CHEMICAL BONDING - II

PART - I

- **By:**

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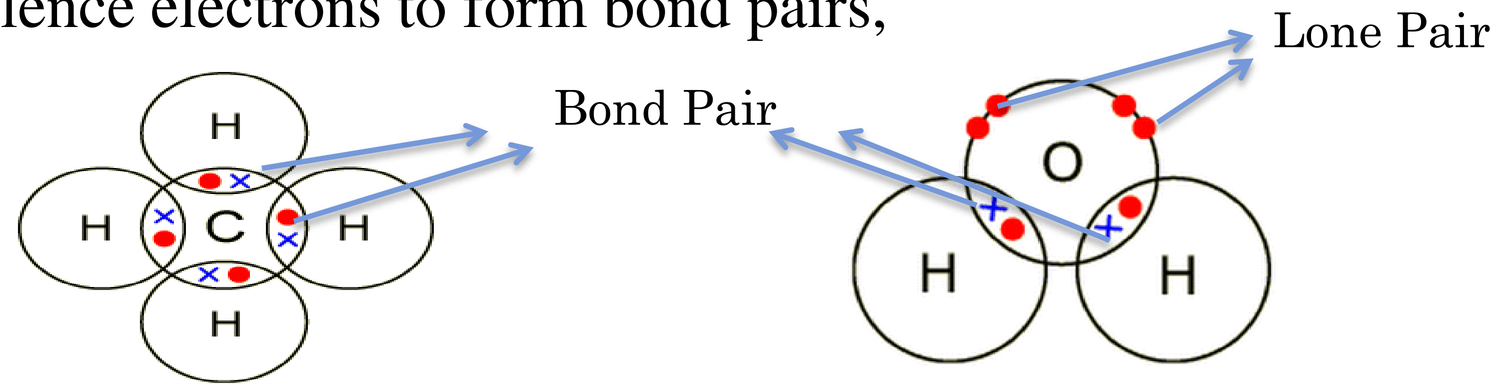
VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- The directional nature of the covalent bond leads to definite shape and geometries of molecules.
- The shape of molecules have been explained by hybridisation.
- The valence shell electron pair repulsion theory is another simple way of predicting the geometries/shape of molecules.
- This theory was given by **Sidgwick and Powell** in 1940.
- It is based on the repulsive interactions between electron pairs in the valence shell of the atoms.
- The theory was later refined by **Gillespie** and **Nyholm** in 1957.

POSTULATES OF VSEPR THEORY

- The shape / geometry of the molecule depends on the total number of bonded as well as lone pair of electrons present in the valence shell of the central atom.

- For e.g. in the formation of methane, Carbon uses all its valence electrons to form bond pairs,



- But in the formation of water, Oxygen uses only two of the six valence electrons it has to form bonds. The remaining four electrons do not take part in bonding and exist as two lone pairs.

- The electron pairs repel one another. So, they try to stay as far apart as possible to acquire a state of minimum energy or maximum stability.

- Repulsion between the lone pair - lone pair is different from lone pair – bond pair and bond pair – bond pair. The repulsive interaction decreases in the order

Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair

- The magnitude of repulsion between the bonded pairs depend on the electronegativity difference between the central atom and the other atoms.

- Repulsive forces decrease with increase in bond angle between the electron pairs.

REGULAR AND IRREGULAR GEOMETRIES

***Regular Geometry*:** Molecules in which the central atom is surrounded by similarly bonded pair of electrons are said to have regular geometry. The central atom only form bonded pairs.

For example: $BeCl_2$, BF_3 , CCl_4 , PF_5 ,etc.

***Irregular Geometry*:** Molecules in which the central atom is not surrounded by similarly bonded pair of electrons or surrounded by bond pair and lone pair of electrons are said to have irregular geometry.

For example:

$CHCl_3$, CH_2Cl_2 , CH_3Cl (Non similar bonded pair of electrons)

NH_3 , H_2O, $SnCl_2$ (Lone pair and bond pair of electrons)

APPLICATIONS OF VSEPR THEORY

- This theory gives the most reliable method for predicting the shapes of covalent molecules and polyatomic ions.

- It is simple to use.

- This theory does not make any distinction between **s and p electrons.**

- It only takes into account the **number of electron pairs** (both bonded and non bonded) present in the valence shell of the central atom.

- The electron pairs try to stay **as far as possible from each other** to attain maximum stability.

AMMONIA MOLECULE (NH_3)

- In ammonia molecule, the central atom is Nitrogen ($Z = 7$).
- The electronic configuration of Nitrogen is [He] $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$ and it has five valence electrons .
- Three of the valence electrons which are half filled, share electrons with three hydrogen atoms resulting in three bond pairs around the nitrogen atom.
- The remaining two electrons do not participate in bond formation and are present as lone pair of electrons.
- So, in ammonia, central atom Nitrogen is surrounded by **four electron pairs**, three bond pairs and one lone pair.

- The four bond /electron pairs adopt tetrahedral geometry and should have bond angle 109.5° .

- But the bond angle is not equal to 109.5° because nitrogen is surrounded by bond pairs and lone pair of electrons.

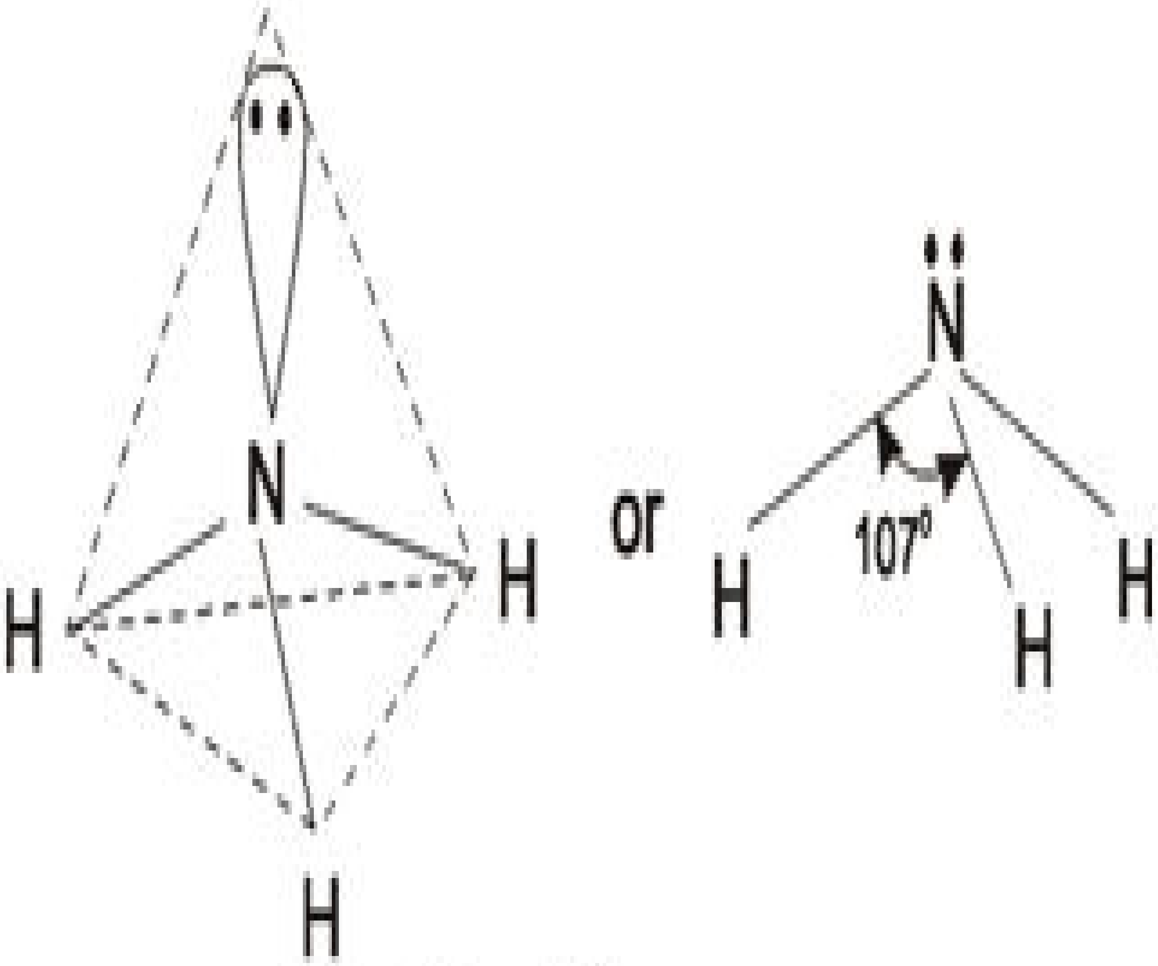
- The repulsion in case of **lone pair – bond pair will be more than bond pair – bond pair.**

- The lone pair of electrons present on the nitrogen atom will repel the bond pairs of electron strongly.

- This results in the **decrease** in bond angle from 109.5° to 107°

- The geometry of the NH_3 molecule is also regarded as **pyramidal.**

Geometry (Irregular)



Shape (Pyramidal)

WATER MOLECULE (H_2O)

- In water molecule, the central atom is Oxygen (Z = 8).
- The electronic configuration of Oxygen is [He] $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$ and it has six valence electrons .
- Two of the valence electrons which are half filled, share electrons with two hydrogen atoms resulting in two bond pairs around the oxygen atom.
- The remaining four electrons do not participate in bond formation and are present as lone pair of electrons.
- So, in water, central atom Oxygen is surrounded by **four electron pairs**, two bond pairs and two lone pair.

- The four bond /electron pairs adopt tetrahedral geometry and should have bond angle 109.5° .

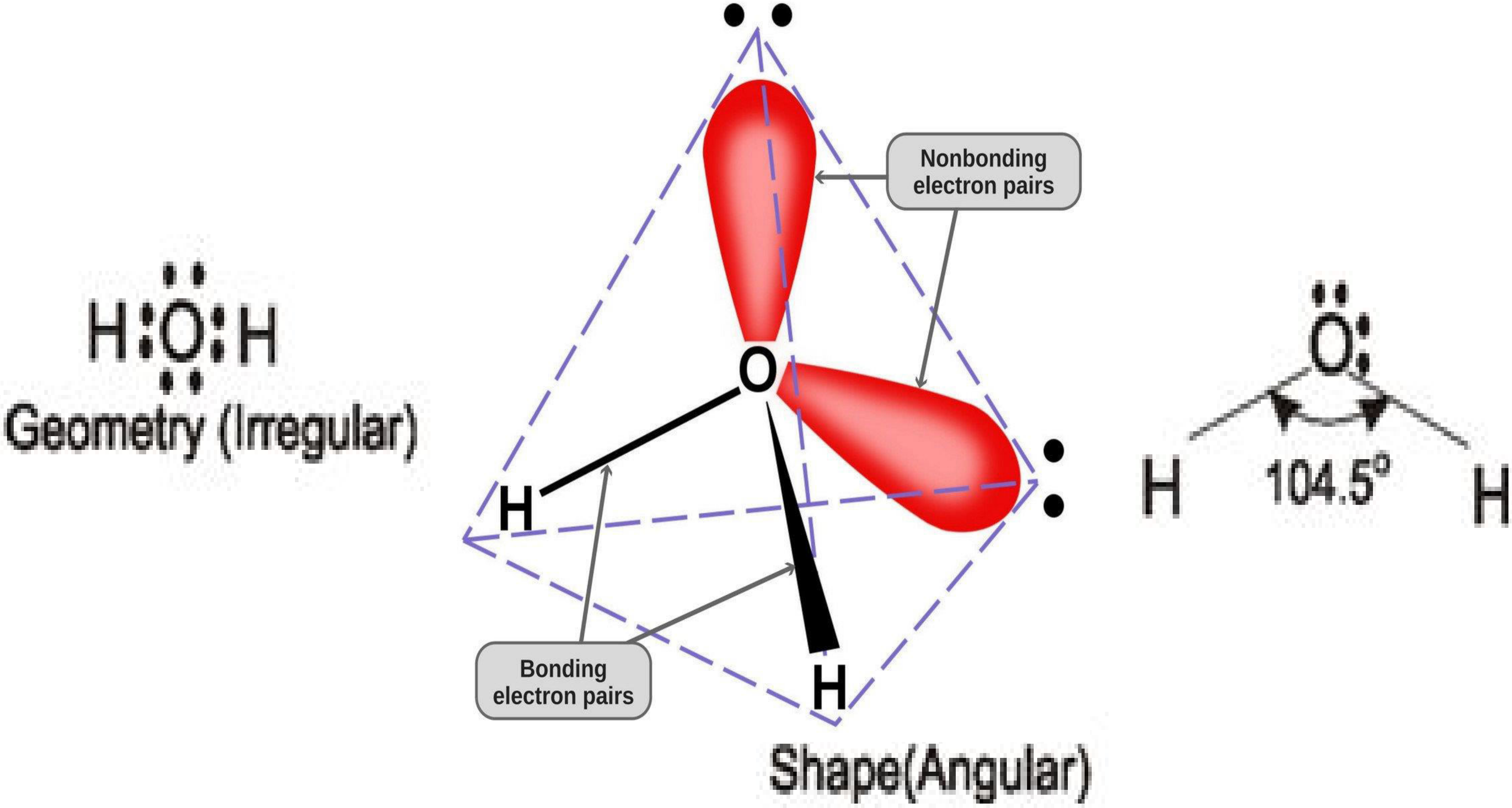
- But the bond angle is not equal to 109.5° because oxygen is surrounded by bond pairs and lone pair of electrons.

- The repulsion in case of **lone pair- lone pair** will be more than **lone pair – bond pair** which in turn will be more than **bond pair – bond pair**.

- The lone pair of electrons present on the oxygen atom will repel each other as well as the bond pairs of electron strongly.

- This results in the decrease in bond angle from 109.5° to 104.5°

The geometry of the H_2O molecule is also regarded as **bent or angular.**



HYDRONIUM ION **(H_3O^+)**

- In water molecule, the central atom is Oxygen (Z = 8).
- The electronic configuration of Oxygen is [He] $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$ and it has six valence electrons .
- Two of the valence electrons which are half filled, share electrons with two hydrogen atoms resulting in two bond pairs around the oxygen atom.
- One completely filled pair of valence electrons of Oxygen share its electrons with H^+ ion.
- This leaves two electrons which do not participate in bond formation and are present as lone pair of electrons.

- So, in Hydronium ion, central atom Oxygen is surrounded by **four electron pairs**, three bond pairs and one lone pair.

- The four bond /electron pairs adopt tetrahedral geometry and should have bond angle 109.5^{o}.

- But the bond angle is not equal to 109.5^{o} because oxygen is surrounded by bond pairs and lone pair of electrons.

