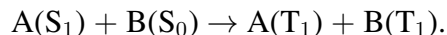


A computational protocol to test new chromophores for singlet fission

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Singlet fission is a process in which a chromophore A in an excited singlet state (S_1) transfers part of its excitation energy to a neighbouring chromophore B in the ground state (S_0) and both are converted into triplet excited states (T_1) [1, 2]:



The process represents an opportunity to improve the solar energy conversion efficiency in photovoltaic devices. In fact, a sensitizer capable of quantitative singlet fission may generate two charge carrier pairs per absorbed photon in a semiconductor material.

We propose here a computational protocol to test the suitability of newly proposed chromophores for singlet fission, both as molecular crystals and covalent dimers. In the former case, the molecular pair is embedded in the crystal, whereas in covalent dimers the system consists of two covalently linked chromophore units. The procedure includes the following steps: (i) determination of the excitation energies of the isolated chromophore, to verify whether the energy criteria for singlet fission are satisfied; (ii, a) computation of a possible crystal structure and identification of the most favorable pair of adjacent monomers within the crystal, in the case of molecular crystals; (ii, b) determination of the most favorable dimeric geometries for singlet fission and selection of a way to covalently connect the two chromophore units, in the case of covalent dimers; (iii) simulation of the excited state dynamics for the dimer, using a trajectory surface hopping approach [3]. For molecular crystals, we used a QM/MM scheme [4], where the QM subsystem is the chosen dimer and the MM subsystem is the rest of the crystal (Figure 1). For covalent dimers, we planned to include the semiconductor material in the simulation.

The excited state dynamics simulation is particularly important not only to determine the singlet fission quantum yield, but also to identify competing processes and other deficiencies of the selected chromophore [5].

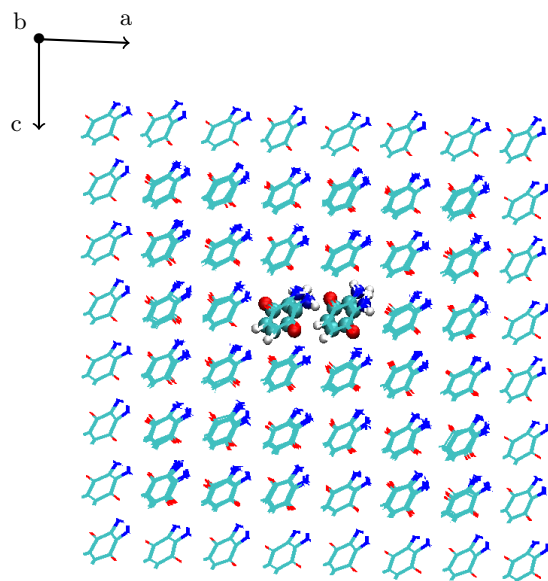


Figure 1: Cluster for the QM/MM simulation of 2,3-diamino-1,4-benzoquinone in the crystalline phase [5]. The QM dimer is represented with ball atoms and stick bonds, while the MM molecules are shown in simple line drawing.

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Identification of the Amino Acids responsible for a 200 cm⁻¹ Spectral Shift of the Chlorophylls Bound to the Water-Soluble Chlorophyll Protein.

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The Water-Soluble Chlorophyll Protein (WSCP) differs from other chlorophyll-binding proteins in that it is not involved in the photosynthetic process. Its low binding stoichiometry (each polypeptide subunit binds no more than one chlorophyll) and its highly symmetric structure¹ make the complex an ideal model system for spectroscopic investigations, as the four bound chlorophylls share the same environment and site energy.

WSCPs are classified in two sub-classes that are characterized by a difference of 9 nm in the position of their S₀→S₁ absorption bands of bound chlorophylls *a*. A mutation in one of the WSCP versions causing roughly half of this shift was previously reported.² We identified few other amino acids in the chlorophyll binding sites that influence the optical properties of the bound chromophores. Combining the two mutations, we achieved an almost complete spectral interconversion between the two sub-classes, as determined by comparing both absorption and circular dichroism spectra.

