

Chapter-3

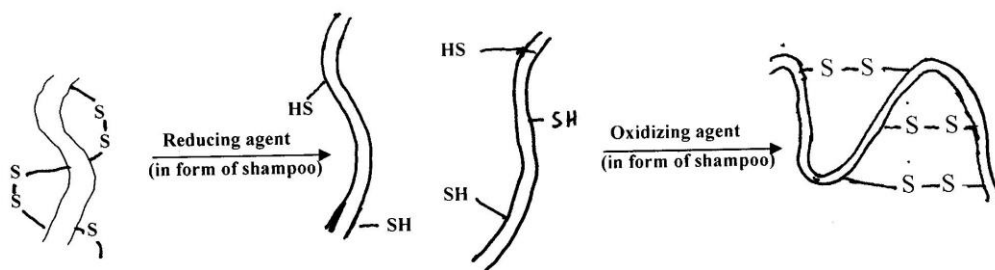
Theories of Covalent Bonds and Shapes of Molecules

“The attractive force which holds two atoms, ions or molecules together in a substance and which bring change in chemical nature is called chemical bond.

Kossel gave the idea that bonds are formed due to transfer of electrons and are called ionic bonds. Later on G. N. Lewis in 1916 gave the idea that bonds are formed due to sharing of electrons pairs and are called covalent bonds.

Science, Society Relationship:

Keratin are major protein component of hair. These protein contains large quantities of sulphur containing amino acids e.g. cysteine. There is formation of a covalent bond called a disulphide bridge between the sulphur atoms of two cysteines on separate chains of keratine. These bonds are stronger than hydrogen bond which are responsible for straight hair or curly hair. This is all due to cross linking in hair between sulphur atoms. Shampoos can be used to make hair style. Shampoos containing reducing agent make hair straight while shampoos containing oxidizing agent make hair curly.



Theories of Covalent Bonds:

There are three theories of covalent bonds.

These are

- (i) VSEPR, Resonance Theory
- (ii) VBT
- (iii) MOT.

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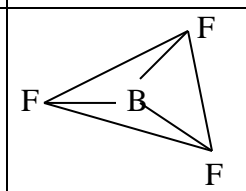
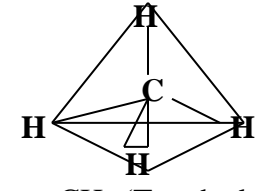
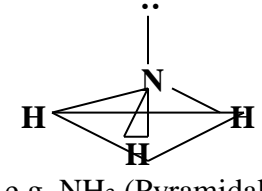
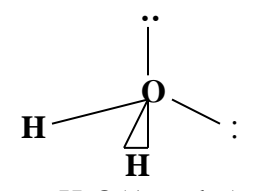
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Valence Shell Electron Pair Repulsion (VSEPR)

Theory:

VSEPR theory is good enough to explain molecule geometries and bond angles.

Summary of molecular shapes is given in following table:

Total no of electrons pairs in valence shell of central atom	No of lone pairs of electrons around the central Atom	No of bond pairs of electrons around the central Atom	Electrons geometry	Molecular geometry
2	0	2	$: - x - :$ Linear	$A - x - A$ e.g. BeCl_2 Linear
3	1	2	$: - x \begin{matrix} : \\ / \\ \backslash \\ : \end{matrix}$ Trigonal planar	$\begin{matrix} & A & \\ & / & \\ : - x & & \\ & \backslash & \\ & A & \end{matrix}$ e.g. SnCl_2 (Angular)
3	0	3	$: - x \begin{matrix} : \\ / \\ \backslash \\ : \end{matrix}$ Trigonal planar	 e.g. BF_3 (Trigonal planar)
4	0	4	$\begin{matrix} : \\ \\ X \\ / \quad \backslash \\ : \quad : \end{matrix}$ Tetrahedral	 e.g. CH_4 (Tetrahedral)
4	1	3	$\begin{matrix} : \\ \\ X \\ / \quad \backslash \\ : \quad : \end{matrix}$ Tetrahedral	 e.g. NH_3 (Pyramidal)
4	2	2	$\begin{matrix} : \\ \\ X \\ / \quad \backslash \\ : \quad : \end{matrix}$ Tetrahedral	 e.g. H_2O (Angular)

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This theory considers two types of electron pairs around central atom of a molecule and it has following postulates:

- (i) Two types of electron pairs are present around central atom of a molecule. Electron pair which is shared between two atoms and is responsible for covalent bond is called "bond pair" while electron pair which is not shared between two atoms is called "lone pair"
- (ii) These electrons pair repel each other and their order of repulsion is
Lone pair-lone pair > Lone pair-bond pair > Bond pair-bond pair
- (iii) To reduce repulsion these electron pairs move to maximum angle apart each other and are directed in different directions in space. So they are responsible for molecular geometries.
For two electron pairs geometry is linear and bond angle is 180° .
For three electron pairs geometry is triangular planar and bond angle is 120° .
For four electron pairs geometry is tetrahedral and bond angle is 109.5° .
- (iv) If more than one electron pairs are there in the same region they behave like a single pair. e.g.

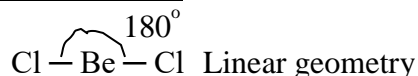
$$\begin{array}{c} \text{O} :: \overset{\cdot\cdot}{\text{S}} :: \text{O} \end{array}$$
 Sulphur in SO_2 shows three electron pairs behaviour.
- (v) Deviation from ideal bond angle occurs if lone pair of electrons is there.
- (vi) The effect of a bonding electron pair decreases with increasing electronegativity of an atom forming a molecule.

Shape of molecules with two electron pairs:

e.g (i) BeCl_2



or



The central atom Be has two electron pairs so molecule is linear with bond angle 180° .

e.g (ii) CO_2



or



Four pairs around central Carbon atom behave like two pairs so CO_2 molecule is linear with bond angle 180° .

e.g (iii) HCN



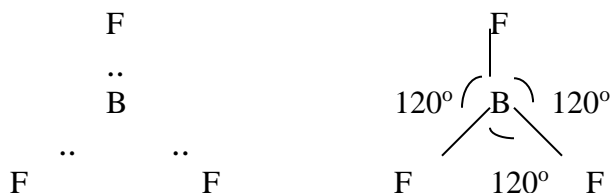
or



Four pairs around central Carbon atom behave like two pairs so HCN molecule is linear with bond angle 180° .

Shape of molecules with three electron pairs:

e.g (i) BF_3



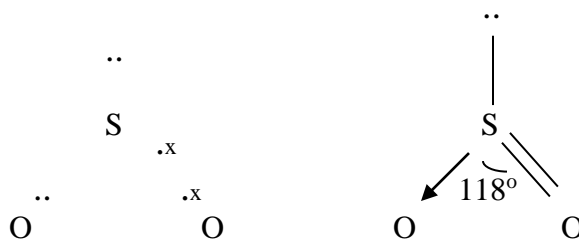
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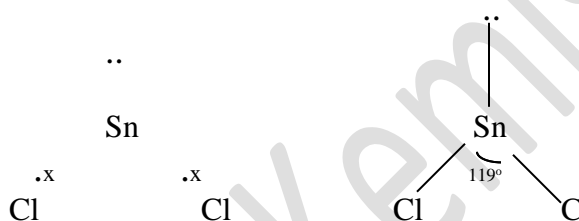
The central atom B has three electron pairs so molecule is triangular planner with bond angle 120° .

e.g (ii) SO_2



Two electron pairs that Sulphur has shared with one of the oxygen act as single pair so SO_2 shows behaviour of three electron pairs. Hence electron geometry in SO_2 is triangular planner while molecule geometry is angular or bent structure. In SO_2 deviation from ideal bond angle occurs due to presence of a lone pair.

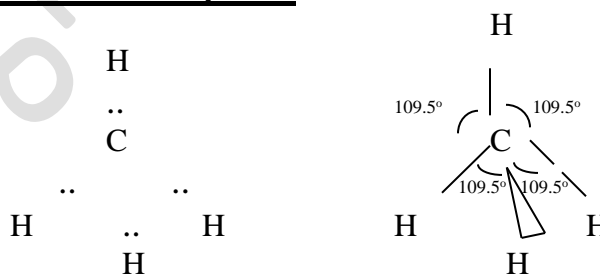
e.g (iii) SnCl_2



In stannous chloride, Sn has $5s^2 5p^2$ valence electrons. The two unpaired electrons of 5p orbital take part in bond formation of covalent bond with chlorine, while pair of electrons of 5s remains as lone pair and not participate in bond formation. Hence electron geometry in SnCl_2 is triangular planner while molecule geometry is angular or bent structure. In SnCl_2 deviation from ideal bond angle occurs due to presence of a lone pair.

