

UNIT 4 : CHEMICAL BONDING & MOLECULAR STRUCTURE

CONCEPT WISE HANDOUTS

KEY CONCEPTS :

1. Kossel-Lewis Approach to chemical Bonding & Formal Charge
2. Bond Parameters
3. VSEPR Theory
4. Resonance
5. Valence Bond Theory
6. Hybridisation
7. Molecular Orbital Theory

Concept 1. Kossel -Lewis Approach to Chemical Bonding & Formal Charge



WALTHER KOSSEL

G.N. Lewis, an American chemist introduced simple notations (LEWIS SYMBOLS) to represent valence electrons in an atom.



G.N. LEWIS

G. N. Lewis and Kossel studied the electronic

configuration of noble gases and observed that the inertness of noble gases is due to their complete octet or duplet in case of Helium which has 2 electrons in its last shell and gave a generalization which states, "the atoms of different elements combine with each other in order to complete their octets or duplets (in case of H, Li and Be) to attain stable electronic configuration".

Significance of Lewis Symbols :

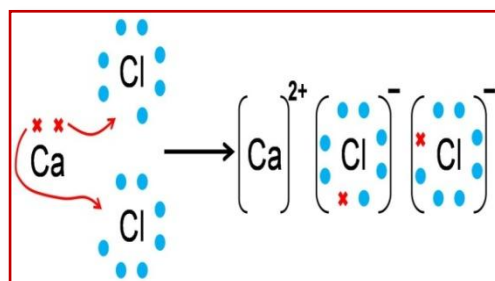
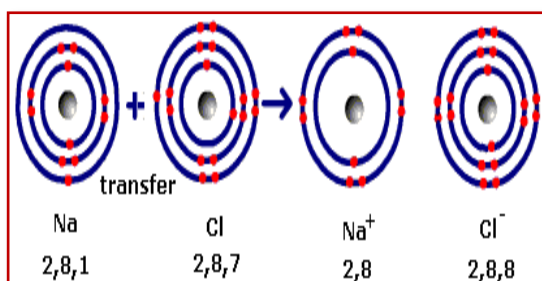
- The number of dots around the symbol represents the number of valence electrons.
- This number of valence electrons helps to calculate the common or group valence of the element.

HYDROGEN 1 H ·	PERIODIC TABLE ELEMENTS 1-20						HELIUM 2 He ·
LITHIUM 3 Li ·	BERYLLIUM 4 Be ·	BORON 5 B ·	CARBON 6 C ·	NITROGEN 7 N ·	OXYGEN 8 O ·	FLUORINE 9 F ·	NEON 10 Ne ·
SODIUM 11 Na ·	MAGNESIUM 12 Mg ·	ALUMINUM 13 Al ·	SILICON 14 Si ·	PHOSPHORUS 15 P ·	SULFUR 16 S ·	CHLORINE 17 Cl ·	ARGON 18 Ar ·
POTASSIUM 19 K ·	CALCIUM 20 Ca ·						

According to Kossel – Lewis approach, the atoms of different elements take part in chemical combination in order to complete their octet (to have eight electrons in the outermost valence shell) or duplet (to have two valence electrons in some cases such as H, Li, Be etc, or to attain the nearest noble gas configuration. This is known as **OCTET RULE**.

Ionic Bond: Ionic bond is a bond is formed by the complete transference of a certain number of electrons from one atom to another atom, so that both acquire stable electronic configuration".

Elements of group 1 and group 2 on combining with halogens, oxygen and sulphur generally form ionic bonds.



Conditions necessary for the formation of an ionic bond

1. Atoms forming positive (Cat) ions should have: (Usually Metals)

Low Ionization Energy Low electron affinity

Low electro negativity High Lattice Energy

2. Atoms forming negative (An) ions should have (Usually Non-Metals)

High Electron affinity High Electro negativity

High ionization energy High Lattice energy

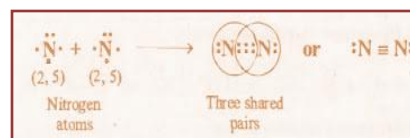
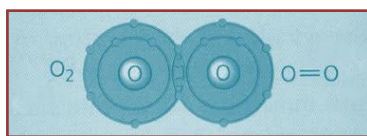
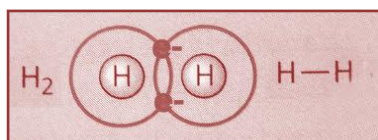
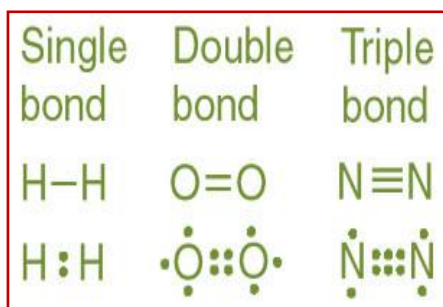
An ionic or electrovalent bond has the following characteristics:

- An ionic bond is formed due to the columbic attraction between the positively and negatively charged ions.
- An ionic bond is non-directional i.e., the strength of interaction between two ions depend upon distance, but not on the direction.
- An ionic bond gets broken when the substance is dissolved in a polar solvent or when the substance is melted.

Covalent Bond

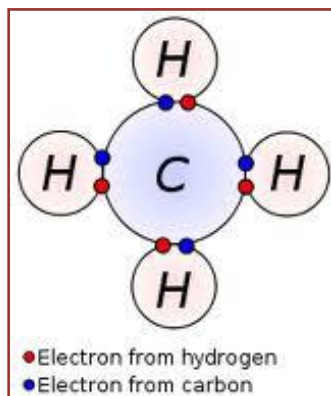
A covalent bond is formed when the atoms of same or different elements combine by mutual sharing of electrons". The compound, thus formed, is known as a Covalent Compound.

Such chemical bonds are formed by sharing of electrons, eg. formation of O_2 molecule.



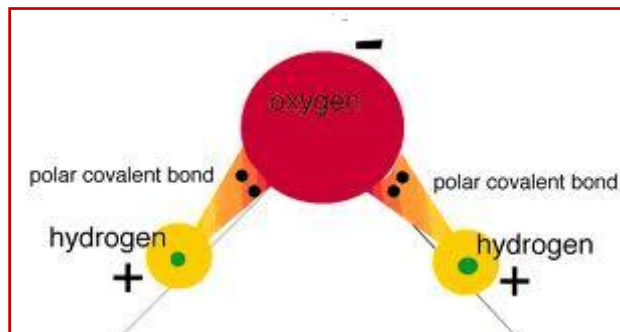
Conditions necessary for the formation of covalent bonds:

- A bond formed by mutual sharing of electrons
- Formed between two or more non-metals – difference in electro negativity should not be high.
- A single bond represents 2 electrons
- They satisfy the octet rule by sharing of electrons
- These molecules have a definite shape



Polar Covalent Bond

A bond in which electrons are shared between elements having a difference of electronegativity of between 0.5 & 2.0.



Dipole Moment

Dipole moment is defined as the product of the magnitude of charge on any one of the atoms and the distance between them.

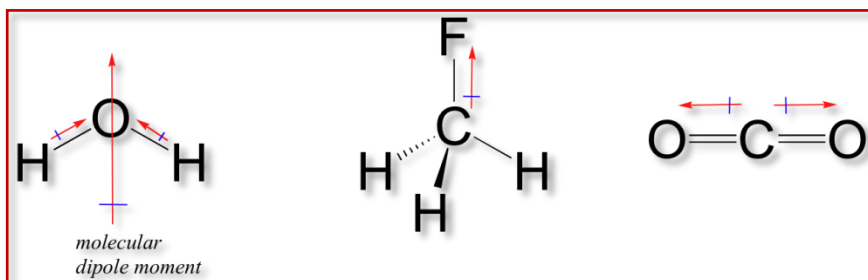
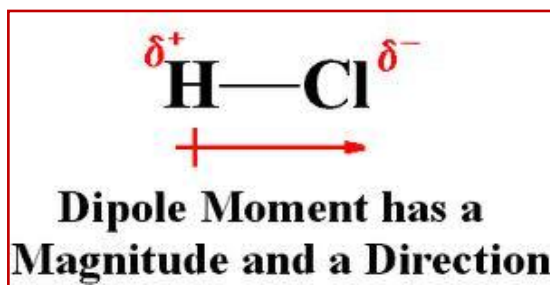
Dipole moment is represented by a Greek letter ' μ '. It can be expressed mathematically, as:

$$\mu = e \times d$$

Where, e = charge on any one of the atoms

d = distance between the atoms.

Its unit in CGS system is debye (D).



