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Hybrid Simulations of Transient Absorption Spectra

Photochemical reactions – chemical reactions brought about by the action of light – occur wherever on Earth the light of the Sun reaches, from the atmosphere to hundreds of meters deep into oceanic waters. One of the most important methods to study these processes in the laboratory is transient absorption (TA) spectroscopy. In this technique, a first laser pulse (the so-called pump) triggers a photochemical reaction in the sample, and then a second laser pulse (the probe) is used to monitor its progress. An inherent complication of this method is that TA spectra are often difficult to interpret, which necessitates the use of computer modeling to aid in their analysis. However, the simulation of TA spectra of large molecules remains very challenging.

In this project, I will address this issue by developing a new, hybrid algorithm for the computer simulation of TA spectra from first principles (without recourse to experimental data). The novelty of my approach is that the two main stages of the overall simulation will be done at different levels of approximation, achieving an optimal compromise between the usage of computing time and accuracy. The computer program implementing my algorithm will be released as free and open-source software, enabling it to be used by other researchers.

Moreover, I will apply the hybrid method to some unresolved questions in photochemistry where I expect it will yield new insights. The first problem that I have in mind is the photophysics of fluorescent probes based on two aromatic moieties connected with an acetylene “bridge.” Compounds of this class have potential applications as fluorescent probes for the detection of amyloid beta aggregates – protein deposits whose accumulation in the brain is related to Alzheimer’s disease. Unfortunately, little is known about the behavior of these compounds in excited electronic states. Within the framework of this project, I will employ the hybrid method to interpret the available spectroscopic data on these compounds. In doing so, I explain the nature of their interactions with amyloid beta aggregates.

The second problem that I will address is the photochemistry of the nitronaphthalenes, a pair of compounds which occur in the environment as byproducts of combustion, and which are known to be harmful to human health (mutagenic and carcinogenic). The importance of their photochemistry is due to the fact that the main process responsible for eliminating them from the environment is decomposition under the action of solar light. Despite extensive spectroscopic studies, the key aspects of this process remain the subject of debate. I will simulate the TA spectra of the nitronaphthalenes with the use of my hybrid algorithm, and use the simulation results to clear up the controversy surrounding their photochemistry.