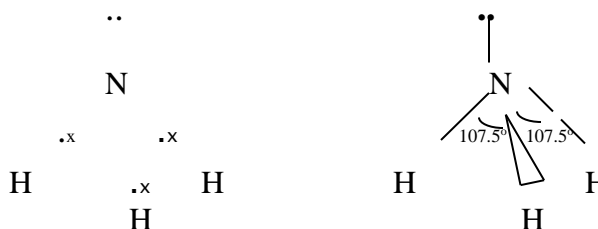
Shape of molecules with four electron pairs:

e.g (i) CH_4



The central atom C has four electron pairs so molecule is tetrahedral with bond angle 109.5° .

e.g (ii) NH_3



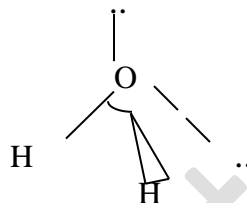
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The central atom N has four electron pairs so electron geometry in NH_3 is tetrahedral while molecule geometry is pyramidal. In NH_3 deviation from ideal bond angle occurs due to presence of a lone pair of electrons and angle reduces to 107.5° .

e.g (iii) H_2O



The central atom O has four electron pairs so electron geometry in H_2O is tetrahedral while molecule geometry is angular or bent structure. In H_2O deviation from ideal bond angle occurs due to presence of two lone pairs of electrons and angle reduces to 104.5° .

Limitations of VSEPR Theory:

Although this theory is good enough to explain molecular shapes and bond angles but:

- (i) it fails to explain the mechanism of formation of covalent bonds.
- (ii) it fails to explain why two electrons of same pair do not repel each other.
- (iii) it fails to explain paramagnetic nature of oxygen.

Resonance Theory:

According to resonance theory some molecules are represented by two or more than two structures and the actual structure is weighed average of these and is called resonance hybrid.

There are certain molecules which cannot be represented by single structure, so we write various possible structures for such molecules. These possible structures are called resonating structures or canonical structures. The real structure is weight average of these resonating structures and is called resonance hybrid. The resonance hybrid is imaginary structure which is obtained by mental combination of resonating structures.

Each resonating structure contributes to real structure. Some structures contribute more (Major contributors) and other contributes less (Minor contributors). More is the stability of a resonating structure more is its contribution to resonance hybrid (real structure).

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Ingold in 1933 called this phenomenon as mesomerism, later; Heisenberg explained it theoretically and called it as resonance.

Necessary conditions for resonance are:

- The position of nuclei of atoms in each structure must be the same.
- The structures differ only in position of electrons.
- The number of unpaired electrons in each structure must be the same.

The resonance hybrid is always lower in energy than resonating structures, therefore, it is stable. The difference in energy of resonance hybrid and that of most stable resonating structures is called resonance energy. Higher is the resonance energy, more will be stability of the compound.

Ozone O₃:

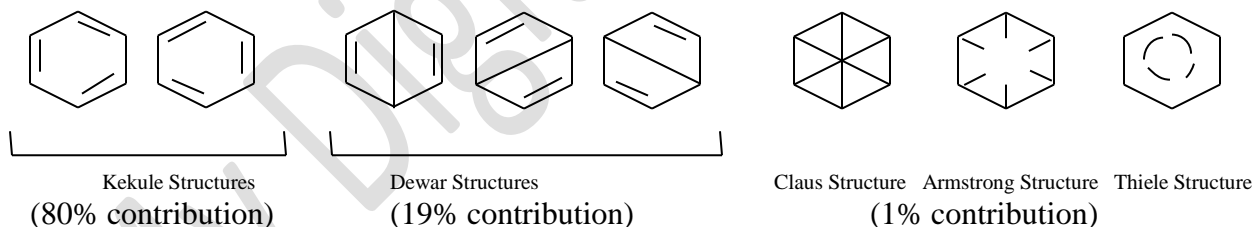
Lewis gave two resonating structures for Ozone, which are following:



But actual structure of ozone is weight average of these resonating structures and is called resonance hybrid. The resonance hybrid is imaginary structure which is obtained by mental combination of resonating structures.

Benzene C₆H₆:

There are several resonating structures for benzene which are following:



But actual structure of Benzene is weight average of these resonating structures and is called resonance hybrid. The resonance hybrid is imaginary structure which is obtained by mental combination of resonating structures. Kekule structures are main contributing structures their contribution to resonance hybrid is 80% that of Dewar structures is 19% while other structures contribute only 1%.

Valence Bond (VB) Theory:

This theory has following postulates:

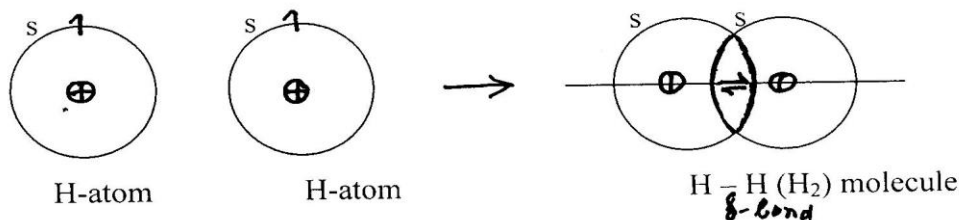
- (i) Covalent bonds are formed by overlapping of atomic orbitals.
- (ii) Electron density is high in the overlapped area and is thus responsible for holding atoms together.
- (iii) Only half filled atomic orbitals take part in covalent bond formation.
- (iv) The half filled atomic orbitals must contain electrons with opposite so they cancel the magnetic lines of force and can live together.
- (v) By the overlapping of orbitals two types of bonds are formed sigma bonds and pi bonds.
- (vi) Atomic orbitals of different shapes and energies some time are mixed to form hybrid orbitals.

Sigma (δ) Bond:

When half filled atomic orbitals are overlapped on bond axis the overlapping is called sigma overlapping and the bond formed is called sigma bond. Sigma bond is formed due to s-s or s-p or p-p overlapping. As sigma overlapping is larger so sigma bond is very strong.

s-s Overlapping:

The sigma bond which is formed between Hydrogen atoms is due to s-s overlapping.



The electronic configuration of Hydrogen is $1S^1$. The half filled s-orbital of one Hydrogen atom overlaps with half filled s-orbital of other Hydrogen atom on bond axis. So H – H bond is sigma bond.

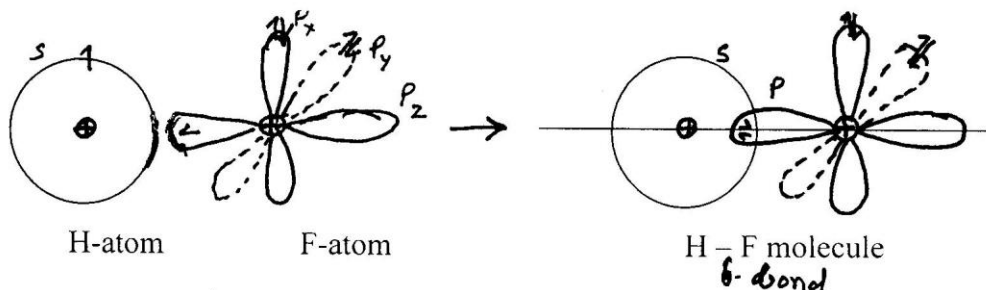
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s-p Overlapping:

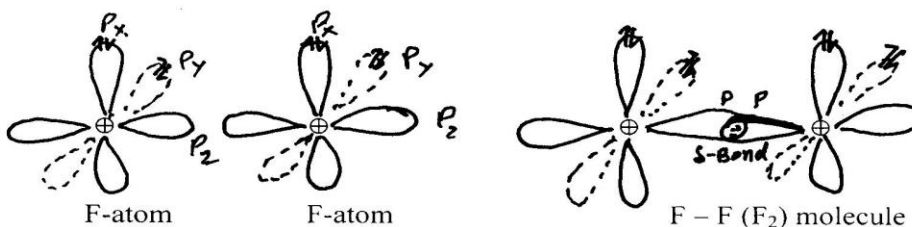
The sigma bond which is formed between Hydrogen atom and Fluorine atom is due to s-p overlapping.



