

Inorganic Chemistry

M.S.C. / First Semester

(6) Lecturer

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Pro .Dr. Mohammed Hamid

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Lewis-Langmuir concept of covalent bonding is unable to explain the shapes of the covalent molecules. In case of covalent molecules having three or more atoms, one of the atoms acts as a central atom and rest of the atoms are linked to it in definite directions in space. **This definite arrangement of the bonded atoms with the central atom in a molecule is known as shape or geometry of the molecule.**

The first simple theory that was put forward to predict the geometry or shape of a covalent molecule is known as **Valence Shell Electron Pair Repulsion Theory (or VSEPR theory)**. This theory was first proposed by **Sidgwick and Powell** in 1940 and was further developed by **Nyholm and Gillespie** in 1957.

The theory, known as VSEPR theory, is primarily based on the fact that in a polyatomic molecule, the direction of bond around the central atom depends upon the total number of electron pairs (bonding as well as non-bonding) in its valence shell. These electron pairs place themselves as far apart as possible in space in order to have minimum forces of repulsion between them. The minimum repulsions correspond to the state of minimum energy and maximum stability of the molecule.

The main postulates of VSEPR theory are as follows:

(i) The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

(ii) Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.

(iii) The positions of the electron pairs in space around central atom are such that minimise repulsion and thus maximise distance between them.

(iv) The magnitudes of the different types of electronic repulsions follows the order given below:

Lone pair – Lone pair > Lone pair - Bonding pair > Bonding pair - Bonding pair

These repulsive forces alter the bond angles of the molecule or ion.

(v) The electronic repulsion between two pairs of electrons will be minimum if they are as far apart as possible. On this basis, the following geometrical arrangements are most suited.

No. of electron pairs	2	3	4	5	6
Geometrical figure	Linear	Triangular planar	Tetra-hedral	Trigonal bipyramidal	Octa-hedral
Examples	BeCl ₂ , CO ₂ , ZnCl ₂	BCl ₃ , SO ₃ , CO ₃ ²⁻	CH ₄ , H ₂ O, NH ₃	PF ₅ , ClF ₃ , SF ₄	SF ₆ , IF ₅ , SiF ₆ ²⁻

(vi) If the central atom is linked to similar atoms and is surrounded by bond pairs of electrons, the repulsions between them are similar. As a result the shape of the molecule is symmetrical and the molecule is said to have a regular geometry. On the other hand, the molecules in which the repulsive interactions between the electron pairs around the central atom are unequal have irregular or distorted geometry. In fact, the presence of lone pairs in addition to bond pairs in the molecule causes distortion in the geometry of the molecule. For example, in the NH₃

and H₂O molecules, the bond angles are not 109°28' but 106.5° and 104.5° respectively due to presence of one lone pair in NH₃ and two lone pairs in H₂O.

[In the VSEPR notation used to describe molecular geometries, the central atom is denoted as A, terminal atoms as X and lone pairs as E. AX₂E₂ describes a structure with two terminal atoms and two lone pairs around a central atom, for example water molecule. Similarly, AX₃E₂ describes a structure with three terminal atoms and two lone pairs around a central atom. For example ClF₃ molecule.]

(vii) A multiple bond is treated as if it is a single electron pair and two or three electron pairs of a multiple bond are treated as a single super pair.

(viii) Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

A Strategy for Applying VSEPR Method

To predict the shape of a molecule or polyatomic ion, the following four steps can be followed:

Step 1: Draw a Lewis structure of the molecule or polyatomic ion. The structure must be plausible but it does not need to be the best one.

Step 2: Determine the number of electron groups around the central atom (bonding and non-bonding both). A double and a triple bond each is counted as one electron group.

Step 3: Identify the electron group geometry. This may be linear, trigonal planar, tetrahedral, trigonal bipyramidal or octahedral corresponding to two, three, four, five and six electron groups respectively.

Step 4: Identify the molecular geometry. This is based on the positions around the central atom occupied by other atoms (not by lone pairs).

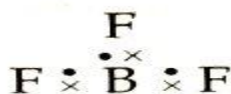
Illustration of the Theory by Considering a Few Examples

(A) Molecules containing bond pairs only

(i) **Shape of BeF₂ molecule:** Be-atom is surrounded by two bond pairs of electrons. These should be localised in such a way that there is minimum repulsion between them, i.e., bond angle should be 180°, hence BeF₂ molecule is Linear.

Molecules such as BeCl₂, ZnCl₂, HgCl₂ etc., have a linear shape.

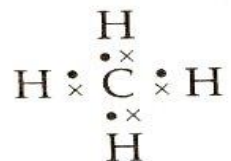
(ii) **Shape of BF₃ molecule :** Lewis structure of BF₃ is:



B-atom is surrounded by three bond pairs. According to VSEPR theory they must be situated at an angle of 120° as they will experience minimum repulsion, i.e., shape of BF₃ is triangular planar.

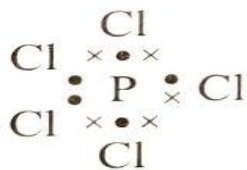
Molecules such as BCl₃, AlCl₃, etc., have a triangular planar shape.

(iii) **Shape of CH₄ molecule:** The Lewis structure of CH₄ is

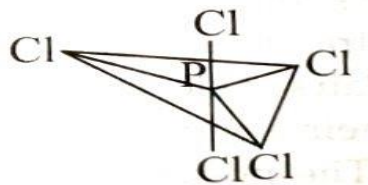


C-atom is surrounded by four bond pairs. These four bond pairs adopt tetrahedral structure as to remain as far apart as possible in order to have minimum repulsion. The bond angle is 109°28' (or approximately 109.5), Species such as SiF₄, CCl₄, SiH₄, NH₄⁺, etc., have tetrahedral structure.

