

ATOMIC ENERGY CENTRAL SCHOOL-3 TARAPUR

- ▶ MODULE-2
- ▶ UNIT- CHEMICAL BONDING

Syllabus

Chemical Bonding and Molecular Structure 14 Periods : Valence electrons, ionic bond, covalent bond, bond parameters, Lewis structure, polar character of covalent bond, covalent character of ionic bond, valence bond theory, resonance, geometry of covalent molecules, VSEPR theory, concept of hybridization, involving s, p and d orbitals and shapes of some simple molecules, molecular orbital theory of homonuclear diatomic molecules(qualitative idea only), Hydrogen bond.

THE VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

- ▶ As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further modified and redefined by Nyholm and Gillespie (1957).

VSEPR THEORY

- ▶ The main postulates of VSEPR theory are as follows:
- ▶ • The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non bonded) around the central atom.
- ▶ • Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- ▶ • These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximize distance between them.
- ▶ • The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- ▶ • A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- ▶ • Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- ▶ The repulsive interaction of electron pairs decrease in the order:
- ▶ Lone pair (lp) - Lone pair (lp) > Lone pair (lp)- Bond pair (bp) > Bond pair (bp) -Bond pair (bp)

VSEPR THEORY

- ▶ Why lone pair(lp) - lone pair repulsion is more than others ?
- ▶ Since lps are localized to the central atom occupies large space over the bps therefore lp -lp repulsion is more than lp-bp and bp-bp repulsion.
- ▶ Effect of lp on the shape of molecule : They can alter the bond angle hence change ideal shape of the molecule.
- ▶ **VSEPR Theory in short we can understand as follows:** When central atom in a molecule is surrounded by only bond pairs of electrons the shape of molecule will be ideal(or regular) shape(i.e. 2bps shape is linear, 3bps shape is trigonal planar etc.)
- ▶ But if central atom in a molecule is surrounded by lps as well as bps then the shape of molecule will not remain ideal(or regular) it deviate from ideality for example if the central atom is surrounded by 1lp and 2bps then ideal trigonal planar shape destroyed and molecule adopts another shape i.e. bent shape here in this case.

VSEPR THEORY

- ▶ **Merits** : 1. The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of *p*-block elements accurately.
- ▶ 2. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small.
- ▶ **Demerits**: 1. It is also quite successful in determining the geometry quite-accurately
- ▶ even when the energy difference between possible structures is very small.
- ▶ 2. It could not provide any information about magnetic behavior of molecule and molecule ions.

valence bond theory

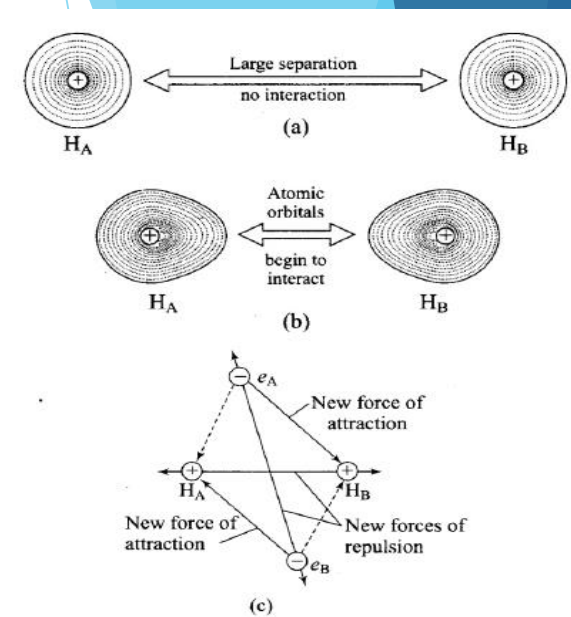
- ▶ As we know that Lewis approach helps in writing the structure of molecules but it fails
- ▶ to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in different molecules.
- ▶ Similarly the **VSEPR** theory gives the geometry of simple molecules but **theoretically**, it does not explain them and also it has limited applications. To overcome these limitations the two important theories **based on quantum mechanical principles** are introduced. These are **valence bond (VB) theory** and molecular orbital (MO) theory.

