: Octahedral Geometry

Keep in mind

In octahedral molecule, can not use the terms 'axial' 'equatorial' as in triang bipyramidal molecule beca all the six bonds a equivalent.

Limitations of VSEPR Theory

This theory was failed to explain:

i) The sharing of electrons in the valence shell.

ii) The paramagnetic nature of O_2 molecule.

iii) The shapes of molecules having delocalized π-electrons.

3.2 Resonance

The process in which two or more structures are written for a compound wh differs only in the arrangement of electrons is called resonance. The diffe structures obtained are called resonance structures. Resonance structures are actual structures. They are hypothetical and exist only on paper. They are, there cannot be prepared or isolated in the laboratory. The real or actual structure is hybrid of all the resonance structures. The resonance is represented by a dou headed arrow (⟷). There are some molecules and polyatomic ions for wh no single Lewis structure can be written. Let us take the example of oxygen. It ex in two allotropic forms; the dioxygen, O_2 (oxygen molecule) and the trioxyge (ozone). Ozone is present in larger amounts in the upper atmosphere wh shields life on earth from harmful UV radiation from the sun. It is also pres trace amounts in the lower atmosphere where it may damages plants and an tissues. There are two possible Lewis structures "A" and "B" for Ozone which

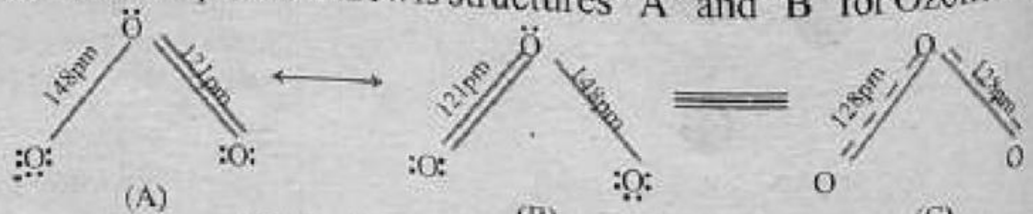


Figure 3.10: Lewis structures for Ozone

The O – O single bond in O_3 should be longer than the O=O double bond because the double bonds should be shorter than single bonds. But experimental evidence shows that the oxygen-to-oxygen bonds are equal in length (128 pm). This bond length is shorter than the O – O single bond length of 148 pm in hydrogen peroxide, H – O – O – H, but it is longer than the double bond length of 121 pm in diatomic oxygen, O = O. Hence neither of the above structures can be correct. The bond identity cannot be satisfactorily represented by any single structure and it becomes necessary to write more than one Lewis structures. To describe such situations a concept called resonance is used. The bonds in ozone are equivalent and intermediate in strength and length between a double bond and a single bond. The resonance structures of ozone are:

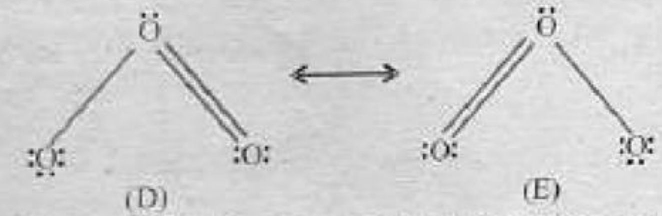


Figure 3.11: Resonance Structures of Ozone

They both are identical. They have same number of electrons (18 electrons) and both have octets around all three oxygen atoms. Which resonance structure is correct? Neither structure accurately represents the structure of ozone. The actual structure is the average (hybrid) of these two Lewis structures. They both have equal contributions to the real structure (hybrid structure) of ozone (structure "C" given above). A common analogy might help to clarify this concept. A horse and a donkey may be crossbred to produce a hybrid, the mule. The mule doesn't look or behave exactly like either parent, yet it has attributes of both. The resonance hybrid of a molecule has properties of each resonance form but is not identical to any one form.

Keep in Mind:

- Resonance structures are not real.
- The real structure is the hybrid of resonance forms.
- Resonance forms are not in equilibrium with each other.
- Resonance forms are not isomers. Resonance forms have different arrangement of electrons while isomers have different arrangement of both electrons and atoms. In witting resonance structures we are allowed to move electrons and not the atoms.

3.3 Theories of Covalent Bonding

VSEPR theory explains the shapes of simple molecules but it does not explai formation of chemical bond. There are two important quantum mechanical theo which explain the concept of bond formation, bond enthalpies, bond lengths a shapes of molecules. These are valence bond theory (VBT) and molecular orb theory (MOT). Neither theory completely explains all aspects of chemical bondi They both help us to understand the observed properties of molecules.

3.3.1 Valence Bond Theory and Hybridization

Valence Bond Theory (VBT)

This theory was first proposed by W. Heitler and Fritz London in 1927 and later developed by Linus Pauling and J.C. Slater in 1931. This theory expl bond formation (sharing of electrons), bond strength, and geometry of molecule

Main Points

Linus Pauling
(1901-1994)

i) Covalent bonds are formed by overlapping of half-filled atomic orbitals.

ii) A single covalent bond is formed by the overlap of two half-filled atomic orbitals.

iii) A multiple bond (double or triple covalent bond) is formed by the overlap of more than two half-filled atomic orbitals. Overlapping means a common region of two orbitals with high electron density.

iv) As a result of overlapping, the electrons with opposite spins paired up and become stable by releasing energy.

v) When they form a bond, the atomic orbitals maintain their identities; onl outermost shell electrons lose their identities.

vi) Greater the overlapping, the stronger is the bond.

vii) The direction of bond is determined by the direction of the two overlap orbitals when other than s-orbital are involved.

Types of Overlapping and Nature of Covalent Bonds:

On the basis of overlapping of orbitals, covalent bonds can be divided into two i.e. Sigma bond and pi-bond.

i) Sigma bond (σ – bond)

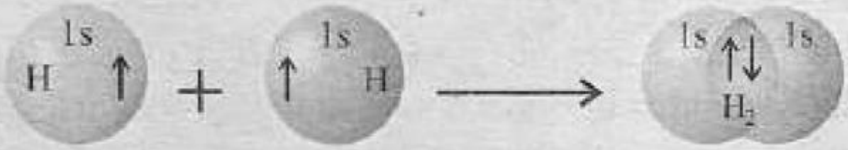
A covalent bond formed by head to head or linear overlap of two atomic orbit which electron density is the maximum around the bond axis) is called sigma

(Sigma is the English word for the Greek letter, which corresponds to the English letter *s*). Overlapping of s – s and s – p orbitals always form σ – bonds but p – p may form sigma bonds. It may also be formed by overlapping of atomic-hybrid and hybrid-hybrid orbitals. All single covalent bonds are sigma bonds.

Types of Overlapping

s – s Overlapping (Formation of H_2)

This type of overlapping takes place between half-filled s-orbitals of two atoms along the bond axis. For example, consider the formation of H_2 molecule from two hydrogen atoms. Each atom has the electronic configuration $1s^1$. The half-filled atomic orbitals ($1s^1$) of both H-atoms overlap to form a sigma bond. The electron density is maximum between the two nuclei.

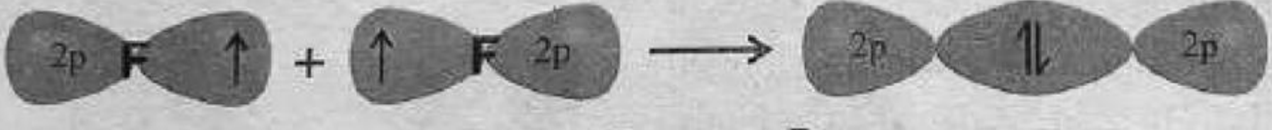


$$H + H \longrightarrow H_2$$

Figure 3.12: s-s overlapping

p – p Overlapping (Formation of F_2)

This type of overlap takes place between half-filled p-orbitals of the two atoms when they approach each other. The formation of fluorine, chlorine and bromine are the common examples of this type of overlapping. Consider the bonding between two fluorine atoms. The electronic configuration of each fluorine atom is $1s^2, 2s^2, 2p_x^1, 2p_y^2, 2p_z^2$. The F – F sigma bond is formed by overlap of half-filled p-p orbitals of two fluorine atoms. The electron density is maximum between two nuclei.

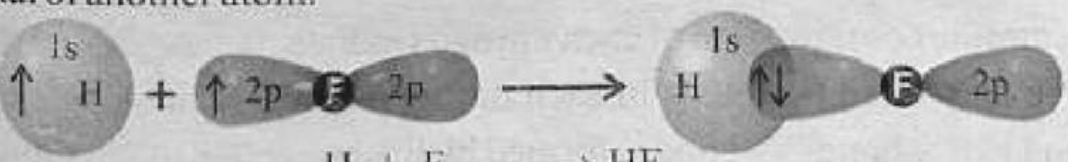


$$F + F \longrightarrow F_2$$

Figure 3.13: p-p overlapping

s-p Overlapping (Formation of HF)

This type of overlap takes place between half-filled s-orbital of one atom and half-filled p-orbital of another atom.



$$H + F \longrightarrow HF$$

Figure 3.14: s-p overlapping

Consider the bonding between a hydrogen atom and a fluorine atom. T electronic configuration of fluorine atom is $1s^1, 2s^2, 2p_x^1, 2p_y^2, 2p_z^2$. The half-f p-orbital (2Px) of fluorine atom overlap with $1s$ orbital of one hydrogen ato form a σ-bond. The other filled $2s$ and $2p$ orbitals of fluorine do not participate i bonding to the hydrogen.

Conceptual Check Point:

How can you explain the bonding in Cl_2 and HCl with respect to VBT?

ii) Pi Bond (π-bond)

The bond formed by sidewise or parallel overlap of two p-orbitals is called Pi bo Examples are: O=O, N=N, $CH_2=CH_2$.

This bond is named after the Greek letter π. The overlap of electronic cl in pi bonds is not as good as in sigma bonds, and they are correspondingly wea Pi bonds are often found in molecules with double or triple bonds. In π-bond, two p-orbitals are in one plane. In π-bond, molecular orbital (bonding) has region of electron density i.e. above and below the bond axis. In almost all ca single bonds are sigma bonds. A double bond consists of one pi bond and one si bond, and a triple bond consists of one sigma bond and two pi bonds.

Formation of O_2 Molecule

The electronic configuration of each oxygen atom is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^2$. There are two half-filled p-orbitals on each oxygen atom. Oxygen has one sigma bond which is formed by head to head overlap of $2p_x$ orbitals. It has one π-bond which is formed by side to side overlap of $2p_x$ orbitals. The electron density is maximum above and below the bond axis.

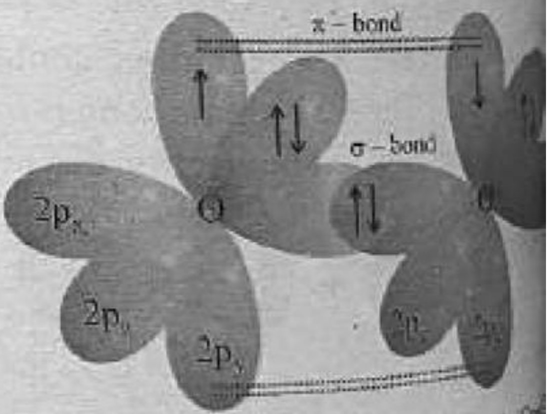


Figure 3.15: Orbital diagram of O_2 (O

Formation of N_2 Molecule

The electronic configuration of each nitrogen atom is $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p$ are three half-filled p orbitals in each nitrogen atom. N_2 molecule has one bond and two π-bonds. σ-bond is formed by linear overlap of $2p_x$ orbitals wh π-bonds are formed by parallel overlap of $2p_y$ and $2p_z$ orbitals.

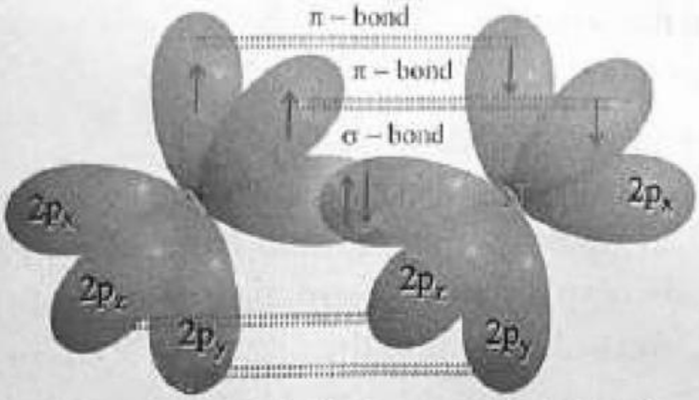


Figure 3.16: Orbital diagram of N_2 ($N \equiv N$).

Table 3.2: Difference between Sigma and Pi Bonds

Sigma Bond	Pi Bond
A covalent bond formed by linear overlap of two half-filled atomic or hybrid orbitals is called sigma bond.	A covalent bond formed by parallel overlap of two half-filled atomic orbitals is called pi bond.
It has electron density around the bond axis.	It has electron density above and below the bond axis.
All single covalent bonds are sigma bonds.	In a multiple bond, one is essentially a sigma bond which is formed earlier than pi bond.
It is stronger due to greater overlap of orbitals.	It is weaker due to lesser overlap of orbitals.
It is less reactive than pi bond.	It is more reactive than sigma bond.
Its formation does not depend on pi bond.	It is formed after the formation of sigma bond.
The shape of a molecule is determined only by the orbitals forming sigma bonds	The shape of a molecule is not determined by the orbitals forming pi bonds.
We can easily rotate the atoms around the bond axis of sigma bond.	Rotation about the double bond is not possible. The rotation is restricted because pi bond has two regions of electron density.
Example: In the molecule of NH_3, all bonds between nitrogen and hydrogen are sigma bonds.	Example: N_2 molecule has one sigma and two pi bonds.

