Comparison of DFT Basis Sets for Organic Dyes

Kaden Shaw, Maia Ketteridge, Lan Li
Micron School of Materials Science and Engineering
Boise State University, Boise, ID 83725
sha17016@byui.edu

BOISE STATE UNIVERSITY

1. Introduction

Density Functional Theory (DFT) and Time-Dependent (TD) DFT calculating excitonic properties of dyes.

- When molecules absorb light, they form an electron-hole pair, called an exciton.
- When the exciton recombines, the molecule releases a photon (fluorescence).
- Understanding excitonic behavior will help us build better organic photovoltaics (solar cells), biological labeling dyes, and quantum information systems.

Much work has been done with the Cyanine (Cy) and Squaraine (Sq) dyes[1,2] This work is to test with different basis sets (i.e., a set of basic functions combined linearly to approximate molecular orbitals) to predict dye properties and substituent effects.

- Current work done with these dyes used the basis set 6-31G+(d,p) (abbr. G6), which cannot compute atoms beyond the 3rd row of the periodic table.
- Lanl2DZ (DZ) and Lanl2MB (MB) basis sets can calculate most of the periodic table.
- This work is to compare the calculations of transition dipole moments and static dipole differences of different substituted dyes with basis sets G6, DZ and MB.

2. Computational Methods

All DFT calculations were performed using the Gaussian 16 software package[3], using the following parameters:

- Exchange Correlational Functional: M062X
- Basis Sets: 6-31+g(d,p) (G6), Lanl2DZ (DZ), Lanl2MB (MB)
- Dyes: Substituted Cy5 and Sq dyes (Fig 1a & b)

The calculated results include:

- Static dipole difference Δd between ground state and excited state
- Transition dipole moment μ

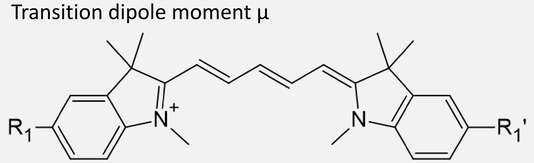

Fig 1a: Cy5 structure, substituents (H, Cl, $N(CH_3)_2$, NO_2, $(NO_2)_2$, and OCH_3) are added at R_1 and R_1'

2. Computational Methods, cont.

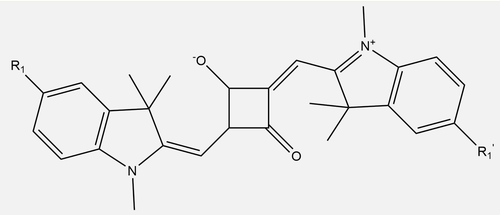

Fig 1b: Sq structure, substituents (H, Cl, $N(CH_3)_2$, NO_2, $(NO_2)_2$, and OCH_3) are added at R_1 and R_1'

Fig 2: General workflow for deriving dye properties with DFT and TDDFT

3. Results

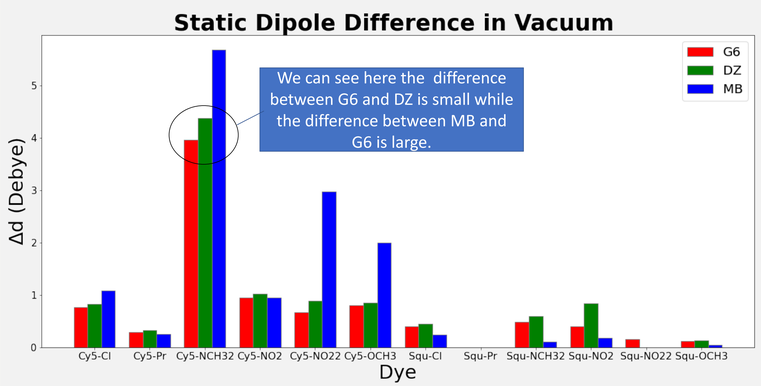

Fig 3a: Static Dipole differences Δd of 12 different dyes and 3 different basis sets

3. Results, cont.

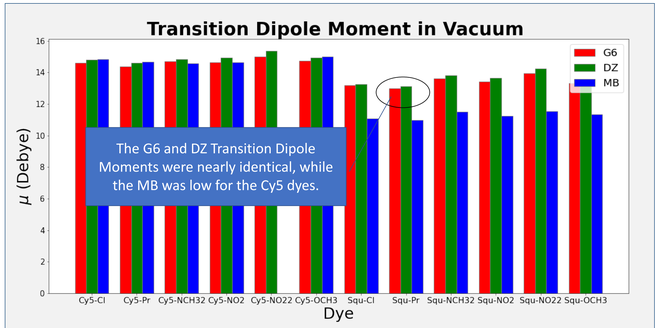

Fig 3b: Transition Dipole Moments μ of 12 different dyes and 3 different basis sets

4. Conclusions and Future Work

- Basis sets G6 and DZ could provide similar results in static dipole difference and transition dipole moment.
- Basis set MB did not demonstrate an ability to accurately reproduce literature results.
- For future work, basis set DZ can be used to predict the excited state properties of dyes besides basis set G6.
- Further validation with experimental data is needed.

5. References and Acknowledgments

Scan the code above to read more!

[1] Biaggne, A., Knowlton, W. B., Yurke, B., Lee, J. & Li, L. Substituent Effects on the Solubility and Electronic Properties of the Cyanine Dye Cy5: Density Functional and Time-Dependent Density Functional Theory Calculations. Molecules 26, 524 (2021). || [2] Barcenas, G. et al. First-principles studies of substituent effects on squaraine dyes. RSC Adv. 11, 19029–19040 (2021).|| [3] Gaussian 16, Revision C.01 M.J. Frisch, et .al

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