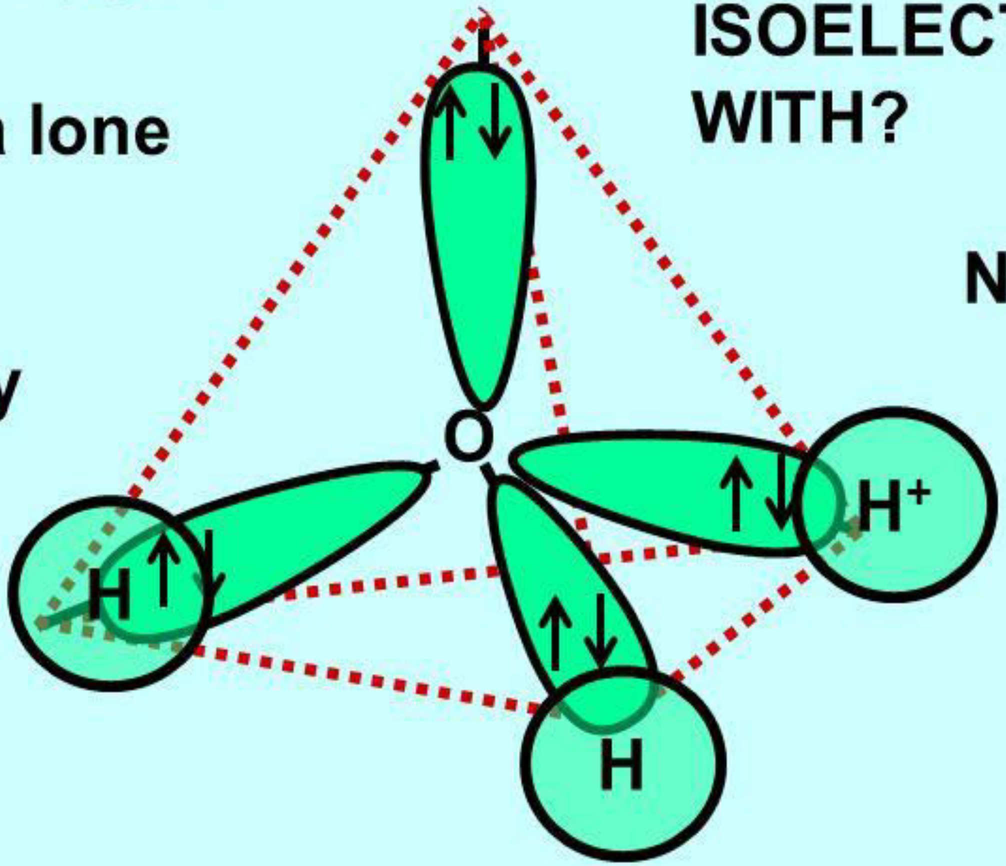
- The lone pair of electrons present on the oxygen atom will repel the bond pairs of electron strongly and the geometry gets distorted.

- This results in the decrease in bond angle from 109.5^{o} to 107^{o}

HYDRONIUM ION.

Overlap of Oxygen sp^3 hybrids containing a lone pair

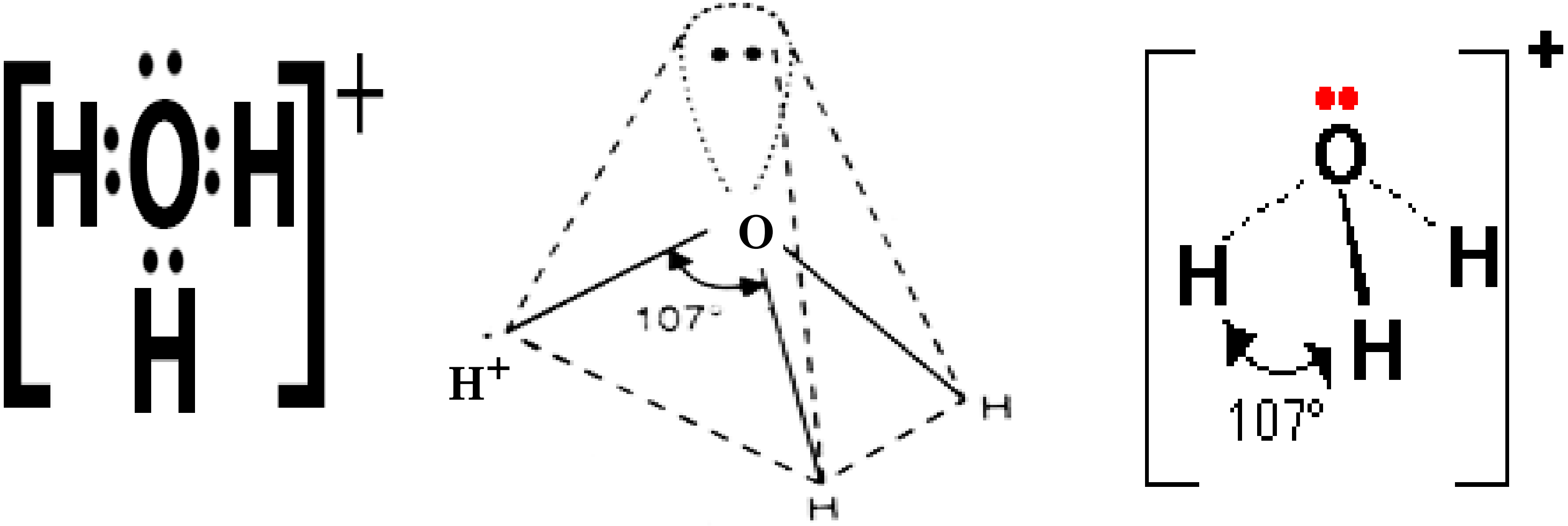
H^+ ion empty 1s orbitals.



ISOELECTRONIC WITH?

NH_3

The geometry of the H_3O^+ molecule is also regarded as **pyramidal or distorted tetrahedral** as in the case of ammonia**.**



Distorted Tetrahedral / Pyramidal geometry

Sulphur tetrafluoride molecule (SF_4)

- In Sulphur tetrafluoride molecule, the central atom is Sulphur (Z = 16).

- The ground state electronic configuration of Sulphur is [Ne] $3s^2$, $3p_x^2$, $3p_y^1$, $3p_z^1$, $3d^0$ and it has six valence electrons .

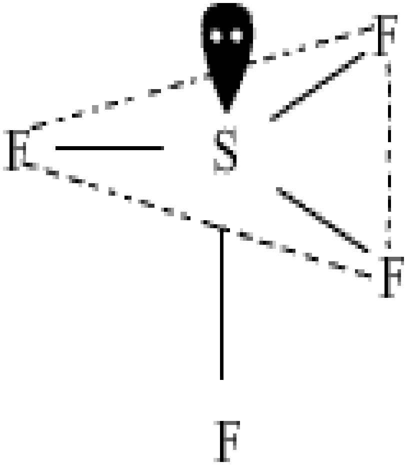
- Four of the valence electrons of Sulphur share electrons with four fluorine atoms resulting in four bond pairs around the Sulphur atom.

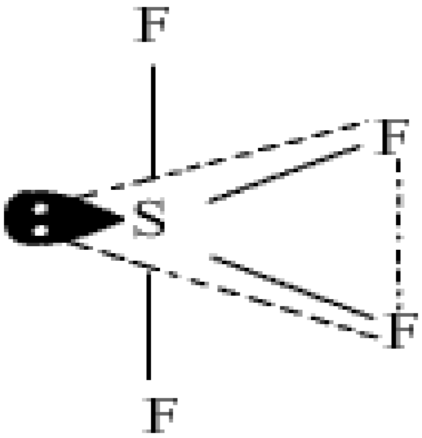
- This leaves two electrons which do not participate in bond formation and are present as lone pair of electrons.

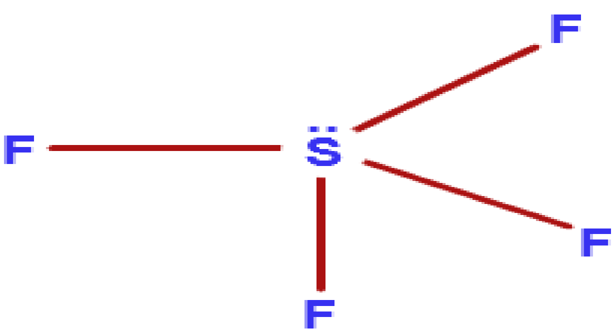
- So, in Sulphur tetrafluoride, central atom Sulphur is surrounded by **Five electron pairs**, four bond pairs and one lone pair.

- The Five bond /electron pairs geometry is **predicted to be trigonal bipyramidal**.

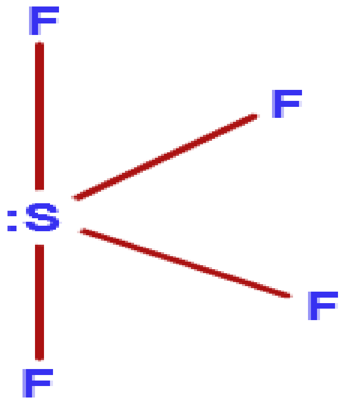
- The lone pair can occupy either the axial position or the equatorial position.



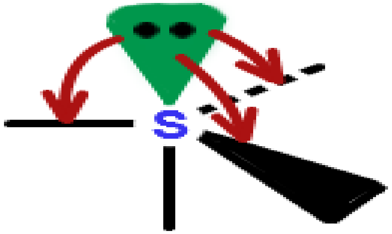


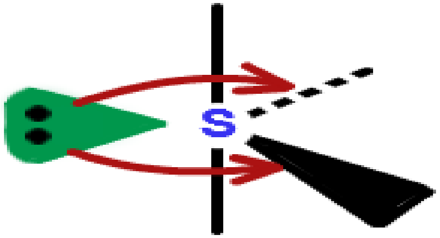


Lone pair in axial Position



Lone pair in equatorial position





(Preffered arrangement)

lp – bp = 3 (at 90°)
lp – bp = 1 (at 180°)

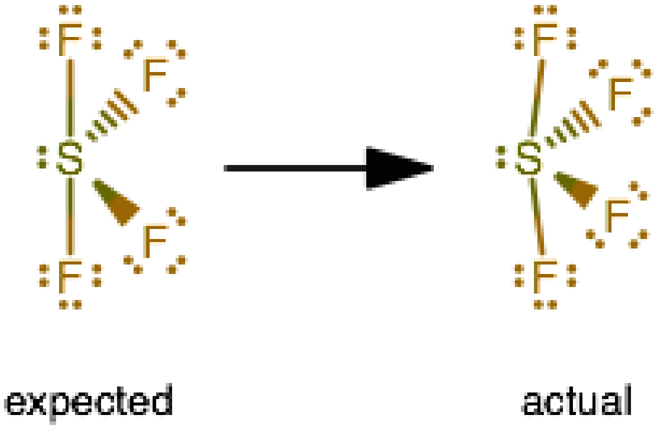
lp – bp = 2 (at 90°)
lp – bp = 2 (at 120°)

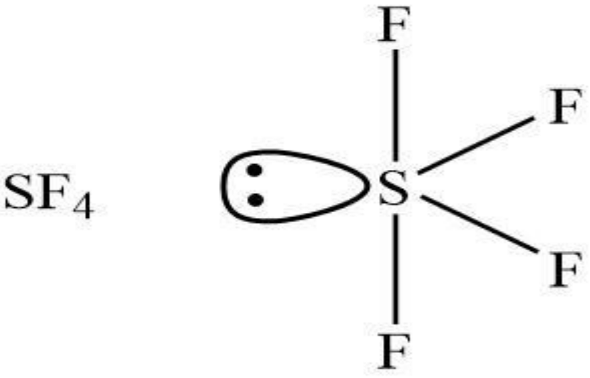
Repulsions decrease with increasing bond angles, so only repulsions at 90° are taken into consideration.

- It has been found out that when the lone pair of electron is present at equatorial position the repulsions **are quite less** as compared to when the lone pair of electron is present at axial position.

- So, the lone pair of electron is present at equatorial position

- The geometry of the molecule is **distorted trigonal bipyramidal** and is also called **see saw** geometry





See-saw shape

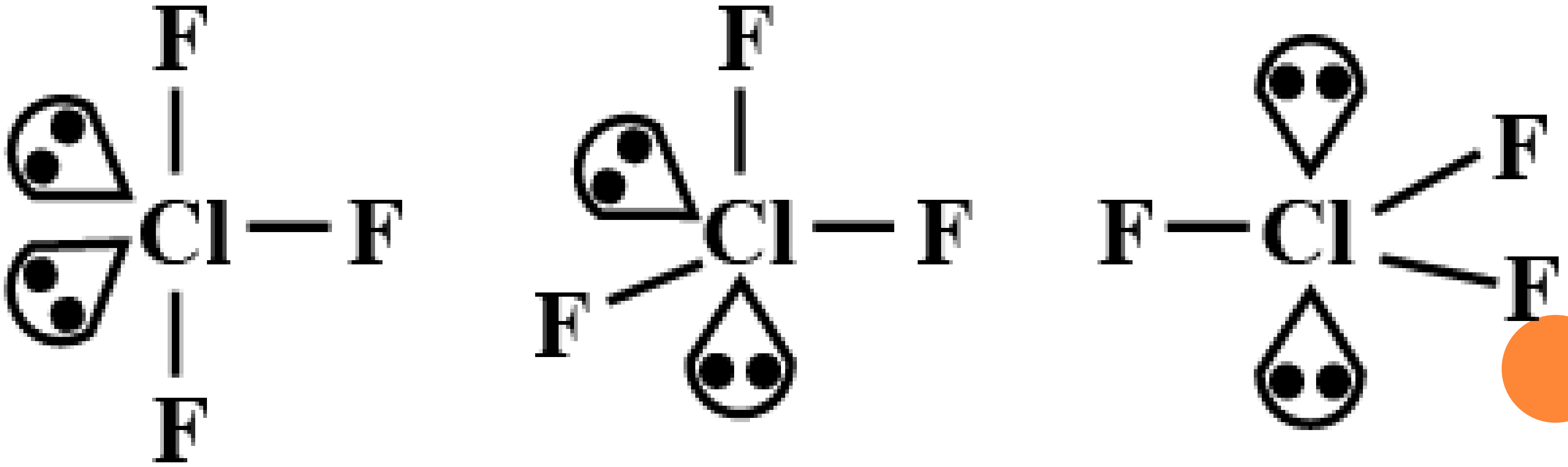
Chlorine trifluoride molecule (ClF_3)