(iv) **Shape of PCl₅ molecule:** The Lewis structure of PCl₅ is

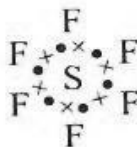
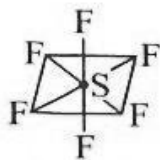


or



P-atom is surrounded by five bond pairs. To have minimum energy, the bond pairs of electrons should be as far apart as possible from each other. This is possible if the molecule acquires a trigonal bipyramidal shape. In this geometry all the bond angles are not equal. The axial bonds are of 90° and the bond angles in the triangle plane are of 120° . Two axial P-Cl bonds are longer as compared to three equatorial bonds. This is due to the fact that axial bond experiences greater repulsion from other bonds. Molecules such as PF_5 , SbCl_5 , etc., have same shape.

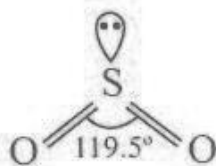
(v) **Shape of SF_6 molecule** : The Lewis structure of SF_6 is



S-atom is surrounded by six bond pairs. According to VSEPR theory these bond pairs adopt an octahedral geometry, In this geometry, all the bond angles are 90° each. The molecule is symmetrical and stable, i.e., less reactive. TeF_6 molecule is also expected to have the same shape.

(B) Molecules containing lone pairs and bond pairs

(1) **Molecules containing two bonding electron pairs and one lone pair (AX_2E):** The molecule contains three electron pairs. Thus, it should have a trigonal planar geometry. Due to the presence of one lone pair, the geometry gets distorted. For example, SO_2 has a V-shaped geometry. The bond angle is reduced to 119.5° .

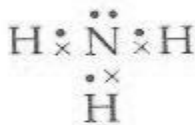


Shape of SO_2 molecule

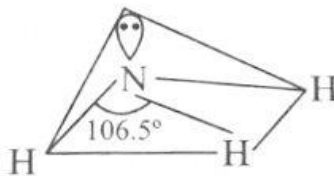
(2) **Molecule containing four electron pairs**

(a) Molecules containing three bonding electron pairs and one lone pair (AX_3E)

Shape of NH_3 molecule : The Lewis structure of NH_3 is



N-atom is surrounded by four electron pairs (three bonded and one lone pair). These four pairs adopt tetrahedral geometry. Due to presence of lone pair, NH_3 has a distorted tetrahedral geometry. The bond angle is not $109^\circ 28'$ but it is 106.5° . The actual shape of ammonia molecule is pyramidal.

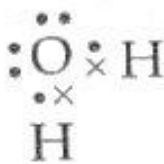


Shape of NH_3 molecule

Molecules such as PCl_3 , NF_3 , H_3O^+ , etc., have same shape.

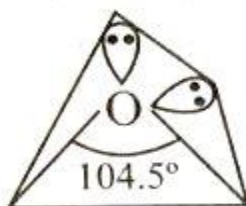
(b) Molecules containing two bonding electron pairs and two lone pairs (AX_2E_2)

Shape of water molecule: The Lewis structure of water is



O-atom is surrounded by four electron pairs (two bonded and two lone pairs). These four electron pairs adopt tetrahedral arrangement. The presence of two lone pairs brings distortion in the geometry of the molecule. The lone pairs repel the bond pairs more effectively resulting in the decrease of bond angle from $109^\circ 28'$ to 104.5° . The actual shape of the water molecule is V-shape.

Molecules/ions such as F_2O , NH_2^- , SCl_2 , PbCl_2 , etc., have shape similar to water molecule.

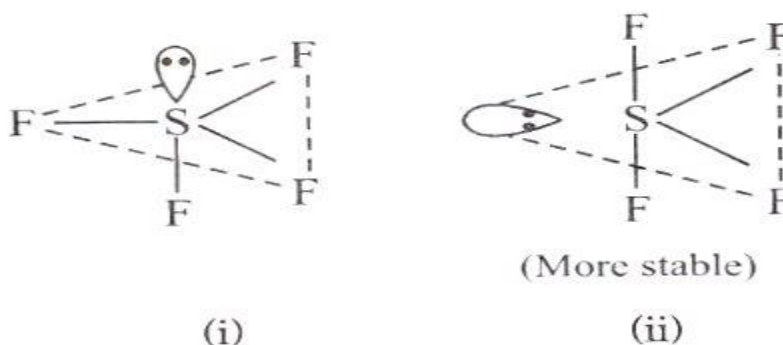


Shape of H_2O molecule

(3) Molecules containing five electron pairs

(a) Molecules containing four bonding electron pairs and one lone pair (AX_4E)

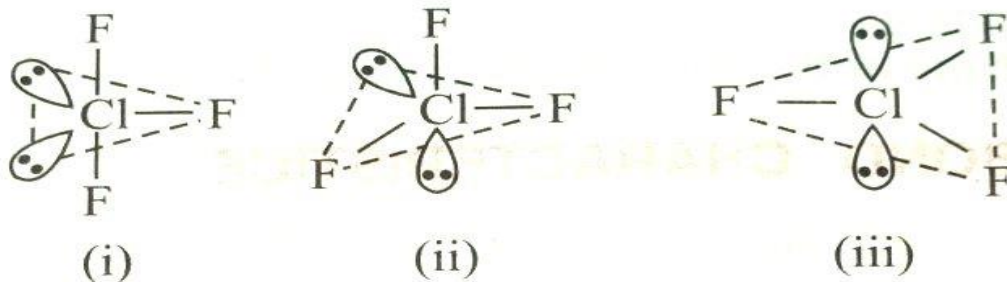
The example is SF_4 molecule. The molecule has five electron pairs and should have trigonal bipyramidal geometry in which one position is occupied by a lone pair. Therefore, SF_4 molecule can have either of the following two structures.