Formal Charge

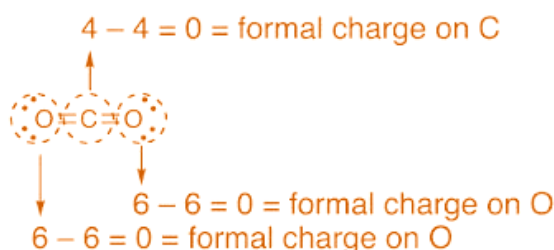
The formal charge is a hypothetical charge assigned from the dot structure. The formal charges is the electrical charge difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis Structure.

Formal Charge = [Number of valence electrons on atom] – [non-bonded electrons + number of bonds].

For Example BH_4

- The number of valence electrons for boron is 3.
- The number of non-bonded electrons is zero.
- The number of bonds around boron is 4.

$$\text{So formal charge} = 3 - (0 + 4) = 3 - 4 = -1$$

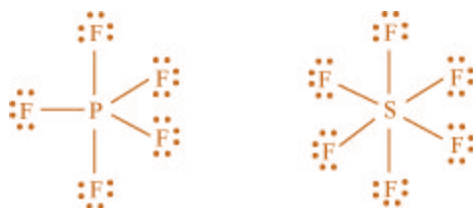


Limitations of Octet Rule

(a) The rule failed to predict the shape and relative stability of molecules.

(b) It is based upon the inert nature of noble gases. However, some noble gases like xenon and krypton form compounds such as XeF_2 , KrF_2 etc.

(c) The octet rule cannot be applied to the elements in and beyond the third period of the periodic table. The elements present in these periods have more than eight valence electrons around the central atom. For example: PF_5 , SF_6 , etc.



(d) The octet rule is not satisfied for all atoms in a molecule having an odd number of electrons. For example, NO and NO_2 do not satisfy the octet rule.



(e) This rule cannot be applied to those compounds in which the number of electrons surrounding the central atom is less than eight. For example, LiCl , BeH_2 , AlCl_3 etc. do not obey the octet rule.

➤ BOND LENGTH

Bond length is the average distance between the centres of the nuclei of two bonded atoms in a molecule. It is expressed in Angstrom units (Å) or picometers (pm).

$1\text{Å} = 10^{-10}\text{m}$ and $1\text{pm} = 10^{-12}\text{m}$. It is determined with the help of X-rays diffraction and other spectroscopic methods.

Bond length depends upon the following factors:

Bond Multiplicity *Bond length decreases with increase in bond multiplicity.*

CC bond length is shorter than C=C bond which in turn is shorter than C-C.

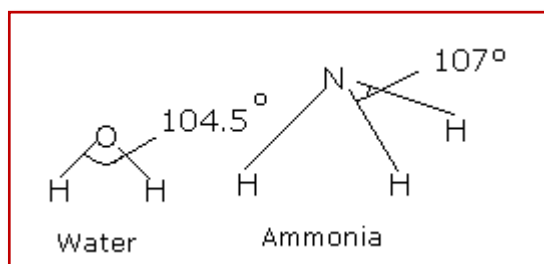
Size of the Atom *The bond length increases with increase in the size of the atom. From the above values it is clear that the bond lengths for a given family increase with increase in atomic number. For example : $\text{C-C} < \text{Si-Si} < \text{Ge-Ge}$*

This is because with the increase in size of the atom, the distance of the electrons from the nucleus increases successively with the addition of a new shell. Therefore the average distance between the bonding nuclei (bond length) increases.

➤ BOND ANGLE

It is defined as the average angle between the orbitals of the central atom containing the bonding electron pairs in the molecule. It is expressed in degree/minute/second. This gives an idea about the distribution of orbitals around the central atom in a molecule. Therefore bond angle determines the shape of a molecule.

For example, the H-O-H bond angle in H_2O is 104.5° and H-N-H bond angle is NH_3 107° .



➤ BOND DISSOCIATION ENTHALPY

It is defined as the enthalpy change involved to break one mole of bonds of a particular type between the atoms of a molecule in the gaseous state. It is expressed in terms of kJ mol^{-1} . When a bond is formed between the atoms, energy is released and the bonded atoms have lesser energy than the separated individual atoms. Then, same amount of energy will be needed to form the bond. This energy is called the bond dissociation energy and is a measure of bond strength. Larger the bond dissociation energy, stronger will be the bond in the molecule.

Bond Dissociation Enthalpy depends upon:

- *Size of Bonded Atoms*
- *Bond Length*
- *Bond Polarity*

➤ BOND ORDER

Bond order is a measurement of the number of electrons involved in bonds between two atoms in a molecule.