valence bond theory

- ▶ A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules. Consider two hydrogen atoms A and B approaching each other having nuclei N_A and N_B and electrons present in them are represented by e_A and e_B . When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate.
- ▶ Attractive forces arise between:
 - ▶ (i) nucleus of one atom and its own electron
 - ▶ that is $N_A - e_A$ and $N_B - e_B$.
 - ▶ (ii) nucleus of one atom and electron of other
 - ▶ atom i.e., $N_A - e_B$, $N_B - e_A$.

valence bond theory

- ▶ Similarly repulsive forces arise between
 - ▶ (i) electrons of two atoms like $e_A - e_B$,
 - ▶ (ii) nuclei of two atoms $N_A - N_B$.
- ▶ Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart. Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm. Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as **bond enthalpy**.



valence bond theory

- ▶ In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo **partial interpenetration**. This partial merging of atomic orbitals is called **overlapping** of atomic orbitals which results in the pairing of electrons (formation of covalent bond). The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to **orbital overlap concept**, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins. As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms.

Valence Bond Theory – H₂

- H₂ bonds form because **1s** atomic valence orbital from each H atom overlaps



Separated H atoms



Overlapping of orbitals



Covalent bond in H₂

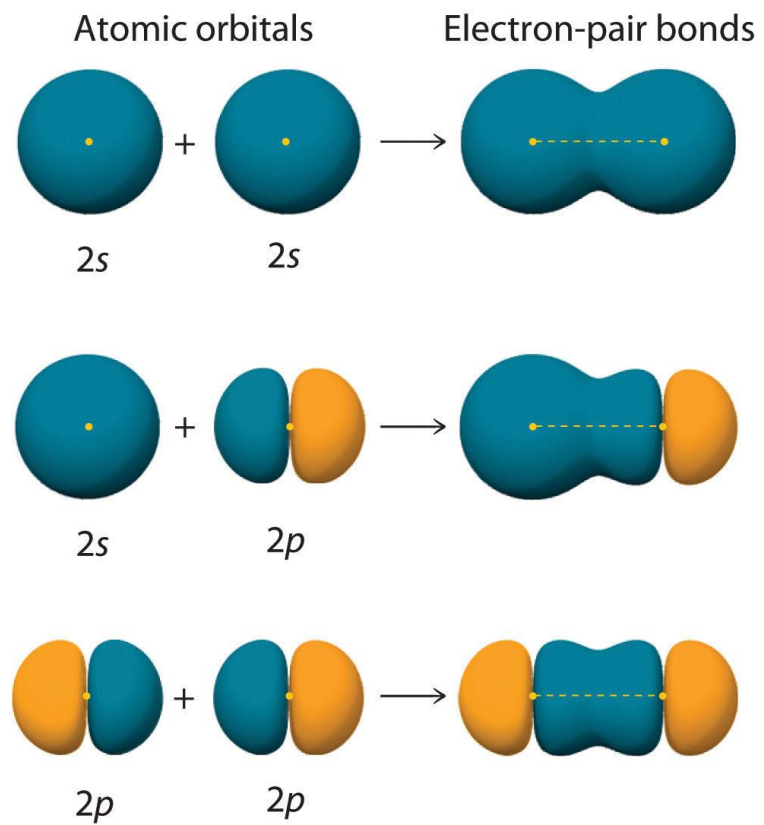
valence bond theory

- ▶ The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH_4 , NH_3 and H_2O , etc. in terms of overlap and hybridisation of atomic orbitals
- ▶ **Overlapping of Atomic Orbitals :**
- ▶ The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. We know that the shapes of CH_4 , NH_3 , and H_2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in terms of the orbital overlaps.

valence bond theory

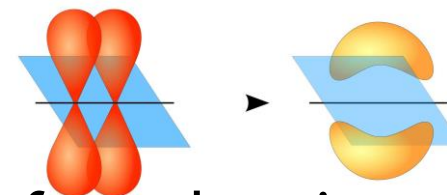
- ▶ **Types of Overlapping and Nature of Covalent Bonds:**
- ▶ The covalent bond may be classified into two types depending upon the types of overlapping:
- ▶ (i) **Sigma(σ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals.
- ▶ (a) **s-s overlapping** : In this case, there is overlap of two half filled s-orbitals along the internuclear axis.
- ▶ (b) **p-p overlapping** : between the two half filled p- orbitals along the internuclear axis.
- ▶ (c) **s-p overlapping.**

Sigma(σ) bond



π -bond

pi(π) bond : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the inter nuclear axis. The orbitals formed due to sidewise overlapping(p-p) consists of two saucer type **charged clouds above and below** the plane of the participating atoms.