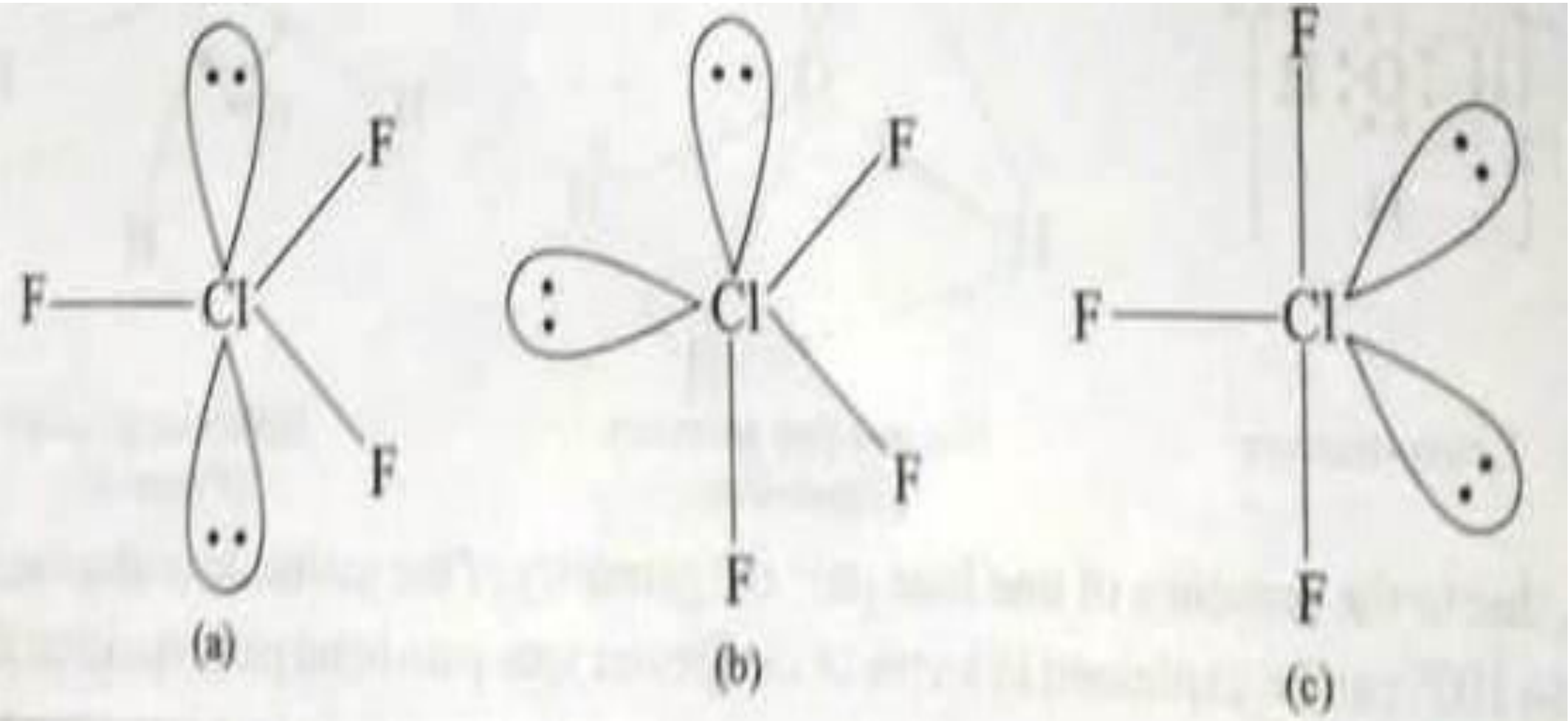
- In Chlorine trifluoride molecule, the central atom is Chlorine (Z = 17).
- The ground state electronic configuration of Chlorine is [Ne] $3s^2$ $3p^5$ and it has seven valence electrons .
- Three of the valence electrons of Chlorine share electrons with three fluorine atoms resulting in three bond pairs around the Chlorine atom.
- This leaves four electrons which do not participate in bond formation and are present as lone pair of electrons.

- So, in Chlorine trifluoride, central atom Chlorine is surrounded by **five electron pairs**, three bond pairs and two lone pair.

- The five bond /electron pair geometry is **predicted to be trigonal bipyramidal**.

- The two lone pairs can occupy either the axial position or the equatorial position or both.





(a) (b) (c)

lp - lp = 0
lp - bp = 6
bp - bp = 0

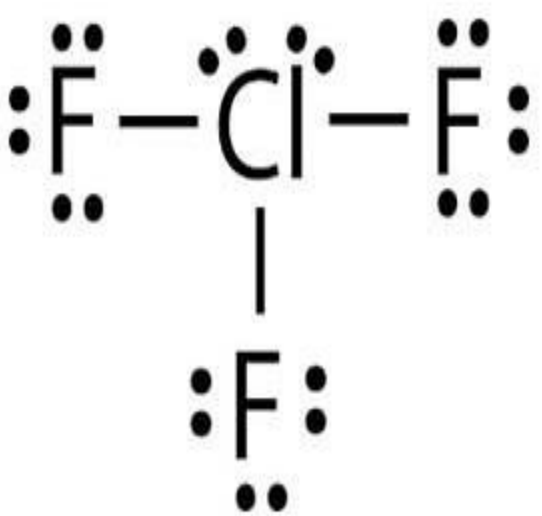
lp – lp = 1
lp - bp = 3
bp - bp = 2

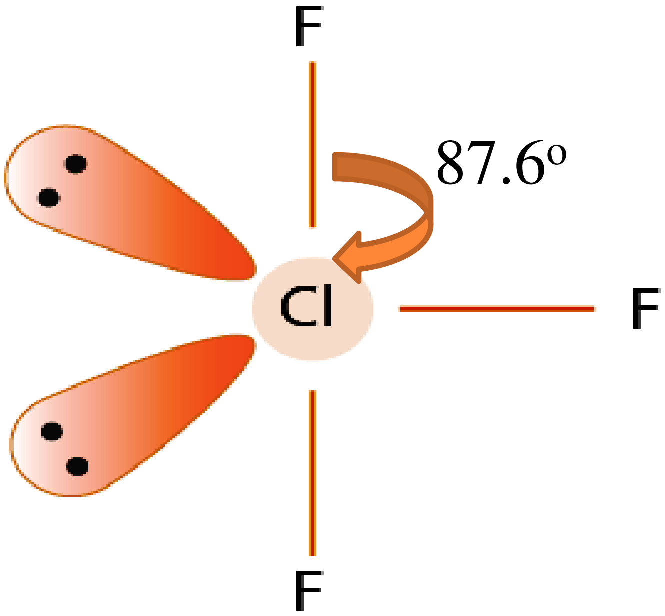
lp – lp = 0
lp - bp = 4
bp - bp = 2

- The lone pairs in trigonal bipyramidal geometry experience more repulsions when they are present at axial positions.

- So, both the lone pairs are present at equatorial positions.

- The molecule has T – shaped geometry with bond angles 87.6^{o} instead of 90^{o} .





Iodine dichloride ion (ICl_2^-)

- In Iodine dichloride molecule, the central atom is Iodine (Z = 53).

- The ground state electronic configuration of Iodine is [Kr] $4d^{10}\ 5s^2\ 5p^5$ and it has seven valence electrons .

- One of the valence electrons of Iodine share electron with one chlorine atom resulting in one bond pair around the Iodine atom.

- This leaves six electrons of iodine which do not participate in bond formation and are present as lone pair of electrons.

- ICl now has eight electrons around Iodine atom.

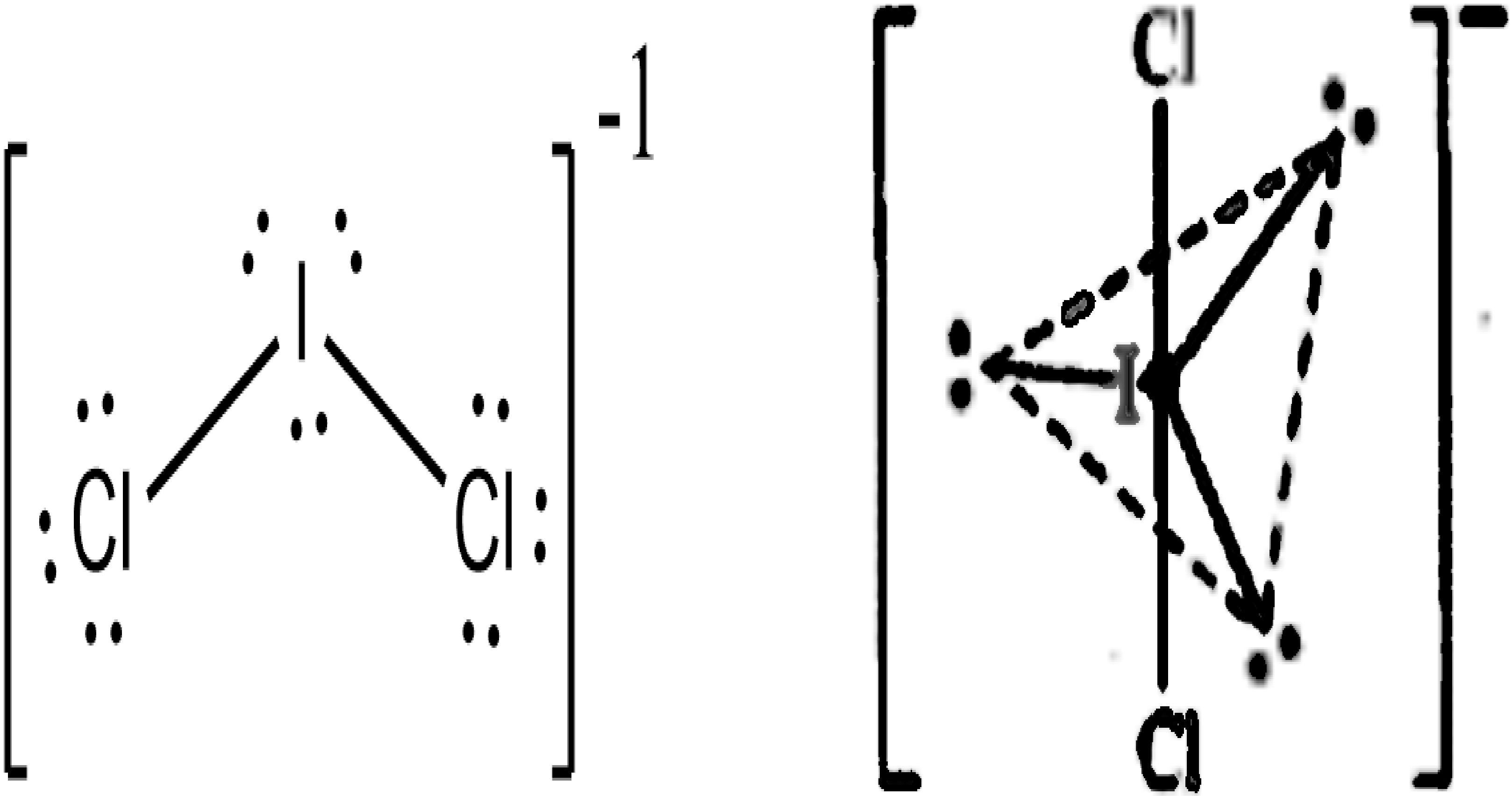
- Iodine can accept a lone pair of electron from one chloride ion (Cl^-) , forming a co-ordinate bond [I← Cl].

- The outer shell of Iodine now has **10** electrons or **5** electron pairs (Three lone pairs and two bond pairs).

- So, the ion acquires **trigonal bipyramidal geometry**.

- To minimize the repulsions, the lone pairs occupy **equatorial positions** and the chloride atom / ion occupy axial positions.

- The molecule has **linear geometry** with bond angle of 180^o .



Linear Geometry of ICl_2^-

MOLECULAR ORBITAL THEORY

- Developed by Hund and Mulliken in 1932.
- Alternative way to explain bonding in molecules.
- Basic idea of MO theory is that atomic orbitals of isolated/ individual atoms combine to form a set of molecular orbitals.
- These molecular orbitals are delocalised over the molecule
- The electrons in these molecular orbitals are under the influence of two or more nuclei depending on the number of atoms in the molecule.

ASSUMPTIONS OF MOLECULAR ORBITAL THEORY

- A molecule is said to be different from the combining atoms from which it is formed.
- All the electrons belonging to the atoms forming the molecule are under the influence of all the nuclei .
- Like an atom, the molecule has orbitals of definite energies called molecular orbitals.
- Molecular orbitals are formed by the merging of atomic orbitals of the atoms forming the molecule.
- The shape of the molecular orbitals depend on the shape of the combing atomic orbitals.

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

- Molecular orbitals are formed by linear combination of atomic orbitals of atoms forming the molecule.

- Linear combination means simple addition and subtraction of the wave function of the atomic orbitals.

- For example, a simple diatomic molecule like AB , consisting of two atoms A and B each having a single valence electron.

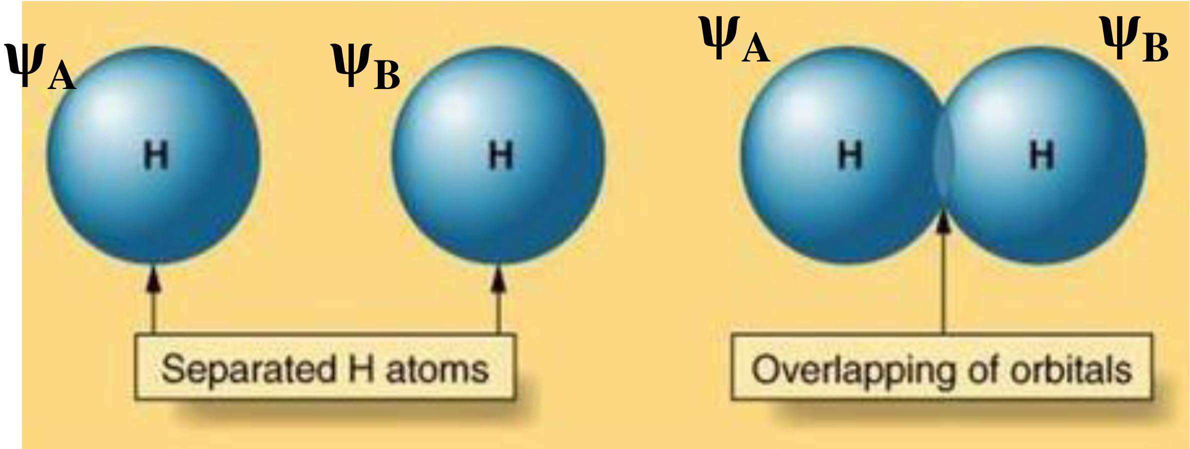
- Let the wave function of the electron of atom A be $\boldsymbol{\psi_A}$ and the wave function of the electron of atom B be $\boldsymbol{\psi_B}$.

- When the atoms come close, their atomic orbitals combine to form molecular orbitals and the valence electrons will be in the region where atomic orbitals overlap.

- The wave function for the electron under the influence of both the nuclei A and B can be written as linear combination of wave function ψ_A **and** ψ_B

$$\psi = C_A \psi_A + C_B \psi_B$$

where C_A and C_B are mixing coefficients and give the relative contribution of each atomic orbital. The values of these coefficients are adjusted in a manner to give molecular orbital of lowest energy.