Most of the time, bond order is equal to the number of bonds between two atoms.

Exceptions occur when the molecule contains antibonding orbitals.

Bond order is calculated by the equation:

$$\text{Bond order} = (\text{number of bonding electrons} - \text{number of antibonding electrons}) / 2$$

If bond order = 0, the two atoms are not bonded.

Examples:

The bond order between the two carbons in acetylene is equal to 3.

The bond order between the carbon and hydrogen atoms is equal to 1.

Concept 3 . Valence Shell Electron Pair Repulsion theory [VSEPR]

There is no direct relationship between the formula of a compound and the shape of its molecules. The shapes of these molecules can be predicted from their Lewis structures, however, with a model developed about 30 years ago, known as the valence-shell electron-pair repulsion (VSEPR) theory.

The VSEPR theory assumes that each atom in a molecule will achieve a geometry that minimizes the repulsion between electrons in the valence shell of that atom. The five compounds shown in the figure below can be used to demonstrate how the VSEPR theory can be applied to simple molecule.

This theory was proposed for the first time by Sidgwick and Powell in 1940 and developed by Gillespie and Nyholm in 1957. According to this theory

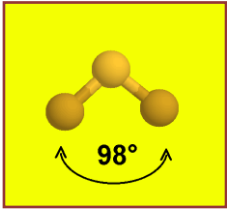
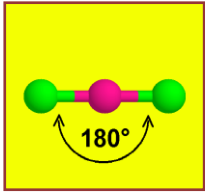
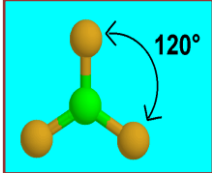
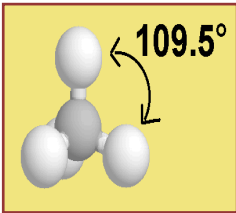
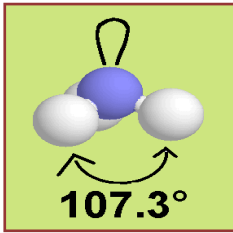
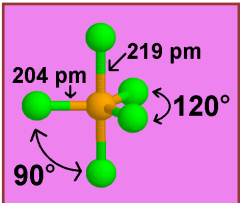
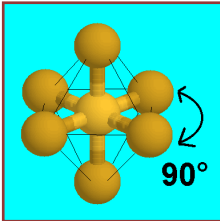
“The shape of a given species (molecule or ion) depends on the number and nature of electron pairs surrounding the central atom/ion of the species.”

Possible Arrangement of Electrons About A Central Metal Atom

MOLECULE CLASS	TOTAL ELECTRON PAIRS	BONDING PAIRS	NON-BONDING PAIRS	ARRANGEMENT OF ELECTRONS	GEOMETRY (OR SHAPE)	EXAMPLE
AB ₂	2	2	0	Linear	Linear	BeCl ₂ , CO ₂
AB ₃	3	3	0	Trigonal planar	Trigonal planar	BH ₃
AB ₄	4	4	0	Tetrahedral	Tetrahedral	CH ₄
AB ₃ E	4	3	1	Tetrahedral	Trigonal pyramidal	NH ₃
AB ₂ E ₂	4	2	2	Tetrahedral	Bent (angular or V-shaped)	H ₂ O
AB ₅	5	5	0	Trigonal bipyramidal	Trigonal bipyramidal	PCl ₅
AB ₄ E	5	4	1	Trigonal bipyramidal	Seesaw	SF ₄
AB ₃ E ₂	5	3	2	Trigonal bipyramidal	T-shaped	ClF ₃
AB ₂ E ₃	5	2	3	Trigonal bipyramidal	Linear	XeF ₂
AB ₆	6	6	0	Octahedral	Octahedral	SF ₆
AB ₅ E	6	5	1	Octahedral	Square pyramidal	BrF ₅
AB ₄ E ₂	6	4	2	Octahedral	Square planar	XeF ₄

A = central atom, B = bonding atom, E = nonbonding electron pair

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SOME MOLECULAR SHAPES

SF_2 BENT	
$BeCl_2$ LINEAR	
BF_3 TRIGONAL PLANER	
CH_4 TETRAHEDRAL	
NH_3 TRIGONAL PYRAMIDAL	
PCl_5 TRIGONAL BIPYRAMIDAL	
SF_6 OCTAHEDRAL	