Strength of Sigma and pi Bonds:

strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent.

Remember : Formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed **in addition to a sigma bond**.

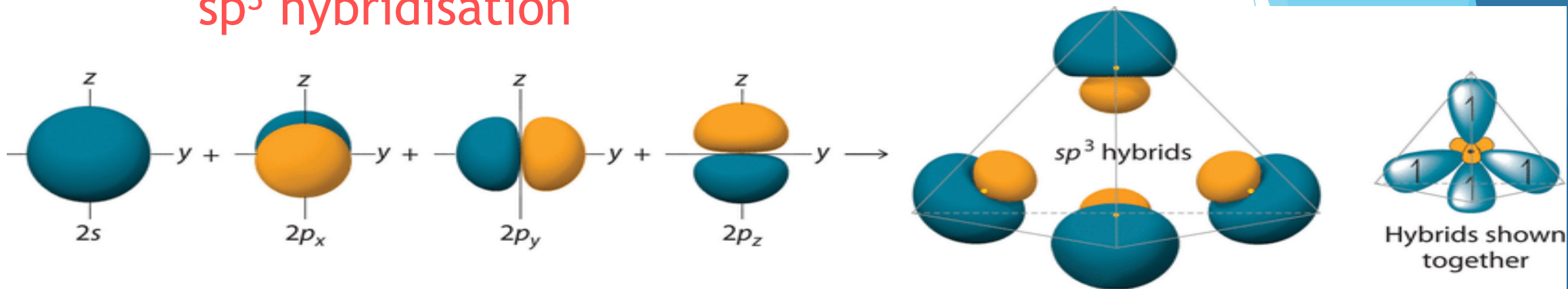
HYBRIDISATION

- ▶ Atomic orbitals of central atom in a chemical species of **nearly equal energies** are undergo intermixing and produce new orbitals of equal energies and similar shapes, these new orbitals here are called as hybrid orbitals and this phenomenon is called as **hybridisation**.
- ▶ **Salient features of hybridisation :**
 1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
 - ▶ 2. The hybridised orbitals are always equivalent in energy and shape.
 3. Unlike pure orbitals, the hybrid orbitals are used in bond formation.
 - ▶ 4. Unlike pure atomic orbitals hybrid orbitals also undergo overlapping.
 - ▶ 5. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
 - ▶ 6. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridization indicates the geometry of the molecules.

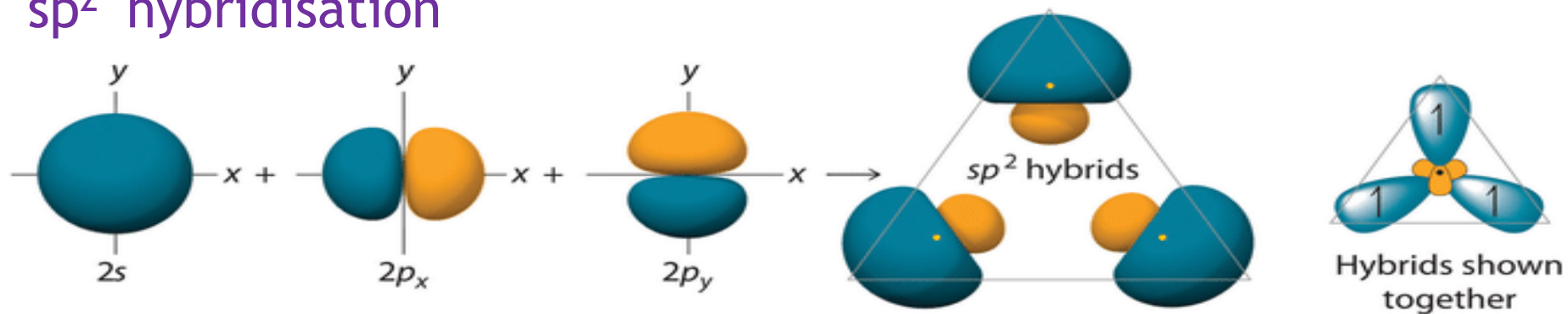
Types of Hybridisation

- ▶ (1) ***sp hybridisation*** : This type of hybridisation involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals.
- ▶ (2) ***sp² hybridisation*** : In this hybridization there is involvement of one *s* and two *p*-orbitals in order to form three equivalent *sp²* hybridised orbitals.
- ▶ (3) ***sp³ hybridisation*** : In this hybridization there is mixing of one *s*-orbital and three *p*-orbitals of the valence shell to form four *sp³* hybrid orbital of equivalent energies and shape.