The collection of well resolved Triplet minus Singlet (T-S) spectra, by Optically Detected Magnetic Resonance (ODMR), allowed us to unravel the electronic interactions among the four chlorophylls, that in the WSCP tetramer are organized in two H-like dimers. Comparing the spectra of the mutated variants with the corresponding native variants, we were able to attribute the effect of the mutations to the sole site energy of the bound chromophores, as the T-S profile, strongly influenced by the chlorophyll-chlorophyll excitonic interactions, remains unaffected upon mutations.

The possibilities that recombinant WSCP offers by manipulating the number of bound chromophores³ and the nature of the surrounding amino acids, makes it a powerful tool to study the modulation of the magnetic and electronic properties of chromophores induced by their surroundings.

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A COMPUTATIONAL ASSESSMENT OF THE PHOTOTOXICITY OF ASPIRIN AND IBUPROFEN

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Drug exposure to light - visible (Vis) and ultraviolet (UV) - is inevitable. The evaluation of their light sensitivity is essential to predict either an eventual loss of potency or a possible production of toxic reactive species induced by electronic photoexcitation [1]. Photosafety recommendations are outlined in the International Council for Harmonization (ICH) S10 guidance.

We have analysed aspirin and ibuprofen behaviour upon photoexcitation. First attempts to predict photostability and phototoxicity of drugs in-silico, were based on the calculation of the HOMO-LUMO energy gap [2]. However, the predictive power of this indicator is limited for non-steroidal anti-inflammatory drugs' (NSAIDs) and therefore they are sometimes complemented with indicators of light absorption intensity, i.e. the molar extinction coefficient.

Initially we computed the absorption spectra. The complexity of the deactivation mechanism, still requires an in detail mapping of the potential energy landscape for the ground and excited states; locating the deactivation funnels to lower lying electronic states and searching the main stationary points. Multistate second order perturbation theory on state average complete active space self-consistent field wavefunctions MS-CASPT2//SA-CASSCF were the computational protocols used for this purpose [2,3,4].

Higher chances of producing phototoxic species are expected the longer the drug remains excited, so the keys behind photostability of a drug is the accessibility of lower lying singlet states. The most probable photophysical deactivation mechanism of the excited molecules will be determined with the help of semi-classical dynamics simulations, performed with the surface-hopping algorithm incorporating spin orbit coupling [5]. These results are also expected to shed light on the lifetime of the excited state.

We aim at generating a model that would translate the deactivation mechanisms in to a phototoxicity alert that could be introduced at early stages of the drug discovery process and help mitigate risks associated with drug exposure to light.

KEYWORDS: NSAIDs, Phototoxicity, In-Silico, Photophysics, Aspirin, Ibuprofen.

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COMPUTATIONAL VIBRATIONAL SPECTROSCOPY OF FLAVIN-BASED PHOTORECEPTORS

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Flavin-binding photosensory proteins such as the sensors of blue light using FAD (BLUF) and light-oxygen-voltage (LOV) domains serve many biological functions (e.g. phototropism) and are also invaluable in optogenetics. Upon photoexcitation, they undergo a variety of processes ranging from protein conformational changes to oligomerization and binding to other biomolecules. Apart from sharing a common isoalloxazine chromophore, a number of residues are conserved in their ligand binding pocket. These include the adduct-forming cysteine in LOV proteins and the flavin binding glutamine residue in both LOV and BLUF. The latter is postulated to alter the hydrogen bonding map and initiate long range changes in the protein.¹

To monitor the light-triggered changes of key residues involved in signal transduction, a combination of isotopic labelling and time-resolved vibrational spectroscopy is utilized. Cluster and QM/MM calculations are employed to predict the vibrational shifts of glutamine residues with distinct combinations of isotopes, which are then correlated with the experimental infrared spectra of BLUF and LOV photosensors.²⁻⁴ The effects of protein hydration and deuteration and the geometry of the excited states are also taken into account. The computational results provide a valuable assistance in the IR spectral assignment and help to interpret the appearance of transient peaks that are coupled to the electronic and structural changes the flavoprotein undergoes through its photocycle.

