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Simulating Photochemical Processes with Approximate Methods

Preface

Computers have been used in chemical research ever since they emerged in the 1950s. Using computations to predict the outcome of reactions or the properties of molecules bears great potential to design new compounds, catalysts, and functional materials. This way, time and resource demanding experiments could potentially be avoided. Deriving predictions from so-called machine learning models that rely on existing data is becoming increasingly popular. However, these are still hampered by the shortage of suitable reference data. Different from that, computational physical models rely only on the laws of physics and are, in principle, capable of describing arbitrary chemical problems. Applied to molecules, this eventually leads to the field of quantum chemistry where the laws of quantum mechanics are used to compute the energy and other properties of a molecule. The resulting equations can be implemented in computer programs and solved for a variety of chemical problems. However, the simulation of large molecules and many chemical phenomena can quickly become prohibitively expensive. Our research is centered around enabling predictive simulation with efficient quantum chemical models. Of particular interest to our group is the simulation of photoinduced physical and chemical processes.

Predictive Quantum Chemical Simulations of Molecules under Equilibrium Conditions

The internal energy of a molecule is an extensive quantity. As such, its magnitude grows linearly with the system size. However, the complexity to calculate the internal energy of a molecule with physical models grows non-linearly with the system size. On the one hand, one needs to solve the electronic Schrödinger equation to compute the molecular energy for a given atomic arrangement. Various approximations to this problem have been presented by theoretical chemists since the advent of quantum mechanics in the 1920s. Still, the most efficient models retain a formal cubic scaling with the system size: That means, if we double the system size, the computation will take

at least eight ($=2^3$) times longer. On the other hand, the number of possible molecular conformations is also growing exponentially with the system size. From all possible conformers, it is necessary to identify the most stable ones to accurately compute the molecule's internal energy. This requires screening of many conformers and determining their energies, which is currently impossible with accurate electronic structure theory methods, due to their computational demands. Consequently, significantly faster though more approximate methods are employed for this purpose. Classical force fields and so-called semi-empirical quantum chemical methods are, nowadays, established choices since they are several orders of magnitude faster than *ab initio* electronic structure theory methods. After the conformational sampling, the latter can be applied to the much smaller set of structures to compute energies and other properties of those molecules. This interplay between comparably inaccurate semi-empirical and high-level quantum chemical methods, mostly from the realm of density functional theory, has achieved a level of sophistication that enables predictive simulation of thermodynamic and spectroscopic properties for most molecules with up to 200 atoms.

This achievement was recently enabled through the development of suitable semi-empirical quantum chemical methods. Here, rather severe approximations are made to the energy expressions, which may partially be compensated for by introducing empirical parameters. The latter are generally non-trivial to determine. Hence, semi-empirical quantum chemical methods were not available for many chemical elements and, furthermore, have been very limited with respect to their accuracy. In 2019, the semi-empirical electronic structure theory method GFN2-xTB was developed [1]. Through its design, this method could be parametrized for all elements of the periodic table through radon. In comparison to related methods, it includes an improved treatment of electrostatics through the inclusion of higher multi-pole interactions, leading to an improved description of molecular structures and intermolecular energies. This method is now an integral part of the aforementioned conformational exploration procedures and has, hence, played a key role in enabling predictive quantum chemical simulations of molecules under equilibrium conditions.

Simulation of Photophysical and Photochemical Processes

However, equilibrium conditions may not hold in many cases. Among these are photoinduced processes that play an important role in photocatalysis, photoresponsive materials, and photoluminescence.

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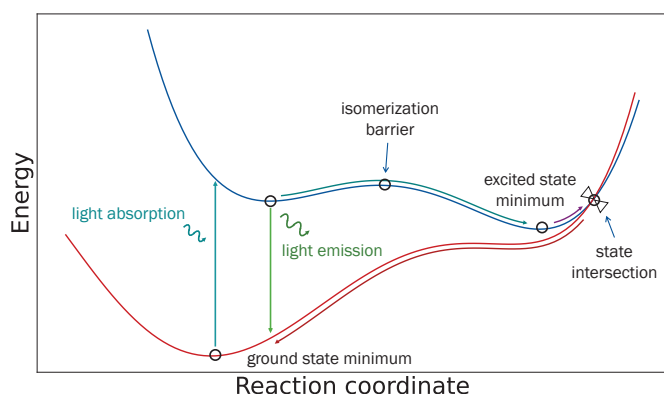


Fig. 1: Schematic potential energy curves indicating the relevant structures in a photoinduced process. Determination of minima, barriers, and state intersections (black circles) is necessary to simulate the kinetics of photophysical and photochemical processes following light absorption. Efficient semi-empirical electronic structure theory methods may be used to quickly sample these points. Then, higher levels of theory can be applied to determine rate constants to be used in kinetic modeling.

The simulation of photoinduced processes in molecules is far from being trivial and typically requires very system-specific modifications of the theoretical framework. In general, these processes are initiated when a molecule is promoted to an excited electronic state via absorption of an incoming photon (see Figure 1). The molecule cannot equilibrate immediately and will typically undergo more directional motions on the excited state potential energy surface. These may then lead to isomerization or reactions with neighboring molecules. Eventually, the molecule will return to the ground state either by emission of a photon (fluorescence) or by internal conversion. In the latter case, one may think of the molecule passing through a state intersection. A common approach to describe this non-equilibrium process is by non-adiabatic dynamics simulations. These can quickly become computationally demanding and technically cumbersome, since costly multi-configurational electronic structure theory methods are employed that, furthermore, require molecule-specific tailoring and may become unstable during the dynamical simulations. Hence, only small molecules with less than 30 atoms are treated routinely. During my postdoctoral research, we could show that the simple density functional theory-based hh-TDA method is a robust choice to treat the energetically low-lying electronic states, including their intersections, and enables more routine investigation of photochemical processes [2]. This method enabled the first non-adiabatic dynamics simulation of the wavelength-dependent photochemistry of the azobenzene molecule [3]. The latter is a core component in many photoswitches and dye molecules.