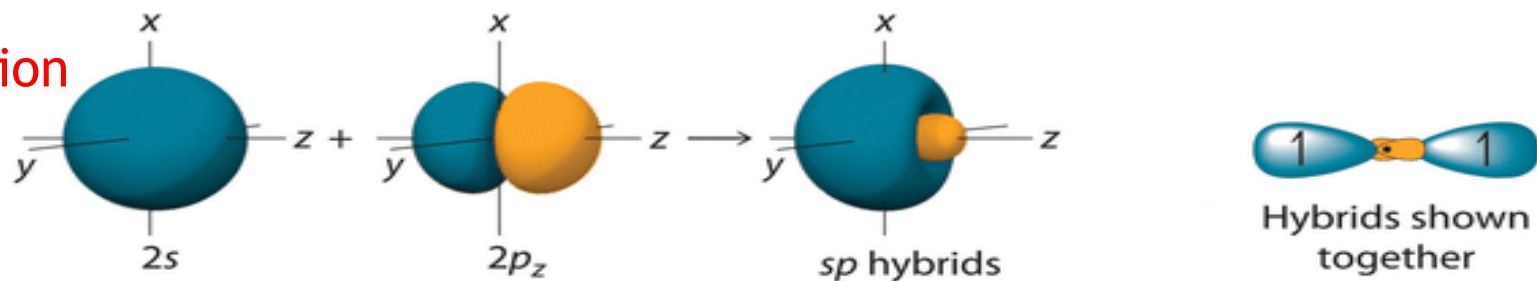
sp^3 hybridisation



sp^2 hybridisation

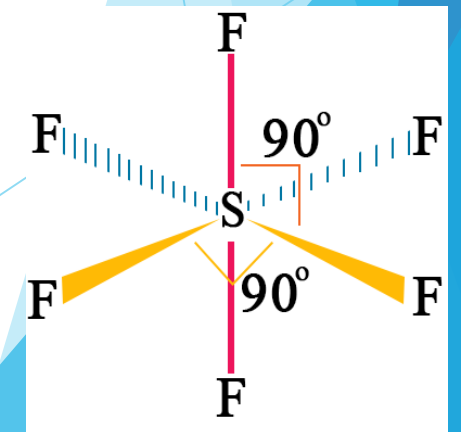
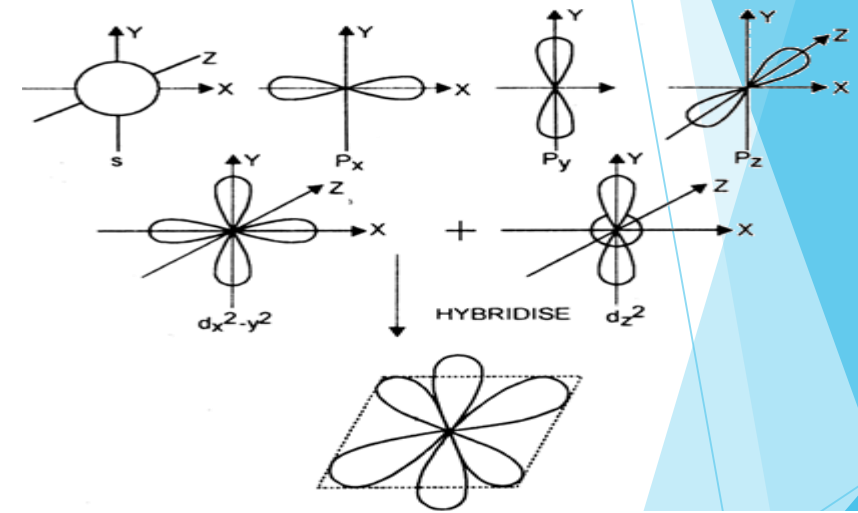
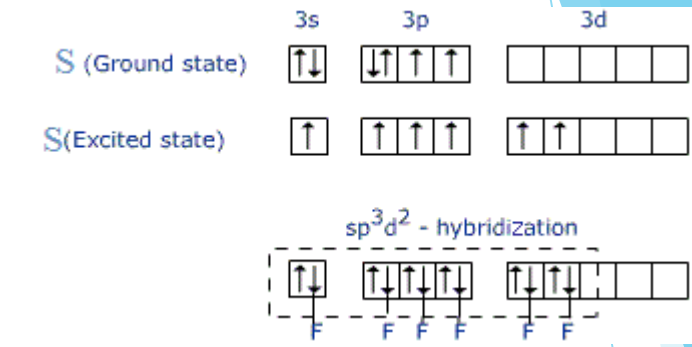
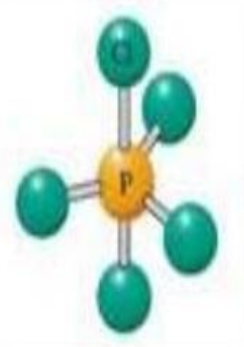
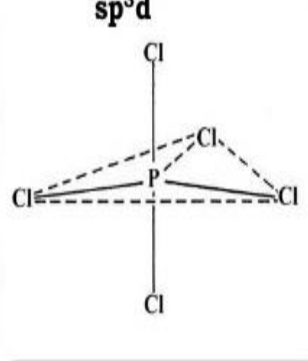
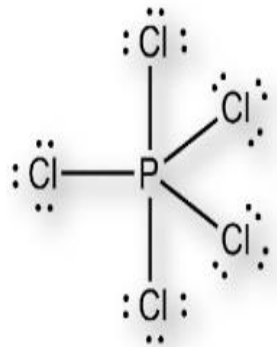
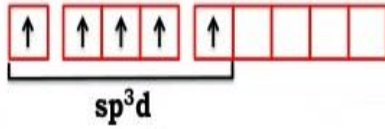
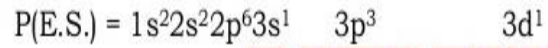
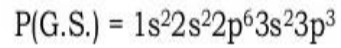


