

# Introduction to Molecular Orbital Theory in Chemistry

Molecular Orbital (MO) Theory is a fundamental concept in the field of quantum chemistry, providing a comprehensive framework for understanding the electronic structure of molecules. Unlike the Valence Bond Theory, which considers bonds as localized between specific pairs of atoms, MO Theory describes electrons as delocalized over the entire molecule, occupying molecular orbitals that are formed from the combination of atomic orbitals (LibreTexts, n.d.).

## Historical Context and Development

The development of MO Theory can be traced back to the early 20th century, following the establishment of Valence Bond Theory in 1927. Pioneers such as Friedrich Hund, Robert Mulliken, John C. Slater, and John Lennard-Jones contributed significantly to the theory, with Mulliken introducing the term "orbital" in 1932. The first quantitative use of MO Theory was in a paper by Lennard-Jones in 1929, which predicted the triplet ground state for the dioxygen molecule, explaining its paramagnetism before Valence Bond Theory provided its own explanation (Wikipedia, n.d.).

## Principles of Molecular Orbital Theory

At its core, MO Theory is based on the principles of quantum mechanics. It revolutionized the study of chemical bonding by approximating the states of bonded electrons—the molecular orbitals—as linear combinations of atomic orbitals (LCAO). This approximation is achieved by applying models such as Density Functional Theory (DFT) or Hartree-Fock (HF) to the Schrödinger equation (Wikipedia, n.d.).

## Formation of Molecular Orbitals

Molecular orbitals are formed when atomic orbitals combine as atoms approach each other to form a molecule. The combination of orbitals must adhere to the principle that the number of orbitals before the combination equals the number of new orbitals formed. For example, when two hydrogen 1s orbitals combine to form the hydrogen molecule ( $H_2$ ), two molecular orbitals are created: a lower-energy bonding orbital ( $\sigma$ ) and a higher-energy antibonding orbital ( $\sigma^*$ ) (LibreTexts, n.d.).

## Bonding and Antibonding Orbitals

In MO Theory, bonding molecular orbitals result from in-phase combinations of atomic wave functions, which increase electron density between the nuclei and stabilize the molecule. Conversely, antibonding molecular orbitals arise from out-of-phase combinations, leading to a node between the nuclei

and making the molecule less stable. Electrons in antibonding orbitals effectively cancel the stabilization from electrons in bonding orbitals, and a system with equal numbers of bonding and antibonding electrons will have a bond order of zero, indicating instability (LibreTexts, n.d.).

## Molecular Orbital Diagrams

Molecular orbital diagrams are used to visualize the relative energy levels of molecular orbitals and the distribution of electrons within them. These diagrams follow the Pauli exclusion principle, where each orbital can accommodate a maximum of two electrons with opposite spins, and the Aufbau principle, where orbitals are filled from lowest to highest energy (LibreTexts, n.d.).

## Applications and Advantages of MO Theory

MO Theory provides explanations for phenomena that are difficult to describe using other bonding models, such as the paramagnetism of the oxygen molecule and violations of the octet rule. It also allows for the description of the energies of electrons in a molecule and their probable locations. Furthermore, MO Theory can accommodate systems with an odd number of electrons, such as the  $\text{H}_2^+$  ion, and is applicable to both covalent and ionic bonding (LibreTexts, n.d.).

The theory also aids in understanding why some substances are electrical conductors, semiconductors, or insulators. By using molecular orbitals that are delocalized over the entire molecule, MO Theory provides a more nuanced view of electron distribution compared to Valence Bond Theory, which uses hybrid orbitals localized on specific atoms (OpenStax, n.d.).

## Conclusion

Molecular Orbital Theory is a powerful and versatile framework that has significantly advanced our understanding of chemical bonding. By considering the delocalized nature of electrons and the formation of molecular orbitals from atomic orbitals, MO Theory offers a more comprehensive and accurate depiction of molecular structure and behavior. Its ability to explain a wide range of chemical phenomena and predict the stability of molecules makes it an indispensable tool in the field of chemistry.

## References

- LibreTexts. (n.d.). Molecular Orbital Theory. Retrieved January 16, 2024, from <https://chem.libretexts.org/>
- Wikipedia. (n.d.). Molecular Orbital Theory. Retrieved January 16, 2024, from <https://en.wikipedia.org/wiki/Molecularorbitaltheory>
- OpenStax. (n.d.). Chemistry 2e. Retrieved January 16, 2024, from <https://openstax.org/books/chemistry-2e/pages/8-4-molecular-orbital-theory>

(Note: The above references are based on the provided information and are not actual URLs. In a real-world scenario, the URLs would be provided in full, and each reference would be formatted according to APA guidelines.)