- In case of bonding between two similar atoms (homonuclear), the magnitude of their coefficients $\mathbf{C_A}$ and $\mathbf{C_B}$ must be the same.

$$\mathbf{C^2_A = C^2_B \qquad or \qquad C_A = \pm C_B}$$

- If $\mathbf{C_A}$ = 1 , then $\mathbf{C_B}$ = ±1, so there will be two molecular orbitals. They are

$$\boldsymbol{\psi = \psi_A + \psi_B \;\; (C_A = 1, C_B = +1)}$$

$$\boldsymbol{\psi^* = \psi_A - \psi_B \;\; (C_A = 1, C_B = -1)}$$

- The molecular orbital associated with $\boldsymbol{\psi}$ is called **bonding molecular orbital** and the molecular orbital associated with $\boldsymbol{\psi^*}$ is called **anti - bonding molecular orbital .**

POINT TO REMEMBER :

The number of molecular orbitals formed will always be equal to the number of atomic orbitals involved in bonding.

PHYSICAL STRUCTURE OF BONDING & ANTI – BONDING MO

The physical structure/ picture of bonding & anti – bonding molecular orbitals can be obtained by considering the atomic orbitals.

For this lets take the case where an **s atomic orbital overlaps with another s atomic orbital .**

Combination of the **two s atomic orbitals** leads to the formation of **two molecular orbitals.**

The atomic orbitals can combine in two ways to form molecular orbitals,

First way :

- By **addition of overlapping** of the two s orbitals.
- The region between the two nuclei where overlapping of the two s orbitals occur has **high electron density**.
- The molecular orbital formed due to addition of the orbitals is called **bonding molecular orbitals**.

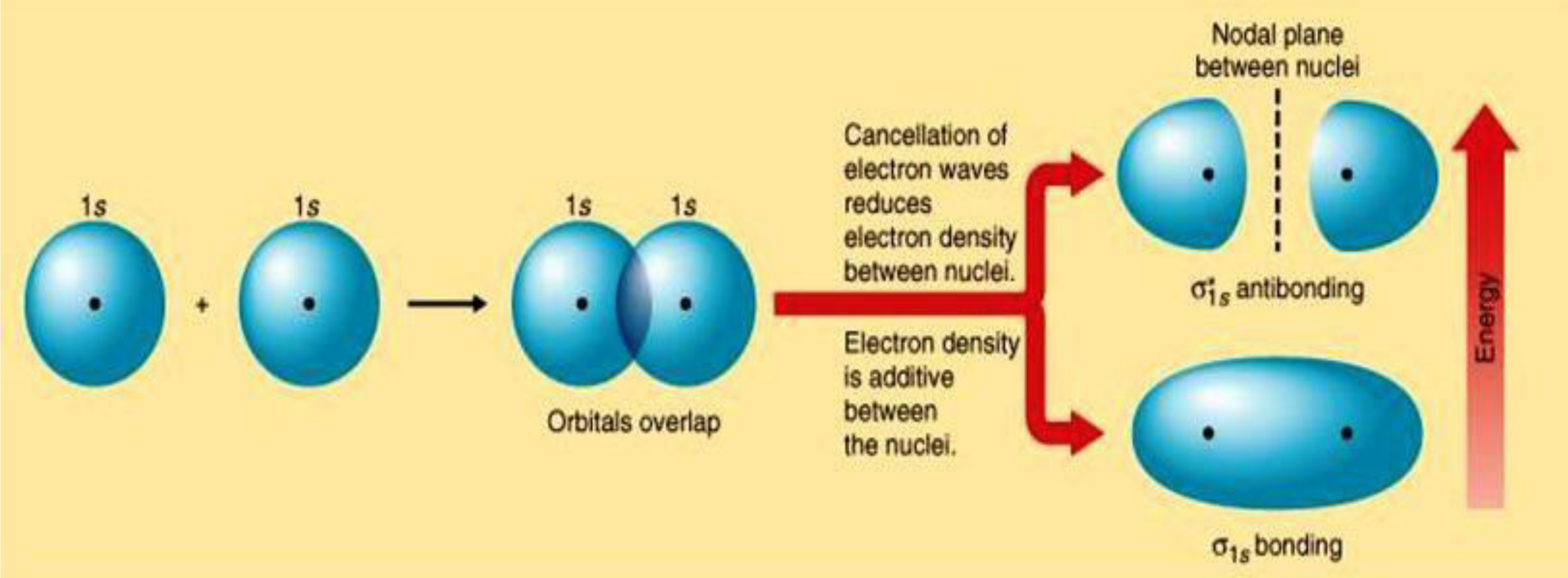
Second way :

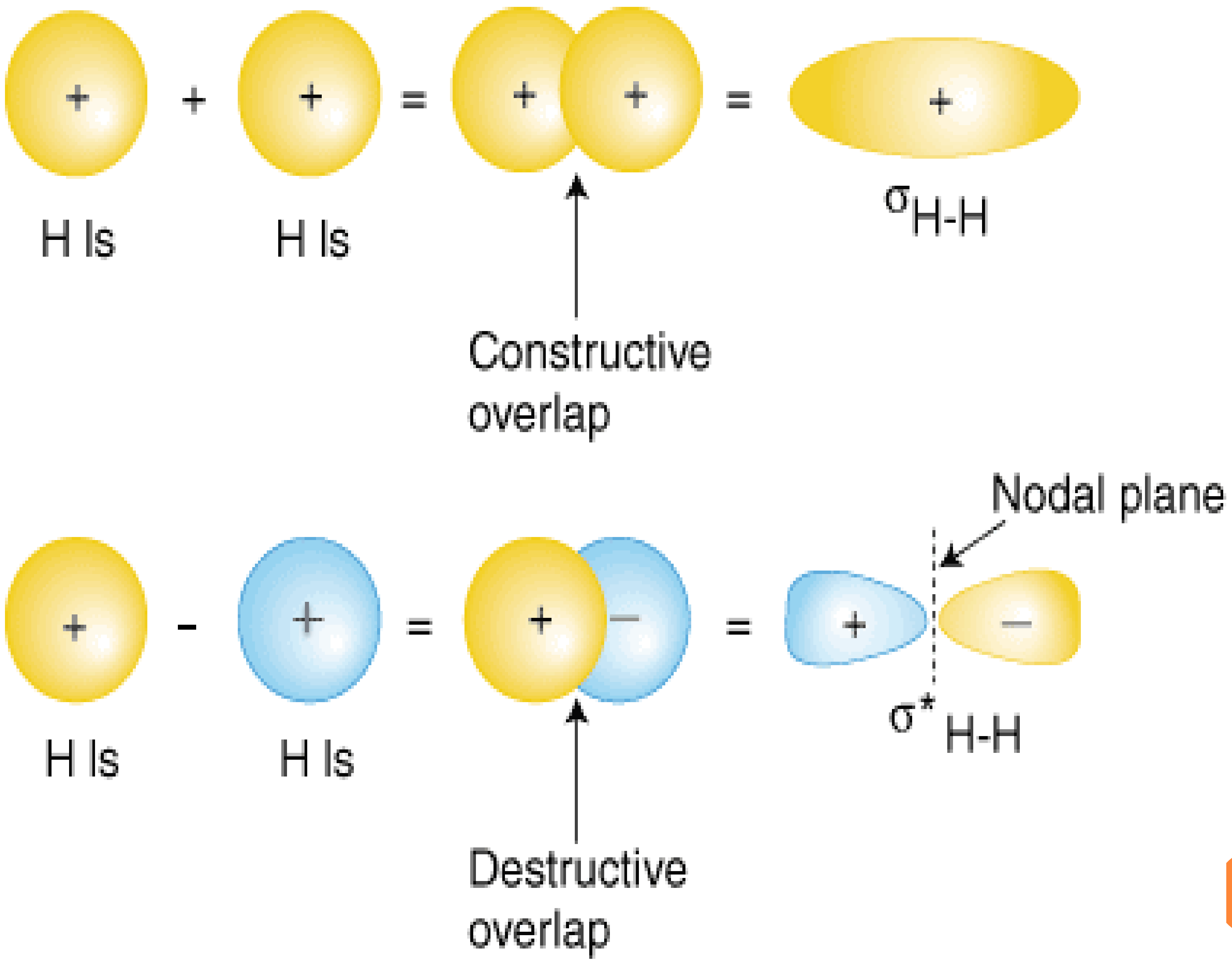
- By **subtraction of overlapping** of the two s orbitals.
- The region between the two nuclei where overlapping of the two s orbitals occur has **zero electron density**.
- This plane of zero electron density between the two nuclei is called the **nodal plane.**

- The molecular orbital formed due to subtraction of the orbitals is called **anti - bonding molecular orbitals**.

- The bonding and anti – bonding molecular orbitals are labelled as **σ ns** and **σ* ns.**

- The term **σ** is used for orbitals that are symmetric to rotation about the internuclear axis.




+
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H ls
$\sigma_{H\text{-}H}$
Constructive overlap
Nodal plane
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H ls
H ls
$\sigma^*_{H\text{-}H}$
Destructive overlap

GRAPHICAL REPRESENTATION OF BONDING & ANTI BONDING MO

A bonding molecular orbital has **high electron density** in the overlap/bonding region whereas the anti - bonding molecular orbital has **zero electron density** in the overlap/bonding region

- This can be shown graphically by plotting ψ^2 (probability density) vs **'r'** (internuclear distance).

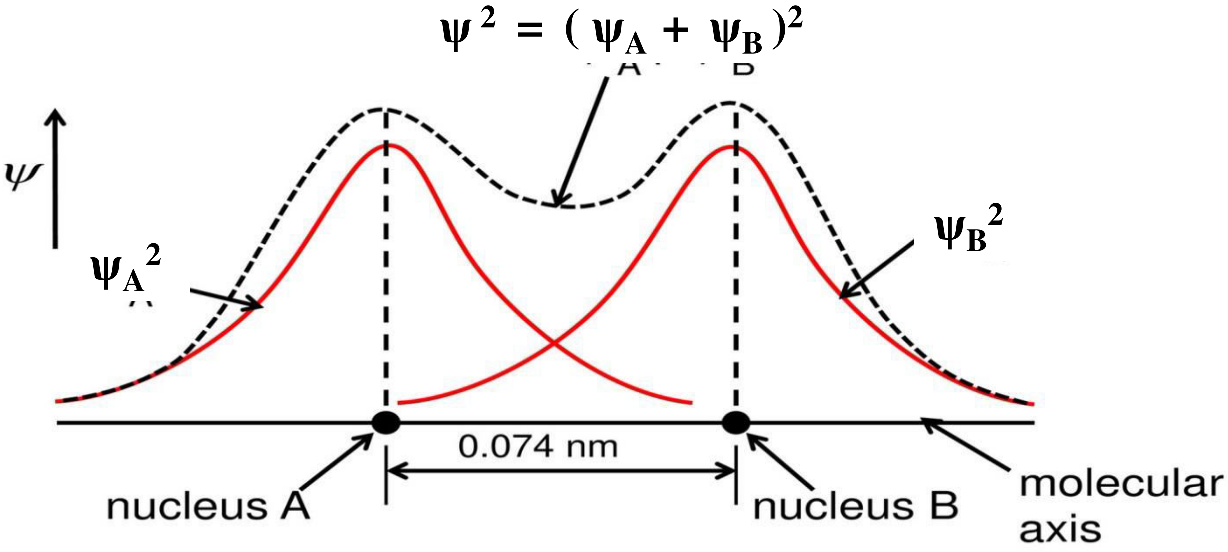
- The wave function for a bonding molecular orbital is given as

$$\psi = \psi_A + \psi_B$$

So, the probability density can be given as

$$\psi^2 = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

- The probability density of the molecular orbital is greater than the sum of the individual probability densities of the atoms by **$2\psi_A\psi_B$.**
- So, the probability of finding the electrons in the bonding molecular orbital is more than in the atomic orbitals.



The symmetric overlapping of two 1s wavefunctions, showing the separate wavefunctions and the combined wavefunction

- The wave function for an antibonding molecular orbital is given as

$$\psi = \psi_A - \psi_B$$

So, the probability density can be given as

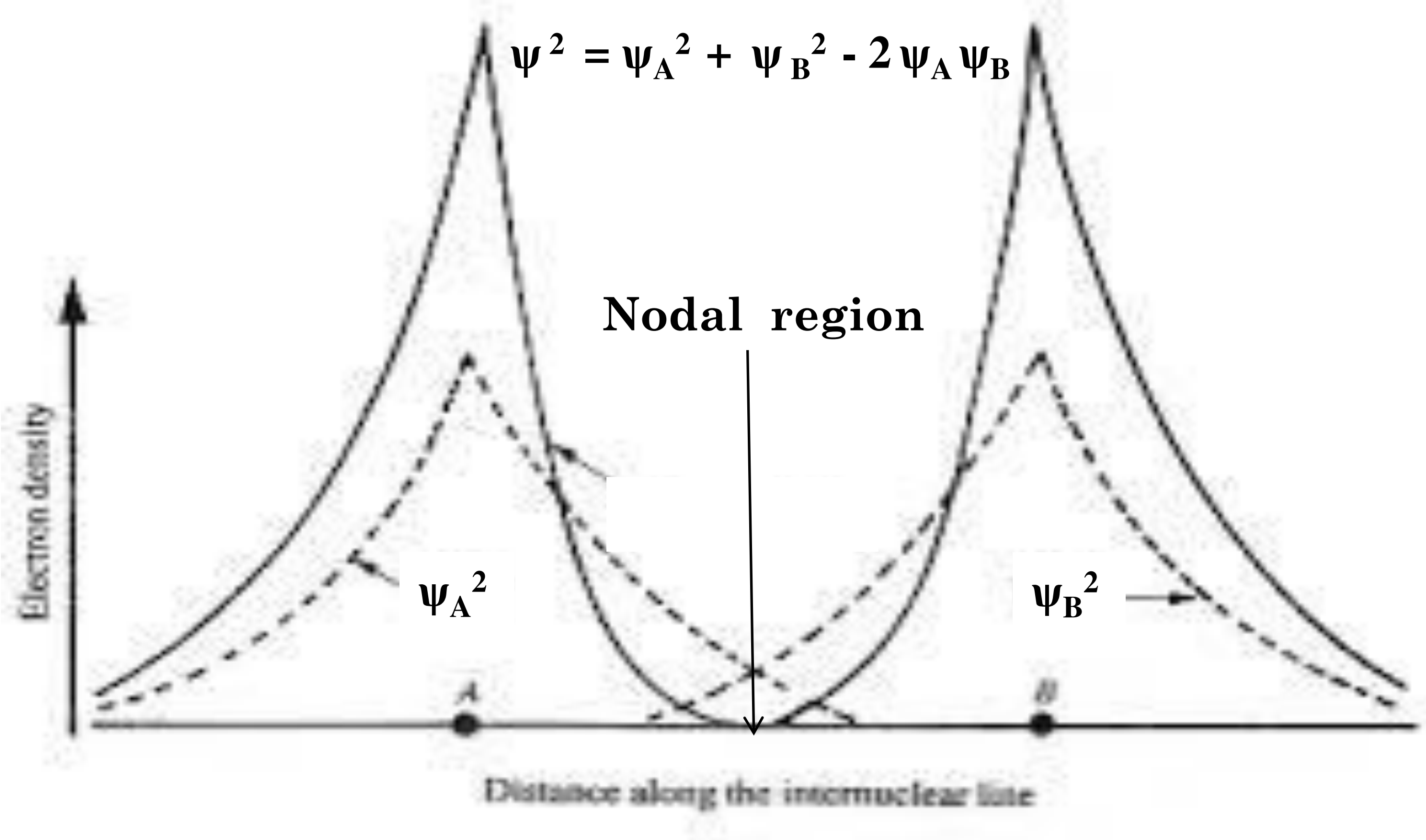
$$\psi^2 = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

- The probability density (ψ^2) of anti – bonding molecular orbital is less than the sum of the individual probability densities of the atoms by $2\psi_A\psi_B$.