sp hybridisation



Types of Hybridisation involving d-

One 's', three 'p' and one 'd' orbitals of same shell participates to give sp^3d hybrid. with trigonal bipyramidal shape with bond angles 90° & 120° . **Example:** PF_5 & PCl_5 ,



MOLECULAR ORBITAL THEORY

- ▶ **The salient features of this theory are :**
- ▶ (i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- ▶ (ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.
- ▶ (iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus,
- ▶ an atomic orbital is mono centric while a molecular orbital is polycentric.
- ▶ (iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called anti bonding molecular orbital.
- ▶ (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- ▶ (vi) Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- ▶ (vii) The molecular orbitals like atomic orbitals are filled in accordance with the *aufbau* principle obeying the Pauli's
- ▶ exclusion principle and the Hund's rule.

MOLECULAR ORBITAL THEORY

- ▶ **LCAO** : Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals(LCAO) that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below :

- ▶
$$\psi_{MO} = \psi_A \pm \psi_B$$

- ▶ Therefore, the two molecular orbitals σ and σ^* are formed as :

- ▶
$$\sigma = \psi_A + \psi_B$$

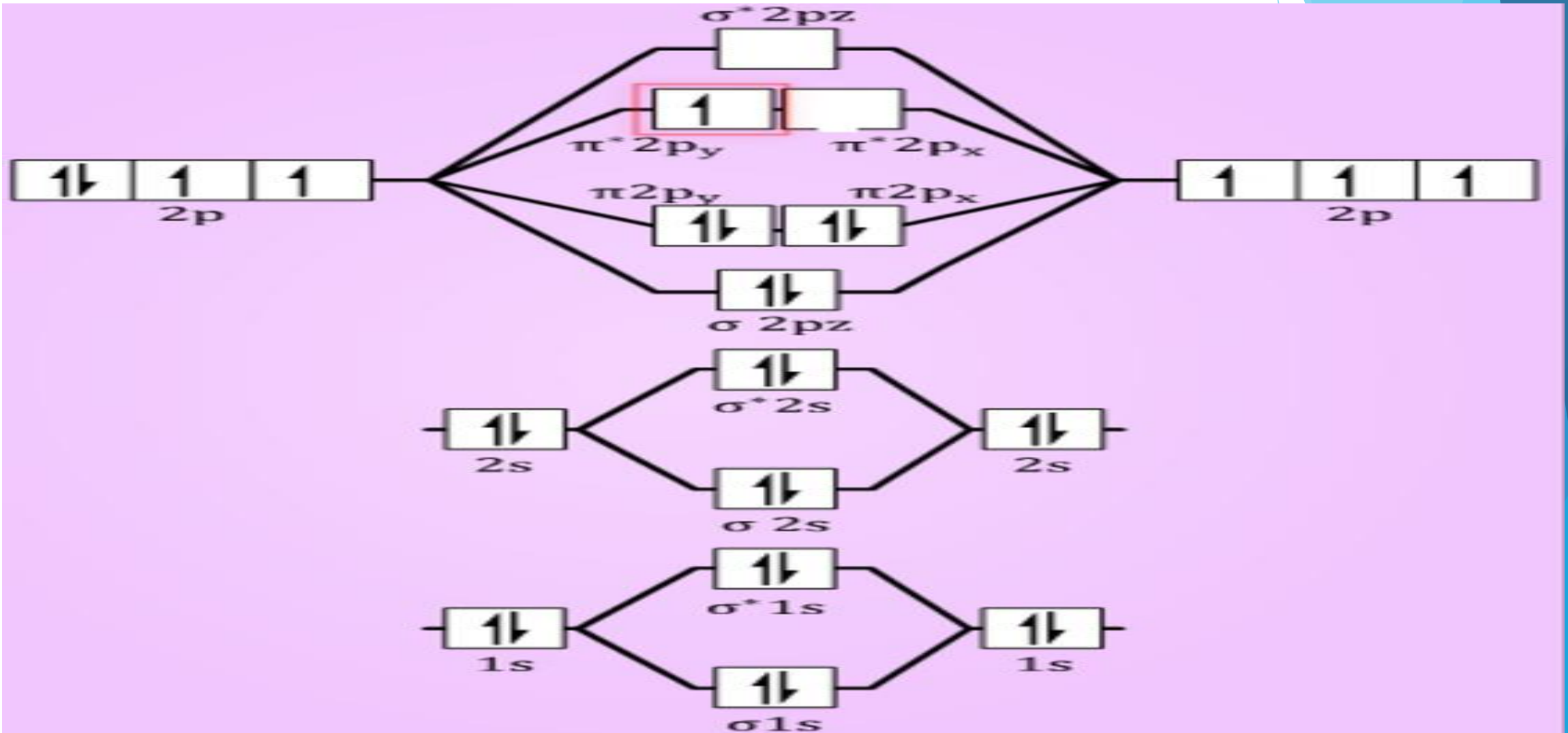
- ▶
$$\sigma^* = \psi_A - \psi_B$$

- ▶ The molecular orbital σ formed by the addition of atomic orbitals is called the **bonding molecular orbital** while the molecular orbital σ^* formed by the subtraction of atomic orbital is called **antibonding molecular orbital**

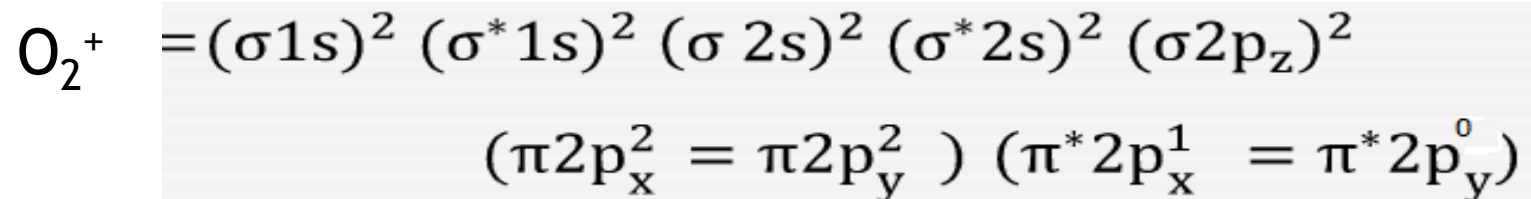
- ▶ The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied:

- ▶ 1.The combining atomic orbitals must have the same or nearly the same energy.
- ▶ 2. The combining atomic orbitals must have the same symmetry about the molecular axis.
- ▶ 3.The combining atomic orbitals must overlap to the maximum extent.