In my research group at RWTH Aachen University, we now aim towards predictive simulations of photophysical and photochemical processes also in larger molecules. We mostly abstain from performing time-consuming non-adiabatic dynamics simulations. Instead, we simulate photoinduced processes with a multi-level setup like the one for systems in equilibrium described above. In addition to the conformational minima, also the state intersections and barriers must be determined

(see Figure 1). We have recently presented an approach that leverages the computational efficiency of the semi-empirical GFN2-xTB method to quickly determine the most favorable state intersections [4]. This way, the points on the potential energy surfaces that are crucial for the studied photoinduced process can be quickly identified and, subsequently, be treated with more accurate quantum chemical methods. In collaborative studies, we have successfully used such a treatment to elucidate the mechanisms of different photocatalytic deracemization reactions [5, 6]. Here, we could also demonstrate that the long-known Dexter energy transfer process occurring in donor-acceptor systems may be modeled by means of conical intersection as well [5].

By assuming quasi-equilibrium conditions, one may also determine rate constants for the internal conversion and fluorescence processes based on the sampled crucial points on the excited state and ground state potential surfaces (c.f. black circles in Figure 1). These rate constants can then be employed in a kinetic model that allows to efficiently simulate the photoinduced process. Compared to the computationally more demanding non-adiabatic dynamics simulations, higher levels of theory can be afforded in the calculation of the rate constants. That includes the use of accurate *ab initio* electronic structure theory methods and the consideration of nuclear quantum effects. The trade-off is, of course, the assumption of quasi-equilibrium conditions in the computation of the rate constants, which may require some *ad hoc* corrections. Our group is currently using and improving the above-described approach to computationally determine fluorescence quantum yields of organic and organometallic molecules. This may open new pathways to computer-aided design of new fluorescent and photoswitchable molecules.

Current and Future Direction

The current achievements pave the way for routine simulations of photophysical and photochemical processes that can be afforded for a variety of molecules. However, some remaining issues still need to be addressed. The automatized identification and modeling of the involved electronic states in the photoinduced process need to be improved. The same is true for the computation of rate constants via transition states on a specific electronic state. Furthermore, the accuracy and computational efficiency of the employed physical models should be improved. Our current research is directed towards these goals. For this purpose, we are developing new approaches and also explore the use of low-scaling and data-driven models to achieve an overall better cost-to-accuracy ratio in our simulations. Central to our research is the use of inexpensive computing hardware, i.e. our computational setup hardly differs from the setup that is commonly found in computers that are used in gaming. With algorithms and workflows running efficiently on such computers, predictive computations become feasible for many researchers around the world, which may promote computer-aided design in chemical research.

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ZITATE

“Nature has a great simplicity and therefore a great beauty.” – Richard P. Feynman

“When you ask what are electrons and protons I ought to answer that this question is not a profitable one to ask and does not really have a meaning. The important thing about electrons and protons is not what they are but how they behave, how they move. I can describe the situation by comparing it to the game of chess. In chess, we have various chessmen, kings, knights, pawns and so on. If you ask what chessman is, the answer would be that it is a piece of wood, or a piece of ivory, or perhaps just a sign written on paper, or anything whatever. It does not matter. Each chessman has a characteristic way of moving and this is all that matters about it. The whole game of chess follows from this way of moving the various chessmen.” – Paul A.M. Dirac

“Life is not easy for any of us. But what of that? We must have perseverance and above all confidence in ourselves. We must believe that we are gifted for something and that this thing must be attained.” – Marie Curie

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Christoph Bannwarth obtained his bachelor's and master's degrees in chemistry from the RWTH Aachen University in 2009 and 2012, respectively. Given his interests in sustainable chemistry and chemical engineering on the one hand, and the physical foundation of chemistry on the other hand, he elected the specializations “catalysis” and “computational chemistry and spectroscopy” in the newly formed master's course of studies. At that time, he was undecided about a career path in industry or in academia. During the master's studies, he quickly fell in love with theoretical chemistry and joined the group of Robert W. Woody at the Colorado State University (Fort Collins, CO, USA) for his master's thesis. There, he worked on an approximate model to include charge transfer excitations in the simulation of protein circular dichroism spectra. This experience strongly impacted him in the decision to pursue an academic career. Christoph then joined the research group of Stefan Grimme at the University of Bonn. There, he worked on the development and application of various efficient quantum chemistry methods, mainly focusing on the simulation of electronic absorption and circular dichroism spectra. He obtained his doctoral degree in 2018. Shortly afterwards, he completed his work on the semiempirical GFN2-xTB method that is, by now, widely used by quantum chemists around the world. Funded by a Leopoldina Postdoc Scholarship, he joined the group of Todd J. Martínez at the Stanford University in August 2018. There, he became more interested in the simulation of photochemical processes. He drove the development of the, until then, neglected electronic structure theory method hh-TDA with particular aim to employ it in photochemical investigations. During his postdoctoral research at Stanford, he also started leveraging consumer-grade GPUs to accelerate computationally demanding steps in electronic structure theory calculations. In 2021, he was appointed as junior professor for Theoretical Physical Chemistry of Large Molecules at the RWTH Aachen University. His group is working on efficient methods to enable solving chemical problems on standard desktop computers. For this purpose, his group makes use of efficient electronic structure theory methods, kinetic models, fast screening approaches, as well as machine learning models and low-rank approximations. Currently, his group is funded by the NRW Rückkehrprogramm, the RWTH Junior Principal Investigator Fellowship, and the DFG.