In structure (i) the lone pair is on axial position while in structure (ii) the lone pair is on equatorial position. The structure (ii) will therefore, experience lesser repulsions than structure (i). Thus the structure (ii) which is described as distorted tetrahedron or a folded square or see-saw will be a more stable correct structure of SF_4 . The bond angles are 89° and 117° instead of 90° and 120° respectively.

(b) Molecules containing three bonding electron pairs and two lone pairs (AX_3E_2)

The example is ClF_3 . The molecule has five electron pairs and it should have a trigonal bipyramidal geometry in which two positions are occupied by lone pairs. Therefore, the molecule, ClF_3 , can have either of the following three structures.

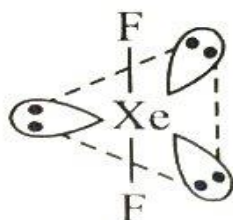


Structure (i) is most stable as it will experience lesser repulsions in comparison to structures (ii) and (iii). Thus, the molecule has a T-shaped structure and bond angle is 87.6° .

(c) Molecules containing two bonding electron pairs and three lone pairs (AX_2E_3)

The example is XeF_2 . It has five electron pairs and it should have a trigonal bipyramidal geometry in which three positions are occupied by lone pairs. If the three lone pairs are present on the corners of an equatorial triangle, the net repulsion will be zero.

Thus, the most correct and stable shape will be linear.

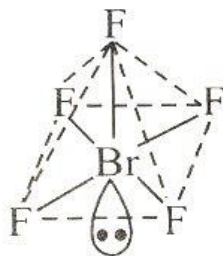


Linear shape

(4) Molecules containing six electron pairs

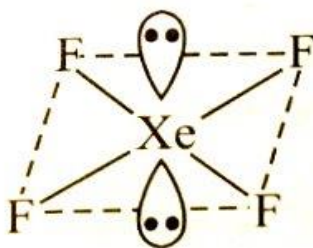
(a) Molecules containing five bonding electron pairs and one lone pair (AX_5E)

The example is BrF_5 . It has six electron pairs and it should have an octahedral geometry in which one position is occupied by a lone pair. Since all the six positions in octahedron are equivalent, the lone pair can be present on any one position. Thus, the molecule has a square pyramidal geometry.



(b) Molecules containing four bonding electron pairs and two lone pairs (AX_4E_2)

The example is XeF_4 . It has six electron pairs and should have octahedral geometry in which two positions are occupied by lone pairs.



The shape of the molecule square planar

Molecular Orbital Theory:-

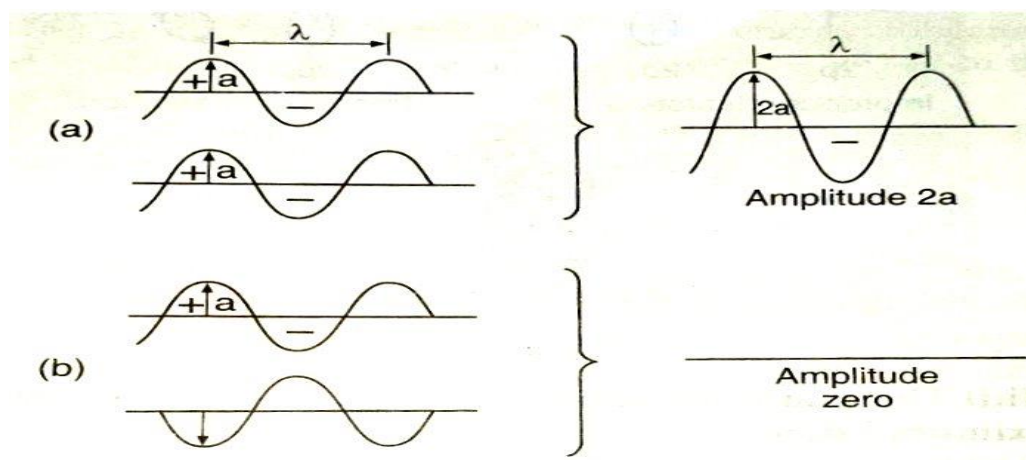
The valence bond theory is based on the assumption that the formation of a molecule involves an interaction between the electron waves of only those atomic orbitals of the participating atoms which are half filled. These atomic orbitals mix with one another to form a new orbital of greater stability while all other orbitals on the atoms remain undisturbed or maintain their individual identity. But this cannot be correct because the nucleus of one approaching atom is bound to affect the electron waves of nearly all the orbitals of the other atom. Besides this, the valence bond theory fails to explain the formation of coordinate bond, the paramagnetic character of O_2 molecule and the formation of odd electron molecules or ions such as H_2^+ ion where no pairing of electron occurs.

Molecular orbital theory of chemical bonding is more rational and more useful in comparison to valence bond theory. This theory was put forward by **Hund and Mullikan**. According to this theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called **molecular orbitals**. The electrons belonging originally to the participating atoms are now considered to be moving along the molecular orbitals under the influence of all the nuclei. Thus, **molecular orbitals are polycentric**. Molecular orbital is defined as **the region in space comprising the nuclei of the combining atoms around which there is maximum probability of finding the electron density**.

