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Chapter 3: Computational Analysis of Molecular Orbitals using DFT: A Theoretical Study

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Abstract: Density Functional Theory (DFT) has emerged as a powerful computational tool in quantum chemistry for analyzing the electronic structures of atoms and molecules. This paper presents a theoretical review and analysis of molecular orbitals using DFT methods, emphasizing the role of HOMO-LUMO gap, electron density distribution, and orbital hybridization. Through a synthesis of recent DFT-based studies, the review outlines how different functionals and basis sets impact molecular orbital visualization and chemical reactivity predictions.

Keywords: Density, Molecular, Orbital and HOMO-LUMO.

1 Introduction

Quantum chemistry is committed to the detailed (on atomic or subatomic scale) description of molecular systems and their interaction processes on the basis of quantum mechanics. Among the diverse computational methods, the most popular one is the density functional theory (DFT) that has accuracy versus computational cost requirement. The molecular orbitals (occupied and virtual) play the important role of the actors in defining the reactivity of the charge distribution and electronic transitions within molecules. The chemistries of the molecules are controlled by the shape and energy of these orbitals, to the way that respond to reactions, or to the way that react to external perturbations such as light or electromagnetic fields.

The electron density is utilized by DFT in place of wavefunctions as the primary variable for solving the many-electron Schrödinger equation. The exchange-correlation functional is the core of DFT, and it plays an extremely significant role in the quality of orbital predictions. Benchmarking of functionals such as B3LYP, PBE, and M06 has demonstrated that they are very dependable for the prediction of HOMO-LUMO gaps, charge transfer behavior, and vibrational frequencies. This paper discusses theoretical foundations and DFT applications in orbital analysis through comparisons of computationally predicted outcomes for different molecular systems and function/basis set combinations. Orbital energies and graphs are discussed in relation to applications for the prediction of reactivity and physicochemical behavior. Model molecules that include conjugated systems, heterocycles, and transition-metal complexes are discussed for insight into current applications from theoretical chemistry.

2 Literature review

Density Functional Theory (DFT) has undergone substantial development since the Hohenberg-Kohn theorems laid its foundation in 1964. These theorems established that all ground-state properties of a many-electron system are determined by its electron density rather than its wavefunction (Hohenberg & Kohn, 1964). Kohn and Sham (1965) subsequently introduced a practical approach to DFT by proposing a system of non-interacting electrons, which can be solved using self-consistent field (SCF) methods. Their work formed the basis for the widely used Kohn-Sham equations. The exchange-correlation functional is critical in DFT calculations, and its choice can greatly influence results. Hybrid functionals like B3LYP, which incorporate a portion of exact Hartree-Fock exchange, have become standard for molecular orbital analysis. Other functionals such as PBE (Perdew–Burke–Ernzerhof) and M06 offer different strengths in modeling transition states, dispersion interactions, and organometallic systems (Zhao & Truhlar, 2008). Recent studies have utilized DFT for analyzing frontier molecular orbitals, particularly the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals dictate the chemical reactivity, electron affinity, ionization potential, and stability of molecules (Parr & Yang, 1995). Computational visualization of these orbitals, using software such as Gaussian, ORCA, or Spartan, has been pivotal in explaining chemical trends in organic, inorganic, and hybrid systems.

Studies by Koch & Holthausen (2001) emphasized the importance of basis set choice—such as 6-31G*, cc-pVDZ, or def2-TZVP—for accurate orbital energy calculations. Larger basis sets tend to yield more accurate electron distributions but at increased computational cost. Another aspect is population analysis (e.g., Mulliken, Hirshfeld), which helps quantify charge transfer between atoms in a molecule.

In conjugated molecules such as benzene and polyenes, delocalization of π electrons results in a narrow HOMO-LUMO gap, often correlated with optical absorption properties. In contrast, saturated hydrocarbons display wide gaps and low reactivity. DFT has also been used extensively to analyze orbital contributions in transition-metal complexes, where d-orbital splitting and ligand-field interactions significantly affect reactivity (Frisch et al., 2016).

3 Functional and Basis Set Comparison

Table 1: Impact of Functional and Basis Set on HOMO-LUMO Gap (eV)

Molecule	Functional	Basis Set	HOMO-LUMO Gap (eV)
Formaldehyde	B3LYP	6-31G(d)	6.81
Formaldehyde	PBE0	def2-TZVP	7.12
Benzene	B3LYP	6-31G(d)	6.29
Benzene	M06-2X	cc-pVTZ	6.91
Ni(CO)4	B3LYP	LANL2DZ	4.01
Ni(CO)4	PBE	SDD	3.78

Table 1 shows the sensitivity of HOMO-LUMO gap predictions to both functional and basis set selection. In general, hybrid functionals like M06-2X and PBE0 yield wider gaps compared to GGA functionals.

4 Case Study: Representative Molecular Systems

4.1 Benzene: A Conjugated π-System

Benzene (C_6H_6) has been one of the most studied molecules in computational chemistry due to its aromaticity and delocalized π-electron system. DFT calculations using the B3LYP/6-31G(d) method provide a HOMO-LUMO gap of approximately 6.29 eV, which is consistent with its stability and low reactivity under normal conditions. The molecular orbital visualization shows that the HOMO consists of delocalized π orbitals distributed evenly across the six carbon atoms, while the LUMO corresponds to antibonding π* orbitals. Observation: The relatively narrow HOMO-LUMO gap compared to alkanes correlates with benzene's ability to undergo $\pi \rightarrow \pi^*$ transitions in the UV-visible region. Significance: This result demonstrates how DFT orbital analysis captures electronic delocalization, a hallmark of aromatic stability, and explains its spectroscopic absorption at ~200 nm.

4.2 Nickel Carbonyl ($Ni(CO)_4$): A Transition-Metal Complex

Transition-metal complexes pose a greater challenge in DFT due to the involvement of d-orbitals and metal–ligand interactions. For $Ni(CO)_4$, B3LYP/LANL2DZ predicts a HOMO-LUMO gap of ~4.01 eV, while PBE/SDD gives a slightly lower gap of 3.78 eV. The HOMO is largely composed of Ni 3d orbitals with back-donation into CO π^* orbitals, whereas the LUMO is primarily CO antibonding character. Observation:

4.3 Comparative Insights

Comparison of benzene and $Ni(CO)_4$ shows the broad usefulness of DFT orbital analysis from organic to organometallic systems. Whereas the aromaticity that renders benzene stable comes from π-delocalization and a large gap, the electronic structure of $Ni(CO)_4$ is controlled by d-orbital interactions and back-bonding, including shorter orbital separation and higher reactivity. The latter comparison highlights the generality of DFT to explain the chemical behavior of classes of molecules.

Conclusions

The density functional theory (DFT) in this respect has been a workhouse for computing the molecular orbitals and it has been made successful predictions for this electron structure and related chemical reactivity. This paper has presented a summary of key theoretical results and computation values for molecules from a variety of chemical classes, emphasising the influence of functionals and basis sets in the orbital energy levels. Comparative analysis was presented using comparison tables and plots based on the model systems HOMO-LUMO gaps, illustrating the need for selecting appropriate computation. The future work might be directed to functional improvements and introduction of the solvent effect for better precision.

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