- **The electron probability densities of the two atomic orbitals cancel out each other in the centre.**

- There is no probability of finding the electrons in the overlapping region.

- This region corresponds to the nodal region/ plane.
- So, the probability of finding the electrons in the antibonding molecular orbital is less than the probability in the atomic orbitals.

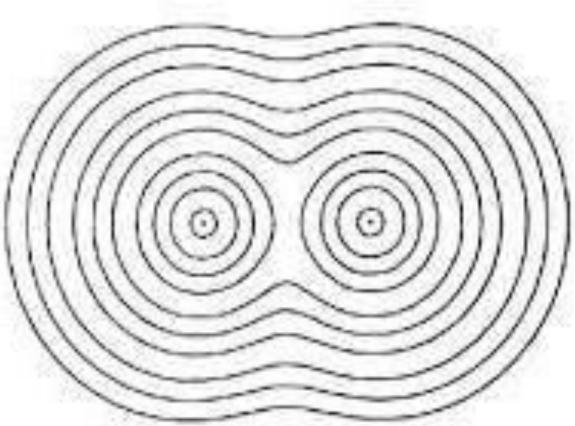


ELECTRON DENSITY MAP OF BONDING & ANTI BONDING MO

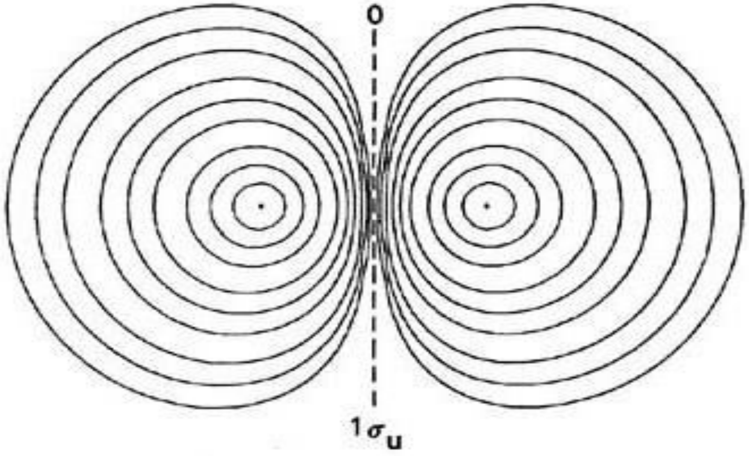
- Another way of representing bonding and anti bonding molecular orbitals is by drawing electron density maps/ **contour diagrams**.

- As seen there is an increased electron density in between the nuclei in bonding molecular orbitals.

- In antibonding molecular orbitals there is very small or zero electron density between the nuclei.



MOLECULAR CHARGE DENSITY



RELATIVE ENERGIES OF BONDING & ANTI BONDING MO

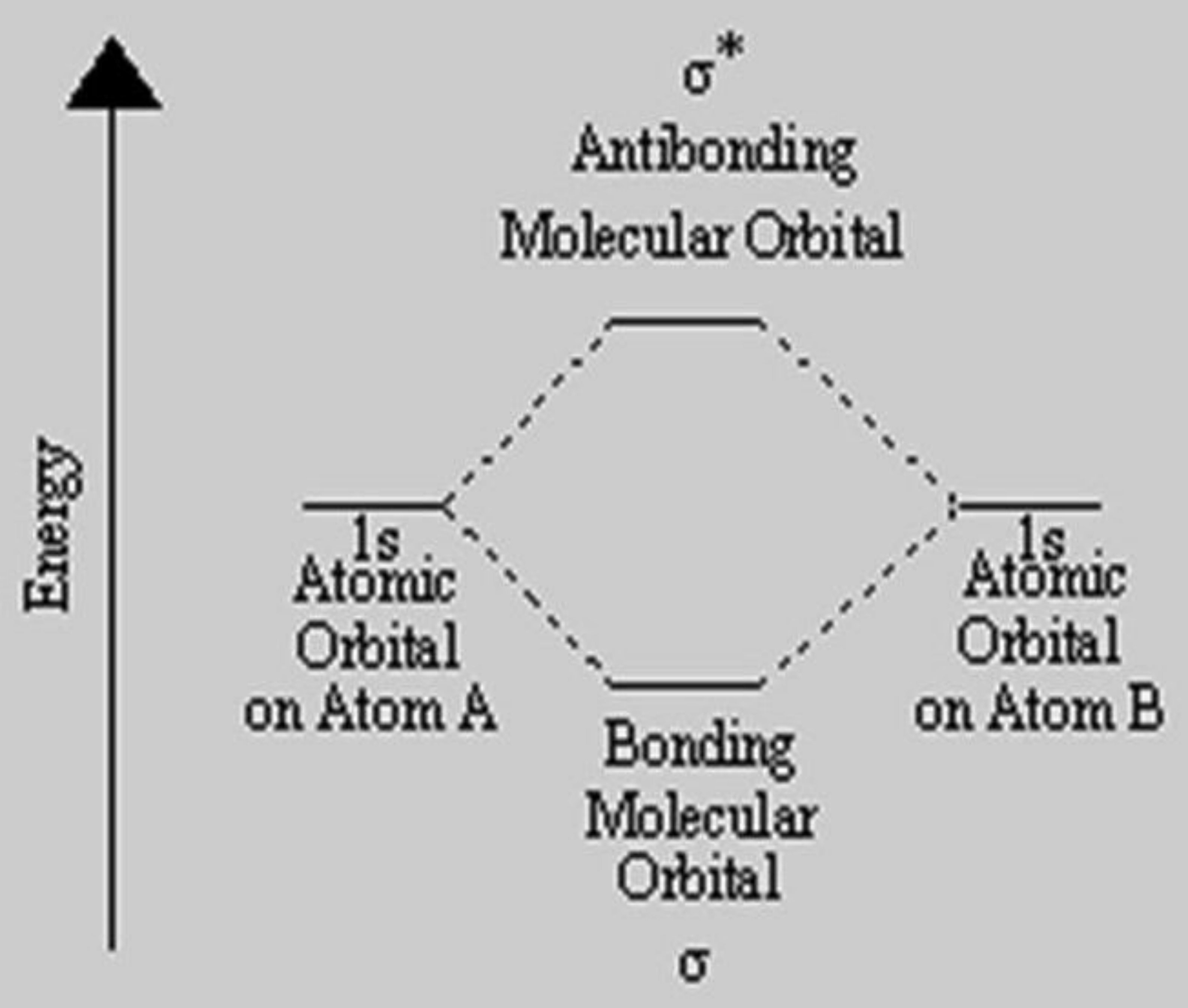
- In bonding molecular orbital, the attraction of both the nuclei for the electron increases.

- So, the energy of the bonding molecular orbital is always lower than the atomic orbitals.

- The energy of the anti - bonding molecular orbital is always greater than the atomic orbitals.

- In other words, bonding molecular orbital are stabilized whereas anti - bonding molecular orbital are destabilized with respect to isolated atoms.

- The stabilization and destabilization occurs to the same extent in homo nuclear diatomic molecule


σ*
Antibonding
Molecular Orbital
Energy
1s
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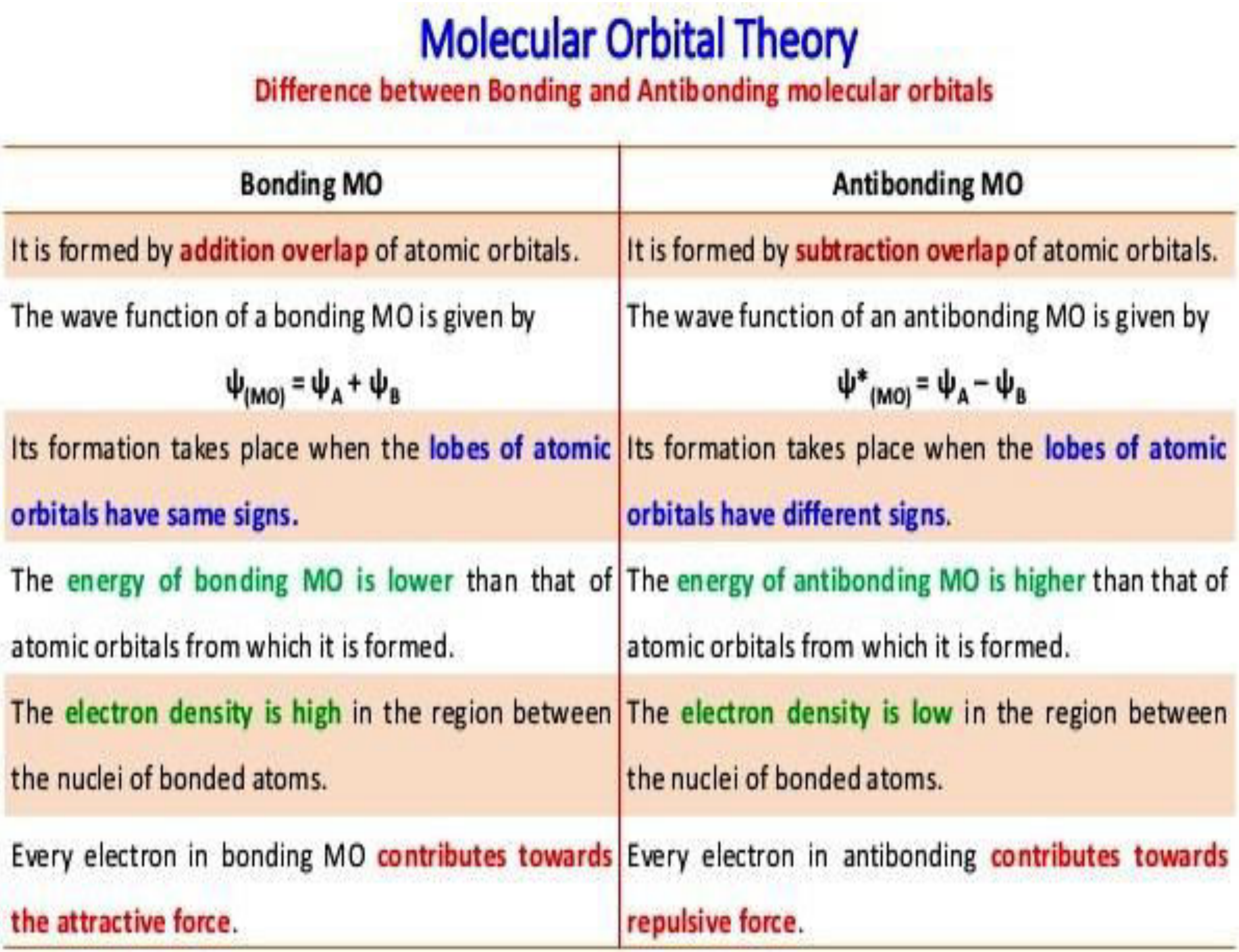


Molecular Orbital Theory

Difference between Bonding and Antibonding molecular orbitals

Bonding MO	Antibonding MO
It is formed by **addition overlap** of atomic orbitals.	It is formed by **subtraction overlap** of atomic orbitals.
The wave function of a bonding MO is given by $\psi_{(MO)} = \psi_A + \psi_B$	The wave function of an antibonding MO is given by $\psi^*_{(MO)} = \psi_A - \psi_B$
Its formation takes place when the **lobes of atomic orbitals have same signs.**	Its formation takes place when the **lobes of atomic orbitals have different signs.**
The **energy of bonding MO is lower** than that of atomic orbitals from which it is formed.	The **energy of antibonding MO is higher** than that of atomic orbitals from which it is formed.
The **electron density is high** in the region between the nuclei of bonded atoms.	The **electron density is low** in the region between the nuclei of bonded atoms.
Every electron in bonding MO **contributes towards the attractive force**.	Every electron in antibonding **contributes towards repulsive force**.

COMBINATION OF 2s AND 2p ATOMIC ORBITALS TO FORM MOLECULAR ORBITALS

COMBINATION OF 2s ORBITALS

2s orbitals like 1s are formed by addition and subtraction of overlap of atomic orbitals to form bonding and anti – bonding molecular orbitals.