Molecular orbitals are of varying energies and are arranged in the order of increasing energy levels as in the case of atomic orbitals. The filling of electrons in the molecular orbitals follows, aufbau principle and Hund's rule.

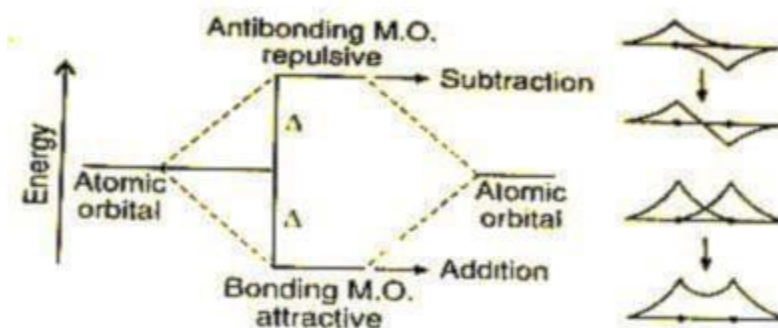
Linear Combination of Atomic Orbitals (LCAO)

Molecular orbitals of a molecule are obtained by the linear combination of atomic orbitals of the bonded atoms. The electron waves that describe the atomic orbitals have positive and negative phase or amplitude just as there are positive (upward) and negative (downward) amplitudes associated with standing wave. When waves are combined, they may interact either constructively or destructively. If the two identical waves are added, they combine constructively to produce the wave with double the amplitude and same wavelength. Conversely, if they are subtracted, they combine destructively to produce the wave with zero amplitude. This has been shown in Fig below



Likewise when two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interaction occurs in the region between two nuclei and a **bonding orbital** is

produced. When they overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and **antibonding orbital** is produced.



Formation of bonding and antibonding molecular orbitals

This can be shown mathematically also. Suppose Ψ_A and Ψ_B represent the amplitude (or also called wave functions) of the electron waves of the atomic orbitals of the two atoms A and B respectively. When these waves overlap, two cases may arise:

Case I. When the two waves are in phase, i.e., constructive interference occurs, the waves are added so that the amplitude of the new wave is

$$\phi = \Psi_A + \Psi_B$$

Case II. When the two waves are out of phase, i.e., destructive interference occurs, the waves are subtracted from each other so that the amplitude of the new wave is

$$\phi' = \Psi_A - \Psi_B$$

The probable electron density is given by the square of the amplitude, therefore, we have

$$\begin{aligned}\phi^2 &= (\Psi_A + \Psi_B)^2 \\ &= \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B\end{aligned}$$

and

$$\begin{aligned}\phi'^2 &= (\Psi_A - \Psi_B)^2 \\ &= \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B\end{aligned}$$

i.e.,

$$\phi^2 > \Psi_A^2 + \Psi_B^2$$

$$\text{whereas } \phi'^2 < \Psi_A^2 + \Psi_B^2$$

The above relation shows that the probability of finding the electrons in the bonding molecular orbital increases whereas it decreases in the antibonding molecular orbital. In other words, it can be said that electron density is high between the nuclei of two bonded atoms due to increased attraction in case of bonding molecular orbital whereas most of the electron density is located away from the space between the nuclei due to repulsion in case of antibonding molecular orbital. In fact, there is a nodal plane between the two nuclei of antibonding molecular orbital where electron density is zero.

Just as letters s , p , d , etc., are used to denote the atomic orbitals, similarly Greek symbols, σ , π , δ , etc., are used to denote the bonding molecular orbitals and asterisk symbols σ^* , π^* , δ^* , etc., are used to represent antibonding molecular orbitals.

Note : Crests of the electron waves are given '+' sign and troughs a '-' sign. Thus, bonding molecular orbital is formed by combination of '+' with '+' and '-' with '-' part of the electron waves whereas antibonding molecular orbital is formed by combination of '+' with '-' part of the electron waves.

The energy of the bonding molecular orbital is always lower than the energy of the atomic orbitals of the combining atoms whereas the energy of the antibonding molecular orbital is higher than the energy of the combining atomic orbitals as bonding molecular orbital is more stable and antibonding molecular orbital is less stable. However, it should be noted that compared with the energy of the combining atomic orbitals, the energy of the antibonding molecular orbital is raised by an amount greater than the amount by which the energy of the bonding orbital is lowered but the sum of the energies of bonding molecular orbital and antibonding molecular orbital is equal to the sum of energies of the combining atomic orbitals. The lowering in energy (Δ) of the bonding molecular orbital than the combining atomic orbital is called stabilization energy while increase in energy (Δ') of the antibonding molecular orbital is called destabilizing energy.

Distinction between Atomic and Molecular Orbitals

Atomic orbital	Molecular orbital
1. Atomic orbital is monocentric, <i>i.e.</i> , electron cloud extends around the nucleus of a single atom.	Molecular orbital is polycentric, <i>i.e.</i> , the electron cloud extends around all the nuclei of bonded atoms in the molecule.
2. It is less stable.	It is more stable.
3. It has simple shape.	It has complex shape.
4. Atomic orbitals are designated as s , p , d , etc.	Molecular orbitals are designated as σ , σ^* , π , π^* , etc.

