Theory of solar energy materials

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Preface

Theory of solar energy materials

Understanding mechanisms of operation of photovoltaic [1] and photocatalytic [2] systems and devices, or more generally, solar energy materials, is important for advancing our capability to sustain steadily increasing demands in energy and fuels. With the number of possible materials scaling combinatorially, it is unlikely that a brute-force study of each and every new compound could lead to a successful practical strategy for finding novel efficient materials. Direct experimental techniques alone cannot provide sufficient details for solving such problems. In addition, experiments can be very expensive and time-consuming. The role of theoretical modeling of materials for solar energy conversion is thus hard to overestimate. A theoretical description provides atomic and sub-atomic details inaccessible to experimental characterization. Theory allows for ultra-fine time and space resolution. It helps with exploring additional hypothetical opportunities and establishing qualitative dependencies of the materials properties on various factors at the molecular and electronic structure levels.

Charge and excitonic energy transfer, non-radiative relaxation and electron–nuclear interaction occur in solar energy materials and are essential for their operation. Interrelation of the rates of all these processes determines the overall efficiency of the materials for a specific task. The processes rely on a quantum mechanical description of electronic states and require explicit treatment of dynamics. Theoretical modeling of this type of process is hence of special interest [3]. The present issue combines papers that showcase the development and application of modern techniques for accurate simulation of coupled electron–nuclear dynamics, as they occur in real time.

One of the common themes of the presented works is the realization that even the simplest in silico models of solar energy materials are already quite large for a straightforward application of the existing methods of electronic structure calculations. For example, modeling dye-sensitized oxide semiconductors may require a large substrate unit to accommodate a bulky organic sensitizer [4, 5], modeling photoinduced processes in metal-organic frameworks (MOFs) [6] requires a significant simulation cell whose size is determined by the intrinsic structure of a MOF. Consideration of long-range electron transfer (ET) [5] requires large system size by definition. One should also be aware that dynamics simulations are significantly more computationally expensive than the standard single-point calculations. Thus, various approximations are employed by the authors to reduce computational costs. In particular, da Silva et al [5] and Bowman et al [4] use the semiempirical extended Hückel (EH) method as an efficient scheme for obtaining electronic structure along simulated trajectories. Li et al [7] utilize a model Hamiltonian derived from ab initio calculations. Neukirch et al [6] employ density functional theory (DFT) with the pre-computed and parameterized electron integrals, to allow faster on-the-fly calculations. Vazhappilly et al [8] and...

The level of theory may vary notably while providing reasonable results, if a thoughtful judgment and a model construction are exercised. Still, the problem of construction of accurate and efficient Hamiltonians for time-domain simulation exists. As demonstrated by Micha et al [10], a correction to pure DFT-derived properties may be needed for accurate modeling of absorption and dielectric functions of Si materials. At the same time, a simple EH method can give a reasonable description of interfacial ET dynamics, although it is possible that some qualitative and quantitative trends will change if the model is systematically improved. Generally, it is advantageous to combine different levels of theory to accomplish distinct tasks. For example, one can compute nuclear dynamics using DFT or even classical mechanics, electronic spectra using time-dependent DFT (TD-DFT), while ET dynamics can be computed using simple semiempirical or model Hamiltonian.

The formulation and choice of the time-propagation method constitute the second main theme of the papers presented in this issue. The dynamics methods add a second dimension to the diversity of methodologies, beyond the first dimension arising from different descriptions of electronic state. The time-propagation techniques address a dominant problem of the field—coupling between electronic and nuclear degrees of freedom. If the electronic structure theory mostly affects the simulation results quantitatively, the dynamics methods exhibit major qualitative differences. Hence, they constitute an extremely important study topic.

The authors of the present issue address critical questions regarding the role of electron–nuclear coupling. Many previous works have customarily adopted the classical path approximation [11], which neglects the electron back-reaction [12–16]. According to such method, the nuclear dynamics is decoupled from the electronic evolution, while the propagation of the electronic state is determined by a pre-computed, usually ground state trajectory. The electronic evolution depends parametrically on nuclear geometry. da Silva et al [5] reintroduced the neglected back-reaction in the combined classical mechanical/quantum dynamics approach. They concluded that for large systems it plays a minor role, thus validating the assumption utilized as granted by other authors previously [12–16]. Bowman et al [4] employs an extreme version of such approximation—the nuclear dynamics is frozen and only electronic degrees of freedom are propagated. On the opposite extreme, Neukirch et al [6] study photoinduced isomerization of small organic chromophores in MOFs. The electron back-reaction is important and cannot be neglected under these circumstances.

Li et al [7] study another important dynamical effect. The authors utilize the multilayer multi-configurational time-dependent Hartree (ML-MCTDH) method for accurate quantum dynamics. Using this approach supplemented with a model Hamiltonian, they have been able to elucidate the role of anharmonicity of nuclear vibrations. They also study the role of the Dushinsky rotation, which arises due to variation in the forces exerted on the system in different electronic states. The authors found that these effects are rather small in the weak electron-coupling limit. In the strong coupling regime, the effects slow down the ET dynamics.

The works in the present issue excel in demonstrating the utility of the simulation techniques for modeling quantum dynamics processes. For example, the work of Bowman et al [4] suggests that hydroxamate is the most suitable anchor among a variety of moieties, leading to the most efficient electron injection from a Fe-based dye to the TiO2 substrate. Applying the surface hopping [11] method implemented within the FIREBALL software, Neukirch et al [6] demonstrate how
it can be used to predict the photo-physical properties of MOF-embedded chromophores with various side groups. The theoretical predictions are supported by the corresponding experimental measurements.

In addition to the interfacial structures, many solar energy materials rely on bulk and surface properties. Vazhappilly et al [8] studied Ni-doped TiO$_2$ for applications in photocatalytic water splitting. They showed that the dopant can be used to tune properties of the solar material by lowering the energy gap, although the absorption cross section must still be optimized. Importantly, the authors showed using the reduced density matrix simulation that holes relax faster than electrons. Since the hole ground state is localized on the surface, the surface is charged during a short period after the photo-excitation. The electron arrives later. Maximizing the time delay between the hole and electron relaxation may provide a strategy for improving photocatalytic properties of such materials. The reduced density matrix simulation technique is also used by Micha et al [10], who studied surface photo-voltage on Si slabs. Nanotechnology allows fabrication of slabs of varying thickness. Yet, it was unknown how the generated photo-voltage depends on slab thickness. The results of the modeling show that the gap decreases and absorption grows with increasing thickness. Since these two properties define the surface photo-voltage, it can be tuned as a function of the number of layers in the Si slabs.

Finally, Shang et al present studies of bulk phases of TiO$_2$ [17]. Photo-physical properties central to solar energy harvesting and transformation may depend strongly on details of structural organization. The work reports a structure search technique applied to exploration of phases in TiO$_2$ materials. The authors show that a number of high-pressure phases may show an improved photocatalytic activity. The work demonstrates that not only dynamical factors, but also structural details carry high importance for finding novel efficient materials for solar energy applications.

We thank all contributors to the special issue and hope that it illustrates the diverse modern methodologies for simulating complex solar energy materials. The issue highlights the importance of electron–nuclear dynamics, electronic coupling and structural effects in determining the optimality conditions for novel materials. We also emphasize that further theoretical developments are needed for accurate modeling of quantum dynamics, and building efficient semiempirical and model Hamiltonians applicable to large systems. Thorough investigation of the validity of different schemes in electron–nuclear dynamics is required.

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References