The electronic configuration of hydrogen is $1S^1$ and that of Fluorine is $1S^2, 2S^2, 2P^5$. The half filled s-orbital of Hydrogen atom overlaps with half filled p-orbital of Fluorine atom on bond axis. So H - F bond is sigma bond.

p-p Overlapping:

The sigma bond which is formed between Fluorine atoms is due to p-p overlapping.



The electronic configuration of Fluorine is $1S^2, 2S^2, 2P^5$. The half filled p-orbital of one Fluorine atom overlaps with half filled p-orbital of other Fluorine atom on bond axis. So F - F bond is sigma bond.

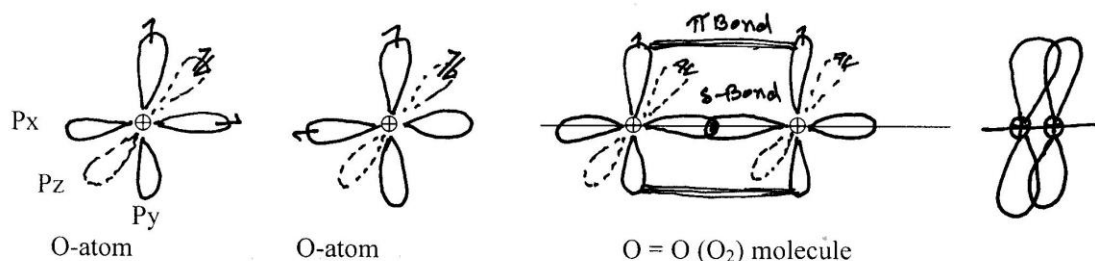
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Pi (π) Bond:

When half filled atomic orbitals are overlapped away from bond axis (side wise or lateral overlapping) the overlapping is pi overlapping and the bond formed is called pi bond. Pi bond is formed due to lateral overlapping of two parallel p-orbitals. As pi overlapping is little so pi bond is weak bond. e.g Oxygen molecule has one sigma bond and one pi bond.



The electronic configuration of oxygen atom is $1S^2, 2S^2, 2P^4$. Thus oxygen has two half filled p-orbitals.

One of the half filled p-orbital of one oxygen atom overlaps with a half filled p-orbital of other oxygen atom on bond axis thus a sigma bond is formed. The half filled p-orbitals of two oxygen atoms which are parallel to each other are side wisely or laterally overlapped and form pi bond. Thus a double bond is formed between two oxygen atoms consisting of a sigma and a pi bond.

Hybridization:

Mixing of atomic orbitals of different shapes and different energies to give same number of identical orbitals is called hybridization and the atomic orbitals thus formed are called hybrid orbitals. Total energy of the hybrid orbitals is less than unhybridized orbitals. However hybrid orbitals are equivalent in energy and shape among themselves. There are various type of hybridizations including sp^3 , sp^2 and sp - hybridization.

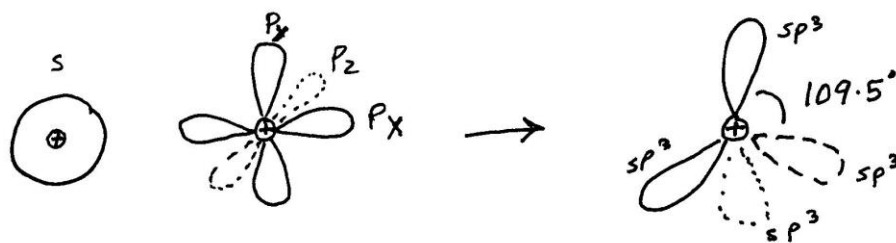
sp^3 hybridization:

Mixing of one s and three p orbitals to form four identical hybrid orbitals is called sp^3 hybridization. The four sp^3 hybrid orbitals are tetrahedrally arranged having an angle of 109.5° between them. Each sp^3 hybrid orbital has $\frac{1}{4}$ or 25% s-character and $\frac{3}{4}$ or 75% p-character.

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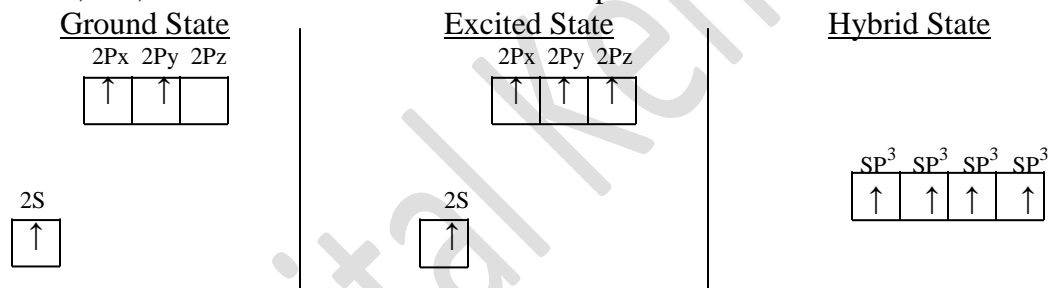
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e.g (i) CH_4 (Methane)

In methane and all other alkanes, C-atom shows sp^3 hybridization. The electronic configuration of Carbon is $1s^2, 2s^2, 2p^2$. Valence shell of carbon has a pair of electrons in its s-orbital while



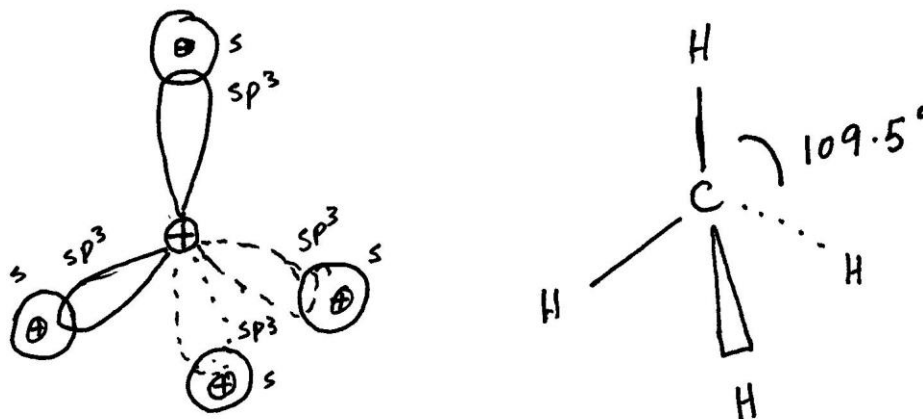
single electrons in two p-orbitals and one p-orbital is vacant in ground state. Then by absorbing energy one of the 2s electron promotes to the vacant p-orbital in excited state. To gain a state of stability one s orbital and three p orbitals are mixed together and form four sp^3 hybrid orbitals. Each hybrid orbital has a single electron thus carbon shows tetravalency.

The half filled s orbital of one of hydrogen atom overlaps with one of the half filled sp^3 hybrid orbital of carbon on bond axis thus forms a C-H sigma bond. Similarly other three hydrogen atoms also form C-H sigma bonds. The shape of CH_4 molecule is tetrahedral with H-C-H bond angle 109.5° . Carbon atom is at the centre of regular tetrahedron while four hydrogen atoms at the four corners of the tetrahedron.

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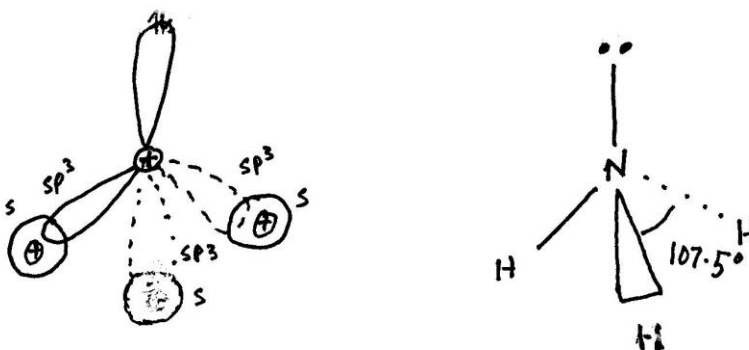
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Methane (CH_4)

e.g. (ii) NH_3 (Ammonia)

In ammonia the central atom nitrogen has electronic configuration $1s^2, 2s^2, 2p^3$ and is sp^3 hybridized. The four hybrid orbitals are directed towards the four corner of tetrahedron. One of the hybrid orbitals is completely filled that it has a pair of electrons. Due to this lone pair the s character of the hybrid orbital is increased (32.2% instead of 25%) as lone pair occupy more space. Also due to greater repulsion of the lone pair for bond pairs deviation occurs from ideal bond angle. So angle reduces from 109.5° to 107.5° .