Bonding molecular orbitals are labelled as **σ2s** and anti – bonding molecular orbitals are labelled as **σ*2s.**

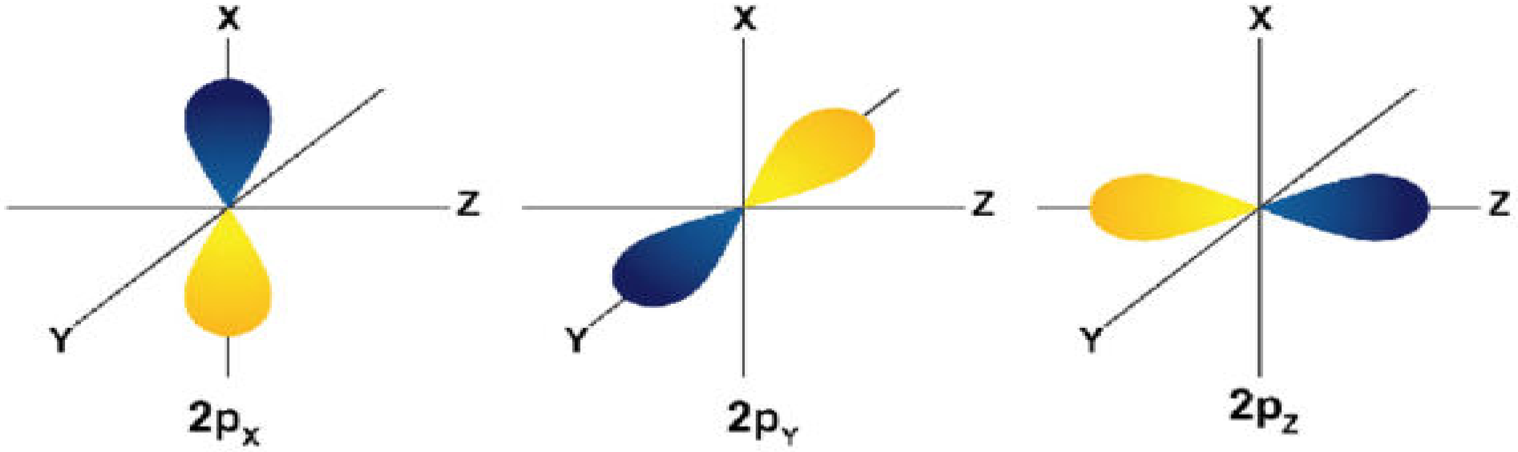
The molecular orbitals of 1s and 2s **differ only in their size**. 2s molecular orbitals **are larger in size** than 1s molecular orbitals

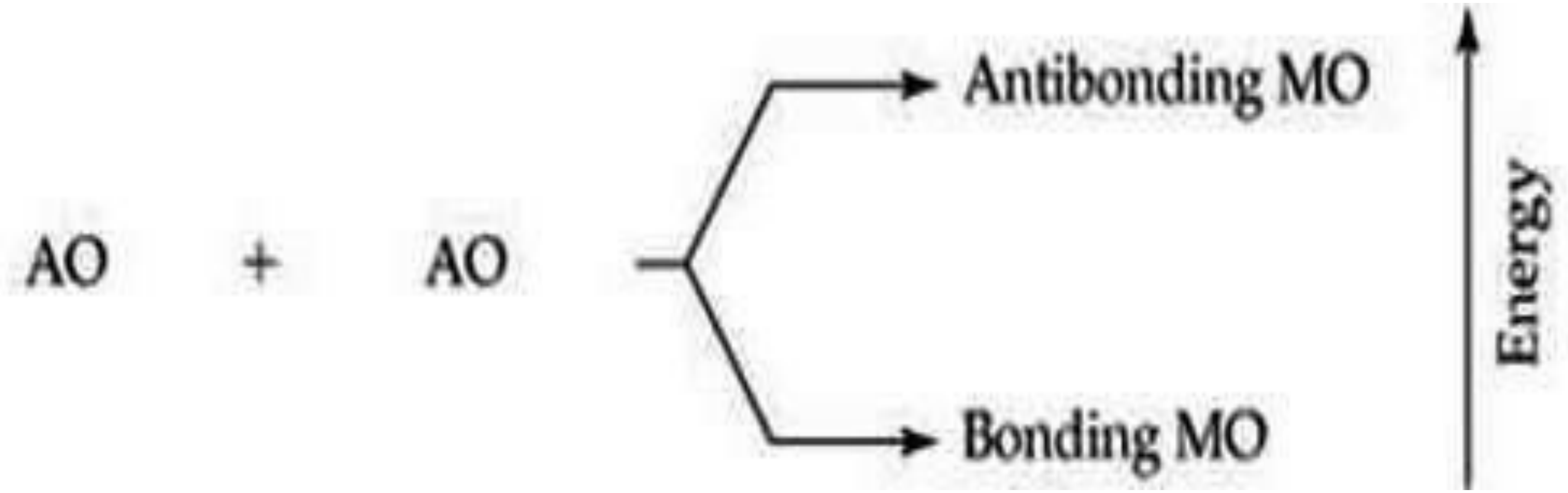
COMBINATION OF 2p ORBITALS

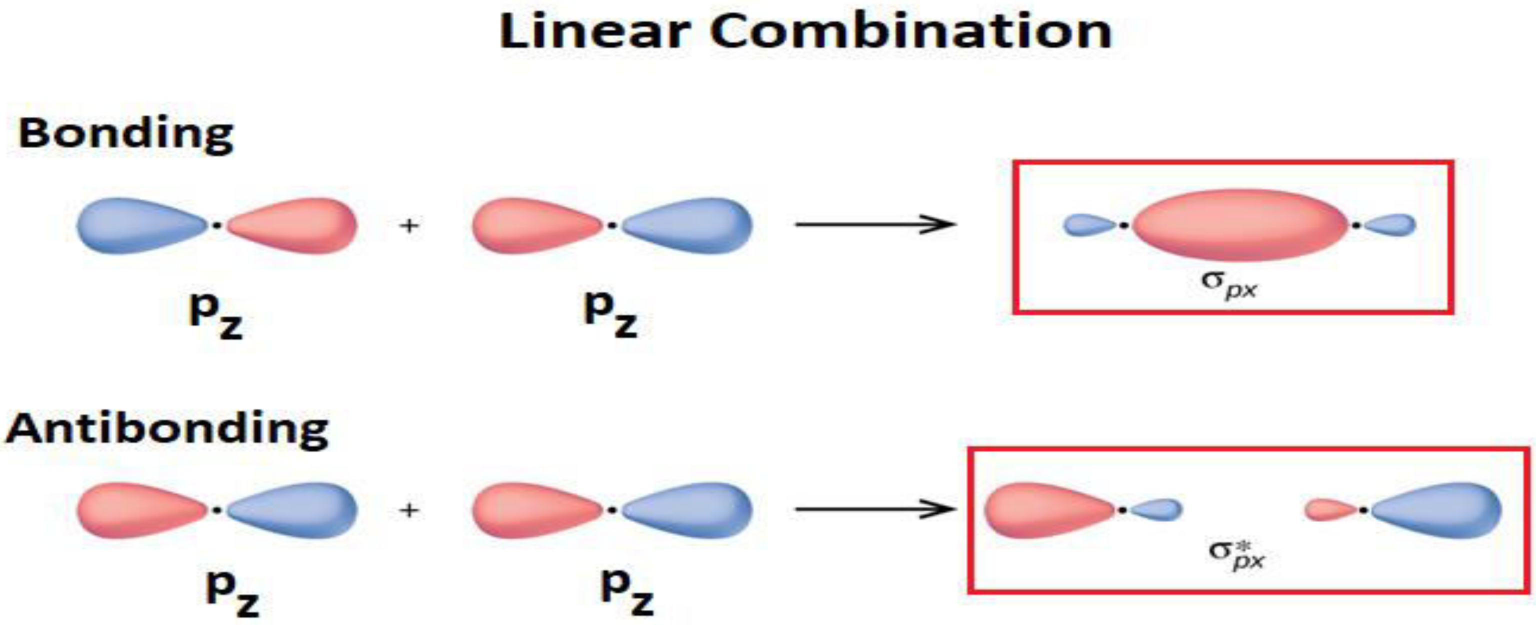
- There are three p - orbitals which are directed along the x, y and z axis in space.

- By convention, z – axis is taken to be the internuclear axis.

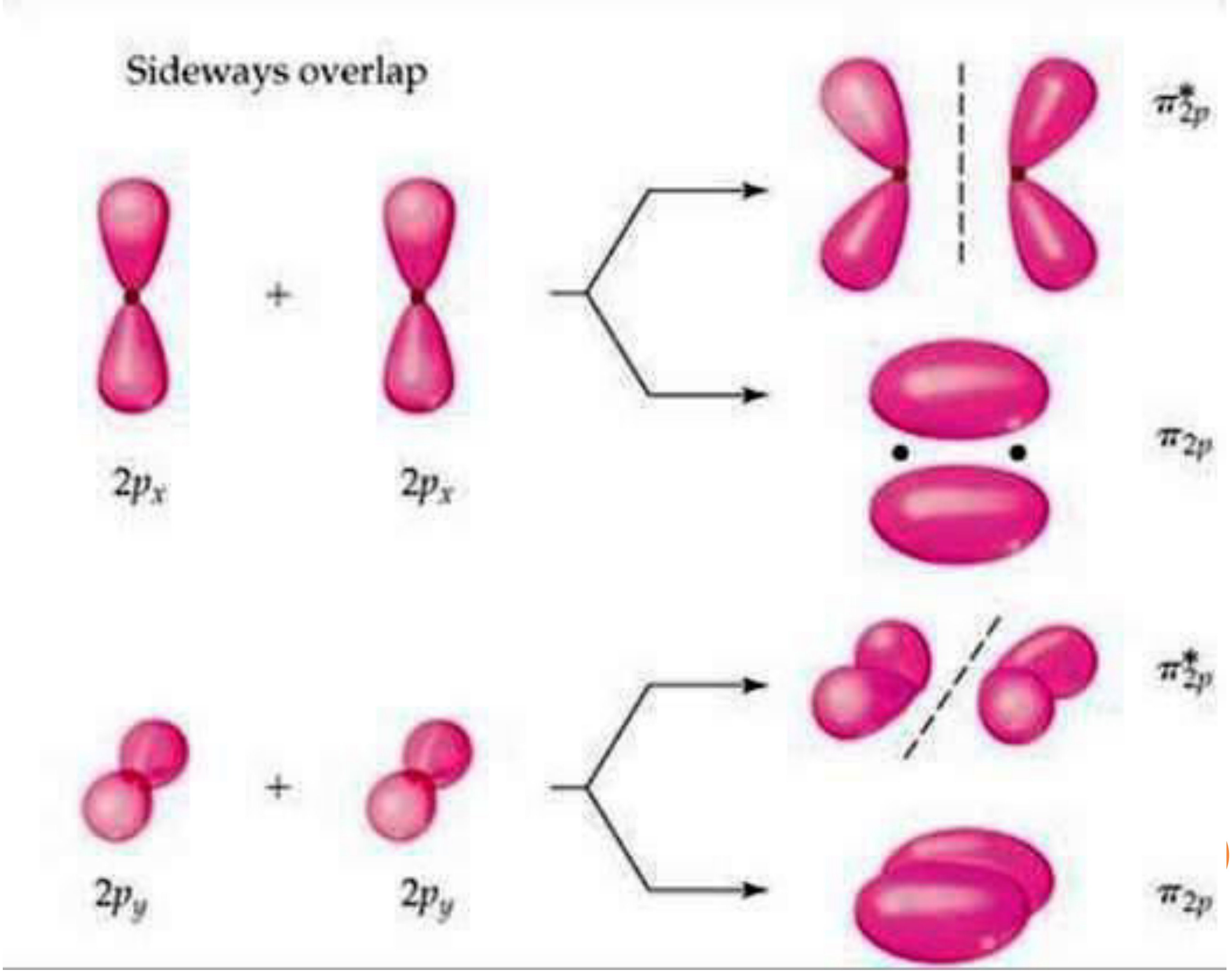
- So, the y and x axes are at right angles (perpendicular) to the internuclear axis.







Sigma (σ) bonds are symmetric about the internuclear axis

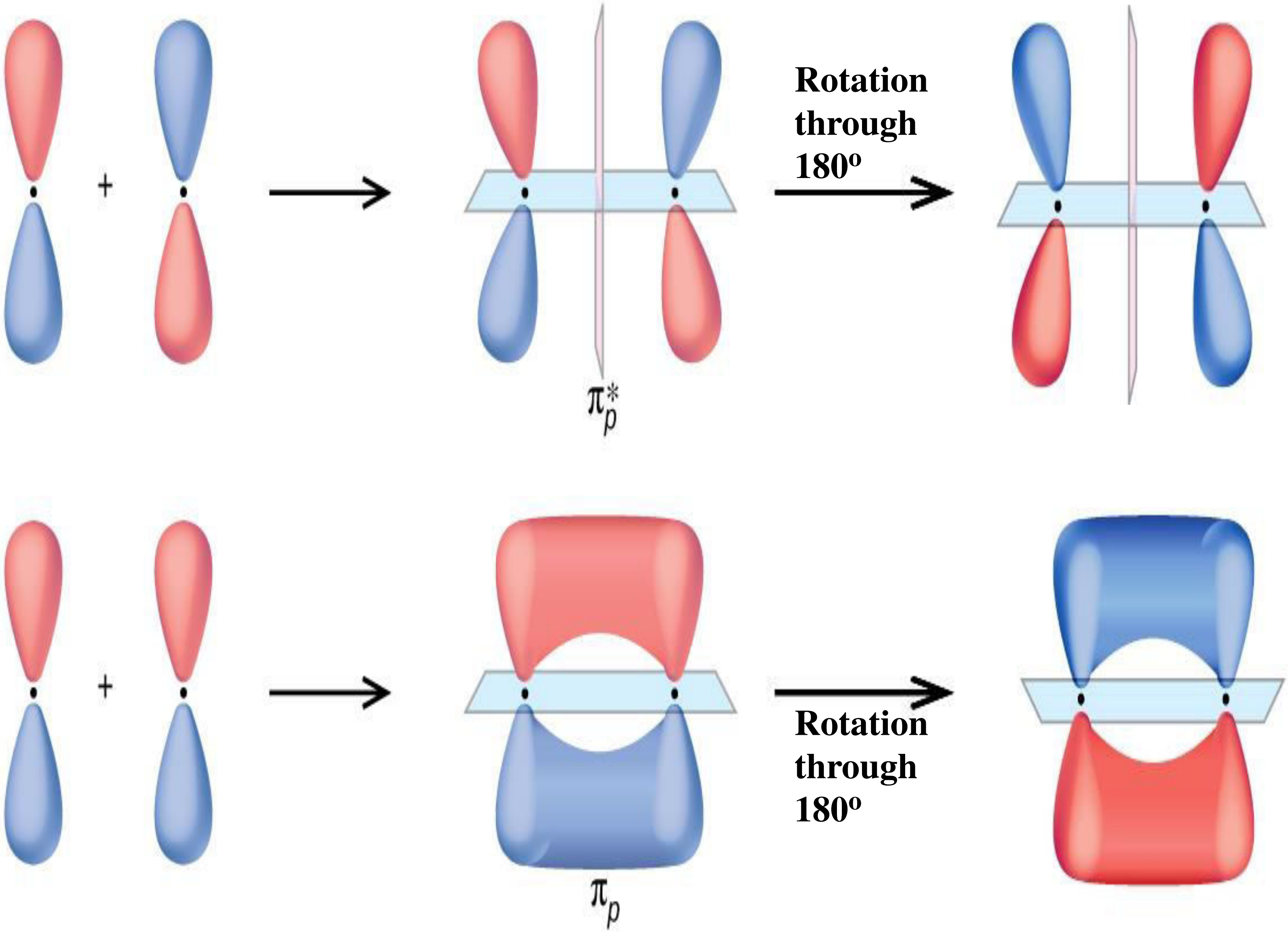

Sideways overlap
$2p_x$
+
$2p_x$
π^*_{2p}
π_{2p}
$2p_y$
+
$2p_y$
π^*_{2p}
π_{2p}

- Unlike Sigma (σ) bonds **pi (π) bonds are not symmetric about the internuclear axis.**

- This can be seen by rotating the bonding **$\pi 2p_x$ or** anti – bonding **$\pi^* 2p_x$** molecular orbital through an angle of 180^o

- On rotating through an angle of 180^o, a change in the sign of the lobe is observed.

- **So, pi (π) molecular orbitals are anti symmetric to rotation**.



