# MOLECULAR ORBITAL THEORY

The valence bond theory operates on the assumption that when a molecule forms, it results from the interaction between the electron waves of specific atomic orbitals in participating atoms that are only half-filled. These atomic orbitals combine with each other, creating a new, more stable orbital, while the rest of the orbitals on the atoms remain undisturbed, maintaining their individual identities. However, this perspective has its flaws because when one atom's nucleus approaches another, it inevitably influences the electron waves of nearly all the orbitals in the other atom. Additionally, the valence bond theory cannot account for the formation of coordinate bonds, the paramagnetic properties of the O$^2$ molecule, or the creation of odd-electron molecules or ions like the H- ion, where electron pairing doesn't occur.

In contrast, the molecular orbital theory of chemical bonding offers a more rational and practical explanation. This theory, initially proposed by Hund and Mullikan, posits that when atoms come closer together in the process of forming a molecule, all their atomic orbitals are perturbed. These orbitals blend to produce an equivalent number of new orbitals specific to the molecule being formed, known as molecular orbitals. The electrons originally associated with the participating atoms are now considered to move within these molecular orbitals under the influence of all the atomic nuclei involved. Consequently, molecular orbitals are polycentric, defined as regions in space around the combining atoms where there is the highest probability of finding electron density. Molecular orbitals possess varying energy levels and are organized in increasing order of energy, akin to atomic orbitals. The filling of electrons in these molecular orbitals follows principles such as the 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. | Molecular orbital is polycentric, i.e., 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 $\sigma, \sigma^*, \pi', \pi^*$, 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. | 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 $\sigma, \pi$, 8, etc. | Designated by $\overset{*}{\alpha}, \overline{\pi}, \dot{\delta}$, etc. |

## Salient Features of Molecular Orbital

(i) Similar to the valence bond theory, this concept initiates with atomic orbitals, but when atoms approach each other for bonding, their atomic orbitals overlap. This overlap results in both constructive and destructive interference, leading to the creation of molecular orbitals. Consequently, the individual identity of the atomic orbital's fades, and all the electrons within the molecule become associated with these molecular orbitals.

(ii) When two atomic orbitals come into contact, they give rise to two new orbitals known as molecular orbitals, or "betels." These new orbitals are categorized as the bonding molecular orbital and the antibonding molecular orbital. They are formed through the addition and subtraction of wave functions, respectively.

(iii) Molecular orbitals represent the energy states of a molecule, housing the electrons of the molecule.

(iv) The bonding molecular orbital has lower energy compared to the original atomic orbitals involved in the combination, while the antibonding orbital has higher energy than these atomic orbitals.

(v) Only atomic orbitals with similar energies and proper alignment can overlap and form molecular orbitals.

(vi) Electrons residing in the bonding molecular orbital enhance the molecule's stability, whereas electrons in the antibonding molecular orbital contribute to the repulsion between the atomic nuclei.

(vii) Bonding molecular orbitals are typically denoted as $\sigma$, $\pi$, $\delta$, etc., while antibonding molecular orbitals are indicated as $\sigma^*$, $\pi^*$, $\delta^*$, etc.

(viii) Each molecular orbital, whether bonding or antibonding, can hold a maximum of two electrons, and these electrons must possess opposite spins, adhering to Pauli's exclusion principle.

(ix) Molecular orbitals are filled in order of increasing energy, starting with the orbital of the lowest energy, in line with the Aufbau principle.

(x) In cases where molecular orbitals have the same energy (referred to as degenerate or betels), electron pairing only occurs when all of them are singly occupied, following Hund's rule.

(xi) The specific shapes of the molecular orbitals formed are contingent upon the type of atomic orbitals that are combining.

## Molecular Orbital Formation

## Conditions for Combination of Atomic Orbitals to form Molecular Orbitals

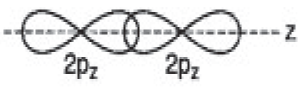
The formation of molecular orbitals by linear combination of atomic orbitals can take place only if the following conditions are fulfilled:

(i) To facilitate the formation of molecular orbitals, it's crucial that the atomic orbitals being combined have similar or closely matching energies. In the case of homonuclear diatomic molecules, like in the example of two gold atoms, the 1s atomic orbital of one atom can effectively combine with the 1s atomic orbital of another atom, and similarly, 2s can pair with 2s, 2p with 2p, and so forth. However, combining dissimilar orbitals, such as 1s with 2s or 2s with 2p, is not feasible due to a significant disparity in energy levels. Nevertheless, these dissimilar combinations can occur in heteronuclear diatomic molecules like AB if the energy difference is relatively modest.

(ii) For the formation of molecular orbitals, it's essential that the atomic orbitals being combined are properly oriented, meaning they exhibit the same symmetry around the molecular axis.