Limitations of VBT

It does not explain:

- Bivalency of Be, trivalency of B and tetravalency of C.

ii) The angle between the bonds.
iii) The paramagnetism of O_2 molecule.

Atomic Orbital Hybridization

In 1931 Linus Pauling introduced the concept of hybridization to explai characteristic geometrical shapes of polyatomic molecules like CH_4, NH_3, B $AlCl_3$ and H_2O etc. He also explained the formation of multiple bonds in mole such as C_2H_2 and C_2H_4. According to him the atomic orbitals of different shape energy combine to form a new set of equivalent orbitals called hybrid orbitals the phenomenon is known as hybridization.

Keep in Mind

- The number of hybrid orbitals formed is always equal to the number of ato orbitals that are combined.
- The hybridized orbitals are always equivalent in energy and shape.
- Hybridization is the mixing of at least two nonequivalent atomic orbitals, example, s and p orbitals. Therefore, a hybrid orbital is not a pure atomic orbital.
- The shape of any hybrid orbital is different from the shapes of the original ato orbitals.
- The geometries are exactly as predicted by VSEPR theory.
- Hybridization takes place in an atom (usually the central atom) before bo formation. The concept of hybridization is not applied to isolated atoms.
- The hybrid orbitals form stable bonds than the pure atomic orbitals.

Types of Hybridization

There are three main types of orbital hybridization i.e. sp^3, sp^2, sp depending the number and nature of orbitals. They are as follows:

(i) sp^3-Hybridization (ii) sp^2-Hybridization (iii) sp-Hybridization

i) sp^3-Hybridization

The process of mixing of one s and three p-orbitals to give four identical sp^3- orbitals is called sp^3-hybridization.

Each sp^3-hybridized orbital has 25% s-character and 75% p-character. Examples are methane, water and ammonia.

Formation of Methane

Consider the example of methane. In methane the ground state ele configuration of carbon ($1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$) shows that the 2s orbital is and two of the p-orbitals are half-filled. But how can carbon form four bonds of its valence electrons are already paired and only two unpaired elect available for sharing? To account for the four C–H bonds in methane, one electrons is promoted from the lower-energy 2s orbital to the empty, higher-

2p orbital, giving an excited-state configuration ($1s^2, 2s^1, 2p_x{}^1, 2p_y{}^1, 2p_z{}^1$) which has four unpaired electrons. Now we have four orbitals, each of which could overlap with the 1s orbital of hydrogen atom to form a sigma bond. Experiment shows, however, that the four C–H bonds in methane are identical. If excited-state carbon uses two kinds of orbitals for bonding, 2s and 2p, how can it form four equivalent bonds? The p-orbitals are at right angles to each other, so three of the bond angles would be 90°, and the position of the sigma bond formed by overlap with the 2s orbital is unclear. This is where hybridization comes in. For this reason, the four valence orbitals of the carbon atom combine during the bonding process to form four new, but equivalent, hybrid orbitals. In this case, one s-orbital and three p orbitals are mixed to form four identical sp^3 (pronounced as "s-p-three") hybrid orbitals. Each hybrid orbital has one large lobe pointing in one direction and one small lobe pointing in the opposite direction.

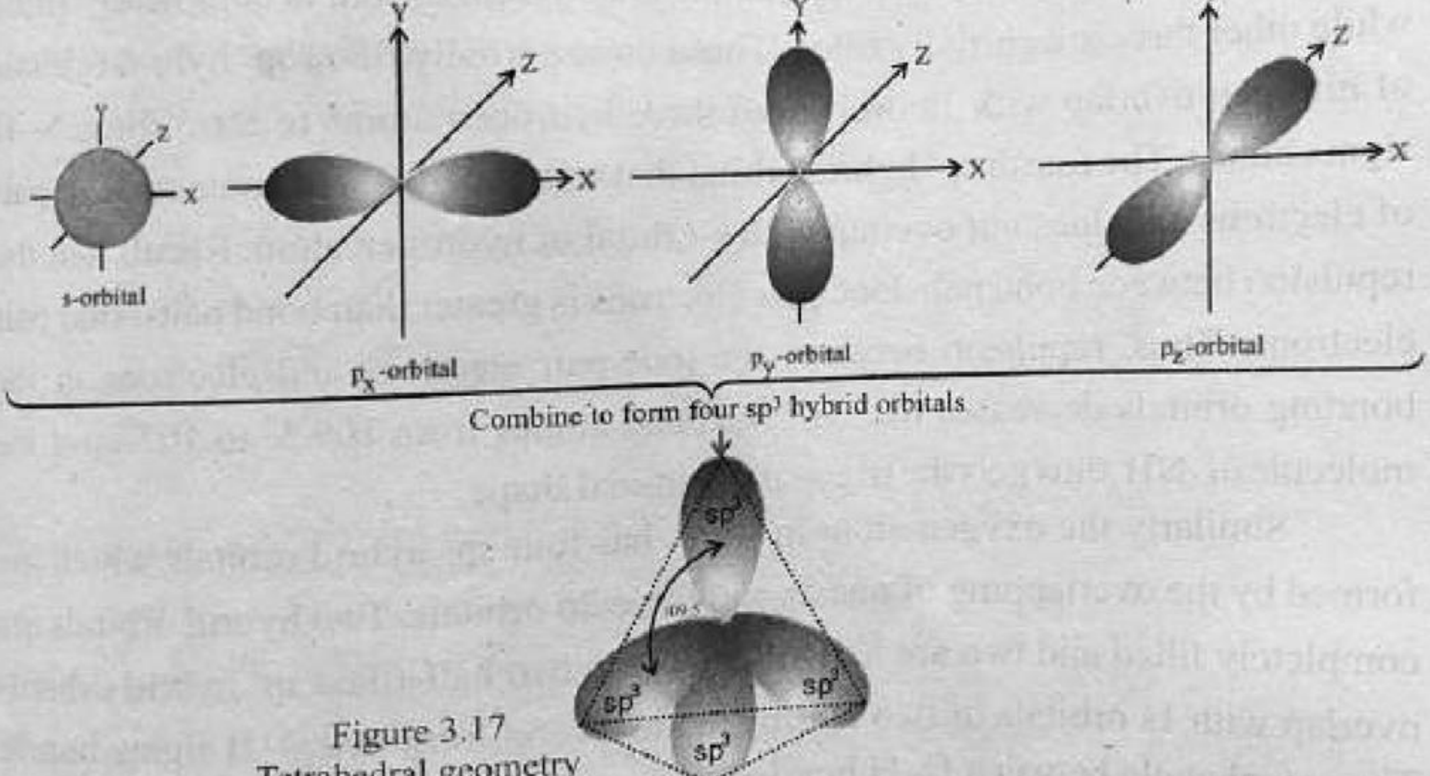


Figure 3.17
Tetrahedral geometry

In methane molecule, these four sp^3-hybrid orbitals of carbon overlap with 1s half-filled orbitals of four H-atoms to give four identical C–H bonds. The four C–H bonds are sigma bonds and formed due to s–sp^3 overlap.

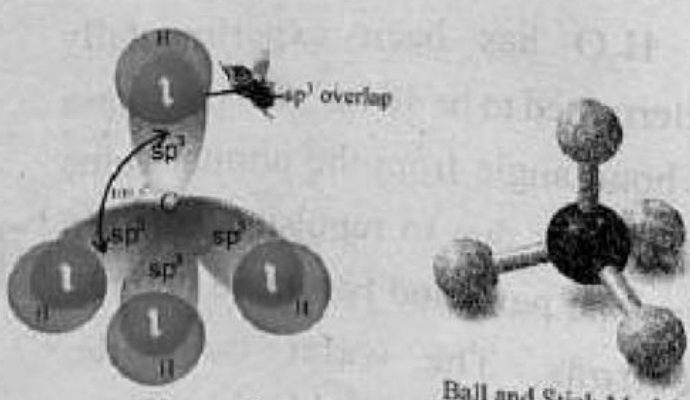


Figure 3.18: Methane Molecule

Covalent bonds made with sp^3 hybrid orbitals are often strong ones. In fact, the energy released on forming the four strong C–H bonds in CH_4 is greater in amount than the energy required to produce the excited state of carbon. Methane has tetrahedral shape with an angle of 109.5°. The shape of methane is the same as predicted by VSEPR theory.

Formation of Ammonia and Water

The shapes of NH_3 and H_2O molecules can be best explained with the help of sp^3–hybridization. In ammonia, the ground state electronic configuration of nitrogen is $1s^2, 2s^2, 2px^1, 2py^1, 2pz^1$ having one filled 2s-orbital and three half-filled 2p- orbitals. Here one 2s and three 2p orbitals of nitrogen atom are combined together and give four sp^3 hybrid orbitals. One hybrid orbital is completely filled while other three are partially filled. These three partially filled sp^3 hybrid orbitals of nitrogen overlap with 1s orbitals of three hydrogen atoms to form three N–H sigma bonds. The fourth sp^3 hybrid orbital that was already filled contains lone pair of electrons and does not overlap with s-orbital of hydrogen atom. Recall that the repulsion between bond pair-lone pair electrons is greater than bond pair-bond pair electrons. Thus, repulsion between the lone-pair electrons and electrons in the bonding orbitals decreases the $H\widehat{N}H$ bond angles from 109.5° to 107° and the molecule of NH_3 thus gets the trigonal pyramidal shape.

Similarly the oxygen atom in water has four sp^3 hybrid orbitals which are formed by the overlapping of one 2s and three 2p orbitals. Two hybrid orbitals are completely filled and two are half-filled. These two half-filled sp^3 hybrid orbitals overlap with 1s orbitals of two hydrogen atoms and form two O–H sigma bonds. The actual angle between O–H bonds in H_2O has been experimentally determined to be 104.5°. This decrease in bond angle from the normal value (109.5°) is due to repulsion between two lone pairs and two bond pairs of electrons. The water molecule, therefore, has angular or V-shape.

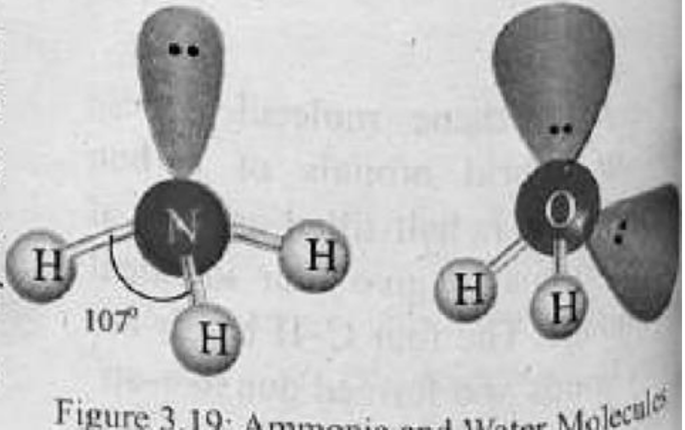


Figure 3.19: Ammonia and Water Molecules

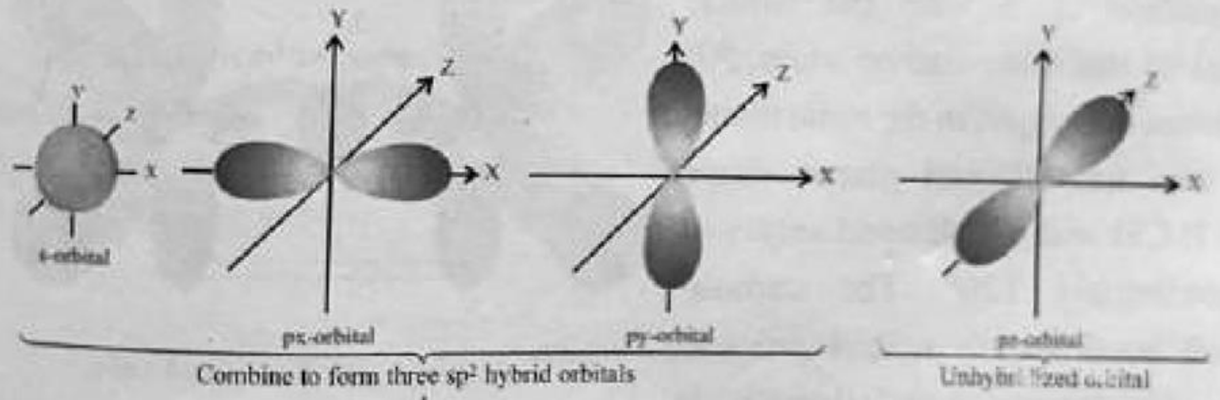
ii) sp^2-Hybridization

The process of mixing of one s and two p-orbitals to give three identical sp^2-hybrid orbitals is called sp^2-hybridization.

Each sp^2-hybrid orbital has 33% s-character and 67% p-character. Examples are boron tri-fluoride and ethene.

Formation of Boron Tri-fluoride:

In BF_3 molecule, the ground state electronic configuration of central boron atom is $1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$. First we promote one of the lower energy 2s electrons to an empty higher energy 2p-orbital giving an excited state electronic configuration $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^0$ in which boron has three unpaired electrons. These three orbitals (one 2s and two 2p) having unpaired electrons are mixed together to produce three sp^2 hybrid orbitals of same shape and energy. Note that one of the 2p orbitals of boron remains un-hybridized and is unoccupied by the electrons. This un-hybridized orbital will be important when we will discuss double bonds in the next examples.