Pi (π) orbitals are antisymmetric about the internuclear axis

COMPARISON OF σ AND π - OVERLAP

S. No	*σ - OVERLAP*	*π - OVERLAP*
1	Formed by end to end overlap of atomic orbitals.	Formed by side ways overlap of atomic orbitals.
2	Region of overlap is maximum	Region of overlap is minimum
3	Symmetrical to rotation about the inter - nuclear axis	Anti symmetric to rotation about the inter - nuclear axis
4	Results in strong bonds	Results in weaker bonds

CONDITIONS FOR COMBINATION OF ATOMIC ORBITALS

- Molecular orbitals are formed by linear combination of atomic orbitals.
- But all atomic orbitals cannot combine to form molecular orbitals.
- In order to form molecular orbitals certain conditions have to be obeyed by the atomic orbitals. These are

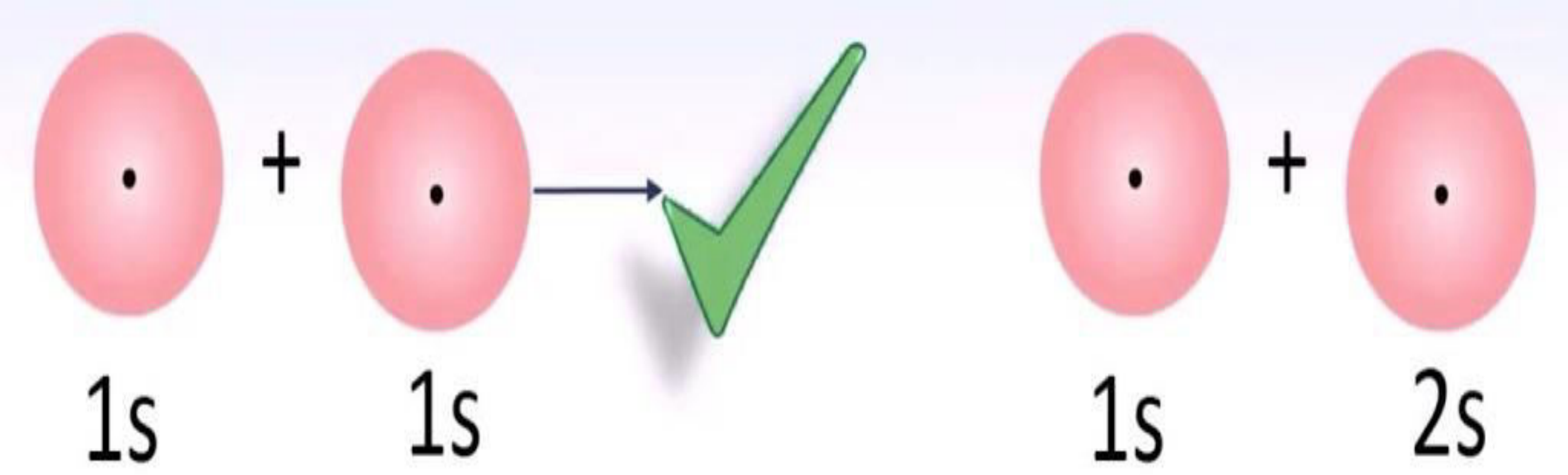
1. Combining atomic orbitals should have approximately same energy

For example, in **homonuclear diatomic molecule (A_2)**

- 1s orbital of one atom will combine with 1s orbital of second atom , similarly 2s will combine with 2s and 2p will combine with 2p.

- 1s and 2s will not combine, neither will 2s and 2p.

However this condition may not apply to **heteronuclear diatomic molecule (AB)**



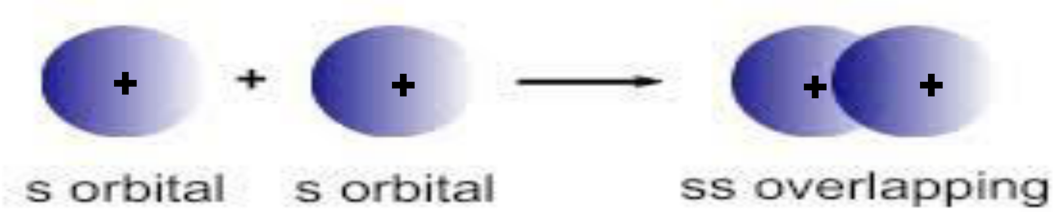
2. Combining atomic orbitals should overlap effectively

Atomic orbitals should not only overlap but should overlap effectively i.e. the extent of overlap should be large.

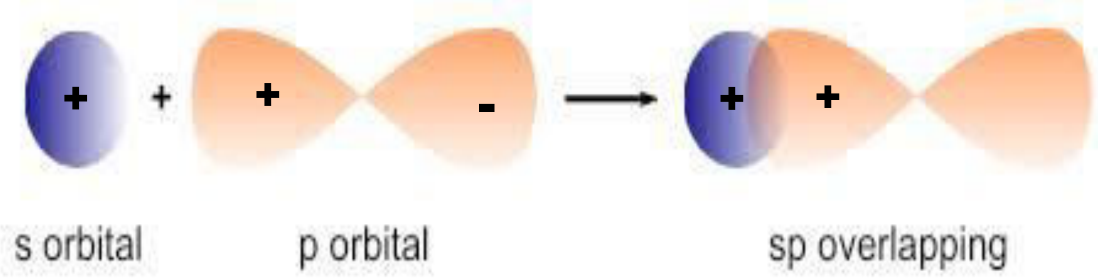
3. Combining atomic orbitals should have same symmetry about the internuclear axis

- The symmetry of the atomic orbitals which undergo overlapping must be the same about the inter - nuclear axis.

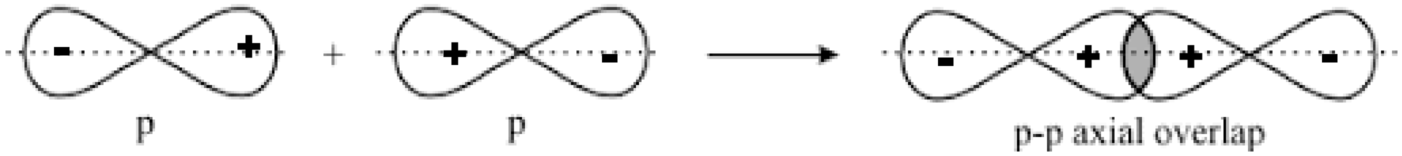
- s orbital can combine with an s orbital



- s orbital can combine with an p_z orbital



- p_z orbital can combine with an p_z orbital



- s orbital cannot combine with an p_x or p_y orbital as they do not have the same symmetry about the inter - nuclear axis

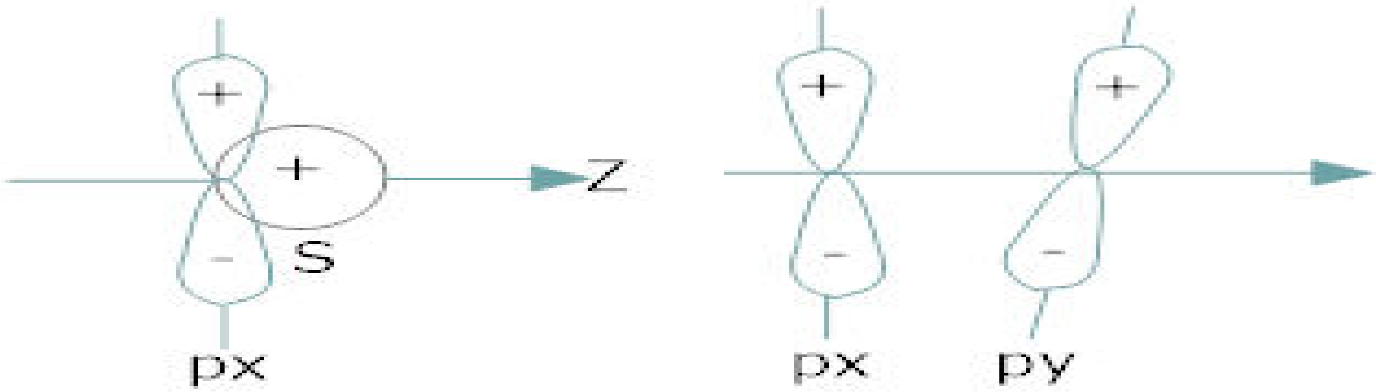


fig. zero overlap.

The s- and the p- atomic orbitals that can combine together along the internuclear axis to form molecular orbitals are

First orbital	Second orbital	Type of molecular orbital formed
s	s	σ
s	p_z	σ
p_z	p_z	σ
p_x	p_x	π
p_y	p_y	π

ENERGY LEVEL DIAGRAM FOR MOLECULAR ORBITALS

- The relative energies of the molecular orbitals depend upon:

a) Energies of the participating atomic orbitals.
b) Extent of overlapping between the atomic orbitals.

- Energy level diagram of the first row elements, show two types of molecular orbitals **namely σ1s and σ*1s.**

σ1s is lower in energy than **σ*1s.**

- In case of second row elements, 2s and 2p atomic orbitals of two atoms overlap.

- Eight atomic orbitals of two atoms overlap resulting in eight molecular orbitals.

Bonding MOs : $\sigma 2s,\ \sigma 2p_z,\ \pi 2p_x,\ \pi 2p_y$

Antibonding MOs : $\sigma^* 2s,\ \sigma^* 2p_z,\ \pi^* 2p_x,\ \pi^* 2p_y$

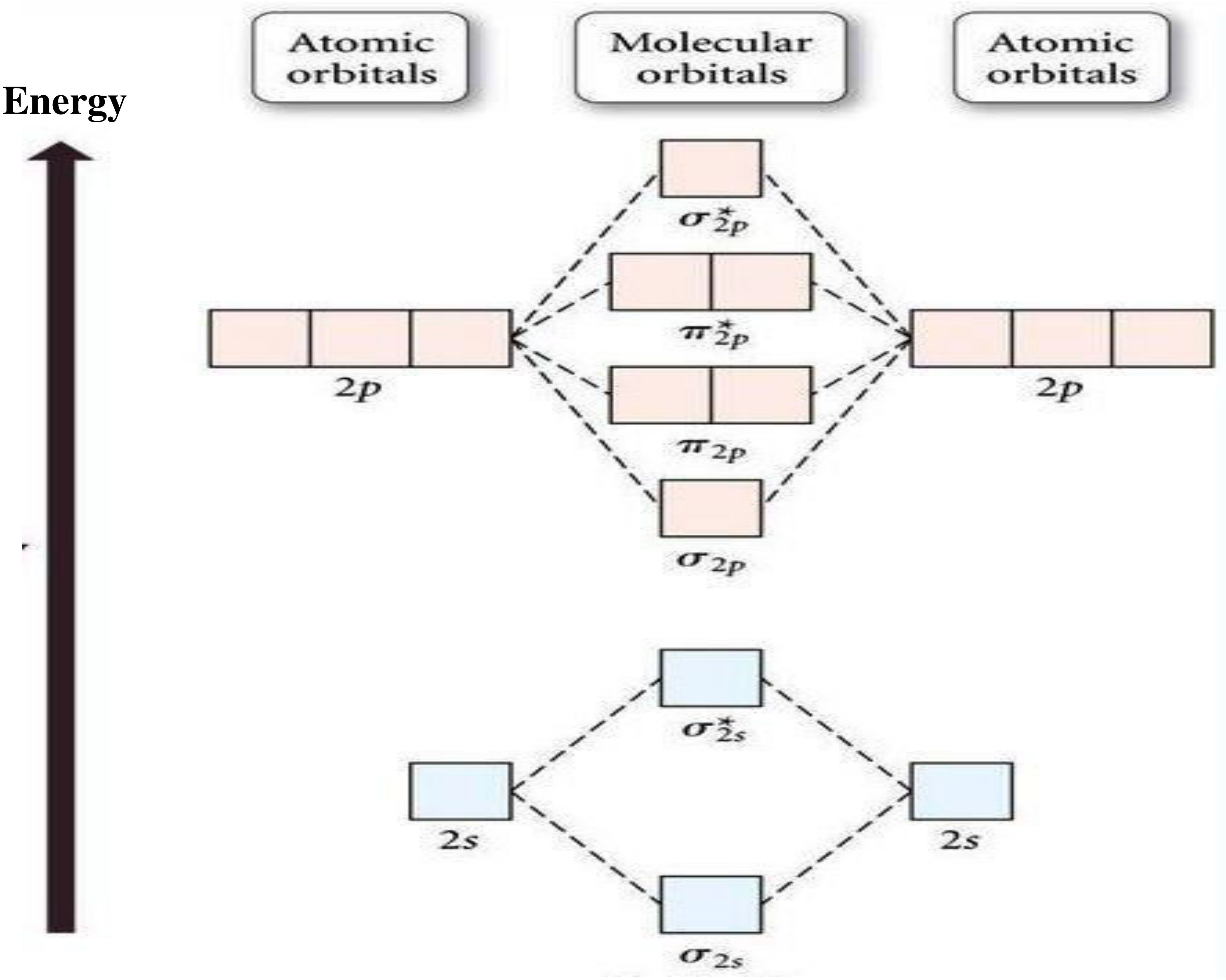
- The energies of these molecular orbitals obtained by the overlap of 1s, 2s and 2p orbitals have been experimentally determined to be in the order

$$\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ \sigma 2p_z,\ \pi 2p_x = \pi 2p_y,\ \pi^* 2p_x = \pi^* 2p_y,\ \sigma^* 2p_z$$

Increasing Energy

- MO energy level diagram show atomic orbitals at the extreme left and extreme right and molecular orbitals at the centre.

Energy


Atomic orbitals
Molecular orbitals
Atomic orbitals
σ^*_{2p}
π^*_{2p}
2p
2p
π_{2p}
σ_{2p}
σ^*_{2s}
2s
2s
σ_{2s}

- The atomic orbitals of the same energy are shown at the same level

- whereas the bonding MOs are shown lower and the antibonding MOs are shown higher than the corresponding atomic orbitals.

- Difference between the energies of atomic orbitals and the bonding of MOs depend on the extent of overlap between the atomic orbitals .

- However, experimental evidences in case of some diatomic molecules have shown that the sequence of energy levels of MOs shown is not correct for all molecules.

- This order is correct only for oxygen and fluorine molecules.

- In case of other diatomic molecules like Li_2 , Be_2 , B_2 , C_2 and N_2 , the **$\sigma 2p_z$** MO is of higher energy than the **$\pi 2p_x$ and $\pi 2p_y$** MOs.

- This change in sequence of energy level of MOs is due to mixing of the **2s** and **$2p_z$** atomic orbitals.

- Due to mixing of **2s** and **$2p_z$** atomic orbitals, the energies of **σ2s, σ^*2s, $\sigma 2p_z$, $\sigma^* 2p_z$** molecular orbitals change.

MIXING OF ORBITALS

- **σ2s and σ^*2s** are formed by the overlap of **2s** atomic orbitals of two atoms whereas the **$\sigma 2p_z$ and $\sigma^* 2p_z$** are formed by the overlap of **$2p_z$** atomic orbitals of two atoms.