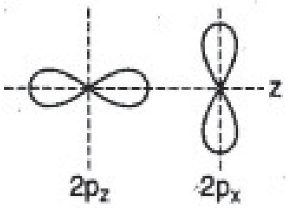
### For example:

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.

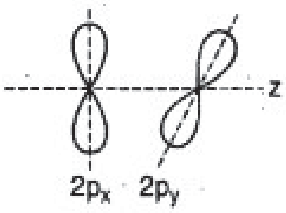


Proper orientation

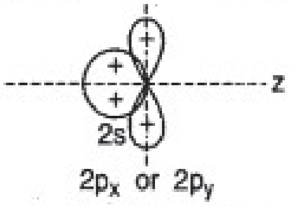
Proper orientation



Improper orientation



Improper orientation



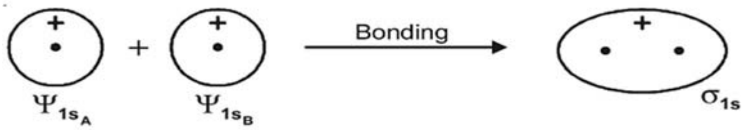
Improper orientation

(iii) It is imperative that the atomic orbitals involved in bonding exhibit a high degree of overlap. The more extensive the overlap, the higher the electron density will be situated between the nuclei within a molecular orbital.

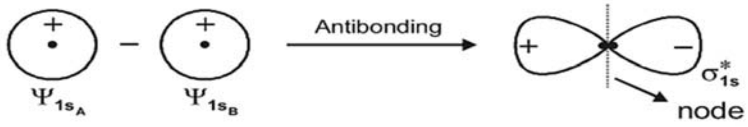
## Types of Molecular Orbital Formed

**S – S overlap (sigma overlap):**

Construction overlap

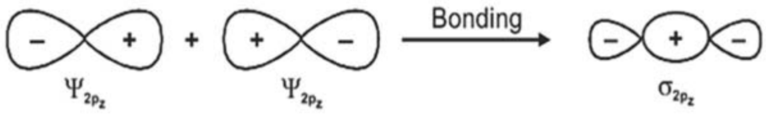


Destructive overlap

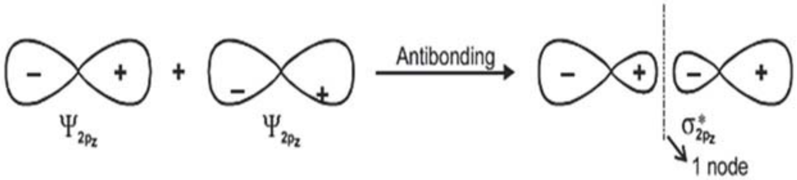


**P – P overlap (sigma overlap):**

Construction overlap

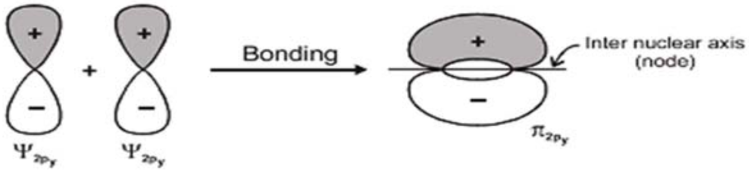


Destructive overlap

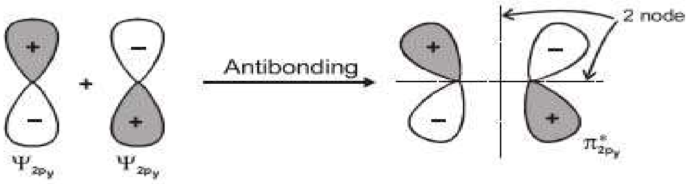


**P – P overlap ($\pi$ overlap):**

Construction overlap



Destructive overlap



## Applications of Bond Order

Consider the number of bonding electrons as $N_b$ and the number of antibonding electrons as $N_a$.

(i) When $N_b$ exceeds $N_a$, the molecule attains stability. This is attributed to the favorable condition where the occupancy of bonding orbitals surpasses that of antibonding orbitals, resulting in a net force of attraction.

(ii) In the scenario where $N_b$ equals $N_a$, the molecule becomes unstable.

The stability of a molecule is directly linked to its bond order; higher bond orders signify greater stability.

Bond length exhibits an inverse relationship with bond order, where an increase in bond order leads to a decrease in bond length.

### Magnetic Character:

The magnetic properties of a system are determined by the presence of paired or unpaired electrons within its molecular structure. Specifically, a system exhibiting exclusively paired electrons is classified as diamagnetic, while a molecule with unpaired electrons is characterized as paramagnetic.

### Example:

$O_2$ is paramagnetic, while $N_2$ is diamagnetic. The rationale behind this behavior can be elucidated through Molecular Orbital Theory (MOT).