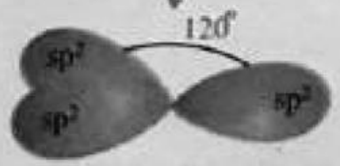


Figure 3.20: Trigonal Planar Geometry

These three sp^2 hybrid orbitals of boron overlap with p-orbitals of three fluorine atoms and form three sigma F-B bonds. The BF_3 molecule is planar with all the $F\hat{B}F$ angles equal to 120°. The geometry of BF_3 is trigonal planar.

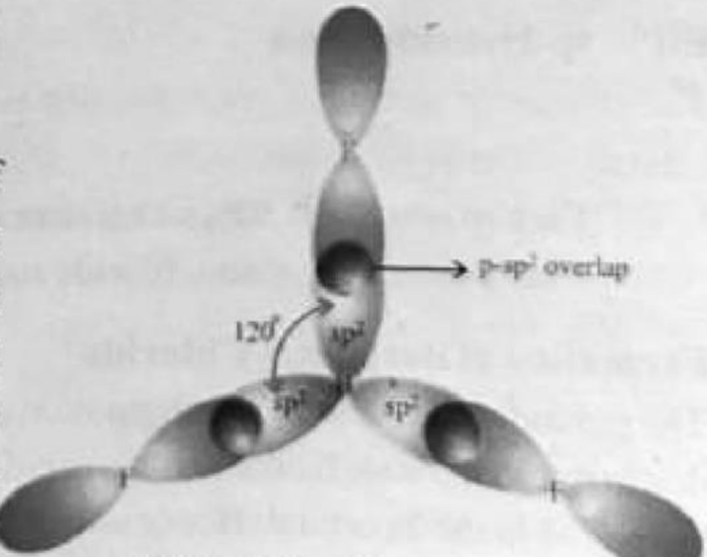


Figure 3.21: BF_3 molecule

Formation of Ethylene

Consider the example of ethylene molecule, C_2H_4 which has a C=C double bond this case, three sp^2 hybrid orbitals are required, because each carbon atom is bond to three other atoms (one carbon and two hydrogen atoms) and there is no lone p of electrons. As we know, the excited state electronic configuration of carbon is 1 $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. In ethylene, one 2s and two 2p orbitals of carbon atom are mi together to give three sp^2 hybrid orbitals of same shape and energy. The remaini $2p_z$ orbital does not take part in the hybridization. In ethylene, each C–H sig bond is formed by overlap of sp^2 hybrid orbitals on carbon with the 1s orbitals each hydrogen atom. There is one sigma bond between two carbon atoms which formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom one π-bond which is formed due to overlap of un-hybridized p-orbital of one carbon atom with the similar orbital of the other carbon atom. All six atoms in C_2H_4 lie in the same plane. Ethylene has trigonal planar shape with $H\hat{C}H$ and $H\hat{C}C$ bond angles of approximately 120°. The carbon-carbon bond length is 134 pm and carbon-hydrogen bond length is 108pm.

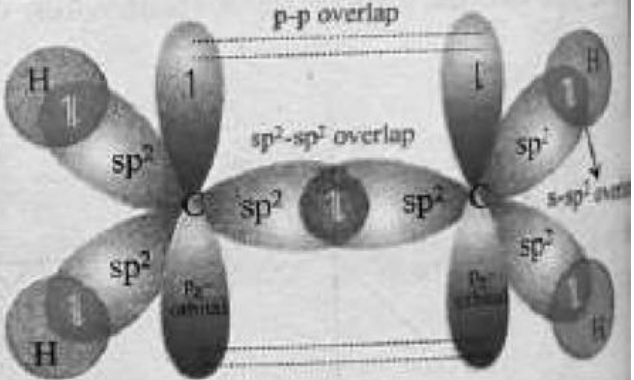


Figure 3.22: C_2H_4 molecule

iii) sp-Hybridization

The process of mixing of one s and one p-orbital to give two identical sp hy orbitals is called sp-hybridization.

Each sp orbital has 50% s-character and 50% p-character.

Examples are beryllium chloride and acetylene.

Formation of Beryllium Chloride

The ground state electronic configuration of Be is $1s^2, 2s^2, 2p_x^0, 2p_y^0, 2p_z^0$. We k that in its ground state Be does not form covalent bonds with Cl because its ele are paired in the 2s orbital. Hence one of the 2s electrons is promoted to vac orbital. Therefore the excited state electronic configuration of Be is $1s^2, 2s^1$,

$2p_y$, $2p_z$. Now there are two Be orbitals available for bonding, the 2s and 2p. The filled (2s and $2p_x$) orbitals of Be are mixed together to give two sp hybrid itals. These two new orbitals are identical in shape.

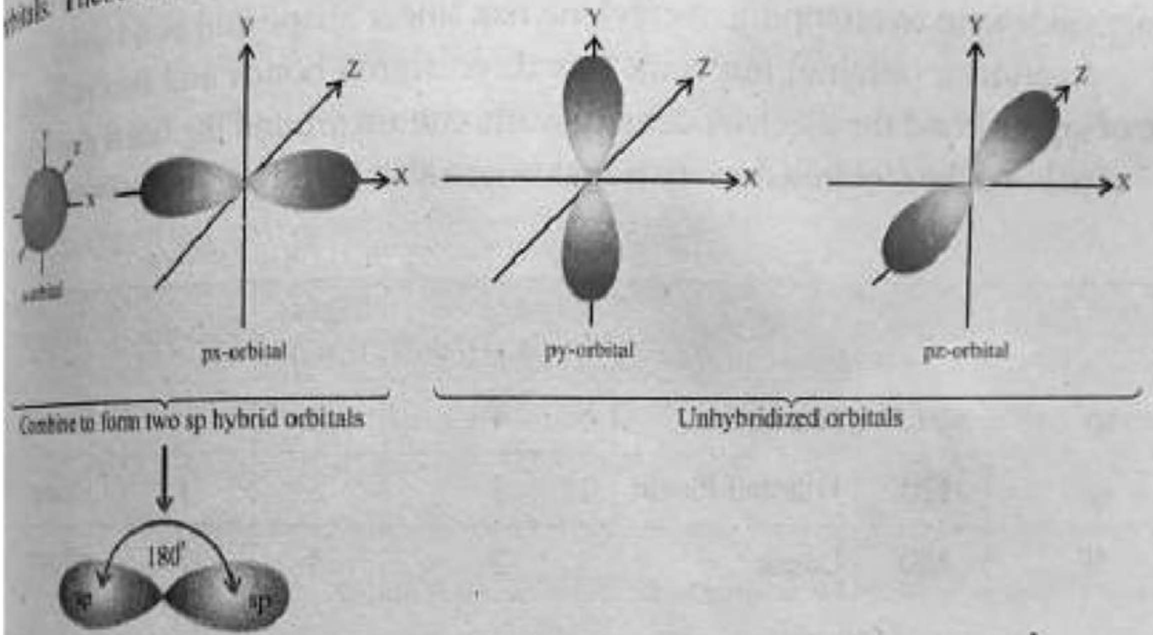


Figure 3.23: Linear Geometry

The remaining vacant $2p_y$ and $2p_z$ orbitals do not take part in hybridization. two sp-hybrid orbitals of Be overlap with half-filled p orbitals of two chlorine ms and form two Be–Cl sigma bonds. The bond angle between Cl–Be–Cl is It has a linear geometry.

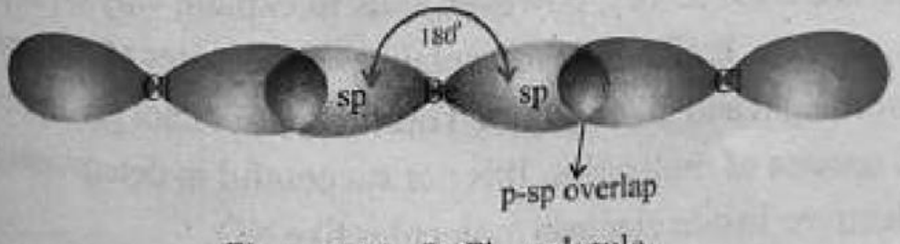


Figure 3.24: $BeCl_2$ molecule

ation of Acetylene

cited state electronic configuration of carbon is $1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, In acetylene, one s ($2s^1$) and one p orbitals of carbon get hybridized two hybrid sp orbitals. One of sp hybrid orbitals of each atom overlaps with 1s half-orbital of hydrogen atom and C–H sigma bonds, while the

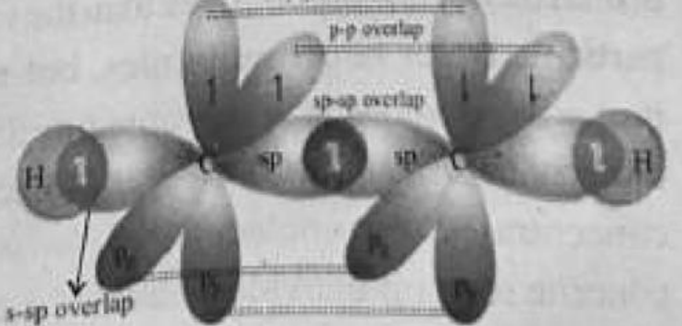


Figure 3.25: C_2H_2 molecule

other sp hybrid orbital of one carbon atom overlaps with sp hybrid orbital of other carbon atom to form C–C sigma bond. The remaining $2p_y$ and $2p_z$ orbita not take part in hybridization. They form two pi bonds between two carbon at through sidewise overlapping. Acetylene has linear shape and bond angle is 1

Acetylene (ethyne) molecule has three sigma bonds and two pi bonds case of sigma bond the electron density is maximum around the bond axis whil case of pi bond the electron density is maximum above and below the bond axis.

Table 3.3: Nature of Bonds and Shapes of Hybrid Orbitals

Hybridization	Angle	Shape	Number of Hybrid Orbitals	Sigma Bonds	Pi-bond	Exampl
sp^3	109.5°	Tetrahedral	4	4	0	Methane
sp^2	120°	Trigonal Planar	3	5	1	Ethene
sp	180°	Linear	2	3	2	Ethyne

3.3.2 Molecular Orbital Theory (MOT)

Valence bond theory provides an explanation of bonding in molecules and stabi of the covalent bond in terms of overlapping atomic orbitals. With the help hybridization we can explain molecular geometries predicted by the VSEPR the It also helps to explain bivalency of beryllium, trivalency of boron and tetravale of carbon. Valence bond theory, however, fails to explain why O_2 is paramag and N_2 is diamagnetic. It also fails to explain excited states of molecules that molecules absorb light and give colours. This theory does not give an explanatio the electronic spectra of molecules. It is not successful in determining the loca of unpaired electrons in odd electron molecules like NO.

For this reason, in about 1932, a German physicist Friedrich Hund (1 1996), and American chemist Robert Sanderson Mulliken, gave the concept of molecular orbital theory. The molecular orbital model is more complex than the valence bond model, particularly for larger molecules, but magnetic and other properties of molecules are some times better explained by molecular orbital (MO) theory. Molecular orbital theory concentrates on molecule as a whole rather than concentrating on individual atoms. A wave function whose square gives the probability of finding an electron within a

Robert Sand
Mulliken
(1896-198

given region of space in an atom is called atomic orbital while a wave function whose square gives the probability of finding an electron within a given region of space in a molecule is known as molecular orbital. Like atomic orbitals, molecular orbitals have specific energy levels and specific shapes, and they can be occupied by a maximum of two electrons with opposite spins. The difference between a molecular orbital and an atomic orbital is that an atomic orbital is associated with only one atom while molecular orbitals spread over all the atoms in the molecule. We may say that in an atomic orbital the electron is influenced by one nucleus while in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule.

Main Points of MOT

i) The number of molecular orbitals formed is equal to the number of combining atomic orbitals. For example, two atomic orbitals overlap and give two molecular orbitals. One is bonding molecular orbital and the other is anti-bonding molecular orbital.

ii) The overlapped atomic orbitals do not maintain their identity.

iii) The molecular orbital which has less energy than parent atomic orbital is called bonding molecular orbital e.g. σ, π-orbitals.

iv) The molecular orbital which has greater energy than parent atomic orbitals is called anti-bonding molecular orbitals e.g. σ^*, π^*-orbitals. The asterisk, which you read as "star," tells us that the molecular orbital is anti-bonding.

v) The electron density in bonding molecular orbital is the maximum between the nuclei of the bonded atoms while in case of anti-bonding molecular orbital the electron density is the minimum between the nuclei of the bonded atoms.

vi) The bonding molecular orbital has greater stability than the corresponding anti-bonding molecular orbital because bonding molecular orbital is lower in energy than its corresponding anti-bonding molecular orbital.

Formation of Molecular Orbitals

Two types of molecular orbitals are formed as atoms approach each other and their atomic orbitals overlap.

i) The low energy molecular orbitals (bonding molecular orbitals).

ii) The high energy molecular orbitals (anti-bonding molecular orbitals).

These two types of molecular orbitals are formed due to s-s and p-p overlap.

s-s Overlap

Two types of molecular orbitals are formed due to s-s overlap, one is a bonding molecular orbital at a lower energy than the original atomic orbitals. The other is an anti-bonding molecular orbital at a higher energy than the original atomic orbitals.