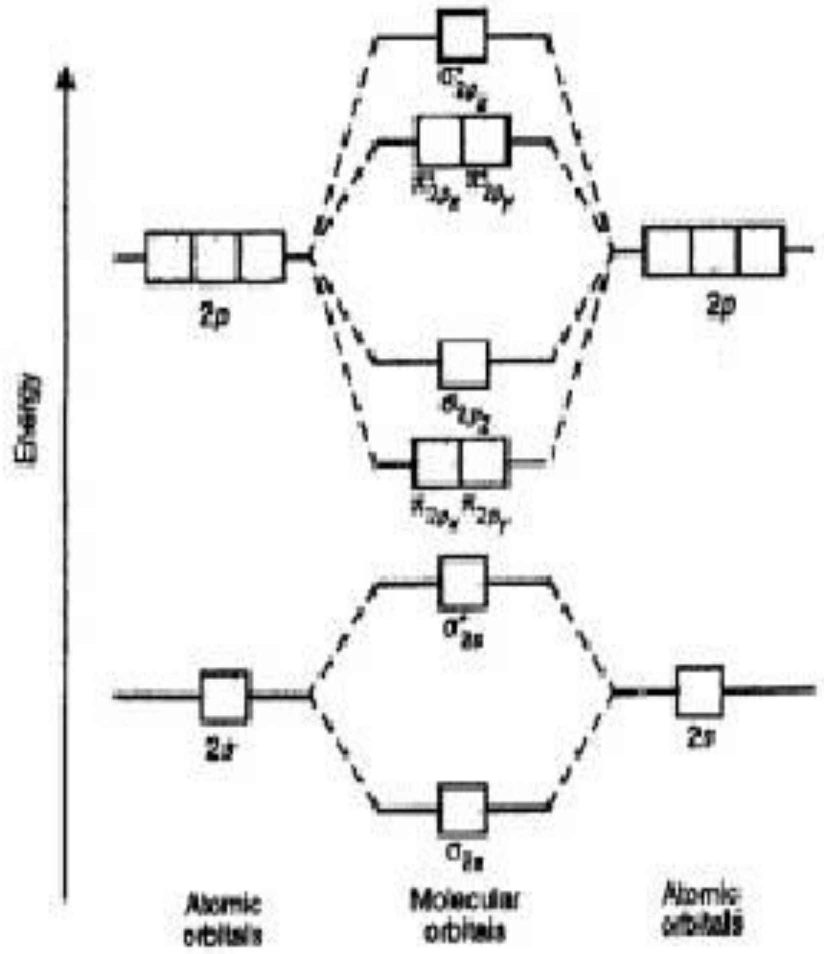


Fig. a Molecular orbital energy level diagram for diatomic homonuclear molecules of first and second period (except O_2, F_2 etc.)

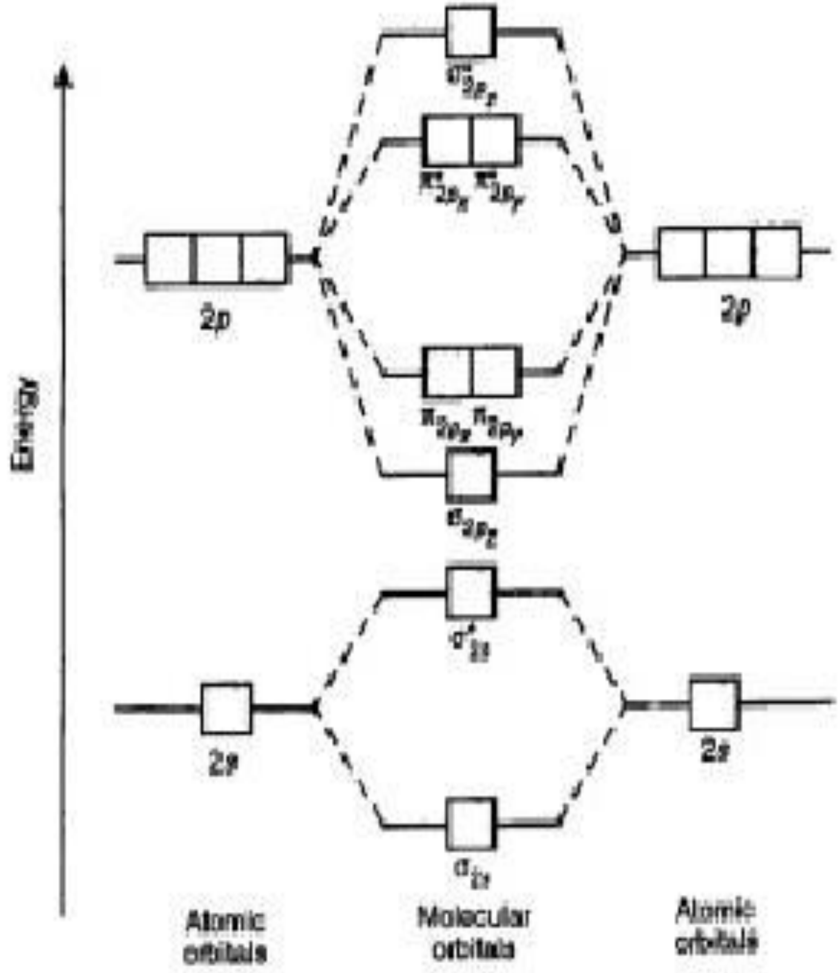


Fig. b. Molecular orbital energy level diagram for homonuclear diatomic molecules of O_2 and other heavier elements

- If the energy difference between **2s** and **$2p_z$** atomic orbitals is small, then the **2s** atomic orbital can combine / overlap with the **$2p_z$** atomic orbital .

- So, the resulting **σ2s and σ*2s** molecular orbitals may not have pure s- character and similarly the resulting **σ$2p_z$ and σ*$2p_z$** molecular orbitals may not have pure p- character.

- All the four above molecular orbitals may have **mixed sp – character.**

- Also due to this s-p mixing, **the energies** of all the four orbitals change.

- Whenever two AOs combine, two MOs are formed. One having lower energy and the other having higher energy.

- The same principle is applied when **σ2s** and **σ2p$_z$** MOs interact.

- When **σ2s** and **σ2p$_z$** MOs interact, the energy of the resulting **σ2s** molecular orbital is **further lowered (decreases)** whereas the energy of the resulting **σ2p$_z$** molecular orbital is **further raised (increases).**

- Similarly, when **σ*2s** and **σ*2p$_z$** MOs interact, the energy of the resulting **σ*2s** molecular orbital is **further lowered (decreases)** whereas the energy of the resulting **σ*2p$_z$** molecular orbital is **further raised (increases).**

- The new **σ2s and σ*2s** MOs formed as a result of mixing are **more stable** and **have less energy** whereas the new **σ2p$_z$ and σ*2p$_z$** MOs are **less stable** and **have more energy**.

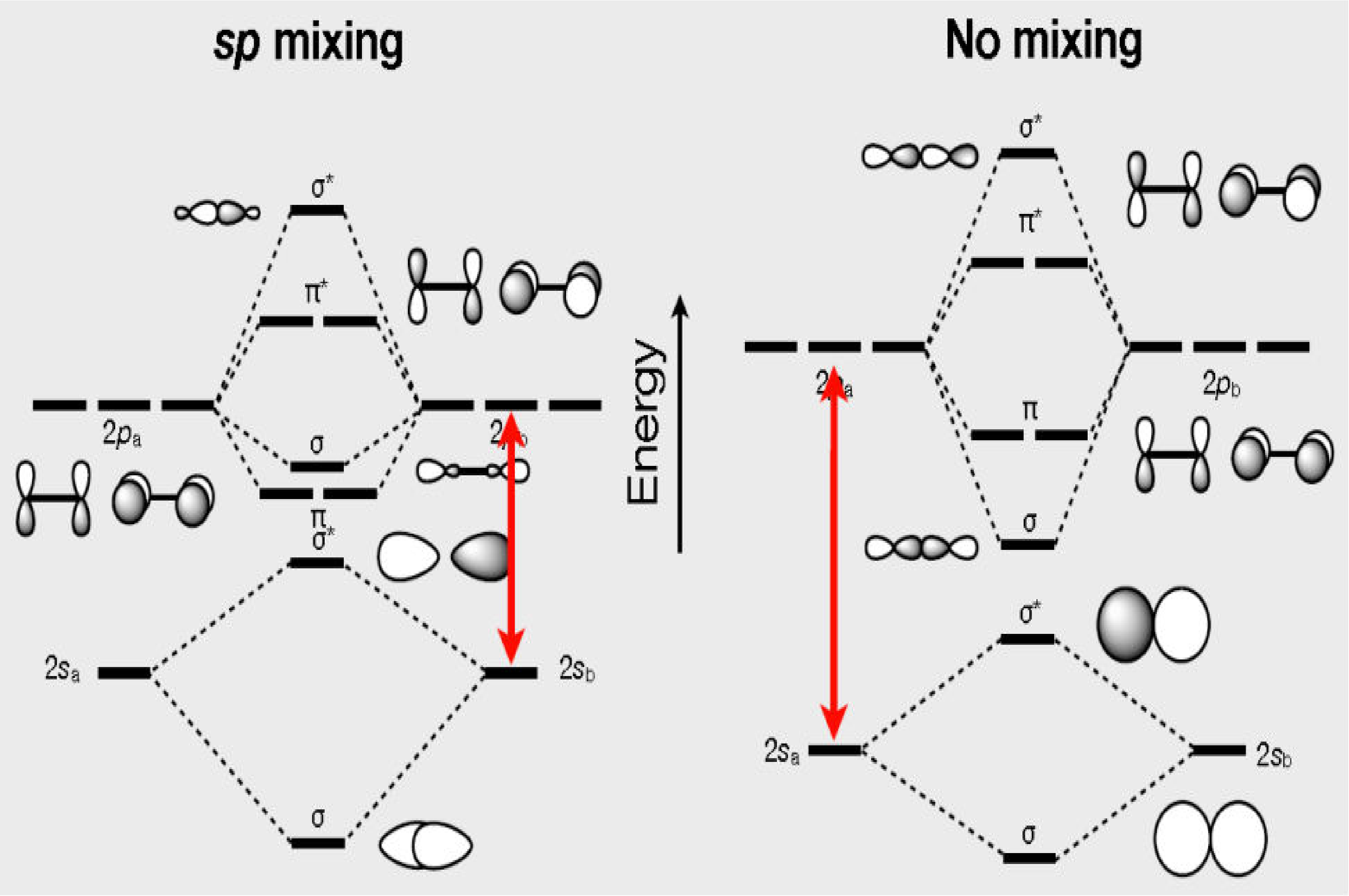
- The **$\pi 2p_x$ and $\pi 2p_y$** MOs are not involved in mixing, so their energies remain the same.

- The new sequence of energy levels as a result of mixing of **2s and 2p** MOs become:

$$\boldsymbol{\sigma 1s,\ \sigma^{*}1s,\ \sigma 2s,\ \sigma^{*}2s,\ \pi 2p_x = \pi 2p_y\ ,\ \sigma 2p_z\ ,\ \pi^{*}2p_x = \pi^{*}2p_y,\ \sigma^{*}2p_z}$$

Increasing Energy →

This sequence of molecular orbitals is observed from Li to N diatomic molecules.



$Li_2, Be_2, B_2, C_2, N_2$

O_2, F_2, Ne_2

Q. Why interaction between 2s and $2p_z$ atomic orbitals occur upto N_2 molecule only ?

The reason for **interaction between 2s and $2p_z$ atomic orbitals** can be explained on the basis of energy difference of **2s and $2p_z$ atomic orbitals** of atoms of second row elements.

Atoms	Li	Be	B	C	N	O	F
Difference between energies of 2s and $2p_z$ AOs (KJ /mol)	180	260	450	510	570	1430	1970

From the table it can be seen that the energy difference between **2s and $2p_z$** orbitals till nitrogen is quite small as compared to that of oxygen and fluorine. So, mixing of **2s and $2p_z$** orbitals till nitrogen can be easily achieved.

RULES FOR FILLING MOLECULAR ORBITALS

Molecular orbitals are filled according to the given rules:

- The molecular orbitals are filled according to increasing energy i.e. molecular orbital with lower energy is filled first followed by that of higher energy (Aufbau's principle).
- Each molecular orbital can accommodate a maximum of two electrons with opposite spin (Pauli's exclusion principle).
- Pairing of electrons will occur only when molecular orbitals of same energy have one electron each (Hund's rule of maximum multiplicity)

ELECTRONIC CONFIGURATION AND MOLECULAR BEHAVIOUR

MO energy level diagram provides important information about the behaviour of molecules. The important information given by the electronic configuration of molecules is :

❖ Stability of the molecule

- The energy of bonding molecular orbitals is **always lower** than the energy of the atomic orbitals from which they are formed.

- So, the electrons in the BMO lead to **attraction** between the atoms and **help in** bond formation.

- The energy of antibonding molecular orbitals is **always higher** than the energy of the atomic orbitals from which they are formed.

- So, the electrons in the ABMO lead to **repulsion** between the atoms and **oppose** the bond formation.

- In other words, electrons in BMO stabilize and electrons in ABMO destabilize the molecule.

- If

$\mathbf{N_b}$ = Number of electrons in BMO's

and $N_{\mathbf{a}}$ = Number of electrons in ABMO's

(i) The molecule will be **stable** if $\mathbf{N_b > N_a}$ i.e. the number of electrons in BMO are **greater** than the number of electrons in ABMO.

(ii) The molecule will be **unstable** if $\mathbf{N_b < N_a}$ **or** $\mathbf{N_b = N_a}$ i.e. the number of electrons in BMO are **lesser or equal** to those in ABMO

- This is because an electron in the ABMO **will cancel out the bonding stability** acquired by an electron in the BMO.

- The relative stability of a molecule can be calculated on the basis of bond order.

❖ ***Bond Order***

- It is defined as the number of covalent bonds present in a molecule.

- It can be calculated as;

$$\textbf{Bond order} = \frac{N_b - N_a}{2}$$

- Bond order can have **whole number as well as fractional values.**

Information conveyed by bond order

- If the bond order is positive, it means the molecule is stable but if the bond order is negative or zero, it means the molecule is unstable.

- The stability of a molecule is measured in terms of ***bond dissociation energy.***

- ***Bond dissociation energy is directly proportional to bond order.*** Greater the bond order, greater is the bond dissociation energy as well as the stability of a molecule and vice- versa.

- ***Bond order is inversely proportional to bond length***. Greater the bond order, smaller will be the bond length.

❖ ***Magnetic character***

- Molecular orbital theory also helps to predict the magnetic nature / character of a molecule.

- If all the electrons in a molecule are ***paired*** then the molecule is ***diamagnetic*** in nature.

- If ***unpaired*** electrons are present in a molecule then the molecule is ***paramagnetic*** in nature.

CHEMICAL BONDING II

CONTINUED IN

PART II

THANK YOU