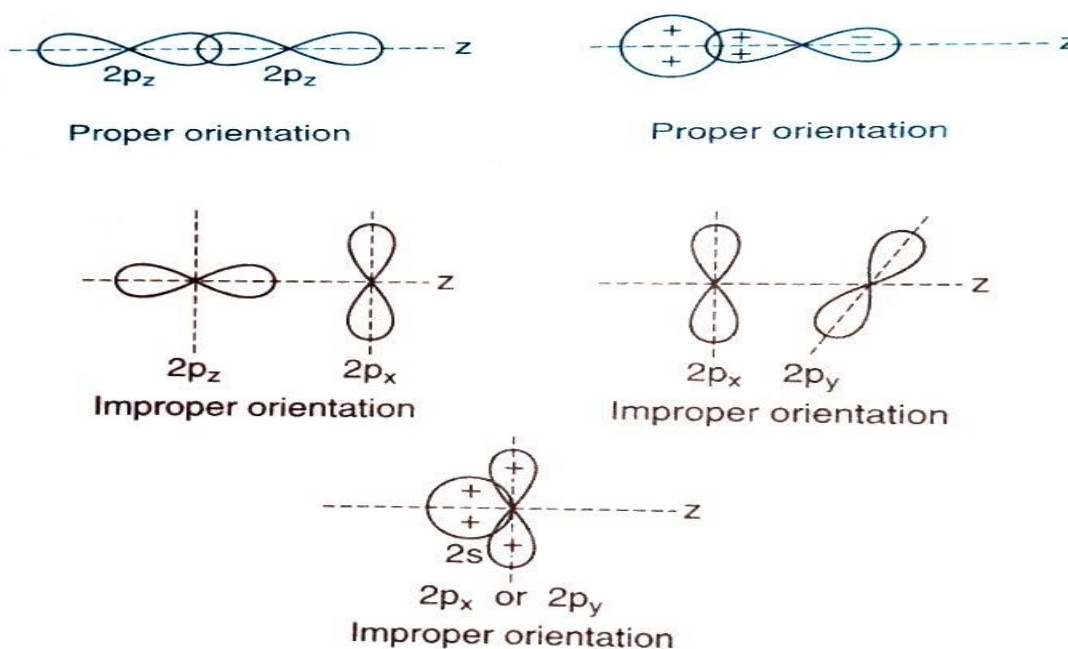
Comparison of Bonding and Antibonding Molecular Orbitals

Bonding molecular orbitals	Antibonding molecular orbitals
1. It is formed by linear combination of two atomic orbitals when their wave functions are added.	It is formed by linear combination of two atomic orbitals when their wave functions are subtracted.
2. Its energy is less than the combining atomic orbitals.	Its energy is more than the combining atomic orbitals.
3. It increases the electron density between the nuclei. It therefore stabilises the molecule.	It decreases the electron density between the nuclei. It therefore destabilises the molecule.
4. It has no nodal plane (plane where electron density is zero).	It has nodal plane.
5. It is symmetrical about inter-nuclear axis.	It is symmetrical about inter-nuclear axis and about a line perpendicular to it.
6. Designated by σ , π , δ , etc.	Designated by σ^* , π^* , δ^* , etc.

Conditions for Combination of Atomic Orbitals to form Molecular Orbitals

The formation of molecular orbitals by linear combination of atomic orbitals can take place only if the following conditions are fulfilled:

- (i) The combining atomic orbitals must have same or nearly same energy, i.e., comparable energy. For homonuclear diatomic molecule, A_2 , 1s atomic orbital of one atom can combine with 1s atomic orbital of another atom or 2s can combine with 2s, 2p with 2p and so on. 1s cannot combine with 2s or 2s cannot combine with 2p as the energy difference is appreciably high. However, such combination can take place for heteronuclear diatomic molecules, AB, if the energy difference is not very high.
- (ii) The combining atomic orbitals must have proper orientation, i.e., same symmetry about the molecular axis. For example, taking z-axis as the molecular axis, $2p_z$ orbital of one atom can overlap with $2p_z$ orbital of another atom but not with $2p_x$ or $2p_y$ orbitals because of their different symmetries. Similarly 2s orbital of one atom can overlap with $2p_z$ orbital but not with $2p_x$ or $2p_y$ orbital of another atom on account of improper orientation.



- (iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron density between the nuclei of a molecular orbital.

Salient Features of Molecular Orbital Theory:-

From the above discussion, the main features of the molecular orbital theory can be summed up as follows:

- (i) Like valence bond theory, this theory starts with atomic orbitals but the atomic orbitals of the atoms approaching for bonding overlap to undergo constructive interference as well as destructive interference to form molecular orbitals. As a result, the atomic orbitals lose their individual identity and all the electrons in the molecule are associated with molecular orbitals.
- (ii) When two atomic orbitals overlap, they form two new orbitals called molecular orbitals. One of which is called bonding molecular orbital and other is called antibonding molecular orbital. These are formed by addition and subtraction of wave function respectively.

- (iii) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule are filled.
- (iv) Bonding molecular orbital has energy lower than the combining atomic orbitals while antibonding orbital has higher energy than the combining atomic orbitals.
- (v) Only those atomic orbitals can overlap to form molecular orbitals which have comparable energies and proper orientation.
- (vi) Electrons present in the bonding molecular orbital contribute towards the stability of molecule while electrons present in antibonding molecular orbital contribute to the repulsions between the nuclei of the atoms.
- (vii) The bonding molecular orbitals are denoted as σ , π , δ , etc., while antibonding molecular orbitals are denoted as σ^* , π^* , δ^* , etc.
- (viii) A molecular orbital (bonding or antibonding) cannot accommodate more than two electrons. Both the electrons must have opposite spins (Pauli's exclusion principle).
- (ix) Molecular orbitals are filled in order of increasing energies starting with the orbital of minimum energy (aufbau principle).
- (x) In molecular orbitals of same energy (degenerate orbitals), the electron pairing occurs only when all of them are singly filled (Hund's rule).
- (xi) The shapes of the molecular orbitals formed depend upon the type of the combining orbitals.