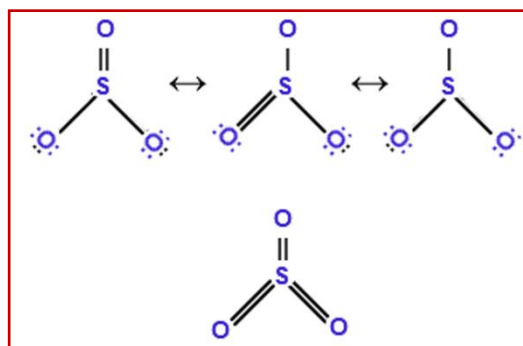
Concept 4. RESONANCE

Resonance is a method of describing the delocalized electrons in some molecules where the bonding cannot be explicitly expressed by a single Lewis structure.

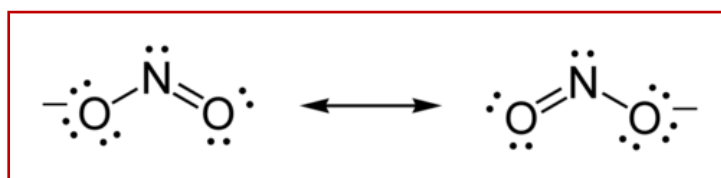
Each individual Lewis structure is called a contributing structure of the target molecule or ion. Contributing structures are not isomers of the target molecule or ion, since they only differ by the position of delocalized electrons.

Resonance is a key component of valence bond theory and arises when no single conventional model using only single, double or triple bonds can account for all the observed properties of the molecule.

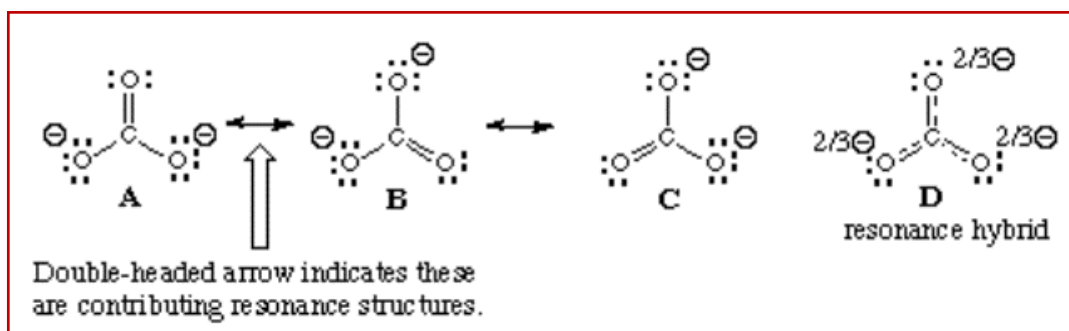
SO_3



NO_2^-



CO_3^{2-}



Concept 5. VALENCE BOND THEORY

Valence Bond theory assumes that electrons occupy atomic orbitals of individual atoms within a molecule, and that the electrons of one atom are attracted to the nucleus of another atom. This attraction increases as the atoms approach one another until the atoms reach a minimum distance where the electron density begins to cause repulsion between the two atoms. This electron density at the minimum distance between the two atoms is where the lowest potential energy is acquired, and it can be considered to be what holds the two atoms together in a chemical bond.

The overlap of atomic orbitals is given by the following postulates:

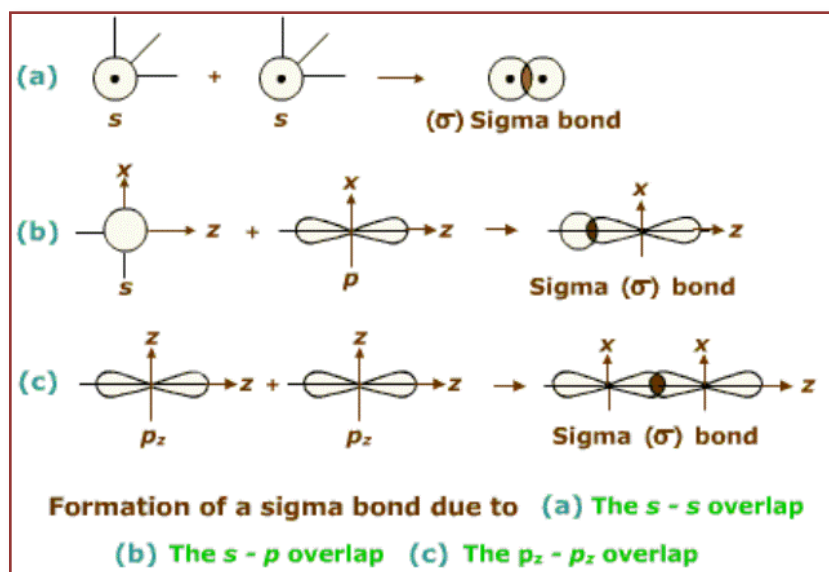
- *The atoms which unite to form a molecule completely retain their identities in the resulting molecule.*
- *The formation of a covalent bond is due to overlap of atomic orbitals .*
- *If the two atoms, each having on unpaired electron, come together, the AO's accommodating these unpaired electrons overlap (i.e, electron waves interact) and the spins of the two electrons get mutually neutralized, resulting in the formation of covalent bond which is localized between the two atoms.*
- *If the electrons present in the AO's have parallel spins, no bond formation will occur, and no molecule will be formed.*
- *If the AO's possess more than one unpaired electrons, more than one bond can be formed. Thus, in N_2 molecule there are three bonds, since N atom has three unpaired electrons. $N = 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$*
- *Electrons already paired in the valence shell cannot take part in the bond formation. They can only take part in the bond formation if they can be unpaired with the use of lot of energy. This is seen in the case of Phosphorus, which forms PF_5 by sharing 5 electrons(three from the three unpaired P electrons and two from paired s).*
- *The strength of the covalent bond is related to the extent of overlapping of the atomic orbitals. The more the two bonding orbitals overlap, The more the bonding electrons are concentrated between the nuclei where they can minimize the nuclear repulsion and maximize the attractive forces between themselves and both nuclei jointly.*

Thus, greater the overlap of the atomic orbitals, the greater will be the strength of the resulting covalent bond.

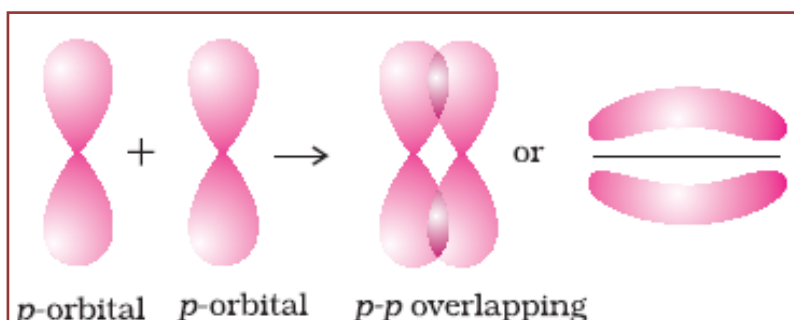
Types of Overlap

Depending upon the type of atomic orbitals involved in bonding, different types of overlap can be seen. Thus, there may be σ or a π covalent bond

Sigma bond: A covalent bond resulting from the formation of a molecular orbital by the end-to-end overlap of atomic orbitals, denoted by the symbol σ .



Pi bond: A covalent bond resulting from the formation of a molecular orbital by side-to-side overlap of atomic orbitals along a plane perpendicular to a line connecting the nuclei of the atoms, denoted by the symbol π .

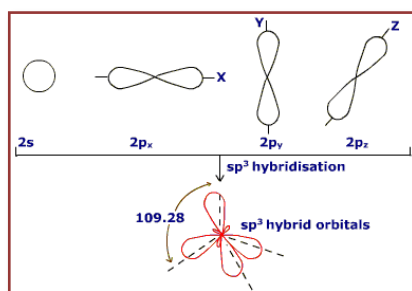
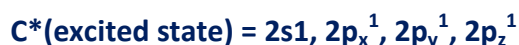


Concept 6. HYBRIDISATION

According to the valence bond theory, a covalent bond resulting from the overlap of atomic orbitals requires the presence of unpaired electron in the overlapping atomic orbital of an atom. Thus carbon, with four electrons in the valence shell would have only two unpaired p electrons. $C = 2s^2, 2p_x^1, 2p_y^1$

To account for the third and fourth valency, it is believed that the 's' electron in the same main level, gets unpaired and occupies the P_z which is empty, thus creating four unpaired levels for the incoming electrons to occupy.

The arrangement of electrons in the atom obtained after the promotion of electrons is sometimes referred to as an excited valence state of the atom.