Ammonia (NH_3)

In ammonia there are three N – H sigma bonds formed due to sp^3 -s overlapping nitrogen and hydrogen respectively and one sp^3 hybrid orbital has lone pair of electrons. Shape of ammonia molecule is pyramidal.

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e.g. (iii) H₂O (Water)

In water the central atom oxygen has electronic configuration $1S^2, 2S^2, 2P^4$ and is sp^3 hybridized. The four hybrid orbitals are directed towards the four corner of tetrahedron. Two hybrid orbitals are completely filled that they have pairs of electrons. Due to these lone pairs the s character of the hybrid orbitals is increased (30% instead of 25%) as lone pair occupy more space. Also due to greater repulsion of the lone pairs for bond pairs deviation occurs from ideal bond angle. So angle reduces from 109.5° to 104.5° .

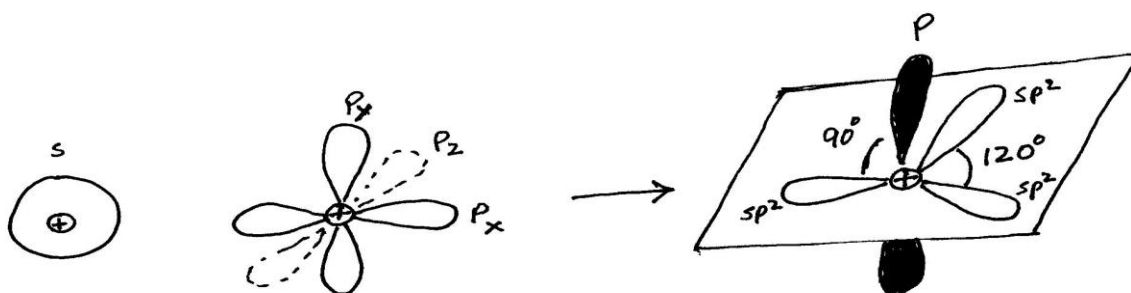


Water (H₂O)

In water there are two O – H sigma bonds formed due to sp^3 -s overlapping of oxygen and hydrogen respectively and two sp^3 hybrid orbitals have lone pairs of electrons. Shape of water molecule is angular or bent structure

sp^2 hybridization:

Mixing of one s and two p orbitals to form three identical hybrid orbitals is called sp^2 hybridization. The three sp^2 hybrid orbitals are planar having an angle of 120° between them. Each sp^2 hybrid orbital has $\frac{1}{3}$ or 33% s-character and $\frac{2}{3}$ or 67% p-character. The third p orbital which is left unhybridized is perpendicular to the plane of hybrid orbitals.



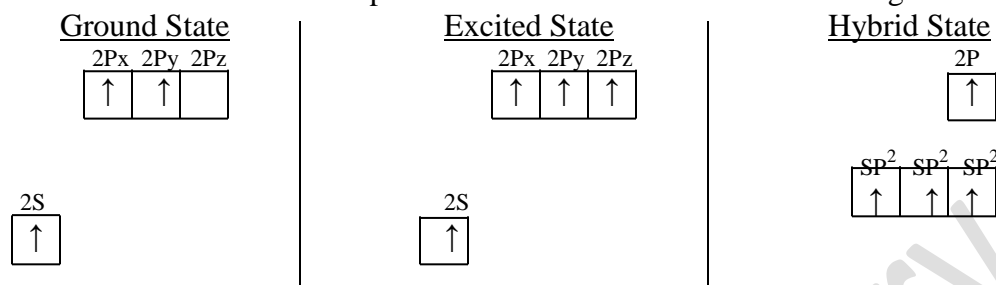
e.g. C₂H₄ (Ethene or Ethylene)

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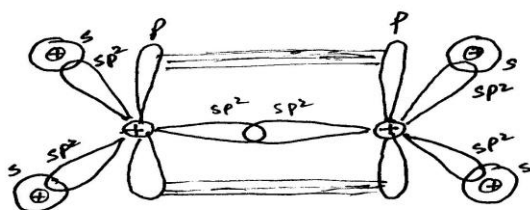
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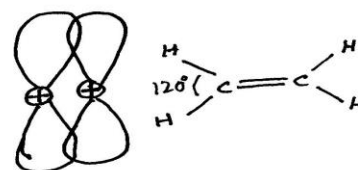
In ethene, each C-atom shows sp^2 hybridization. The electronic configuration of Carbon is $1S^2, 2S^2, 2P^2$. Valence shell of carbon has a pair of electrons in its s-orbital while single electrons in



two p-orbitals and one p-orbital is vacant in ground state. Then by absorbing energy one of the 2S electron promotes to the vacant p-orbital in excited state. To gain a state of stability one s orbital and two p orbitals are mixed together and form three sp^2 hybrid orbitals while the third p orbital remains unhybridized. Each hybrid orbital as well as the unhybridized orbital has a single electron thus carbon shows tetravalency. Both carbons of ethene are sp^2 hybridized.



Ethene (C_2H_4)



Lateral Overlapping
(Sidewise Overlapping)

The half filled s orbital of one of hydrogen atom overlaps with one of the half filled sp^2 hybrid orbital of one carbon atom on bond axis thus forms a C-H sigma bond. Similarly second hydrogen atom makes another C-H sigma bond with this carbon atom by sp^2 -s overlapping. Rest of two hydrogen atoms make two C-H sigma bonds with second carbon atom by sp^2 -s overlapping. The unhybridized p orbitals of carbon atoms which are parallel to each other side wisely or laterally overlaps and form carbon-carbon pi bond.

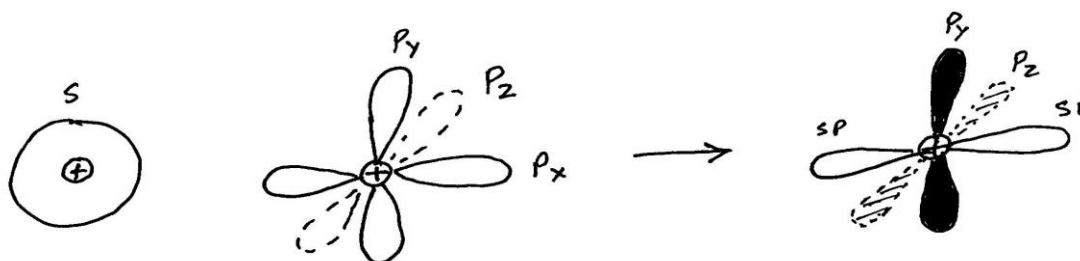
sp hybridization:

Mixing of one s and one p orbital to form two identical hybrid orbitals is called sp hybridization. The two sp hybrid orbitals are planar having an angle of 180° between them. Each sp hybrid orbital has $\frac{1}{2}$ or 50% s-character and $\frac{1}{2}$ or 50% p-character. The other two p orbitals which are left unhybridized are perpendicular to the hybrid orbitals as well as to each other.

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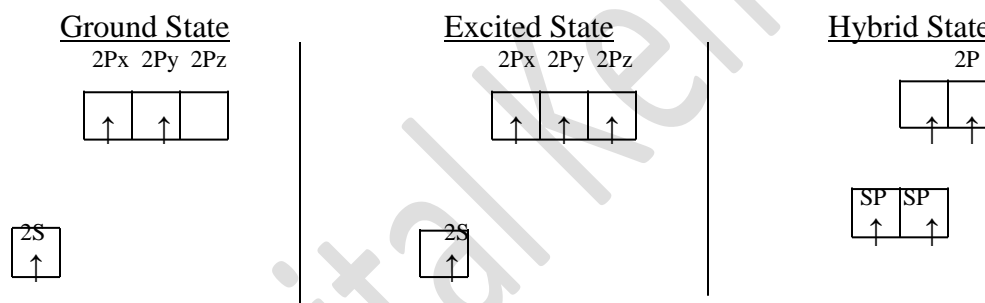
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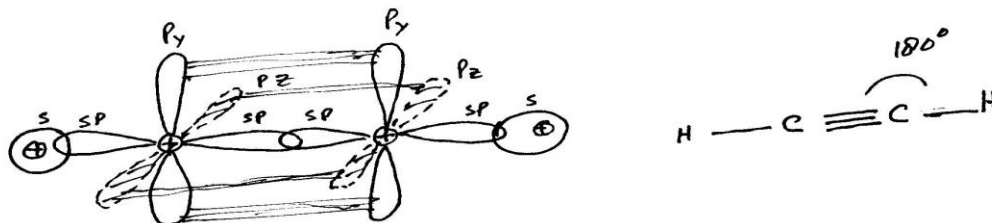
e.g. C_2H_2 (Ethyne or Acetylene)

In ethyne, each C-atom shows sp hybridization. The electronic configuration of Carbon is $1S^2, 2S^2, 2P^2$. Valence shell of carbon has a pair of electrons in its s-orbital while single electrons in



two p-orbitals and one p-orbital is vacant in ground state. Then by absorbing energy one of the $2S$ electron promotes to the vacant p-orbital in excited state. To gain a state of stability one s orbital and one p orbital are mixed together and form two sp hybrid orbitals while the other two p orbitals remain unhybridized. Each hybrid orbital as well as the unhybridized orbital has a single electron thus carbon shows tetravalency. Both carbons of ethyne are sp hybridized.