Consider the formation of H_2 molecule. Each hydrogen atom has one electron in 1s orbital. Hence, two $1s^1$ orbitals of two hydrogen atoms overlap to produce two molecular orbitals designated as σ_{1s} and σ^*_{1s}. The subscripts 1s indicate that the molecular orbital is formed from two 1s orbitals. The σ_{1s} orbital is called **bonding molecular orbital** whereas σ^*_{1s} (read "sigma-star-one-s") orbital is called anti-bonding molecular orbital. The electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an anti-bonding molecular orbital, most of the electron density is located away from the space between the nuclei. This means that in this molecular orbital, the electrons spend little time between the nuclei. Note that the energy of a bonding molecular orbital is less than that of the separate atomic orbitals, whereas the energy of an anti-bonding orbital is higher. The total energy of two molecular orbitals remains the same as that of two original atomic orbitals.

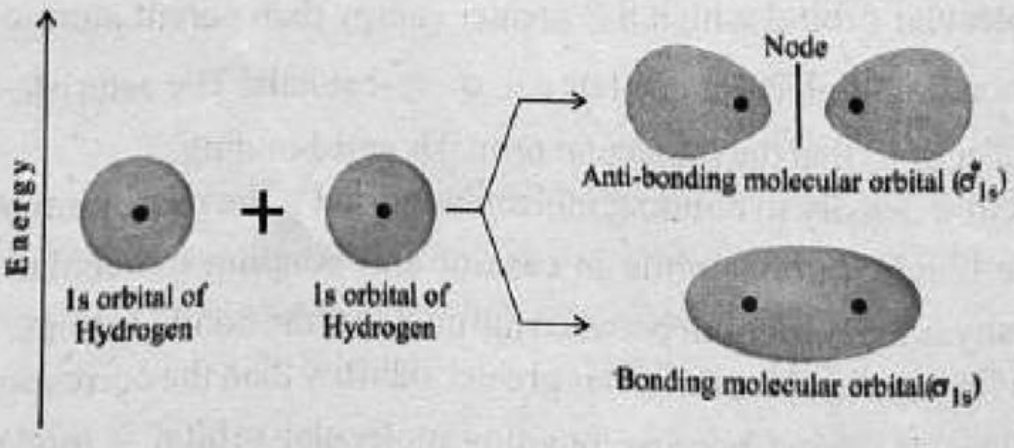


Figure 3.26: Linear overlap of s-s orbitals

It is important to note that 1s orbital of one atom can combine with 1s orbital of another atom but not with 2s orbital because of the higher energy of 2s orbital as compared to 1s orbital. Hence, the overlapping atomic orbitals must have equal or approximately equal energy. It is possible when atoms are different from each other.

p-p Overlap

The situation is more complex when the bonding involves p-orbitals. Two p-orbitals can form either a sigma bond or a pi bond. There are two different ways in which 2 atomic orbitals can combine (overlap).

i) Linear overlap ii) Parallel overlap

One set of 2p orbitals (2px atomic orbitals) can overlap along the same axis (x-axis)to give one bonding and one anti-bonding σ-orbital (σ_{2px} and σ^{*}_{2px}). These orbitals have cylindrical symmetry around the molecular axis.

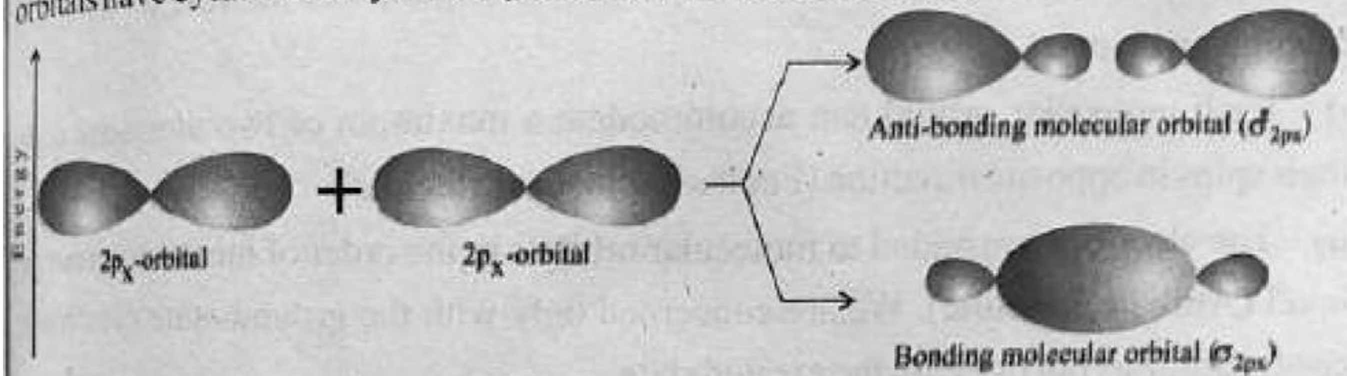


Figure 3.27: Linear overlap of $2p_x$-$2p_x$ orbitals

Keep in Mind

If atomic orbitals do not have the same symmetry then they will not combine. For example, $2p_x$ orbital of one atom can combine with $2p_x$ orbital of the other atom but not with the $2p_y$ or $2p_z$ orbital due to their different symmetries.

The other two sets of 2p orbitals ($2p_y$ and $2p_z$) are perpendicular to the x-axis, and they will overlap sidewise to give two bonding and two anti-bonding π-orbitals. The π molecular orbitals that result from degenerate $2p_y$ and $2p_z$ atomic orbitals are identical and have same energy and are said to be degenerate.

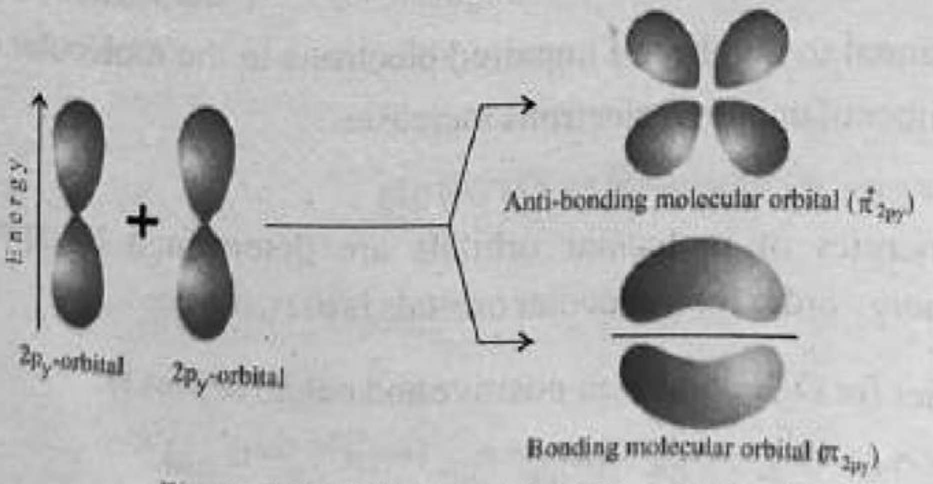


Figure 3.28: Parallel overlap of p_y-p_y orbitals

The overlap of the two p-orbitals is normally greater in a σ– molecular orbital than in a π–molecular orbital. Hence sigma bonds are stronger than pi bonds.

Molecular Orbital Electronic Configuration

The distribution of electrons among various molecular orbitals is called molecular orbital configuration. The method for determining the electro configuration of a molecule is similar to that of the electronic configuration atoms. To write the molecular orbital electronic configuration, we have to know rules given below:

i) Each molecular orbital can accommodate a maximum of two electrons their spins in opposite direction (Pauli's Exclusion Principle).

ii) The electrons are added to molecular orbitals in the order of increasing energ level (Aufbau Principle). We are concerned only with the ground-state electron configurations but not with the excited state.

iii) If two or more same energy molecular orbitals are available then electro prefer to occupy each molecular orbital singly before pairing begins (Hund's rule)

iv) The number of electrons in the molecular orbitals is equal to the sum of all electrons on the bonding atoms.

The molecules are said to be diamagnetic if they have paired electrons in molecular orbitals (bonding and antibonding molecular orbitals) and they are sa to be paramagnetic if they have unpaired electrons in the molecular orbita Paramagnetic substances are attracted by a magnetic field whereas diamagne substances are slightly repelled by a magnetic field. Paramagnetic character directly proportional to number of unpaired electrons in the molecular orbitals increases as number of unpaired electrons increases.

Relative Energies of Molecular Orbitals

The relative energies of molecular orbitals are determined by spectrosco methods. The energy order for molecular orbitals is of two types:

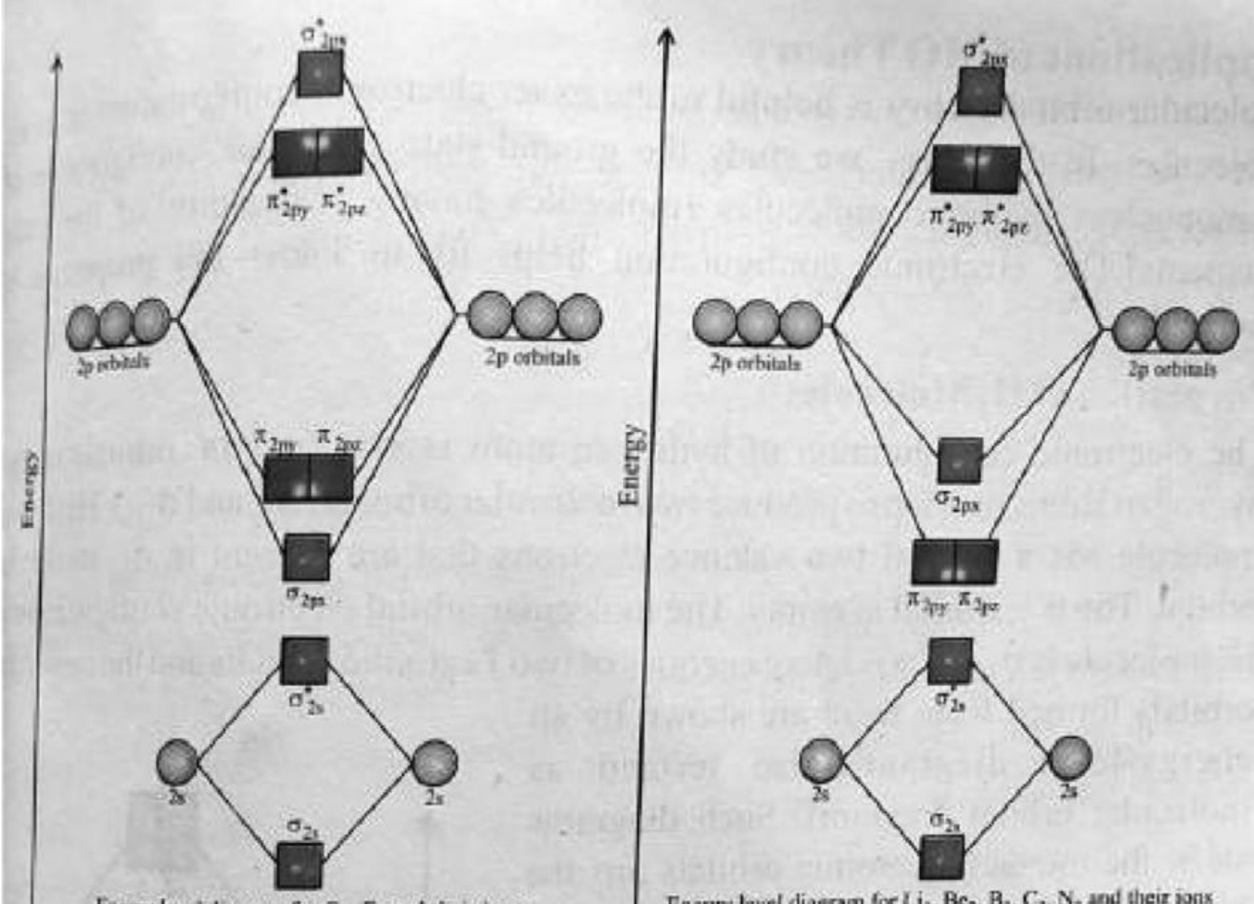
i) Energy order for O_2, F_2 and their positive and negative ions is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < (\pi_{2py} = \pi_{2pz}) < (\pi^*_{2py} = \pi^*_{2pz}) < \sigma^*_{2px}$$

ii) Energy order for Li_2, Be_2, B_2, C_2 and N_2 is:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < (\pi_{2py} = \pi_{2pz}) < \sigma_{2px} < (\pi^*_{2py} = \pi^*_{2pz}) < \sigma^*_{2px}$$

Energy level diagrams are shown as:



Energy level diagram for O_2, F_2 and their ions

Energy level diagram for Li_2, Be_2, B_2, C_2, N_2 and their ions

gure 3.29: Energy level diagrams for first and second period homo-nuclear diatomic molecules d ions

The overlap of the two 2px atomic orbitals is greater than two 2py or 2pz bitals. Because of this the bonding σ_{2px} molecular orbital has lower energy than e degenerate π_{2py} and π_{2pz} molecular orbitals. While in case of Li_2, Be_2, B_2, C_2 and the bonding σ_{2px} molecular orbital has higher energy than the degenerate π_{2py} and molecular orbitals. This U-turn is due to the overlap of a 2s orbital on one of the ms with a 2p orbital on the other. Due to overlapping, the energy difference tween σ_{2s} and σ_{2px} molecular orbitals increases, where the energy of σ_{2s} decreases d that of σ_{2px} increases. The energy of σ_{2px} is raised to such an extent that it comes higher in energy than π_{2py} and π_{2pz} molecular orbitals.

nd Order

e number of bonds formed between two atoms by the overlap of atomic orbitals is led bond order.

diatomic molecules, it can be defined as:

The half of the difference between the number of bonding electrons (n_b) and ber of anti-bonding electrons (n_a) is called bond order.

