CHEMICAL BONDING AND MOLECULAR STRUCTURE

MOLECULAR ORBITAL THEORY

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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 O2 molecule and the formation of odd electron molecules or ions such as H~ 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.

Distinction between Atomic and Molecular Orbitals.	
Atomic orbital.	Molecular orbital
1. Atomic orbital is monocentric, i.e., electron cloud extends around the nucleus of a single atom. 2. It is less stable. 3. It has simple shape. - 4. Atomic orbitals are designated as s, p, d, etc.	Molecular orbital is polycentric, i.e., the electron cloud extends around all the nuclei of bonded atoms in the molecule: It is more stable. It has complex shape. Molecular orbitals are designated as $\sigma, \sigma^*, \pi', \pi^*$, 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 functions are added. 2. Its energy is less than the combining atomic orbitals. 3. It increases the electron density between the nuclei. It therefore stabilises the molecule. 4. It has no nodal plane (plane where electron density is zero) 5. It is symmetrical about inter-nuclear axis. 6. Designated by σ, π,8, etc. .	It is formed by linear combination of two atomic orbitals when their wave functions are subtracted. Its energy is more than the combining atomic orbitals. It decreases the electron, density between the nuclei. It therefore destabilises the molecule. It has nodal plane. It is symmetrical about inter-nuclear axis and about a line perpendicular to it. Designated by $\overset{*}{\alpha}, \bar{\pi}, \dot{\delta}$, etc.

Salient Features of Molecular Orbital Theory

(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 or betels. One of which is called bonding molecular orbital and other is called antibonding molecular orbital. These are formed by addition and subtraction of wave functions respectively.

(iii) Molecular orbitals are the energy states of a molecule in which the electrons of the molecule is 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 or betels), 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.

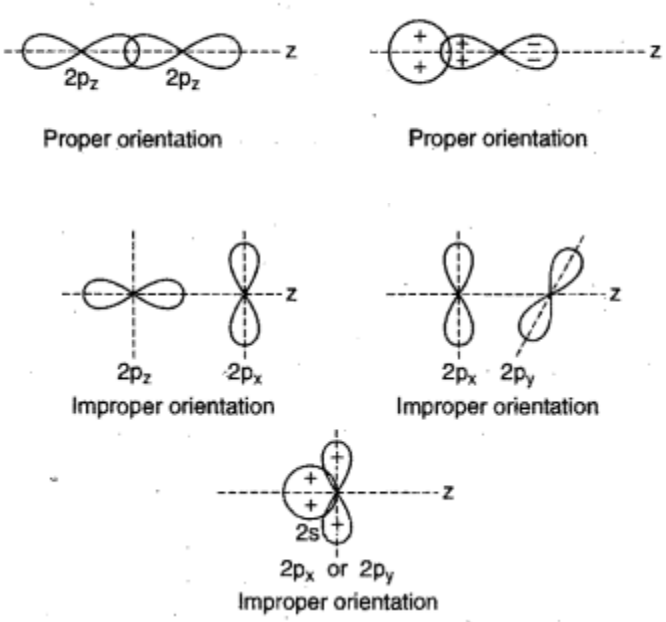
Conditions for Combination of Atomic Orbitals to form Molecular Orbitals

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. Au Is atomic orbital of one atom can combine with Is atomic orbital of another atom or 2s can combine with 2s, 2p with 2 panda so on. Is 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,2pz orbital of one atom can overlap with 2pz orbital of another atom but not with 2px or 2py orbitals because of their different symmetries. Similarly, 2s orbital of one atom can overlap with 2pz orbital but not with 2px or 2py 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.