Types of Molecular Orbitals Formed

When the two atomic orbitals overlap along the internuclear axis, the molecular orbitals formed are called σ and σ^* molecular orbitals and when overlap sideways, the molecular orbitals formed are called π and π^* molecular orbitals. As s -orbitals are spherical symmetrical, their wave function has same sign in all directions while in case of p -orbitals, one lobe is given '+' sign and other a '-' sign. Overlapping of '+' lobes or '-' lobes of two p -orbitals forms bonding molecular orbital and overlapping of one '+' lobe of one orbital and '-' lobe of other orbital forms antibonding molecular orbital. '+' lobe interaction with '+' lobe means addition of wave functions while '+' lobe interaction with '-' lobe means subtraction of wave functions. Few simple cases of combination of atomic orbitals are discussed:

- (i) **Molecular orbitals from s-atomic orbitals:** The formation of molecular orbitals by linear combination of $1s$ atomic orbitals of two atoms is shown in Figure below



The wave functions of two $1s$ atomic orbitals can combine in two ways:

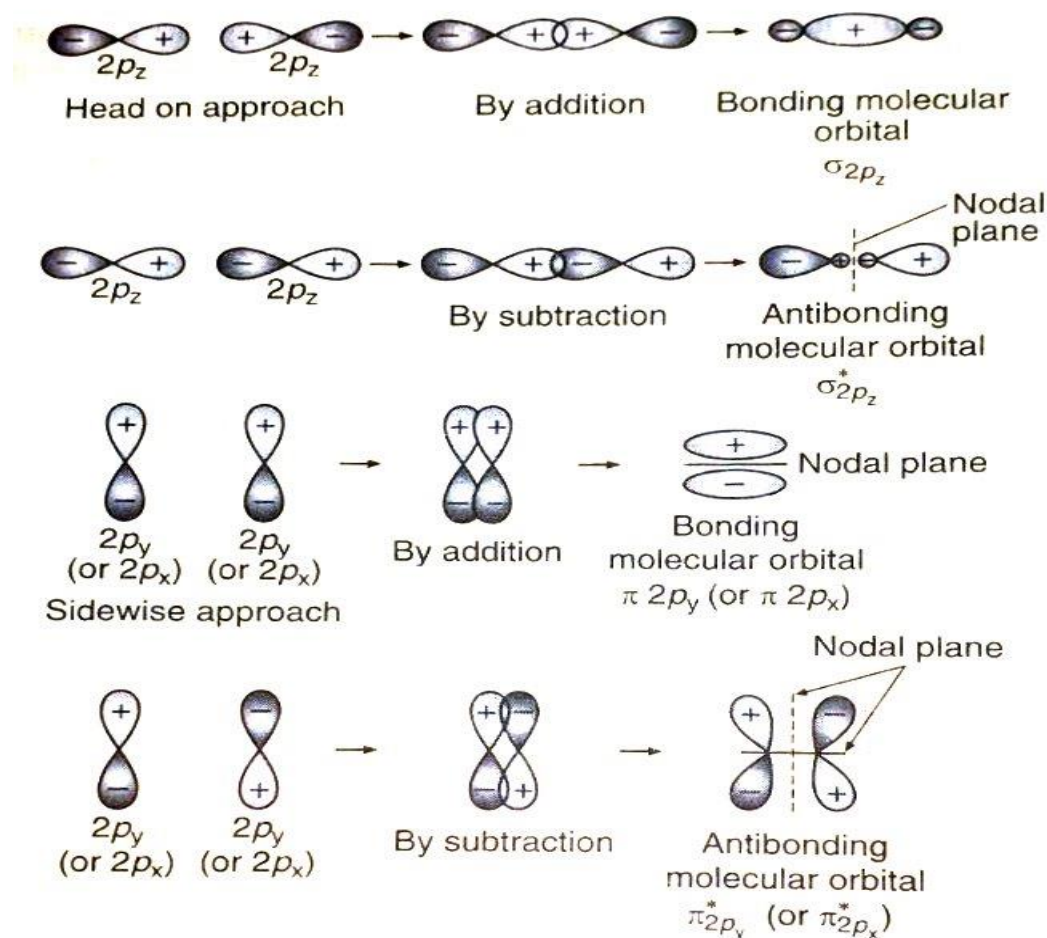
- (a) When both have same sign, i.e., addition of wave functions occur and σ $1s$ molecular orbital is formed. This overlap takes place along the internuclear axis.
- (b) When both have opposite sign, i.e., subtraction of wave functions occur and σ^* $1s$ molecular orbital (antibonding) is formed. This overlap takes place also along the internuclear axis. The dotted line between the two lobes indicates a nodal plane where the probability of finding the electron density is zero.

Each of the two molecular orbitals can accommodate two electrons each and four in all. Similarly, the combination of two $2s$ -orbitals forms two molecular orbitals σ_{2s} (bonding) σ^*_{2s} (antibonding).

(ii) Molecular orbitals from p-atomic orbitals : The two $2p$ -orbitals can combine together in either of the two ways, i.e., end-to-end or side-by-side.