Hybridization

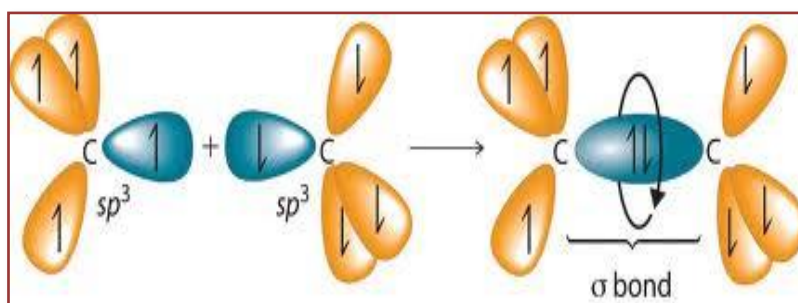
1. In order to account for the equivalence of the four C-H sigma bonds in CH_4 molecule we assume that the four orbitals of C^* atom, $2s$, $2p_x$, $2p_y$ and $2p_z$ are mixed together or hybridized to form four orbitals of equal energy called as the hybrid orbitals.
2. The mixing of pure atomic orbitals to give equal number of hybrid orbitals is referred to as Hybridization.
3. The carbon atom in methane is sp^3 hybridized, because one s and three p orbitals are involved in hybridization.

Hybridization Rules

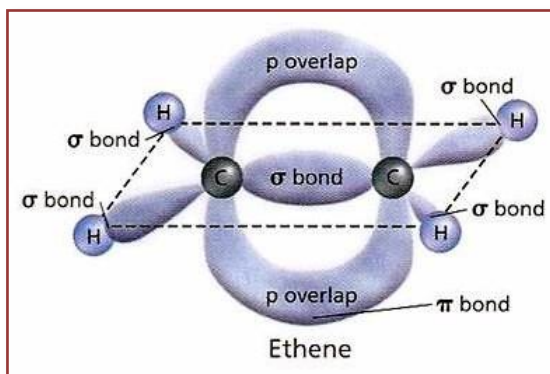
1. Only orbitals of similar energies belonging to the same atom or ion can hybridize together.
2. Number of hybrid orbitals produced is equal to the number of orbitals undergoing hybridization. Hybrid bonds are stronger than the single- non- hybridized bonds of comparable energy.

- Most of the hybrid orbitals are similar but they are not necessarily identical in shape. They differ from one another in their orientation in space.
- For equivalent hybrids the orientation in space is determined by: the number of orbitals mixed and consequently the number of hybrids obtained and which of x, y and z axis are preferred by the orbitals when pure.
- From the type of hybridization one can predict the geometry and bond angles of a molecule.
- An orbital which has been used to build up a hybrid orbital is no longer available to hold electron in its pure form

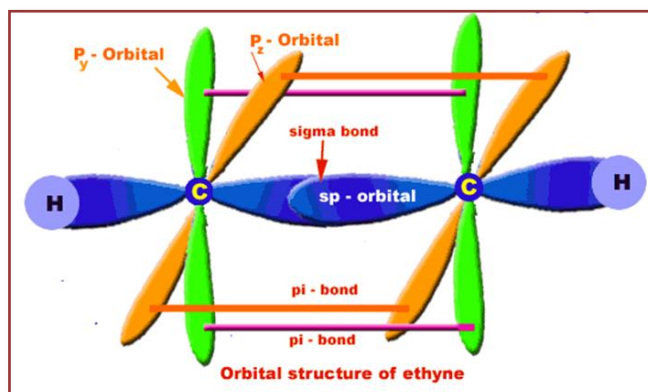
sp³ hybridisation



sp² hybridisation



sp hybridisation



Concept 6. MOLECULAR ORBITAL THEORY

An approach to bonding in which orbitals encompass the entire molecule, rather than being localized between atoms.

Molecular Orbital (MO) theory predicts the actual properties of molecules better than VB theory depicting electron transitions because of the differences in the energy levels of orbitals in the molecule.

Molecular orbitals are formed when the atomic orbitals of two (or more) different atoms are joined together. The orbitals are then spread across all of the atoms that contributed the atomic orbitals.

The same number of molecular orbitals are formed as there were atomic orbitals joined together, and their net energy is the same.