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Computational approach to evaluate hole mobility in the amorphous phase of organic molecule

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Abstract

Hole mobilities for 12 molecules in the model amorphous phase prepared by molecular dynamics simulation were evaluated using the proposed efficient successive conduction (SC) model based on the continuity equation with no adjustable parameter, which could qualitatively reproduce experimental results in a reasonable computational time. Using the SC model, the relationships between hole mobilities and molecular structures were evaluated for the molecular design to control mobilities in the amorphous phase. The SC model assisted by molecular dynamics simulations was demonstrated as a useful approach for evaluating hole mobilities for a wide range of molecules in the amorphous phase. It was confirmed that molecular interactions with only a few neighboring molecules, the high concentration of molecules with significant contributions to the mobility, and small reorganization energies are important factors for increasing hole mobilities. It is indicated that small reorganization energies tend to be obtained from rigid molecules. In addition, molecules with a large S between HOMOs in contact molecular pairs are also good indicators for having a high hole mobility, which is related to short intermolecular distances between adjacent molecules.

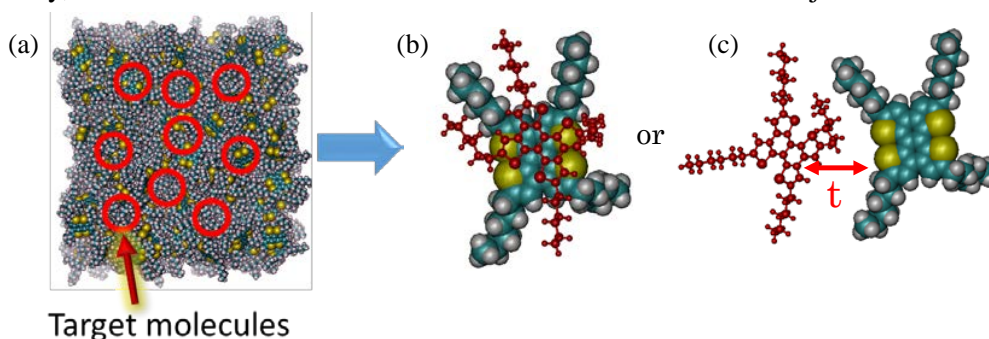


Fig. 1 Computational approach. (a) Model amorphous phase. (b) stacking molecular pair. (c) parallel displaced molecular pair.

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Combining Projector-based Embedding with EOM-CCSD for Excitation Energies

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The calculation of accurate excitation energies using *ab-initio* electronic structure methods such as standard EOM-CCSD can be cost prohibitive due to the computational scaling with respect to system size. We present work showing how a simple projector-based embedding scheme can be used to calculate the EOM-CCSD excitation energies of acrolein solvated in water molecules modelled using DFT¹⁻³. The accuracy of this approach gives excitation energies within 0.01 eV of full all-electron EOM-CCSD, but with significantly reduced computational cost. This approach is also shown to be relatively invariant to the choice of functional used in the environment and allows for the description of systems with large numbers of basis functions (>1000) to be treated using state of the art wavefunction methods. The flexibility of embedding to select orbitals to add to the excited-state method provides insights into the origins of the excitations and can reduce artefacts that could arise in traditional LR-TDDFT.

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The solvent effect on the hydrogen bond of a neutral complex (-OH, H₃O⁺)

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Abstract

The proton transfer [1,2,3] of two water molecules where one is a proton donor and the other is an acceptor forms a neutral complex (-OH, H₃O⁺). The objective of our research is to study the structural, vibrational aspect and to determine the number of ligand by ab initio calculations.

By the choice of two different solvents, one aprotic apolar (CCl₄)_n and the other polar portico (H₂O)_n. The following results show that the distance RO ... H hydrogen decrease each addition of molecules (CCl₄)_n or (H₂O)_n with n varies from 0 to 4 and the frequency ω O ... H confirms this observation.

Keywords: Hydrogen bond, Ion complex neutral, Solvent.

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Benchmark and Application of LC-DFTB on Rhodopsins and Light-Harvesting Complexes

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Recently, a long-range corrected functional (LC) has been implemented into the efficient DFTB method, which now allows extensive sampling of excited states properties of chromophores embedded into proteins using QM/MM methods within the TD-DFTB approach [1,2]. The promise of LC for a better description of (charge-transfer) excited states will be tested for retinal proteins (bR, sRII and Rh) and light-harvesting complexes (FMO and LH2). Critical tests are the change of excitation energies through structural changes of the chromophore and response to external electric fields, which are the key parameters relevant for color tuning, and exciton couplings in case of BChla. While DFT-GGA and hybrid functionals are clearly 'color-blind' [3], LC-functionals exhibit still a significant 'color-weakness'. As examples, we present absorption spectra sampled for bR, sRII and Rh.