The half filled s orbital of one of hydrogen atom overlaps with one of the half filled sp hybrid orbital of one carbon atom on bond axis thus forms a C- H sigma bond.



Ethyne (C_2H_2)
(Acetylene)

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Similarly second hydrogen atom makes another C – H sigma bond with other carbon atom by sp³ overlapping. The unhybridized p orbitals of the two carbon atoms which are parallel to each other side wisely or laterally overlap and form two carbon-carbon pi bonds.

Limitations of VB Theory:

Although this theory is good enough to explain the mechanism of formation of covalent bonds as well as it also explain why two electrons of same pair do not repel each other but it fails to explain paramagnetic nature of oxygen.

Molecular Orbital (M.O) Theory:

This theory gave a new idea about orbitals.

- (i) When atoms combine to form molecules, atomic orbitals (AO) cease to exist and gave molecular orbitals (MO).
- (ii) Two atomic orbitals give two molecular orbitals, a bonding molecular orbital (BMO) and an anti bonding molecular orbital (ABMO).
- (iii) Bonding molecular orbital is lower in energy than parent atomic orbitals while anti bonding molecular orbital is higher in energy. However total energy remains conserved.
- (iv) Names of molecular orbitals are obtained from type of bonding and the parent atomic orbitals. Star is used with name of anti bonding molecular orbital. e.g. $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2p_x$, $\sigma^* 2p_x$, $\pi 2p_y$, $\pi^* 2p_y$, $\pi 2p_z$, $\pi^* 2p_z$ etc
- (v) The electron filling in these molecular orbitals follows same three rules which were followed by atomic orbitals i.e. Auf Bau principle, Pauli exclusion principle and Hund's rule.
- (vi) If electrons enter only in the bonding molecular orbitals and not in anti bonding then strong bond is formed. More is the number of electrons ($n_b > n_a$) weaker will be the bond. If number of electrons is equal ($n_b = n_a$) in bonding and anti bonding molecular orbitals then no bond will be formed.
- (vii) Bond order represents number of bonds and it is calculated as:

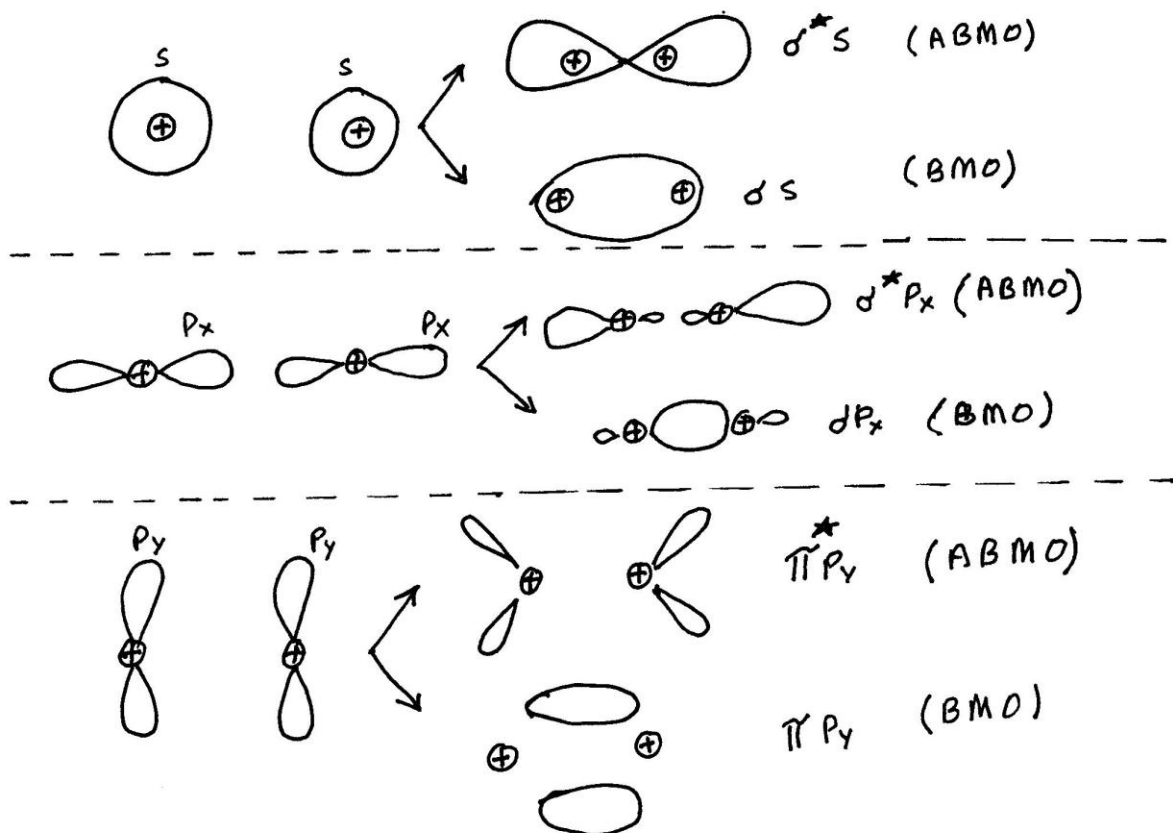
$$\text{Bond order} = \frac{\text{Number of electrons in BMO} - \text{Number of electrons in ABMO}}{2}$$

- (viii) Presence of single (unpaired) electrons shows the paramagnetic nature of the substance. More is the number of unpaired electrons more is the magnetic moment.
- (ix) Shapes of molecular orbitals are:

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Molecular Orbital Treatment of Some Homonuclear Diatomic Molecules:

Hydrogen (H_2) molecule:

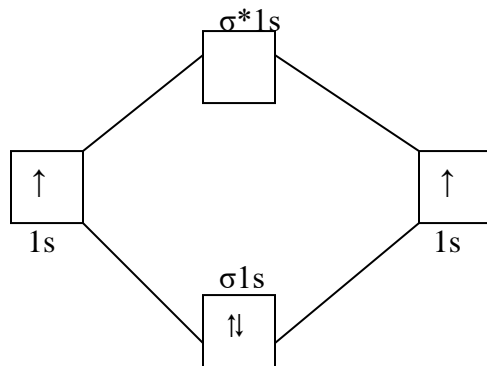
Hydrogen atom has electronic configuration $1s^1$.

$1s$ atomic orbitals of two hydrogen atoms combine to form two molecular orbitals, the bonding molecular orbital $\sigma 1s$ and antibonding molecular orbital $\sigma^* 1s$. The electron filling in these molecular orbitals follow aufbau and Pauli Exclusion Principle. Both electrons go to bonding molecular orbital and no in the antibonding, so a strong bond will be formed.

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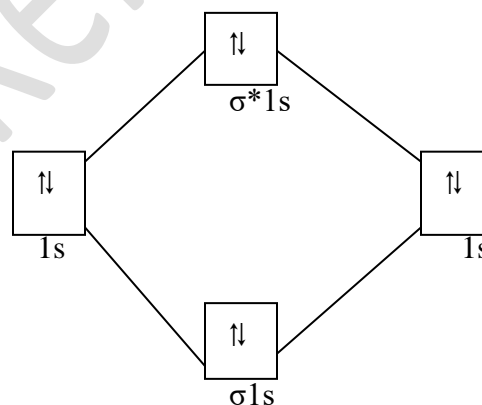


$$\text{Bond order} = \frac{\text{Number of electrons in BMO} - \text{Number of electrons in ABMO}}{2} = \frac{2 - 0}{2} = 1$$

As bond order in H_2 is one so one bond i.e is a single bond is formed between two hydrogen atoms. Further more as there is no unpaired electron in H_2 molecule hence it is diamagnetic.

