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Review of Ph.D. thesis entitled
„Theoretical Investigation of Light-Driven Electron Transfer in Molecular Photosensitizers."

The Ph.D. thesis I was asked to review was written by Aoussaj Sbai. The thesis is written in English and entitled „Theoretical Investigation of Light-Driven Electron Transfer in Molecular Photosensitizers." The Ph.D. project was performed under the supervision of Professor Julien Guthmuller.

The thesis topic is computer simulations exploiting state-of-the-art approaches, namely a few Density Functional Approximations (DFAs) and the Equation of Motion Coupled Cluster Singles and Doubles (EOM-CCSD) model within the DLPNO approximation, and their application to elucidate various BODIPY-based hydrogen production cycles, ultimately addressing how electron-transfer pathways affect efficiency. One major focus is the description of different relaxation pathways, including neutral and reduced dye-cycle variants, and the effects of substitution and solvent on excited-state populations and various relaxation rates. The candidate addresses these questions using quantum chemistry. Most importantly, this task becomes remarkably difficult when electronically excited states are considered, as most quantum chemical methods are developed for electronic ground states and aim for so-called chemical accuracy. Excited-state models are typically more expensive and more complex, with larger error margins (up to 0.5 eV). Furthermore, the thesis focuses on "real-life" models, comparing theoretical predictions with experimental results. For that purpose, "real-life" conditions need to be simulated, like environmental or solvation effects, a wide range of excitation energies, and a series of excited state properties (excited state characters, structural relaxation effects, oscillator strengths, or rate constants) to allow for a sound comparison to experiment. The reliable modeling of excited states and excited-state properties in such "real-life" cases is challenging, primarily because most quantum-chemical excited-state methods are either too expensive or lack implementations for excited-state property calculations. The candidate tackles this difficult task using mostly various DFAs, the workhorse of quantum chemistry, and assesses the validity of their calculations against (their own) DLPNO-EOM-CCSD and (literature-based) RASPT2 reference data. The critical aspect of his thesis consists of 4 parts: (1) Benchmark studies of neutral BODIPY excited states and relaxation pathways to validate a robust theoretical approach used throughout the thesis, simultaneously probing solvent effects, structure relaxation, and substitution effects. (2) Elucidation of the involvement of the reduced doublet state of BODIPY dyes in H_2 reduction. (3) The accurate prediction of absorption and emission spectra and rate constants, including a sound theoretical methodology to reproduce experimental spectra. (4)

Application of the acquired know-how and methodology to study two AIE molecules to increase solar cell efficiency in perovskite solar cells.

The Ph.D. thesis is divided into eight main chapters, a Polish and an English version of the summary, an abstract, an acknowledgment, a list of abbreviations, and a bibliography, totaling 122 pages. The first chapter provides context and motivation, laying the stage for light-driven water splitting as a clean hydrogen source. It also stresses the importance of organic dyes as photosensitizer alternatives. Especially, BODIPY is introduced as a challenging example featuring multiple activation and deactivation pathways.

The second chapter provides a brief overview of BODIPY as a promising candidate for rational molecular design to tune charge transfer (CT), energy transfer, and triplet-state population. It also provides a concise review of previous studies involving BODIPY.

Chapter 3 presents a more in-depth introduction (about 45 pages) to quantum mechanics and quantum chemical approaches, starting with its early foundations and sketching some relevant topics, such as Hund's rule, the Hückel model, the Born-Oppenheimer approximation, Hartree-Fock theory, basis sets, MP2 and CC theory, TDDFT, solvation models, and the calculation of rate constants. Despite its length, this chapter provides the theoretical foundations of all investigated methods and approaches.

In Chapter 4, the candidate studies the excited states and relaxation pathways of neutral BODIPYs. Specifically, they focus on more, higher-lying states than previously reported in the literature to provide a representative excited-state spectrum. Among the computational methods, four DFAs were selected, and their performance (in vacuo) was compared with DLPNO-STEOM-CCSD reference data, where MN15 turned out to be, on average, the best-performing DFA. Based on these results, the candidate further assesses the influence of solvation and substitution effects on excitation energies and the effect of molecular excited-state geometries on electron transfer and catalyst performance. As expected, CT states are most affected by environmental and substitution effects, while substitution effects affect the populations of various CT states, thereby determining catalytic activity. The results of this chapter have been published in a peer-reviewed journal.

Chapter 5 extends the previous study and examines the reduced doublet state of BODIPY dyes and their role in hydrogen reduction. Their theoretical results (obtained with MN15 and two double-hybrid DFAs) are compared with RASPT2 reference data reported in the literature. They again focus on substitution and solvation effects on excited state properties (energies, state ordering, and oscillator strengths). This chapter demonstrates that CT states are challenging to describe (due to spin contamination) and sensitive to structural rearrangements, whereas substitutions affect catalytic activity (either by releasing electrons to the catalyst or by reducing turnover rates).

