

THE ROLE OF ELECTRONIC STRUCTURE AND BAND GAP IN THE OPTICAL PROPERTIES OF CONDUCTING POLYMERS: A QUANTUM- CHEMICAL PERSPECTIVE

Tog'ayev Abdulatif O'ktam o'g'li

Uzbekistan National University

atogayev@gmail.com

Abstract

Conducting polymers are promising materials for optoelectronic devices, chemical sensors, flexible electronics, and energy-conversion technologies because of their tunable electronic and optical properties. Understanding the relationship between electronic structure and optical absorption is essential for explaining their behavior and guiding the development of functional polymeric materials. This thesis examines the theoretical relationship between frontier molecular orbitals, electronic excitation energies, and optical absorption in three representative conducting polymers: polyaniline, polythiophene, and poly(3,4-ethylenedioxythiophene). Particular attention is given to density functional theory (DFT) and time-dependent density functional theory (TD-DFT) as complementary approaches for investigating molecular electronic states and optical transitions. The discussion emphasizes that the HOMO–LUMO energy difference is a useful descriptor of molecular electronic structure but should not be interpreted as directly equivalent to the optical excitation energy. Molecular conjugation, backbone conformation, oxidation state, and doping can substantially influence the electronic states responsible for light absorption. Furthermore, finite oligomer models provide useful molecular-level insights but cannot fully represent the structural and intermolecular complexity of bulk polymeric materials. The analysis highlights the importance of combining quantum-chemical calculations with spectroscopic evidence to obtain a more reliable understanding of structure–property relationships in conducting polymers.

Keywords: Conducting polymers, quantum chemistry, density functional theory, TD-DFT, HOMO–LUMO energy gap, optical absorption, conjugation, electronic structure.

Introduction

Conducting polymers combine the processability and structural versatility of polymeric materials with electronic properties arising from conjugated molecular backbones. Their optical behavior is strongly associated with the distribution of electronic states and the transitions induced by electromagnetic radiation. Polyaniline, polythiophene, and PEDOT are particularly relevant examples because their different molecular architectures and responses to doping produce distinct electronic and spectroscopic characteristics.

Quantum-chemical methods provide a theoretical framework for investigating these relationships. DFT can be used to examine molecular geometry and frontier orbitals, while TD-DFT enables the theoretical analysis of excited-state energies and optical transitions. These approaches help interpret absorption spectra and investigate how molecular structure influences optical response.

Main Discussion

The electronic structure of conducting polymers is governed by π -electron conjugation along their molecular backbones. Greater effective conjugation can modify the distribution of electronic states and the energies of accessible transitions. However, the relationship is influenced by molecular geometry, chain length, and the chemical state of the polymer.

In polythiophene, backbone conformation and oligomer length are important factors in determining electronic delocalization. In polyaniline, oxidation and protonation states affect charge distribution and optical absorption. In PEDOT, doping and the formation of polaronic or bipolaronic states can introduce additional electronic transitions that are not adequately described by a neutral molecular model alone.

An important consideration is the distinction between the HOMO–LUMO energy difference and the optical excitation energy. The former describes the separation between selected molecular orbital energies, whereas the latter relates to an electronically excited state. Their relationship depends on the computational method and the characteristics of the excited state. Consequently, optical properties should be evaluated using excitation energies and transition intensities, together with appropriate experimental evidence where available.

DFT and TD-DFT therefore offer complementary rather than interchangeable information. Their combined application can improve the interpretation of ultraviolet–visible absorption spectra, provided that the molecular model, oxidation state, and computational assumptions are clearly defined.

Conclusion

The electronic structure of conducting polymers provides a fundamental basis for understanding their optical properties. The comparison of polyaniline, polythiophene, and PEDOT demonstrates the importance of conjugation, molecular conformation, oxidation state, and doping in determining electronic transitions. DFT and TD-DFT can support the interpretation of these effects by providing complementary information about molecular orbitals and excited states. Nevertheless, calculated molecular properties should not be directly equated with bulk optical behavior without considering intermolecular interactions and structural complexity. Integrating quantum-chemical calculations with spectroscopic measurements represents a valuable strategy for understanding conducting polymers and guiding the design of materials for optoelectronic applications.

References

1. Hohenberg, P., & Kohn, W. (1964). Inhomogeneous electron gas. *Physical Review*, 136, B864–B871. <https://doi.org/10.1103/PhysRev.136.B864>

2. Kohn, W., & Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. *Physical Review*, 140, A1133–A1138.
<https://doi.org/10.1103/PhysRev.140.A1133>
3. Runge, E., & Gross, E. K. U. (1984). Density-functional theory for time-dependent systems. *Physical Review Letters*, 52, 997–1000.
<https://doi.org/10.1103/PhysRevLett.52.997>
4. Zozoulenko, I., et al. (2019). Polarons, bipolarons, and absorption spectroscopy of PEDOT. *ACS Applied Polymer Materials*, 1(1), 83–94.
<https://doi.org/10.1021/acsapm.8b00061>
5. Sahalianov, I., et al. (2020). UV-to-IR absorption of molecularly p-doped polythiophenes with alkyl and oligoether side chains: Experiment and interpretation based on density functional theory. *The Journal of Physical Chemistry B*, 124(49), 11280–11293.
<https://doi.org/10.1021/acs.jpcc.0c08757>