Mathematically:

$$\text{Bond Order} = \frac{n_b - n_a}{2}$$

Applications of MO Theory

Molecular orbital theory is helpful to the exact electronic configuration of molecules. In this class, we study the ground-state electronic configura homonuclear diatomic molecules (molecules having two atoms of the elements).The electronic configuration helps us to know the properti molecules.

Formation of H_2 Molecule:

The electronic configuration of hydrogen atom is $1s^1$. Two $1s^1$ orbitals of hydrogen atoms overlap to produce two molecular orbitals (σ_{1s} and σ^*_{1s}). Hydr molecule has a total of two valence electrons that are present in σ_{1s} mole orbital. The σ^*_{1s} orbital is empty. The molecular orbital electronic configurati H_2 molecule is σ_{1s^2}. The relative energies of two 1s atomic orbitals and the mole orbitals formed from them are shown by an energy-level diagram (also termed as molecular orbital diagram). Such diagrams show the interacting atomic orbitals on the left and right and the MOs in the middle. The bond order of H_2 molecule can be calculated as:

$$\text{Bond Order of } H_2 = \frac{n_b - n_a}{2} = \frac{2-0}{2} = 1$$

Hence one single covalent bond is formed in H_2. We, therefore, say that the H_2 molecule is stable and can exist.

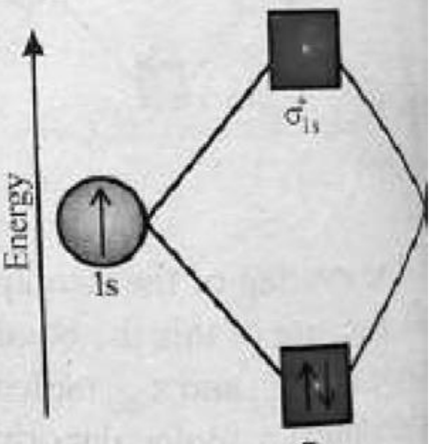


Figure 3.30: Molecular or
diagram for H_2

Formation of He_2 (Hypothetical)

The electronic configuration of helium is $1s^2$. Two $1s^2$ orbitals of two Helium atoms combine to give one bonding (σ_{1s}) and one anti bonding (σ^*_{1s}) molecular orbital. A hypothetical molecule has four electrons, two in σ_{1s} and two in σ^*_{1s} as shown in the figure 3.31. The molecular orbital electronic configuration of helium is $\sigma_{1s^2} < \sigma^*_{1s^2}$.

$$\text{Bond Order of } He_2 = \frac{n_b - n_a}{2} = \frac{2-2}{2} = 0$$

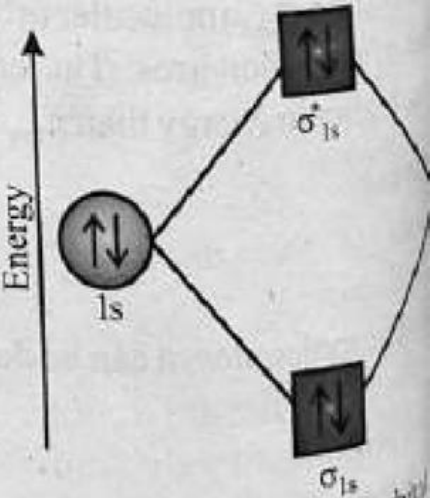


Figure 3.31: Molecular orbit
for Hypothetical He_2 Mo

Zero Value shows that this molecule is unstable and no bond would be formed between two helium atoms. Hence, it is mono-atomic molecule.

Formation of N_2 Molecule

The electronic configuration of nitrogen atom is $1s^2, 2s^2, 2px^1, 2py^1, 2pz^1$. When two nitrogen atoms approach one another to form N_2 molecule, only like orbitals on the two atoms combine. The 1s orbital of one atom combines with 1s orbital of the other atom and the 2s orbital of one atom combines with 2s orbital of the other atom. The 1s orbital of one atom does not combine with the 2s orbital of the other atom, because their energies are quite different. The two 2px orbitals that lie on the same plane (internuclear axis) overlap head on and form σ_{2px} and σ^*_{2px} molecular orbitals. The other two pairs of 2py and 2pz orbitals which are perpendicular to the x-axis overlap sidewise and form two degenerate bonding molecular orbitals (π_{2py} and π_{2pz}) and two degenerate anti-bonding molecular orbitals (π^*_{2py} and π^*_{2pz}).

The molecular orbital diagram of N_2 molecule is shown in figure 3.32. Because of the absence of unpaired electrons in the molecular orbitals, the nitrogen is diamagnetic and is very stable molecule. The molecular orbital electronic configuration of N_2 is:

$$\sigma_{1s^2} < \sigma^*_{1s^2} < \sigma_{2s^2} < \sigma^*_{2s^2} < \pi_{2py^2} = \pi_{2pz^2} < \sigma_{2px^2} < \pi^*_{2py^0} = \pi^*_{2pz^0} < \sigma_{2px^0}$$

Since the inner shell electrons (K-shell) have no significant effect on bonding, therefore, the $\sigma_{1s^2} < \sigma^*_{1s^2}$ is frequently condensed as KK. Now the configuration of nitrogen molecule can be written as:

$$KK < \sigma_{2s^2} < \sigma^*_{2s^2} < \pi_{2py^2} = \pi_{2pz^2} < \sigma_{2px^2} < \pi^*_{2py^0} = \pi^*_{2pz^0} < \sigma^*_{2px^0}$$

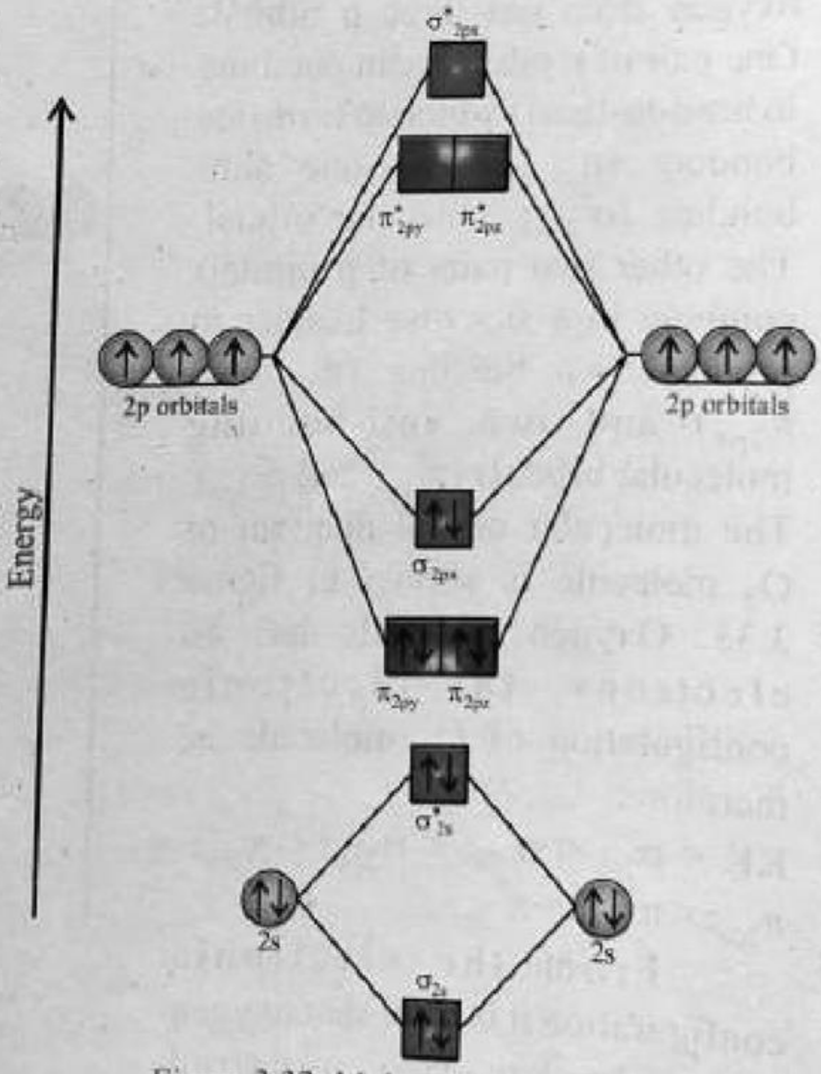


Figure 3.32: Molecular orbital diagram for N_2 molecule

N_2 molecule has eight bonding electrons and two anti-bonding electro therefore the bond order of nitrogen is:

$$\text{Bond Order of } N_2 = \frac{n_b - n_a}{2} = \frac{8-2}{2} = 3$$

The bond order of nitrogen molecule is three which shows that it forms tri bond (N≡N), one is sigma and two are pi-bonds.

Formation of O_2 Molecule

The electronic configuration of oxygen atom is $1s^2$, $2s^2$, $2p_{x^1}$, $2p_{y^1}$, $2p_{z^2}$. As $1s^2$ and $2s^2$ orbitals have no significant effect on bonding, therefore we will not discuss the interactions of these orbitals. Each oxygen atom has three p orbital. One pair of *p* orbitals can combine in head-to-head fashion to form one bonding (σ_{2px}) and one anti-bonding (σ^*_{2px}) molecular orbital. The other two pairs of p orbitals combine in a sidewise manner to produce two bonding (π_{2py} and π_{2pz}) and two anti-bonding molecular orbitals (π^*_{2py} and π^*_{2pz}). The molecular orbital diagram of O_2 molecule is shown in figure 3.33. Oxygen molecule has 16 electrons, the electronic configuration of O_2 molecule is, therefore:

$$KK < \sigma_{2s^2} < \sigma^*_{2s^2} < \sigma_{2px^2} < \pi_{2py^2} = \pi_{2pz^2} < \pi^*_{2py^1} = \pi^*_{2pz^1}$$

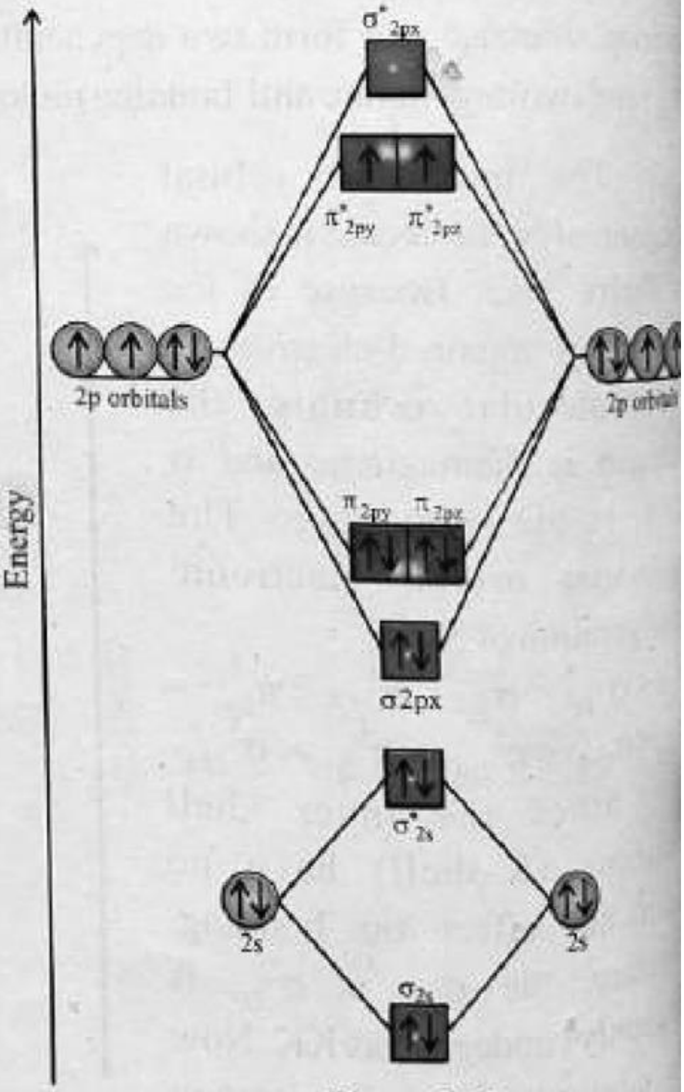


Figure 3.33:
Molecular orbital diagram for O_2 molec

From the electronic configuration it is clear that oxygen molecule has two unpaired electrons in its two degenerate π^*_{2py}

and π^*_{2pz} orbitals and is, therefore, paramagnetic. In the molecular orbital diagram, eight electrons occupy bonding orbitals and four electrons anti-bonding molecular orbitals, so the bond order of O_2 molecule is:

$$\text{Bond Order of } O_2 = \frac{n_b - n_a}{2}$$

$$= \frac{8-4}{2} = 2$$

A bond order of two indicates that there is double covalent bond in O_2 molecule. One bond is sigma and other one is π-bond.

3.4 Bond characteristics

3.4.1 Bond Energy

The average amount of energy needed to break all bonds in one mole of a gaseous substance is called bond energy.

It is also called bond enthalpy as it is a measure of enthalpy change (ΔH) at 298K. For example, the bond enthalpy for the bond in H_2 is the enthalpy change when one mole of gaseous H_2 dissociates into hydrogen atoms.

$$H-H \longrightarrow 2H \qquad \Delta H = +436\,kJ/mol$$

This equation tells us that breaking the covalent bonds in 1 mole of gaseous H_2 molecules requires 436kJ of energy.

The bond energy can also be defined as:

The amount of energy released when one mole of bonds are formed from omponent atoms is called bond energy.