Helium molecule He_2 :

Helium atom has electronic configuration $1s^2$.
 1s atomic orbitals of two helium atoms combine to form two molecular orbitals, the bonding molecular orbital $\sigma 1s$ and antibonding molecular orbital $\sigma^* 1s$.
 The electron filling in these molecular orbitals follow aufbau and pauli exclusion principle.
 Out of four electrons two electrons go to bonding molecular orbital and two to the antibonding molecular orbital, so no bond will be formed.



$$\text{Bond order} = \frac{\text{Number of electrons in BMO} - \text{Number of electrons in ABMO}}{2} = \frac{2 - 2}{2} = 0$$

As bond order in Helium is zero so no bond is formed between two helium atoms. Further more as there is no unpaired electron in Helium molecule hence it is diamagnetic.

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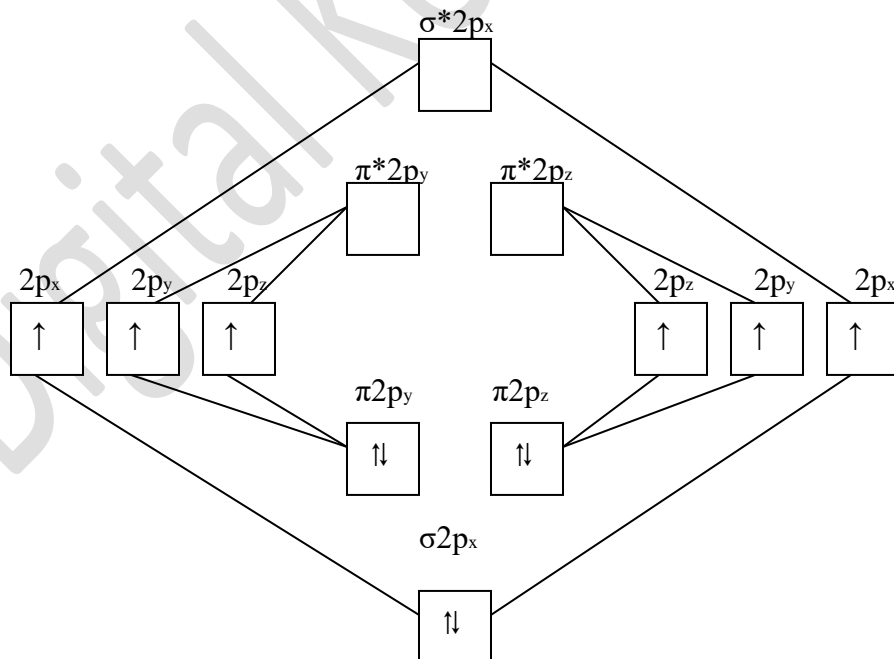
Nitrogen (N₂) molecule:

Nitrogen atom has electronic configuration $1s^2, 2s^2, 2p^3$. Two p-atomic orbitals (one from each nitrogen) atom combine to form two molecular orbitals, the bonding molecular orbital σ_{2p_x} and antibonding molecular orbital $\sigma^*_{2p_x}$. The other four p-atomic orbitals (two from each nitrogen) atom combine to give four molecular orbitals, two bonding molecular orbitals i.e. π_{2p_y} and π_{2p_z} , while two antibonding molecular orbitals i.e. $\pi^*_{2p_y}$ and $\pi^*_{2p_z}$.

The electron filling in these molecular orbitals follow aufbau, pauli exclusion principle and hund's rule. All six electrons go to bonding molecular orbitals, so strong bonds will be formed.

$$\text{Bond order} = \frac{\text{Number of electrons in BMO} - \text{Number of electrons in ABMO}}{2} = \frac{6 - 0}{2} = 3$$

As bond order in Nitrogen is 3 so three bonds i.e. triple bond is formed between two nitrogen atoms ($\text{N}\equiv\text{N}$). Further more as there is no unpaired electron in Nitrogen molecule hence it is diamagnetic.



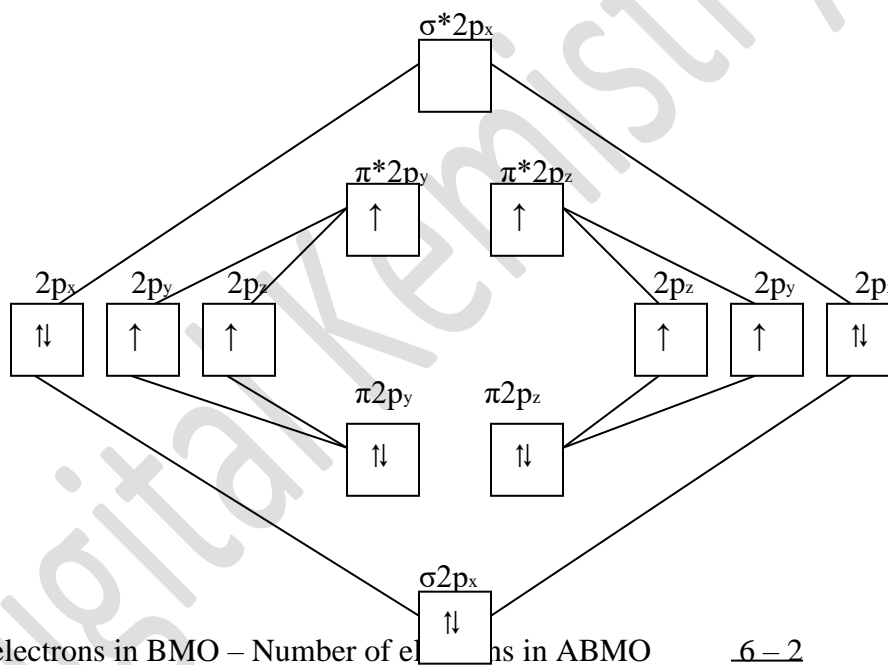
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Oxygen (O₂) molecule:

Oxygen atom has electronic configuration $1s^2, 2s^2, 2p^4$. Two p-atomic orbitals (one from each oxygen) atom combine to form two molecular orbitals, the bonding molecular orbital σ_{2p_x} and antibonding molecular orbital $\sigma^*_{2p_x}$. The other four p-atomic orbitals (two from each oxygen) atom combine to give four molecular orbitals, two bonding molecular orbitals i.e. π_{2p_y} and π_{2p_z} , while two antibonding molecular orbitals i.e. $\pi^*_{2p_y}$ and $\pi^*_{2p_z}$. The electron filling in these molecular orbitals follow aufbau, pauli exclusion principle and hund's rule. Out of eight electrons six go to bonding molecular orbitals and two to the antibonding molecular orbitals. As electrons are also present in antibonding molecular orbitals so weak bonds will be formed.



As bond order in Oxygen is 2 so two bonds i.e. double bond is formed between two oxygen atoms (O=O). Further more as there are two unpaired electrons in Oxygen molecule hence it is paramagnetic.

Significance of MOT:

Molecular Orbital Theory (MOT) predicts following facts.

- (i) MOT predicts either a bond is feasible or not. e.g. bond order in He₂ is zero so no bond is possible in helium.
- (ii) It predicts stability of bond. If no electrons are present in anti bond molecular orbital than strong bond will be formed and vice versa.

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- (iii) It predicts bond dissociation energy, Greater the bond order high will be bond dissociation energy.
- (iv) It predicts bond length, Greater the bond order less will be bond length.
- (v) It predicts about paramagnetic nature of a molecule. If unpaired electrons are present in molecular orbitals then molecule will be paramagnetic e.g. oxygen is paramagnetic as it has 2 unpaired electrons in its molecule.

Bond Energy:

“The energy required for breaking one mole of bonds or energy released during formation of one mole bonds is called bond energy”

Bond energy is the measure of strength of bond. Polar bonds are stronger than non-polar bonds. e.g bond energy of HCl:

Energy required to break one mole H – H bond = 436 kJ/mol bond
 Energy required to break one H – H bond = $436/6.02 \times 10^{23} = 7.242 \times 10^{-22}$ kJ/bond
 Contribution of 1 H-atom to bond energy = $7.242 \times 10^{-22}/2 = 3.621 \times 10^{-22}$ kJ/H-atom

Energy required during breaking of one mole Cl – Cl bond = 243 kJ/mol bond
 Energy required during breaking of one Cl – Cl bond = $243/6.02 \times 10^{23} = 4.037 \times 10^{-22}$ kJ/bond
 Contribution of 1 Cl-atom to bond energy = $4.037 \times 10^{-22}/2 = 2.0185 \times 10^{-22}$ kJ/Cl-atom

By considering H – Cl bond to be non-polar with equal sharing of electron pair, we can calculate bond energy of H – Cl by adding the contribution of Cl-atom and H-atom to the bond.