❖ Bonding molecular orbitals

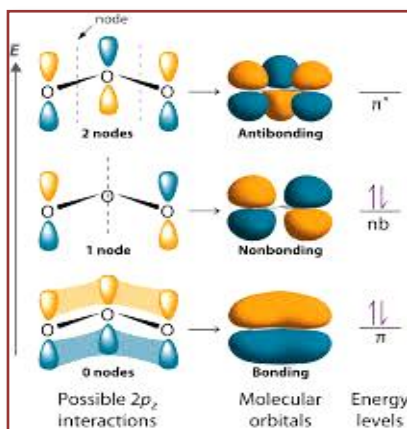
- have electron density between the atom
- are lower in energy than the original atomic orbitals
- when these orbitals are occupied by electrons, it holds the atoms together, forming a bond

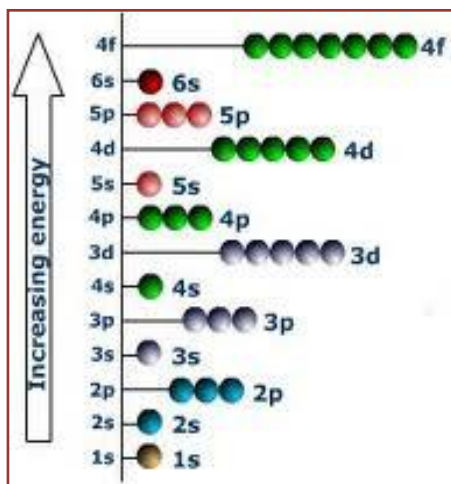
❖ Nonbonding molecular orbitals

- may occur when three or more atomic orbitals are combined
- have the same energy as the original atomic orbitals
- electrons occupying these orbitals do not stabilize or destabilize the molecule

❖ Antibonding molecular orbitals

- have electron density which is not between the atoms (there is a node between the atoms)
- are higher in energy than the original atomic orbitals
- if these orbitals are occupied by electrons, it pulls the atoms away from each other and weakens or prevents bonding.





The relative energies of molecular orbitals depend upon the following two factors:

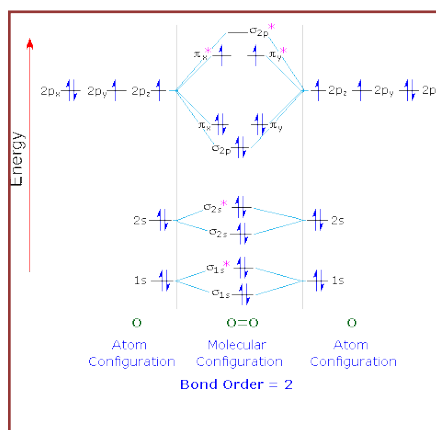
- the energies of the atomic orbitals combining to form molecular orbitals.
- the extent of overlapping between the atomic orbitals.

The greater the overlap, the more the bonding orbital is lowered and the antibonding orbital is raised in energy relative to atomic orbitals.

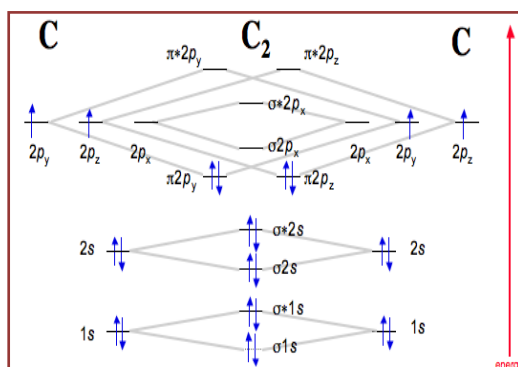
Energy order of various Molecular Orbitals

The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below :

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



However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li_2 , Be_2 , B_2 , C_2 , N_2 . For instance, it has been observed experimentally that for molecules such as B_2 , C_2 , N_2 etc. the increasing order of energies of various molecular orbitals is



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

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

Points to Remember on Molecular Orbital Theory

1. *Bond Order = (no. of bonding electrons – no. of antibonding electrons) / 2*
2. *Bond order is useful in predicting the stability of the molecules.*
 - *If B.O = 0, then the molecule is unstable.*
 - *If B.O > 0, then the molecule is stable.*
 - *Thus, higher the bond order, greater will be the stability of the molecule.*
3. *Atoms or molecules which consist of paired electrons are called as “Diamagnetic” and which consist of one or more unpaired electrons are known as “Paramagnetic”.*
4. *Saturated molecules:- The molecules in which all the valence electrons are involved for single bond formation. Non-bonded lone pairs are absent. These molecules have less energy, hence are more stable.*