For example, the bond energy for the formation of H_2 molecules is:

$$2H \longrightarrow H-H \qquad \Delta H = -436\,kJ/mol$$

Keep in Mind

- Bond breaking is an endothermic process.
- Bond formation is an exothermic process.
- When the net energy value is positive, the reaction is endothermic.
- When the net energy value is negative, the reaction is exothermic.

The unit of bond energy is kJ/mol or kcal/mol. The bond energy is a measure the stability of molecule. The stability of a molecule is related to the strengths of covalent bonds. The strength of a covalent bond between two atoms is ermined by the energy required to break the bond. The greater the bond energy, the stronger the chemical bond and the stable is the molecule. For exam hydrazine (N_2H_4) is highly reactive (unstable) whereas nitrogen (N_2) is a st molecule. Because nitrogen has a very strong nitrogen-nitrogen triple bond (N while hydrazine has a weak nitrogen-nitrogen single bond (N – N).

Bond energies play an important role in thermochemistry. It helps u explain the heat of chemical reactions. For a chemical reaction, the enthalpy cha can be written as:

$$\Delta H = \Sigma BE \text{ (reactants)} + \Sigma BE \text{ (Products)}$$

Where, Σ shows the sum of terms and *BE* shows the bond energy. The enthalpy of the reaction,(ΔH), is the sum of energies needed to break old bo in the reactants plus the sum of the energies released in the formation of new bo in the products. Consider the reaction between hydrogen and chlorine to form H When one mole of hydrogen gas reacts with one mole of chlorine gas then 2 m of HCl gas is formed.

$$H_2 + Cl_2 \longrightarrow 2HCl \qquad \Delta H = -1432 \text{ kJ/mol}$$

This reaction involves breaking one H–H and one Cl–Cl bond and form two H–Cl bonds. The enthalpy change for this reaction is estimated as:

The amount of energy required to break H–H bond = 436 kJ/mol

The amount of energy required to break Cl–Cl bond = 242 kJ/mol

The sum of bond energies of H–H and Cl–Cl = 436kJ/mol + 242kJ/mol = 678kJ

The amount of energy released when H–Cl bonds are formed = –432 kJ/mol

The energy released when 2 moles of H–Cl bonds are formed = –864 kJ/mol

$$\begin{aligned} \Delta H \text{ for HCl} &= \Sigma BE \text{ (reactants)} + \Sigma BE \text{ (products)} \\ &= (+678\text{kJ/mol}) + (-864\text{kJ/mol}) \\ &= -186\text{kJ/mol} \end{aligned}$$

This is an example of an exothermic reaction. In an exothermic reactio energy required to break the bonds is less than the energy released to make th bonds. The excess energy is released as heat. Conversely, in an endoth reaction, the energy required to break the bonds is more than the energy rele make the new bonds. Energy is drawn in from the surroundings to compl reaction.

Table 3.4: Average Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H – H	436	C – Br	276	O – F	190		
H – F	565	C – I	216	O – Cl	203	S – H	347
H – Cl	432			O – Br	234	S – S	266
H – Br	366	N – H	391	O – I	234	S – F	327
H – I	299	N – N	160			S – Cl	271
		N = N	418	Si – H	323	S – Br	218
C – H	413	N ≡ N	941	Si – O	368	S – I	170
C – C	348	N – P	209	Si – Si	226		
C = C	614	N – O	201	Si – S	226	F – F	159
C ≡ C	839	N = O	607	Si – F	565	F – Cl	193
C – Si	301	N ≡ O	631	Si – Cl	381	F – Br	212
C – N	305	N – F	272	Si – Br	310	F – I	263
C = N	615	N – Cl	200	Si – I	234		
C ≡ N	891	N – Br	243			Cl – Cl	243
C – O	358	N – I	159	P – H	320	Cl – Br	215
C = O	745 (799 in CO_2)			P – Si	213	Cl – I	208
C ≡ O	1070	O – H	463	P – P	200		
C – P	264	O – O	204	P – F	490	Br – Br	193
C – S	259	O = O	495	P – Cl	331	Br – I	175
C – F	453	O – P	351	P – Br	272	I – I	151
C – Cl	339	O – S	265	P – I	184		

Factors Affecting Bond Energy

Electronegativity (E.N) Difference

Greater the electronegativity difference of the bonded atoms, greater would be the bond energy. For example, the bond energies for HF, HCl, HBr, and HI are 565, 432, 366 and 299kJ/mol respectively. The bond energies of hydrogen halides decrease in the following order:

$$HF > HCl > HBr > HI$$

The highest value of bond energy of HF is due the greatest E.N difference value and the lowest value of bond energy of HI is due to the smallest E.N difference value.

Multiple Bonds

Bond energies of multiple bonds (= or ≡) are greater than single bond. For example, the bond energy of nitrogen-nitrogen single bond (N–N), double bond (N=N) and triple bond (N≡N) is 160, 418, and 941 kJ/mol, respectively. It shows that the tripl bond is stronger than the double bond, which in turn is stronger than the single bond

Bond Length

Shorter the bond length, greater will be the bond energy and vice versa.

As the number of bonds between the carbon atoms increases, the bond length decreases and the bond enthalpy increase. That is, the carbon atoms are held more closely and more tightly together.

Table 3.5: The Relation between Bon Length and Bond Energy

Bond	Average Bond Length (pm)	Average Bo Energy (kJ/m
C – C	154	348
C = C	133	614
C ≡ C	120	839

Atomic Size

Greater the size of bonded atoms, greater would be the bond length, hence smalle will be the bond energy and vice versa. For example, the bond energy o I_2(151kJmol^{-1}) is smaller than that of Cl_2(243kJmol^{-1}). This is because the I – I bon length is larger than Cl – Cl bond length.

3.4.2 Bond Length

The distance between the nuclei of two covalently bonded atoms is called bo length. It is also known as bond distance. Bond lengths can experimentally b determined by using the physical techniques such as, electron diffraction, x-ra diffraction, and spectral studies. In many cases, bond lengths for single covale bonds in compounds can be roughly predicted from covalent radii. Hence, bo length can be estimated as the sum of the covalent radii of the two atoms. Fo example, because the covalent radius of hydrogen is 37pm (one half the bond leng of H – H i.e. $\frac{1}{2}\times 74 = 37$) and that of chlorine is 99pm which is one-half o the bond length (198pm), therefore the H–Cl bond length in hydrochloric acid approximately 136pm (37pm + 99pm = 136pm). The actual value of bond length HCl is 127pm. The bond length of triple bond is shorter than double bond which turn is shorter than single covalent bond. As the number of bonds (bond order) between two atoms increases, the bonds length decreases. For example, the average bond lengths for carbon-carbon single, double and triple bonds are given here in the table 3.6.

Table 3.6: Bond length of si and multiple bonds of carb

Types of bond	Bond Len
C – C	154pm
C = C	133pm
C ≡ C	120pm

The values of average bond lengths help us:

i) To provide the clue to the type of bonding present.
ii) To understand resonance structures in molecules like ozone.

Table 3.7: Average Bond Lengths (pm)

Bond	Bond Length	Bond	Bond Length	Bond	Bond Length	Bond	Bond Length
$H-H$	74	$C-O$	143	$N-P$	177	$O-F$	190
$H-F$	92	$C=O$	123	$N-O$	144	$O-Cl$	164
$H-Cl$	127	$C\equiv O$	113	$N=O$	120	$O-Br$	172
$H-Br$	141	$C-P$	187	$N\equiv O$	106	$O-I$	194
$H-I$	161	$C-S$	181	$N-F$	139		
		$C-F$	133	$N-Cl$	191	$Si-H$	148
$C-H$	109	$C-Cl$	177	$N-Br$	214	$Si-O$	161
$C-C$	154	$C-Br$	194	$N-I$	222	$Si-Si$	234
$C=C$	133	$C-I$	213			$Si-S$	210
$C\equiv C$	120			$O-H$	96	$Si-F$	156
$C-Si$	186	$N-H$	101	$O-O$	148	$Si-Cl$	204
$C-N$	147	$N-N$	146	$O=O$	121	$Si-Br$	310
$C=N$	127	$N=N$	122	$O-P$	160	$Si-I$	240
$C\equiv N$	115	$N\equiv N$	110	$O-S$	151		
$P-H$	142					$Cl-Br$	214
$P-Si$	227	$S-H$	134	$F-F$	143	$Cl-I$	243
$P-P$	221	$S-S$	204	$F-Cl$	166		
$P-F$	156	$S-F$	158	$F-Br$	178	$Br-Br$	228
$P-Cl$	204	$S-Cl$	201	$F-I$	187	$Br-I$	248
$P-Br$	222	$S-Br$	225			$I-I$	266
$P-I$	184	$S-I$	234	$Cl-Cl$	199		

Factors Affecting Bond Length

Atomic Size

The bond length increases by increasing atomic size and vice versa. For example, bond length of $I-I$ (266 pm) is more than $Br-Br$ (228 pm).

Electronegativity (E.N) Difference

The bond length increases by decreasing the electronegativity difference of two bonded atoms. For example, the HCl bond length is greater than HF bond length.

Heteronuclear Molecules	ΔEN (Electronegativity Difference)	Bond Length (pm)
HF	1.9	92
HCl	0.9	127
HBr	0.7	141
HI	0.4	161

So order of bond length will be:

HF < HCl < HBr < HI

Type of Hybridization

Greater the s-orbital character in the hybrid orbital, shorter will be bond length. F example, the carbon-carbon bond distances in ethane, ethene and ethyne are 15 133 and 120 pm respectively, because ethane, ethene and ethyne have sp^3, sp^2 and hybridization respectively. The bond length also reduces due to the presence of bonds in ethene and ethyne.

3.4.3 Electronegativity (E.N)

The measure of the ability of an atom in a molecule to attract the bonding electr (shared electrons) to itself is called electronegativity.

The electronegativity of elements decreases from top to bottom in a group periodic table due to increase in atomic size. It increases from left to right in a peri of periodic table due to decrease in atomic size.

Table 3.8: The Pauling Electronegativity Values

H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl [illegible]
K 0.82	Ca 1.00	Sc 1.36	Ti 1.50	V 1.63	Cr 1.60	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.60	Ge 1.80	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.86	Sb 2.03	Te 2.10	I 2.66
Cs 0.79	Ba 0.98	Lu 1.27	Hf 1.30	Ta 1.50	W 2.36	Re 1.90	Os 2.20	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.00	At 2.20
Fr 0.70	Ra 0.89	Lr 1.30	Rf ---	Db ---	Sg ---	Bh ---	Hs ---	Mt ---	Ds ---	Rg ---	Cn ---	Nh ---	Fl ---	Mc ---	Lv ---	Ts --
				La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.20	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25
				Ac 1.10	Th 1.30	Pa 1.50	U 1.70	Np 1.36	Pu 1.28	Am 1.30	Cm 1.30	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30

The elements with high electronegativity values, such as fluorine, att bonding electrons more strongly than the elements such as sodium that have l electronegativity values.

3.4.4 Ionic Character

Unequal distribution of bonding electrons between two atoms is called i character or polarity of molecule. The measure of extent of sharing of elec (how equally or unequally the electrons are shared) in a covalent bond is known as bond polarity.

A covalent bond involves the sharing of at least one pair of electrons between two atoms. In a molecule like H_2, in which the atoms are identical, the bonding electrons are shared equally. That is, the electrons spend the same amount of time in the vicinity of each atom. We can say that the electron pair is situated exactly between the two identical nuclei. The bond so formed is called non-polar covalent bond or simply non-polar bond. But when the two atoms are of different elements, the bonding electrons are not shared equally. That is, the bonding electrons spend more time near one atom than the other. For example, in the case of the HCl molecule, the bonding electrons spend more time near the chlorine atom than the hydrogen atom. This "unequal sharing" of the bonding electron pair results in a relatively greater electron density near the chlorine atom and a correspondingly lower electron density near hydrogen. The resultant covalent bond is a polar covalent bond (or Polar bond).

Keep in Mind

Polar covalent bonds are called polar because the unequal electron sharing creates two poles across the bond. The HCl bond has two poles, just like in battery, one positive and one negative. The symbol (delta) is used to denote a partial charge. The symbols δ^+ and δ^- (delta plus and delta minus) are used to show the distribution of partial charges in a polar covalent bond. These symbols, delta plus and delta minus, represent a partial positive charge and a partial negative charge.

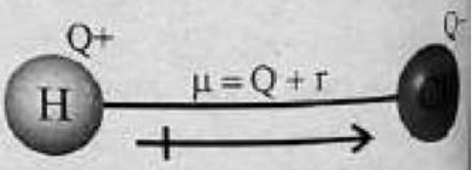
You can consider the polar covalent bond as intermediate between a
onpolar covalent bond (where sharing of electrons is exactly equal), as in H_2, and
n ionic bond (where transfer of the electron(s) is nearly complete), as in NaCl.
rom this point of view, an ionic bond is simply an extreme example of a polar
ovalent bond. We use a quantity called electronegativity to estimate whether a
ven bond is nonpolar covalent, polar covalent, or ionic.