Bond energy per H – Cl bond = $3.621 \times 10^{-22} + 2.0185 \times 10^{-22} = 5.6395 \times 10^{-22}$ kJ/bond

But experimentally measured value = 7.26×10^{-22} kJ/bond

So actual bond energy is higher than calculated value, this is due to polar nature of the bond.

Bond energy depends upon:

- (i) Electronegativity difference between bonded atoms. More is electronegativity difference between atoms more will be the polarity of a bond, stronger will be the bond and higher will be its bond energy. Bond polarity and bond energy order in halogen acids is

	HF	>	HCl	>	HBr	>	HI
Electronegativity difference	1.9		0.9		0.7		0.4
Bond energy (kJ mol ⁻¹)	562		431		366		299

HF being highly polar has higher bond energy so it is difficult to break its bond and hence it is a weak acid.

- (ii) Size of atoms. Larger is the size of atoms weaker will be the bond and low will be bond energy and vice versa e.g.

	Cl ₂	>	Br ₂	>	I ₂
Bond energy (kJ mol ⁻¹)	243		193		151

☞ Bond energy of F₂ is exceptionally low i.e. 159 kJ mol⁻¹.

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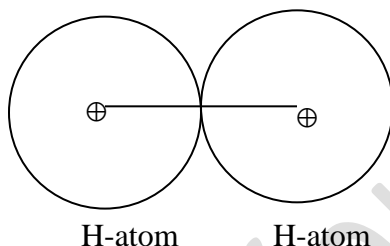
(iii) Bond length. Shorter is the bond high will be bond energy and vice versa.

	HF	>	HCl	>	HBr	>	HI
Bond length (m)	9.17×10^{-11}		1.27×10^{-10}		1.41×10^{-10}		1.61×10^{-10}
Bond energy (kJ mol ⁻¹)	567		436		366		299

S.I unit for bond energy is kJ/mol.

Bond Length:

“The distance between the nuclei of two atoms bonded together through a single covalent bond is called bond length.”



C – C bond length in aliphatic hydrocarbons as well as in diamond is 154 pm (1.54×10^{-10} m). In case of bond between identical atoms the bond length is additive property and can be obtained by adding atomic radii of the bonded atoms.

e.g. Atomic radius of carbon = 77 pm.
 So C – C bond length = 77 + 77 = 154 pm.
 Actual bond length of C – C bond = 154 pm.

In case of bond between un-identical atoms the bond length is not additive property and cannot be obtained by adding atomic radii of the bonded atoms. Due to difference of electronegativities a polar bond is formed between such atoms. And due to formation of positive and negative poles, atoms pull each other thus actual bond length is shortened.

e.g. (i) Bond length of Si^{δ+} – F^{δ-} bond:
 Atomic radius of Silicon = 117 pm.
 Atomic radius of Fluorine = 64 pm.
 So Si^{δ+} – F^{δ-} bond length in SiF₄ = 117 + 64 = 181 pm.
 But actually Si^{δ+} – F^{δ-} bond length in SiF₄ = 155 pm.

e.g. (ii) Bond length of H^{δ+} – Cl^{δ-} bond:
 Atomic radius of Hydrogen = 37 pm.
 Atomic radius of Chlorine = 99 pm.
 So H^{δ+} – Cl^{δ-} bond length in HCl = 37 + 99 = 136 pm.
 But actually H^{δ+} – Cl^{δ-} bond length in HCl = 127 pm.

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Comparisons of experimental and calculated values of bond lengths and bond energies of Halogen acids:

Compound	Bond Length (pm)			Bond Energy (kJ/mol)		
	Calculated	Experimental	Difference	Calculated	Experimental	Difference
H – F	107.7	91.7	16	293	567	274
H – Cl	136	127	9	236	436	200
H – Br	151	141	10	311	366	55
H – I	171	161	10	291	299	8

Ionic Character:

Ionic character is measure of polarity of a bond. It depends upon difference of electronegativity of two bonded atoms, more is difference of electronegativity high will be ionic character. When bond is between identical atoms then electronegativity difference is zero and ionic character is also zero. So bond is 100% covalent. On other hand bond between dissimilar atoms has some ionic character however there is no 100% ionic bond.

Electronegativity difference	Percent Ionic Character	Electronegativity difference	Percent Ionic Character
0.0	0	1.8	55
0.2	1	2.0	63
0.4	4	2.2	70
0.6	9	2.4	76
0.8	15	2.6	82
1.0	22	2.8	86
1.2	30	3.0	89
1.4	39	3.2	92
1.6	47	4.0	100
1.7	51		

Dipole Moment (μ):

“Product of charge +ve or –ve and distance between the centers of charges is called dipole moment”

Dipole moment is the measure of separation of charges and also measure of polarity of bond and polarity of molecule.

$$\mu = q \times r$$

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where

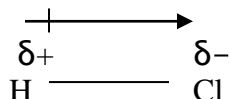
μ = dipole moment

q = charge +ve or -ve

r = distance between the centre of charges

i.e bond length.

Dipole moment is a vector quantity having magnitude " $q \times r$ " and direction from +ve pole to -ve pole. e.g.



Units of dipole moment:

The S.I unit for dipole moment is Coulomb-metre (C-m) beside it other units are electrostatic unit-centimetre (esu-cm) and debye (D). Their relationship is:

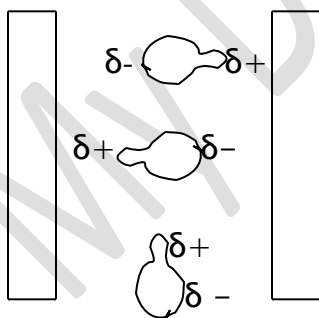
$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C.m}$$

$$1 \text{ D} = 1 \times 10^{-18} \text{ esu-cm}$$

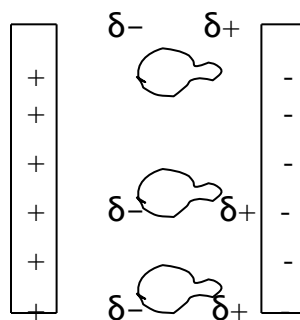
$$1 \text{ esu-cm} = 3.336 \times 10^{-12} \text{ C.m}$$

Measurement of dipole moment:

Dipole moment is measured by electric condenser (Dipole meter). Parallel plates of the condenser are charged by battery.



Field off



Field on

Polar molecules are dipoles. When they are placed between plates with electric field off they are randomly oriented but when electric field is on then the polar molecules are oriented such that their +ve poles towards -ve plate and their -ve poles towards +ve plates. The molecules hung

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between the two plates. The electric potential drops. Drop in potential is proportional to the polarity of molecule. So dipole moment is measured in terms of drop in potential.

Applications of Dipole Moment:

(i) Prediction of Polar nature:

It is used to predict whether molecule is polar or non polar. e.g. dipole moment of CH_4 , CO_2 , Cl_2 is Zero so they are non polar. on other hand dipole moment of CHCl_3 , H_2O , HCl are not Zero so they are polar molecules.