(a) End-to-end overlap : Let z -axis be the line joining the two nuclei in the molecule. Thus, only $2p_z$ orbitals will combine in end-to-end fashion. When $2p_z$ orbitals on two atoms combine in phase (addition), bonding molecular orbital designated as σ_{2p_z} and when these overlap out of phase (subtraction), antibonding molecular orbital $\sigma^*_{2p_z}$ come into existence. The formation is shown in Fieger below.

(b) Side-by-side overlap: When two $2p_y$ orbitals or $2p_x$ orbitals on two atoms, which have mutually parallel axis, interact to give rise molecular orbitals that are not symmetrical about nuclear axis and are called π -molecular orbitals. These are designated as π_{2p_y} (bonding) and $\pi^*_{2p_y}$ (antibonding). Similarly, when two $2p_x$ orbitals on the two atoms interact they form two π -molecular orbitals which are designated as π_{2p_x} (bonding) and $\pi^*_{2p_x}$ (antibonding). The formation has been shown in Fieger below



Thus, in all there are six molecular orbitals arising from two sets of $2p$ atomic orbitals. Since, $2p_y$ and $2p_x$ atomic orbitals on an atom are degenerate (equal energy), the π molecular orbitals formed by these orbitals will also be degenerate, i.e., bonding orbitals,

$\pi 2p_y$ and $\pi 2p_x$ have same energy.

Similarly $\pi^* 2p_y$ and $\pi^* 2p_x$ have same energy.

It may be noted that whereas $\pi 2p_x$ has only one nodal plane, there are two nodal planes in $\pi^* 2p_x$ molecular orbital. Similar is the situation with $\pi 2p_y$ and $\pi^* 2p_y$ also.

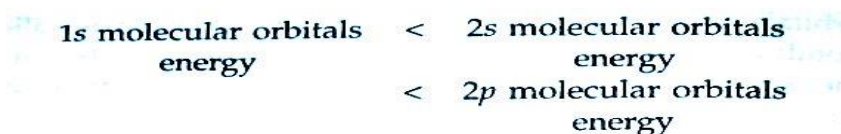
Difference between sigma and pi molecular orbitals

Sigma (σ) molecular orbital	pi (π) molecular orbital
1. It is formed by end-to-end overlap of atomic orbitals along the internuclear axis.	It is formed by sidewise overlap of atomic orbitals perpendicular to internuclear axis.
2. The overlapping is maximum.	The overlapping is comparatively less.
3. The orbital is symmetrical to rotation about internuclear axis.	The orbital is not symmetrical to rotation about internuclear axis.
4. It consists of one electron cloud.	It consists of two electron clouds one above and other below the plane passing through the nuclei.

Energy Level Diagrams for Molecular Orbitals The relative energies of molecular orbitals depend on the following factors:

(i) The energies of the atomic orbitals involved in the formation of molecular orbitals.

For example, pair of molecular orbitals formed by the combination of 2s atomic orbitals will have higher energy than those formed by combination of 1s orbitals. Similarly, molecular orbitals formed by combination of 2p atomic orbitals will have higher energy than those formed by combination of 2s atomic orbitals. Thus,



However, within same pair of molecular orbitals, the bonding molecular orbital has lower energy than the antibonding molecular orbital.

(ii) 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. Therefore, the energy of sigma molecular orbital is expected to be lower than pi molecular orbital.



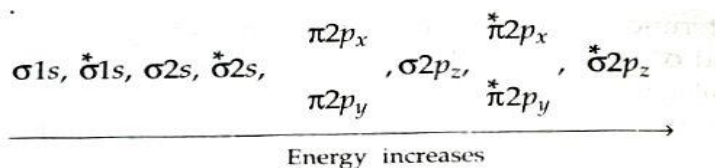
The energy levels of these molecular orbitals have been determined experimentally by spectroscopic methods.

$\pi 2p_x$ and $\pi 2p_y$ orbitals have equal energies as these are degenerate orbitals.

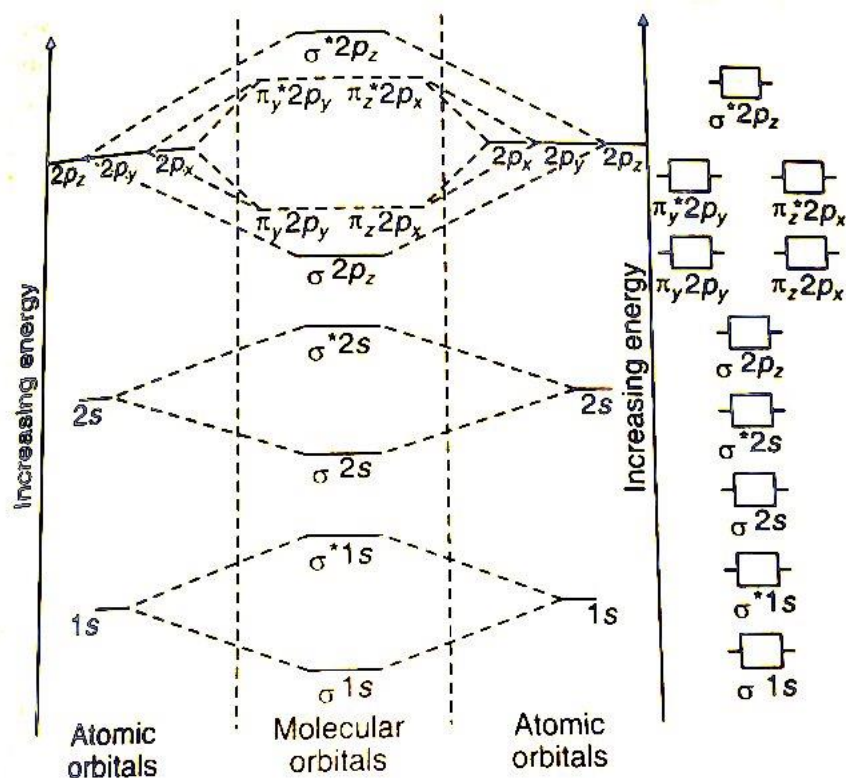
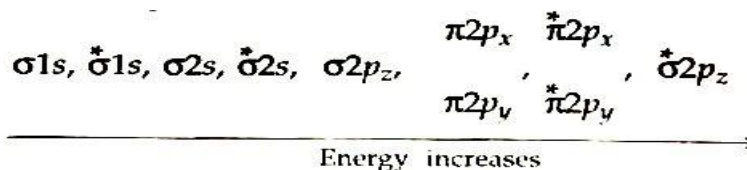
$\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals have equal energies as these are also degenerate orbitals.