Electronegativity is used to predict nature of bond. But predictions may not
ways be correct because there is no clear-cut division between ionic bond and
lar covalent bond. The electronegativity difference of two bonded atoms predicts
e nature of bond or bond polarity. The greater the difference between the
ectronegativity values of the bonding atoms, the greater would be the bond
larity and the stronger will be the bond. The electronegativity difference between

two bonding atoms is often represented by the symbol ΔEN, where EN is a sym for electronegativity and Δ is the Greek letter delta which means "difference." T electronegativity difference (ΔEN) is determined by subtracting the smal electronegativity value from the larger. When ΔEN is zero, the bond will be a p covalent bond (100 % covalent). When the electronegativity difference in a bond 1.8 or greater, the bond will be ionic. If the ΔEN is from 0.5 to 1.6, the bond will b polar covalent bond. When the ΔEN is below 0.5, the bond is normally classified a covalent bond, with little or no polarity. If ΔEN is equal to 1.7 the bond will ha 50% covalent character and 50% ionic character.

3.4.5 Dipole Moment

Dipole moment is the measure of polarity of the bond in a covalently bond molecule. We can say that the polarity of a molecule can be measu experimentally by measuring its permanent dipole moment. The greater the dip moment, the greater is the polarity of molecule. The molecule is considered as no polar when its dipole moment is zero. We know that polar covalent bonds fo between atoms of different electronegativity. In the HCl molecule, the chlor atom is more electronegative than hydrogen, and the chlorine atom thus attracts t electrons towards itself. As a consequence, the electrons are displaced toward t more electronegative chlorine atom and it gets partial negative charge (δ^-). On t other hand, the less electronegative hydrogen atom attains partial positive char (δ^+). The molecule such as HCl which has a partial negative charge at one end and partial positive charge at the other end is said to be polar.



Dipole moment is defined as:

The product of electric charge on either end of a polar bond and the distance between the charges is called dipole moment. It is shown by μ (mu).

Mathematically,

$$\text{Dipole moment} = \text{Charge} \times \text{distance}$$

$$\mu = Q \times r$$

Where Q is charge and r is distance. Q refers only to the magnitude of the charge and not to its sign, so is always positive. Dipole moment is usually measured in debye units (D), (pronounced as duh-bye), named for the Dutch-American chemist and physicist Peter Debye. In SI units, dipole moments are measured in coulomb-meters (C.m).

Peter Deby
(1884 - 196

$1D = 3.34 \times 10^{-30} C.m$

The dipole moment of water is 1.85D and that of ammonia is 1.47D. The larger value for the dipole moment of water means that water is more polar than ammonia. The dipole moment is a vector quantity which has both magnitude and direction. The direction of dipole moment is from positive toward negative. We often represent the dipole using an arrow with a cross at one end ($+\!\!\!\longrightarrow$) to indicate the direction of electron displacement. The point of the arrow represents the negative end of the dipole (δ^-) and the crossed end (which looks like a plus sign) represents the positive end (δ^+). The length of arrow shows magnitude and its head shows direction.

Diatomic molecules containing atoms of different elements (for example, HF, HCl, HBr, HI, CO, and NO) have dipole moments and are called polar molecules. Diatomic molecules containing atoms of the same element (for example, H_2, O_2, N_2, F_2 and Cl_2) do not have dipole moments and are called nonpolar molecules. For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment. Even if polar bonds are present, the molecule will not necessarily have a dipole moment. It is noted that if a molecule is polyatomic and has two or more dipoles, then net dipole moment is the vector sum of individual bond moments. An example is the CO_2 molecule, which is a linear molecule. In this case the opposing bond polarities cancel out, and the carbon dioxide molecule does not have a dipole moment. There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are CS_2, SO_3, CH_4, SiH_4 and CCl_4.

Example 3.1

Calculate the dipole moment, in Debye unit, of a hypothetical 100 % ionic molecule where unit positive and unit negative charges are at a distance of $1A^{\circ}$. The charge on the either ends of the molecule is $1.60 \times 10^{-19} C$.

Ionic 100%.

Solution

Distance $= r = 1A^{\circ} = 1 \times 10^{-10} m = 10^{-10} m$

Charge $= Q = 1.60 \times 10^{-19} C$

Dipole moment $= \mu = ?$

As we know that,

$\mu = Q \times r$

Therefore,

Dipole moment of the hypothetical molecule $= 1.60 \times 10^{-19}\,C \times 10^{-10}\,m$

$= 1.60 \times 10^{-29}\,C.m$

Since, $1D = 3.34 \times 10^{-30}\,C.m$

Hence, $\mu = \dfrac{1.60 \times 10^{-29}\,C.m}{3.34 \times 10^{-30}\,C.m/D} = 4.79D$

Applications of Dipole Moment

Dipole moment can be used to determine:

i) Percentage ionic character

ii) Geometries of molecules.

i) Percentage Ionic Character:

It is defined as:

The observed dipole moment divided by ionic dipole moment and answer is multiplied by 100 is called %age ionic character.

$$\%\text{age ionic character} = \frac{\text{Observed dipole moment}}{\text{Ionic dipole moment}} \times 100$$

%age ionic character of some molecules is:

$HF = 43\%$, $HCl = 17\%$, $HBr = 12\%$, $HI = 5\%$

It decreases by decreasing dipole moment. If dipole moment is zero, bond is 100% covalent.

Example 3.2

The observed dipole moment of HCl is 1.03D and the distance between atoms (bond length) is 127pm. Find the percentage ionic character of the bond?

Solution:

Observed dipole moment of HCl $= \mu_{obs} = 1.03\,D$

Distance between H and Cl atoms $= r = 127 \times 10^{-12}\,m = 1.27 \times 10^{-10}\,m$

When HCl is 100 ionic, then the charge on each atom (Q) is the electronic and it is equal to $1.60 \times 10^{-19}\,C$.

The ionic dipole moment can be calculated as:

Ionic dipole moment $= (1.60 \times 10^{-19}\,C) \times (1.27 \times 10^{-10}\,m) = 2.03 \times 10^{-29}\,C.m$

$$\text{Ionic dipole moment in Debye unit} = \frac{2.03 \times 10^{-29}\,C.m}{3.34 \times 10^{-30}\,C.m/D} = 6.08D$$

The percentage ionic character of HCl can be calculated by dividing the observed dipole moment with ionic dipole moment and the answer is multiplied by 100:

$$\text{Percentage ionic character of HCl} = \frac{1.03\text{D}}{6.08\text{D}} \times 100\% = 16.9\%$$

ii) Geometries of Molecules

The dipole moment helps to determine the geometries of molecules.

Geometries of Diatomic Molecules:

The geometry of diatomic molecules is always linear whether they are polar or non-polar.

Table 3.9: Dipole Moments and Geometries of Some Diatomic Molecules

Name of Molecule	Formula	Dipole Moment (D)	Nature of Bond	Geometry of Molecule
Hydrogen fluoride	HF	1.82	Polar	Linear
Hydrogen chloride	HCl	1.03	Polar	Linear
Hydrogen bromide	HBr	0.78	Polar	Linear
Hydrogen iodide	HI	0.38	Polar	Linear
Carbon monoxide	CO	0.12	Polar	Linear
Hydrogen	H_2	0.00	Non-polar	Linear
Nitrogen	N_2	0.00	Non-polar	Linear

The HF molecule has dipole moment because the electronegativity of fluorine (3.98) is greater than that of hydrogen (2.1). Thus fluorine attains partial negative and hydrogen attains partial positive charge and HF molecule becomes polar. On the other hand hydrogen molecule is non-polar and has no dipole moment. This is because the two hydrogen atoms share electrons equally and no bond polarity occurs.

Geometries of Triatomic Molecules

Whether a triatomic molecule has linear or angular geometry, it can be decided with the help of dipole moment. Triatomic linear molecules have no dipole moment, because the bond moments of the two polar bonds are equal and opposite. They cancel the effect of each other. For example,

i) Carbon dioxide is a molecule with polar covalent bonds. The shape of CO_2 molecule is linear. It has two dipoles. They are equal and have opposite directions. So they cancel the effect of each other. Therefore, the dipole moment of

CO_2 is zero. Although carbon dioxide has relatively strong polar covalent bonds, CO_2 is a nonpolar molecule. On the other hand, if the CO_2 molecule were bent, the two bond moments would partially reinforce each other, so that the molecule would have a dipole moment.

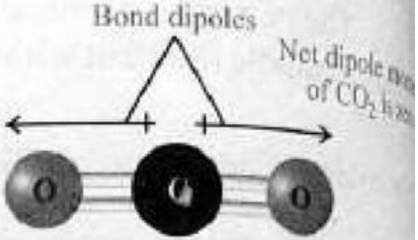


Figure 3.34: Geometry of CO_2 Molecule

Keep in Mind

You can think of two groups (say one group belongs to first year and the other belongs to second year) of students in a tug-of-war. The first year students are at one end of the rope and the second year students are at the other end. Each group pulls the rope towards itself, There is no movement, because each group pulls on the rope with the same force but in the opposite direction. Hence, the net force is zero.

ii) Consider the water molecule which has two polar O–H bonds. The bond dipoles point from the hydrogen atoms toward the more electronegative oxygen. They are equal but do not have opposite directions. So they do not cancel the effect of each other. This is due to non-linear geometry of H_2O. The shape of H_2O is bent or angular. Because of its bent shape, the water molecule as a whole has a negative pole and a positive pole. If the H_2O molecule were linear, the dipole moment would be zero. Similarly, geometries of H_2S and SO_2 are also angular.

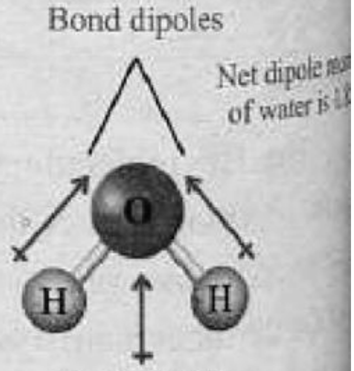
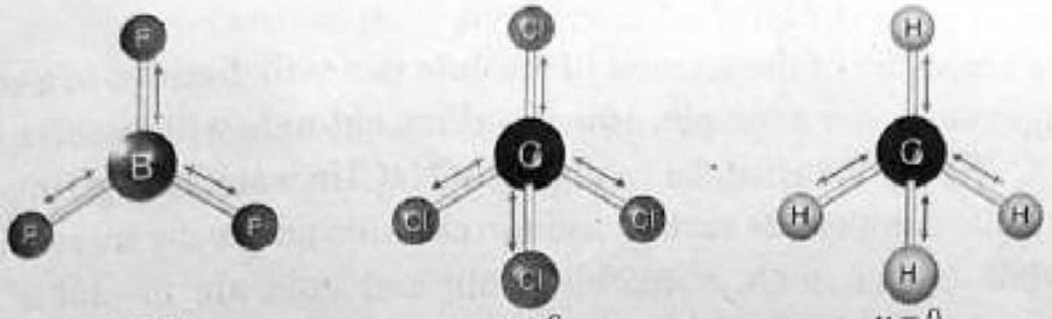


Figure 3.35: Geometry of Water Molecule

Geometries of Symmetrical Molecules

The symmetrical triangular planar molecules (BF_3, $AlCl_3$ and SO_3) and tetrah molecules (CH_4, SiH_4 and CCl_4) have zero dipole moments. In these molecule bond moments cancel effect of one another.



$\mu = 0$
Boron Trifluoride
(Non-polar)

$\mu = 0$
Carbon
Tetrachloride
(Non-polar)

$\mu = 0$
Methane
(Non-polar)

Figure 3.36: Geometries of symmetrical polyatomic molecules

Table 3.10: Dipole Moments and Geometries of Some Polyatomic Molecules

Name of Molecule	Formula	Dipole Moment (D)	Nature of Bond	Geometry of Molecule
Carbon dioxide	CO_2	0.00	Non-polar	Linear
Carbon disulphide	CS_2	0.00	Non-polar	Linear
Hydrogen monoxide	H_2O	1.85	Polar	Angular (or bent)
Hydrogen sulphide	H_2S	0.95	Polar	Angular
Sulphur dioxide	SO_2	1.61	Polar	Angular
Ammonia	NH_3	1.46	Polar	Trigonal pyramidal
Phosphine	PH_3	0.55	Polar	Trigonal pyramidal
Boron fluoride	BF_3	0.00	Non-polar	Trigonal planar
Sulphur trioxide	SO_3	0.00	Non-polar	Trigonal planar
Methane	CH_4	0.00	Non-polar	Tetrahedral
Methyl fluoride	CH_3F	1.81	Polar	Tetrahedral
Methyl chloride	CH_3Cl	1.45	Polar	Tetrahedral
Methyl bromide	CH_3Br	1.85	Polar	Tetrahedral
Methyl iodide	CH_3I	1.35	Polar	Tetrahedral
Methylene chloride	CH_2Cl_2	1.58	Polar	Tetrahedral
Chloroform	$CHCl_3$	1.15	Polar	Tetrahedral
Carbon tetrachloride	CCl_4	0.00	Non-polar	Tetrahedral

3.5 Effects of Bonding on Physical and Chemical Properties

The physical properties such as melting point, boiling point, density, colour, olubility, bond energy, vapour pressure and chemical properties such as reactivity, nd rate of reaction etc. of compounds depend on the nature of bond present in them.

3.5.1 Solubility of Ionic and Covalent Compounds

Solubility is a measure of the amount of a solute that will dissolve in a solvent at specific temperature. For example, 36g of sodium chloride will dissolve in 100g of water at 20°C. We say then that the solubility of NaCl in water is 36g/100g of H_2O at 20°C. Why some compounds such as sodium chloride and sugar are readily soluble in water while others, such as marble, sand and gold are insoluble in water. Solubility is a complex matter, and it is not always possible to make correct predictions. Solubility involves many factors but we will discuss only one factor in this topic. The saying "like dissolves like" helps in predicting the solubility of a substance in a solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) are non-polar liquids. The only intermolecular forces present in these substances are London dispersion forces. When these two liquids are mixed, they readily dissolve in each other, because the attraction between CCl_4 and C_6H_6 molecules is comparable in magnitude to that between CCl_4 molecules and between C_6H_6 molecules. On the other hand, water molecules are very polar and are attracted to other polar molecules or ions. When NaCl is placed in water, polar water molecules become attracted to the sodium and chloride ions on the crystal surfaces and weaken the attraction between Na^+ and Cl^- ions. The positive end of the water molecule is attracted to the Cl^- ions, and the negative end of the water molecule to the Na^+ ions. The weakened attraction allows the ions to move apart, making room for more water molecules. Thus, the water molecules surround the ions. This process is known as hydration.