Energy Level Diagram for Molecular Orbitals



Electronic Configuration and Molecular Behaviour



From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

Stability of Molecules: If N_b is the number of electrons occupying bonding orbitals and N_a the number occupying the antibonding orbitals, then (i) the molecule is stable if N_b is greater than N_a , and (ii) the molecule is unstable if N_b is less than N_a . In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable.

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

$$\text{Bond order (b.o.)} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (10 - 5) = 5/2 = 2.5 \text{ (in case of } \text{O}_2^+)$$

Magnetic behavior :

Paramagnetic : If at least one MO has unpaired electron then chemical species is paramagnetic in nature. since here in O_2^+ molecule ion there is one MO i.e. $\pi^* 2p_x^1$ has unpaired electron therefore this molecule ion is paramagnetic in nature.

Diamagnetic : If electrons are paired in all MO then chemical species is diamagnetic.

HYDROGEN

BONDING

▶ Weak force of attraction formed between hydrogen atom and highly electronegative atom like N, O, F is called as **hydrogen bond or hydrogen bonding**. Hydrogen bond is represented by a dotted line (- - -) while a solid line represents the covalent bond.

▶ Types of H-Bonds or bondings :

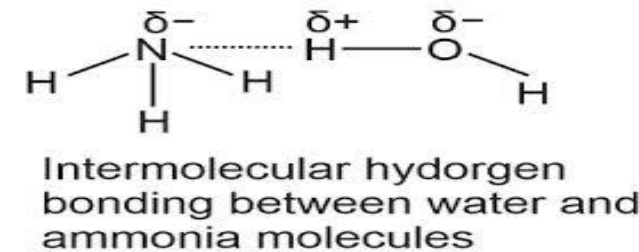
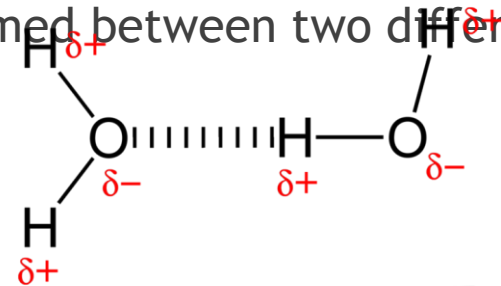
▶ There are two types of H-bonds

▶ (1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds.

▶ Fore example:

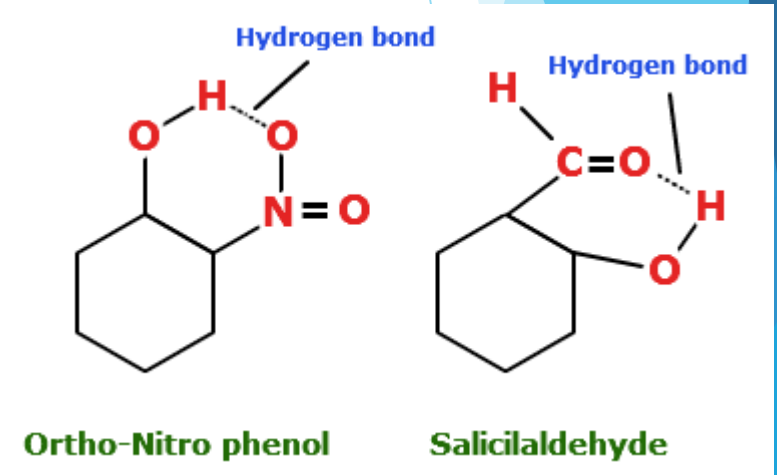
▶ (a) H- bonding between water molecules.

▶ (b) H- bonding between water and ammonia molecules.



HYDROGEN BONDING

- ▶ (2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule.
- ▶ For example,
- ▶ in *o*-nitrophenol and salicylaldehyde
- ▶ Remember : The magnitude of H-bonding depends on
- ▶ the physical state of the compound. It is
- ▶ maximum in the solid state and minimum in
- ▶ the gaseous state. Thus, the hydrogen bonds
- ▶ have strong influence on the structure and
- ▶ properties of the compounds.





THE- END