$\sigma^* 2p_z$ has the maximum energy among the six 2p molecular orbitals.

The energy of $\sigma 2p_z$ not definite. For diatomic molecules Li_2 , Be_2 , B_2 , C_2 and N_2 , the energy of $\sigma 2p_z$ is higher than $\pi 2p_x$ or $\pi 2p_y$ while for diatomic molecules O_2 , F_2 , Ne_2 , the energy of $\sigma 2p_z$ is lower than $\pi 2p_x$ or $\pi 2p_y$. Thus, the energy diagram for first ten molecular orbitals for diatomic homonuclear molecules such as Li_2 , Be_2 , B_2 , C_2 , N_2 is :



For homonuclear diatomic molecules such as O_2 , F_2 , Ne_2 the energy diagram is:



Energy level diagram of molecular orbital for homonuclear diatomic molecules (O_2 , F_2 , Ne_2)

Rules for Filling up of Molecular Orbitals with Electrons

- (i) The molecular orbitals are filled in increasing order of their energy (aufbau principle).
- (ii) The maximum number of electrons which can be accommodated in a molecular orbital is two (Pauli's exclusion principle).
- (iii) If there are two molecular orbitals having the same energy, the electrons will first enter these singly and when both achieve one electron each, pairing will start (Hund's rule).

Electronic Configuration and Molecular Behavior

The distribution of electrons among various orbitals is called the electronic configuration. Electronic configuration of the molecule can give the following information about the behavior of the molecule.

(i) Stability of molecules: A molecule is formed only when the total energy of the system decreases. This is only possible when bonding electrons are more than antibonding electrons. Suppose the number of electrons present in the bonding orbitals is represented by N_b and the number of electrons present in the antibonding orbitals N_a , then

- (a) If N_b is greater than N_a ($N_b > N_a$), the molecule is stable. Stability is due to net force of attraction.
- (b) If N_b is less than N_a ($N_b < N_a$), the molecule is unstable. Antibonding influence is stronger resulting in a net force of repulsion. This brings instability.
- (c) If N_b is equal to N_a ($N_b = N_a$), the molecule is unstable. This is because of the fact that the influence of antibonding electrons is slightly more than that of bonding electrons resulting in a net force of repulsion.

(ii) Stability in terms of bond order:

Bond order is defined as one half of the difference between the number of electrons present in the bonding and the antibonding orbitals, i.e.,

$$\text{Bond Order (B.O.)} = \frac{1}{2}(N_b - N_a)$$
$$= \frac{\text{Number of electrons in bonding orbitals} - \text{Number of electrons in antibonding orbitals}}{2}$$

The bond order provides the following information.

- (a) If the value of bond order is positive, it indicates, a stable molecule or a stable ion. In case, the value of bond order is negative or zero, it indicates that the molecule or ion is unstable or the species does not exist.
- (b) The stability of the bond, i.e., molecule or ion is measured in terms of bond dissociation energy. The bond dissociation energy is directly proportional to the bond order. Higher is the bond order, greater is the bond dissociation energy, i.e., more is the stability. Thus, a molecule with bond order 3 is more stable than a molecule with a bond order 2 which in turn is more stable than a molecule with a bond order of 1 or 1/2
- (c) Bond order 1, 2 and 3 means single, double and triple bonds respectively. [The difference between chemical bond and bond order is that chemical bond is always integral but bond order can be fractional also.]

Bond order	Stability
Less than zero	The species is highly unstable or does not exist
Zero	The species is highly unstable or does not exist
+ 1/2	The species exists but unstable
+1	A stable single bond
+2	A stable double bond
+3	A stable triple bond

(d) Bond length is inversely proportional to the bond order. Greater is the bond order, shorter is the bond length.

Molecule	Bond order	Bond dissociation energy (kJ mol⁻¹)	Bond length (pm)²
F ₂ (F – F)	1	158	142
O ₂ (O = O)	2	497	121
N ₂ (N ≡ N)	3	945	110

(iii) Magnetic nature: If all the electrons in the molecule or ion are paired, it is diamagnetic in nature. In case, if the molecule has any unpaired electron or electrons, it is paramagnetic in nature. Paramagnetic behavior depends upon the number of unpaired electrons, i.e., greater the number of unpaired electrons present in the molecule or ion, greater is the paramagnetic nature. It is expressed in terms of magnetic moment which is equal to $\sqrt{n(n+2)}$ B.M. Where n is the number of unpaired electrons.