Keep in Mind

Most of the covalent compounds are insoluble in water; however, some of them (such as ethyl alcohol and acetic acid.) dissolve in water due to hydrogen bonding.

Conceptual Check Point:

Why sugar is soluble in water and not in benzene?

3.5.2 Reactions of Ionic and Covalent Compounds

The reactions of covalent compounds are much slow, because they involve both breaking and formation of bonds whereas the reactions of ionic compounds are very fast, because their ions are already separated and no energy is needed to break the bonds.

3.5.3 Directional and Non-directional Nature of Ionic and Covalent Bonds

Ionic bonds are non-directional and they do not show the phenomenon of isomerism while covalent bonds are directional and they show the process of isomerism.

Keep In mind

The compounds having same molecular formula but different structures are called isomers and the phenomenon is called isomerism. The covalent compound butane (C_4H_{10}) has two isomers i.e. n-butane and iso-butane.

Summary of Facts and Concepts

- The VSEPR theory explains shapes (geometries) and bond angles of molecules and ions. It assumes that the valence shell electron pairs (bond pairs and lone pairs) of the central atom of a compound being negatively charged will be arranged in space as far apart from each other as possible to minimize the repulsion between electron pairs. Information about the geometry of a molecule can sometimes be obtained from the presence or absence of a dipole moment.
- According to valence bond theory, the covalent bond is formed by the overlapping of half-filled atomic orbitals. Basically the VB theory discusses bond formation in terms of overlap of orbitals.
- The overlapping is of two types:
  (i) Linear overlapping (ii) Parallel overlapping
- The overlapping of orbitals either form sigma bonds or pi-bonds. Sigma bond is formed by head to head or linear overlap of two atomic orbitals where electron density is maximum around the bond axis. Pi-bond is formed bond by sidewise or parallel overlap of two atomic orbitals (p-orbitals) where electron density is maximum below and above the bond axis.
- Linus Pauling gave the concept of hybridization to explain the bi-valency of beryllium, tri-valency of boron, and tetra-valency of carbon. The geometrical shapes and bond angles are better explained by hybridization.
- The sp^3-hybrid orbitals give tetrahedral geometry, sp^2-hybrid orbitals give trigonal planar geometry, and sp-hybrid orbitals give linear geometry.
- Molecular orbital theory can also be used to explain bonding in molecules.

This theory is particularly useful for explaining the paramagnetic character of oxygen molecule and other substances.

- The bond order is the half of the difference between the number of electrons in bonding MOs and the number of electrons in antibonding MOs. A bond order of one corresponds to a single bond; two corresponds to a double bond, and so forth. Bond orders can be fractional numbers.
- The distribution of electrons into molecular orbitals takes place according to Aufbau principle, Pauli's exclusion principle, and Hund's rule.
- A covalent bond in which the electron pair is not shared equally by the two bonded atoms is called polar covalent bond whereas a covalent bond in which the electron pair is shared equally by the two atoms is called non-polar covalent bond.
- The bond energy (bond enthalpy) is defined as the average amount of energy needed to make or break all bonds in one mole of a substance. Energy is released when a bond is formed, and energy is absorbed when a bond is broken.
- The distance between the nuclei of two covalently bonded atoms is called bond distance or bond length. Bond length depends on bond order; as the bond order increases, the bond length decreases.
- Electronegativity is a measure of the ability of an atom to attract bond pair of electrons towards itself in a molecule. Fluorine is the most electronegative element whereas the cesium is the least electronegative element in the periodic table. Electronegativity values range from 0.7 for Cs to 4.0 for F. The difference in the electronegativity of bonded atoms can be used to determine the polarity of a bond. The greater the electronegativity difference between two atoms in a chemical bond, the more polar the bond and the more ionic its character.
- The product of electric charge on either ends of a polar bond and the distance between them is called dipole moment. It is a vector quantity and has both magnitude and direction. Dipole moment is the measure of polarity of molecule. Molecules with zero dipole moment are non-polar while those with resultant dipole moment are polar molecules. The shapes of molecules can also be determined by dipole moment.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one.

i) Which bond is formed first between two atoms?

(a) Sigma bond (b) Pi-bond

(c) Double bond (d) Triple bond

ii) Molecules having four bond pairs and no lone pair give geometry:

(a) Trigonal (b) Tetrahedral

(c) Octahedral (d) Triangular

iii) Which of the following compounds has linear shape?

(a) CO_2 (b) CS_2 (c) $BeCl_2$ (d) All of them

iv) Which of the following molecules show sp^3 hybridization?

(a) NH_3 (b) $AlCl_3$ (c) $MgCl_2$ (d) BeH_2

v) Which one of the following compounds is polar?

(a) H_2 (b) CH_4

(c) CCl_4 (d) $CHCl_3$

vi) The s-character in each sp^2-hybrid orbital is:

(a) 25% (b) 33% (c) 50% (d) None of these

vii) How many lone pairs of electrons are there in NH_3?

(a) 4 (b) 3 (c) 2 (d) 1

viii) Which one of the following atoms is the second most electronegative atom?

(a) Nitrogen (b) Fluorine

(c) Chlorine (d) Oxygen

ix) Bond length of C=C is:

(a) 120 pm (b) 133pm (c) 154 pm (d) None of these

x) Acetylene molecule has:

(a) One sigma and one pi-bond

(b) One sigma and two pi-bonds

(c) Two sigma and two pi-bonds

(d) Three sigma and two pi-bonds

Q.2. Fill in the blanks with suitable words given in the brackets:

i) Resonance structures are _______ structures. (Real/hypothetical)

ii) The carbon-carbon _______ bond length is shorter than carbon-carbon _______ bond. (Single/double)

iii) Energy is _______ when two atoms form a bo
(Evolved/absorbed)

iv) The sigma bond is _______ than pi-bond. (Weaker/stronger)

v) The bond order of O_2 is _______ and that of N_2 is ___
(Two/three)

vi) Molecular orbital theory is _______ to valence bond the
(Superior/non-superior)

vii) N_2 is _______ whereas O_2 is _______. (Paramagnetic
diamagnetic)

viii) Dipole moment of CO_2 is _______ and that of water is ___
(zero/not zero)

ix) H_2S has _______ geometry while CS_2 has _______ geome
(Linear/bent)

x) Ionic bonds are _______. (directional/non-directional)

Q.3. Label the following statements as True or False:

i) The formation of a chemical bond always results in decrease
energy.

ii) Atomic radius decreases down the group.

iii) A shared pair of electrons is called lone pair.

iv) The electronegativity difference for an ionic bond is greater t
1.7.

v) CCl_4 is a polar molecule.

vi) Bond length of C=C is 120 pm.

vii) The SI unit of dipole moment is Debye.

viii) A molecule with zero dipole moment is non-polar.

ix) KCl has covalent bond in it.

x) Hybridization is exothermic process.

Q.4(a) Discuss the basic features of VSEPR theory. Explain the applicati
the theory for predicting the shapes of NH_3 and H_2O.

(b) What is the deference between molecular shape and molecular geom

Q.5. Why the magnitude of repulsion increases in the following order:

Bond pair-bond pair < bond pair-lone pair < lone pair-lone pair

Q.6.(a) The geometry of CH_4 is tetrahedral while that of NH_3 is pyramidal,
As both the molecules have four electron pairs.

(b) The molecules of BF_3 and $AlCl_3$ have planar triangular geometries while the molecules of NH_3 and PCl_3 have triangular pyramidal geometries, as in all of these molecules, the central atom is bonded with three other atoms. Explain this on the basis of VSEPR theory.

Q.7 Predict the shapes of the following species using the VSEPR theory:
$BeCl_2$, $ZnCl_2$, $AlCl_3$, PCl_3, SiH_4, $CHCl_3$, PH_3 and AsF_5

Q.8 When you have three electron pairs around a central atom, how can you have a distorted triangular geometry?

Q.9. How many atoms are directly bonded to the central atom in a linear molecule, tetrahedral molecule, and octahedral molecule?

Q.10. What do you know about bond pair and lone pair of electrons?

Q.11. Is it possible for hydrogen to form double or triple covalent bonds in a molecule?

Q.12. Define the term resonance. Explain the important aspects of resonance with reference to the ozone molecule.

Q.13. The resonance concept is sometimes described by analogy to a mule, which is a cross between a horse and a donkey, discuss.

Q.14. Describe the salient features of valence bond theory. What are the disadvantages of this theory?

Q.15.(a) Why chemical bonds are formed?

(b) Distinguish between a sigma and a pi bond.

Q.16. Explain the structure of HF and N_2 molecules according to VB theory.

Q.17. What is meant by hybridization of atomic orbitals? Discuss different types of hybridization.

Q.18. Why is it not possible for an isolated atom to exist in the hybridized state?

Q.19. Why is it not possible for s and p orbitals to produce sp^4 hybrid orbitals?

Q.20. What do you know about the rules for hybridization of orbitals?

Q.21. What is the hybridization of nitrogen in N_2 molecule and phosphorus in PCl_3?

Q.22. What is the angle between:

i) sp^3 and sp^3 hybrid orbitals, ii) sp^2 and sp^2 hybrid orbitals

iii) sp and sp hybrid orbitals

Q.23. What are the main points of molecular orbital theory? How does it differ from valence bond theory?

Q.24. How molecular orbital theory is superior to VSEPR and VB theories?

Q.25. How would you distinguish between bonding and anti-bon molecular orbitals?

Q.26. What is bond order? Explain the significance of bond order. Calculat bond order of H_2, O_2, N_2 and N_2^+.

Q.27. Do all the sigma molecular orbitals result from the overlap of s-ato orbitals?

Q.28. Explain the following with reasons:

(i) The molecule of hydrogen (H_2) is stable and that of helium (H is unstable.

(ii) N_2 is diamagnetic whereas O_2 molecule is paramagnetic.

(iii) The bond energy of N_2 is greater than O_2.

(iv) The bond order of O_2 is less than O_2^+.

(v) According to MOT the Be_2 molecule does not exist.

Q.29. What is the difference between atomic and molecular orbital?

Q.30. Distinguish between diamagnetic and paramagnetic substances.

Q.31. Draw the molecular orbital diagrams of He_2, C_2, F_2 and Ne_2 molecules

Q.32. Define bond energy. Describe in general how the bond energy of elements changes across a period and down the group.

Q.33. Explain why bond breaking is always endothermic and bond formatio always exothermic?

Q.34. Explain how we can use bond energies to estimate the heat of reaction

Q.35. Estimate the enthalpy change for the combustion of hydrogen gas:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

Q.36. Define bond length. Describe the various factors that affect bond leng

Q.37. What is the relationship between bond order and bond length? Illustra with an example.

Q.38. What is electronegativity? Discuss general trends of electronegativi the periodic table.

Q.39. Explain polar and non-polar covalent bonds with suitable examples.

Q.40. Polar covalent bonds are stronger than non-polar covalent bonds, ho

Q.41. Classify the following bonds as covalent, polar covalent and ioni justify your answer:

(a) The bond in H_2 (b) The bond in HCl

(c) The bond in NaCl

Q.42. The electronegativity difference of two bonded atoms helps us to predict the nature of bond, how?

Q.43. With the help of periodic table, predict which atom in each pair has the smaller values of electronegativity:

(a) N, O (b) K, Ca (c) C, Si (d) Na, K

Q.44. Define dipole moment. What are the units and symbol for dipole moment? Explain the relationship between dipole moment and molecular geometry.

Q.45. How can we calculate the %age ionic character with the help of dipole moment?

Q.46. How dipole moment helps us to find the geometry of molecules?

Q.47. Although the bond in beryllium hydride (BeH_2) molecule is polar but the dipole moment of the molecule is zero. Explain.

Q.48. CO_2 and H_2O are triatomic molecules; the shape of CO_2 is linear while that of H_2O is angular. How are their shapes different?

Q.49. Arrange the molecules in order of increasing dipole moment: HF, H_2O, HI, NH_3, CO_2 and H_2S.

Q.50. The dipole moment of HF is 1.82 D and the bond length is 92 pm. Calculate the percent ionic character of the H – F bond. The unit positive or negative charge is 1.60×10^{-19}C. Is HF more ionic or less ionic than HCl?

.51. Calculate the dipole moment, in Debye, of HCl molecule. The bond length in the HCl molecule is 127pm and the charge on each atom is 1.60×10^{-19}C.

.52. ClF gas is inter-halogen compound (the compound which has bonds between different halogen atoms). The bond length of the molecule is 163pm and the dipole moment of the molecule is 0.88D. Calculate the unit charge on the atom that has partial positive charge.

.53. Separate those molecules, from the molecules given below, which have dipole moment equal to zero:

(i) HBr (ii) Cl_2 (iii) SO_2 (iv) C_2H_2 (v) H_2O

(vi) CS_2 (vii) C_6H_6 (viii) $CHCl_3$ (ix) NH_3 (x) SiH_4.

54. What is the meaning of the expression "like dissolves like"? Explain with suitable examples.