Chapter 6 scrutinizes how reliable, that is, how well they reproduce experimental results, absorption and emission spectra can be determined using BODIPY as a test case. They provide a deep analysis of normal modes and how they show up in the spectrum. Most importantly, they

present a robust numerical recipe for calculating absorption and emission spectra at various temperatures, using a range of harmonic models.

Chapter 7 summarizes the candidate's contribution to a joint project with an experimental group on perovskite solar cells. Their goal was to ultimately increase the solar cell efficiency by studying two AIE molecules. They use the computational machinery from the previous chapters to model the absorption and emission spectra of these two compounds, having reasonable agreement with experiment and hence demonstrating the validity of their approach.

Chapter 8 briefly summarizes all aspects of the thesis, including methodology, numerical results, and an outlook on future work.

In general, the thesis is well written. In my opinion, the language is clear and understandable. Sentences are coherent and concise. The list of references is acceptable for a Ph.D. thesis. Overall, the thesis is complete and well-rounded, with chapters that build logically on each other and guide the reader through a series of computational studies while "building a story."

The vital parts of the thesis include the following:

- Although almost half of the thesis is dedicated to a review and summary of the literature, it provides the fundamental background on the approaches used, which are required to follow and understand the remainder of the thesis, namely the numerical studies and the visualization of the results.
- The Ph.D. candidate developed a numerical recipe that allows for reproducing experimental absorption and emission spectra and predicting various rate constants. This might be of considerable interest for future studies on related compounds or problems.
- They elucidate how environmental effects influence absorption and emission spectra and the corresponding excitation types (local vs. CT). Furthermore, they discuss the structure-property relationships in BODIPY dyes, which can be exploited to tune the catalytic activity of organic photosensitizers. Such knowledge is essential for steering and optimizing device performance.
- Their numerical study highlights the importance of the T_2 state for ISC, challenging the general assumption of an S_1-to-T_1 transition.
- All essential graphs, figures, and tables are included in the thesis, and numerical data properly support the discussion. However, figures could feature a higher resolution.

In light of the aforementioned positive aspects of this thesis, I have only a few general remarks considering its weak parts and questions that have not been addressed:

- The theory part lacks some diligence:
  - $|m_l| < l$ should be $|m_l| \leq l$
  - On page 28: $r_{12} = r_{12}$ is obsolete and not what was intended
  - in eq (3.29), the exchange operator is incorrect
  - eq (3.59): E_0-E_ij^ls does not agree with the definition in the next line
  - eq (3.60): the "<>" notation can be confused with the Physicist's notation of ERI.
  - eq (3.61) misses the E_0^(0) term
- Section 5.3 repeats computational details.

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My major criticism concerns the following:

- What is the point of using small basis sets like def2-SVP, especially when using DFAs? Excited-state calculations are typically very much basis-set dependent. Using the larger TZ-quality basis set yielded significant changes compared to the SVP counterpart.
- The computational details do not specify which DLPNO parameters were used or which QC package was used for the calculations. In general, the set of DLPNO parameters might strongly affect the final results, especially for excitation energies.
- There is no clear statement on how the CT states are identified. DFT or DFAs typically provide delocalized orbitals, which makes it difficult to assign excited states to molecular domains.
- A spin contamination of more than 1.0 for doublet states is significant. And conclusions need to be drawn carefully.

Despite my criticism above, I definitely confirm that this thesis meets the statutory demand for an original solution to a scientific problem. Indeed, no quantum chemistry approach can currently guarantee a balanced description of ground and excited states. Even more challenging are excited-state properties, as most excited-state methodologies either do not allow property calculations or make them computationally expensive. Moreover, providing robust numerical recipes that reproduce experimental spectra is urgently needed. Furthermore, structure-property relationships, especially for excited states, are essential for fine-tuning device performance, thereby accelerating the design of new functional materials. To tackle these problems, one requires fundamental knowledge of the mathematical aspects of quantum chemistry, the skill to understand the physical and chemical nature of the problem, and the ability to perform scientifically sound numerical simulations. The material presented in Chapters 4 to 6 represents an important step toward more reliable modeling of organic dyes and their properties, simultaneously elucidating how BODIPY-based dyes can be tuned to improve catalytic behavior. This is an undoubtedly substantial contribution to the field. Although the Ph.D. candidate published only 2 peer-reviewed papers, which might seem below average in this field of study, the content of this thesis and the amount of QC calculations performed make up for it, especially considering the required workload to study excited-state properties.

To sum up, I rate the work highly, and hence, *in accordance with Art. 191 of the Act of July 20, 2018, on Higher Education and Science, the condition for admitting a candidate for a doctoral degree to the defense*, **apply for admission to further procedural stages of the dissertation**.

Sincerely,

Podpis jest prawidłowy

Digitally signed by Katharina Boguslawski; UMK w Toruniu
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Katharina Boguslawski

Prof. dr hab. Katharina Boguslawski