(ii) Measure of Polarity:

It is the measure of polarity of bond as well as that of molecule. More is the dipole moment more is the polarity of molecule e.g. Consider halogen acids their order of polarity is

HF	>	HCl	>	HBr	>	HI
Dipole moment		1.91D		1.03D		0.79D
						0.38D

(iii) Calculation of percent ionic Character:

Percent ionic character of a compound can be calculated as follows

$$\text{Percent Ionic Character} = \frac{\mu_{\text{obs}}}{\mu_{\text{cal}}} \times 100$$

μ_{obs} = It is the observed dipole moment which is measured by dipole meter

μ_{cal} = It is the dipole moment which is calculated by the formula $\mu = q \times r$ considering molecule to be 100% ionic.

e.g. For H – F $\mu_{\text{obs}} = 1.91 \text{ D}$ or $1.91 \times 3.336 \times 10^{-30} \text{ C.m}$

r = Bond length of H – F = $9.17 \times 10^{-11} \text{ m}$

$q = 1.6 \times 10^{-19} \text{ C}$ consider molecule to be 100% ionic, then complete transfer of electron take place and charge will be equal to the charge of electron.

$$\mu_{\text{cal}} = q \times r = 1.6 \times 10^{-19} \times 9.17 \times 10^{-11} = 1.467 \times 10^{-29} \text{ C.m}$$

$$\text{Percent Ionic Character} = \frac{\mu_{\text{obs}}}{\mu_{\text{cal}}} \times 100 = \frac{1.91 \times 3.336 \times 10^{-30}}{1.467 \times 10^{-29}} \times 100 = 43.4\%$$

Compound	μ_{obs}	Bond length	% ionic character
HF	1.91 D	$9.17 \times 10^{-11} \text{ m}$	43
HCl	1.03 D	$1.27 \times 10^{-10} \text{ m}$	17
HBr	0.79 D	$1.41 \times 10^{-10} \text{ m}$	12
HI	0.38 D	$1.61 \times 10^{-10} \text{ m}$	5

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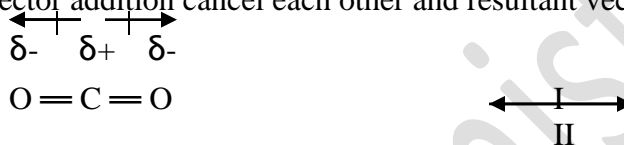
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(iv) Molecular Shapes and Bond Angles:

Dipole moment helps in deciding the molecular shape as well as bond angles. The dipole moment of molecule is obtained by vector addition of its bond moments. Molecular geometry is set such that calculated dipole moment of the molecule should match with observed dipole moment of the molecule.

(a) Shape CO₂ molecule:

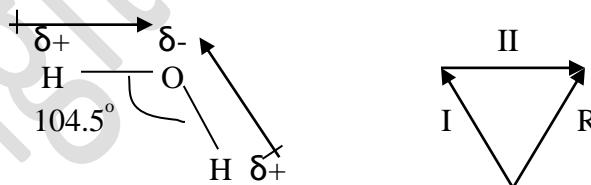
$\mu_{\text{CO}_2} = 0$, this is only possible when CO₂ has linear geometry. So two C=O bond moments on vector addition cancel each other and resultant vector is zero.

(b) Shape CS₂ molecule:

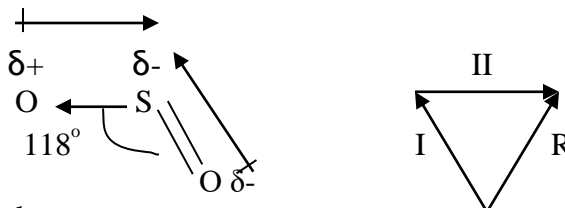
$\mu_{\text{CS}_2} = 0$, this is only possible when CS₂ has linear geometry. So two C=S bond moments on vector addition cancel each other and resultant vector is zero.

(c) Shape of H₂O molecule:

$\mu_{\text{H}_2\text{O}} = 1.84\text{D}$, this is only possible when H₂O has angular or bent structure with bond angle 104.5° . So two O—H bond moments, on vector addition give resultant vector as 1.84D .

(d) Shape of SO₂ molecule:

$\mu_{\text{SO}_2} = 1.62\text{D}$, this is only possible when SO₂ has angular or bent structure with bond angle 118° . So S—O and S=O bond moments, on vector addition give resultant vector as 1.62D .

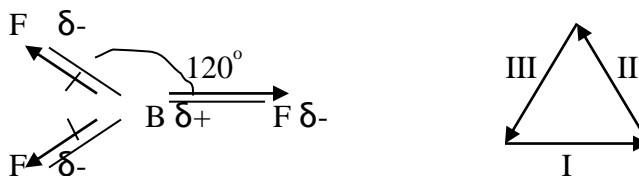
(e) Shape of BF₃ molecule:

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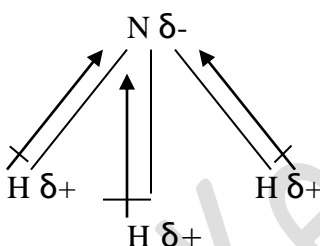
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$\mu_{\text{BF}_3} = 0$, this is only possible when BF_3 has trigonal planar structure with bond angle 120° . So three B—F bond moments, on vector addition give resultant vector zero.



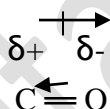
(f) Shape of NH_3 molecule:

$\mu_{\text{NH}_3} = 1.47\text{D}$, this is only possible when NH_3 has pyramidal structure with bond angle 107.5° . So three N—H bond moments, on vector addition give resultant vector 1.47D .



(g) Shape CO molecule:

$\mu_{\text{CO}} = 0.12\text{D}$, there is a double covalent bond between C and O and a coordinate covalent bond.



Compound	μ (in Debye)	Compound	μ (in Debye)	Compound	μ (in Debye)
CO_2	0	HI	0.38	$(\text{CH}_3)_2\text{CO}$	2.70
CO	0.12	CH_4	0	$\text{C}_6\text{H}_5\text{OH}$	1.70
NH_3	1.47	CCl_4	0	$\text{C}_6\text{H}_5\text{NH}_2$	1.56
SO_2	1.62	CHCl_3	1.15	$\text{C}_6\text{H}_5\text{Cl}$	1.50
BF_3	0	CH_2Cl_2	1.59	p-dichloro benzene	0
H_2S	1.10	CH_3Cl	1.86	m-dichloro benzene	1.48
HF	1.91	CS_2	0	o-dichloro benzene	2.25
HCl	1.03	$\text{C}_2\text{H}_5\text{OH}$	1.70	Trans 1,2-dichloro ethane	0
HBr	0.79	CH_3COOH	1.40	Cis 1,2-dichloro ethane	1.89

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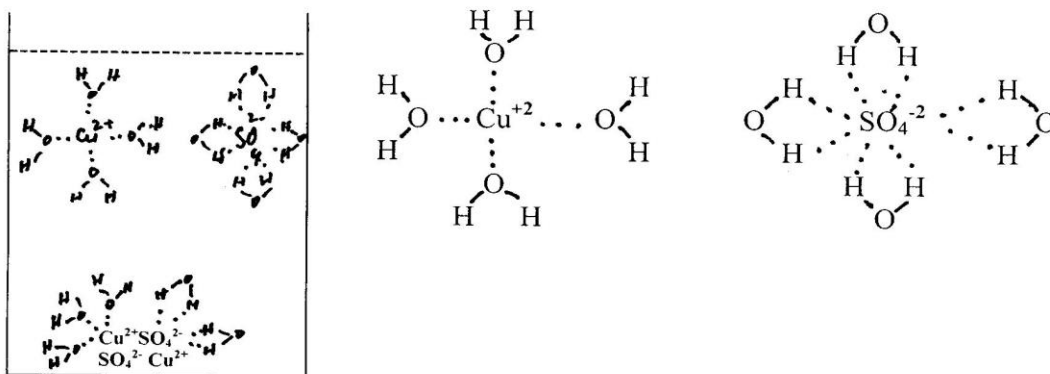
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Effect of bonding on physical and chemical properties:

Physical properties depend upon intermolecular forces (Hydrogen bonding, Dipole-dipole forces & London dispersion forces). While chemical properties depend upon intramolecular forces (Chemical bonds).

(i) Solubility of Ionic and Covalent compounds:

Solubility is based on fact "like dissolve like". e.g. ionic compounds are more soluble in polar solvents like water. Water molecules get attached to solute particles and it is called hydration. Ionic solutes are dissolved in water due to hydration. Partial positively charged hydrogen of water molecules attract negative ions of solute



While partial negatively charged oxygen of water molecules attract positive ions of solute. Thus solute's ions get separated and dissolve in the water. In solution each cation as well as anion of solute is surrounded by many water molecules. But in solid crystalline state only definite number of water molecules are attached per molecule of crystalline substance. The substance is called hydrate. e.g. in solution each copper ion is surrounded by dozens of water molecules similarly each sulphate ion is surrounded by dozens of water molecule but in solid crystalline state only five water molecule are attached per formula unit of CuSO_4 . Number of water molecules attached depends upon the charge density of the ion. More molecules of water are attached to cations due to their high charge density. The high charge density of cations is due to their smaller size or volume. Anions have larger size or volume so their charge density is low and hence less water molecules are attached to them e.g. in hydrated copper sulphate(Blue vitriol) $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ out of 5 water molecules 4 are attached to copper ion and one to sulphate ion. $[\text{Cu} \cdot 4\text{H}_2\text{O}]^{+2}[\text{SO}_4 \cdot \text{H}_2\text{O}]^{-2}$. Some more examples of hydrates are

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