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Real-Time Spectroscopy in an Interactive Quantum Chemistry Framework

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Abstract

A framework for interactive quantum chemistry established in our group allows for the real-time, interactive exploration of chemical reactivity along exploration coordinates [1–4]. In order to facilitate the efficient spectroscopic identification of compounds, an extension of this framework has been developed [5]. We present a real-time spectroscopy tool that seamlessly delivers infrared and ultraviolet-visible spectroscopic information in the interactive exploration. As the determination of the molecular electronic structure by means of very accurate computational methods is too time consuming for its use in an interactive framework, a semi-empirical model is employed. It allows for a fast determination of the molecular properties of interest that may be later refined with more accurate methods if deemed necessary. Molecular properties of interest are, for instance, the dipole moment and its derivative for infrared spectroscopy or the energy difference between HOMO and LUMO as a descriptor for ultraviolet-visible spectroscopy. To best exploit inexpensive, but less accurate, methods, characteristic spectral signals may serve as diagnostic probes that do not require ultimate accuracy with respect to peak position and height. Such diagnostic bands from the interactive spectroscopy software can provide hints on structures with characteristic spectroscopic properties.

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A QM/MM Study of the Dihydroxylation of Nitroaromatic Contaminants Catalyzed by Nitrobenzene Dioxygenase

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Oxygen activating enzymes play an important role in the biodegradation and detoxification of soil and water contamination by organic pollutants. [1] The conversion of persistent aromatic pollutants to their corresponding *cis*-dihydrodiols and catechols acts as the initial step in these processes and is carried out exclusively by *Rieske non-heme Fe dioxygenases*. We present a QM/MM study on the current interpretation of the mechanism of the dioxygenation of nitroaromatic compounds by *nitrobenzene dioxygenase* (NBDO), which has been established by previous experimental and DFT studies [2, 3]. Reaction energies and barriers are compared to DFT results and the effect of the QM region's size is discussed.

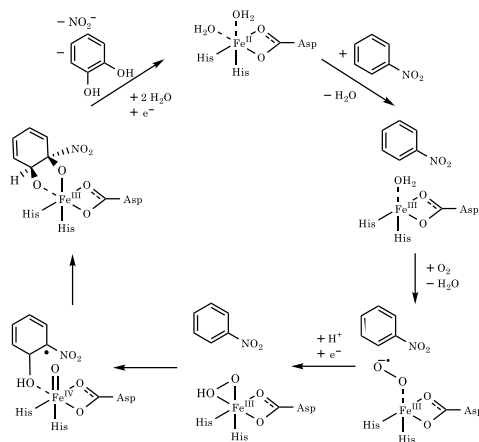


Figure 1: Current interpretation of the O_2 activation and dioxygenation of nitrobenzene based on previous experimental and theoretical studies [2, 3].

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Novel Donor-Acceptor fluorescent quinoxalinone-based chromophores: experimental and theoretical study

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Abstract

π -conjugated push-pull type organic molecules demonstrate a great potential in a number of applications acting as functional layers in non-linear optical (NLO) materials, organic light-emitting diodes (OLEDs), pH and polarity sensors, photovoltaic applications etc. D-A systems often demonstrate perfect sensitivity appearing as changes in their optical absorption/emission properties to the external stimuli. Moreover different strategies including varying of functional D and A groups may dramatically influence photophysical properties of the molecules as well.

D and A parts could be attached directly or through spacer fragment. Recently push-pull systems based on molecules containing two nitrogen atoms like pyridazine, pyrazine, pyrimidine and quinoxalines have been demonstrated as promising candidates in luminescent applications. Diazines, due to their highly π -deficient character effectively act as the electron-withdrawing part in π -conjugated push-pull structures. Intramolecular charge transfer (ICT) into the scaffold of the molecule can induce tunable luminescence. Among the studied diazines quinoxalines derivatives represent a valuable addition to the pool of NLO systems[1], demonstrating high values of first hyperpolarizability and high environmental sensitivity[2]. A set of reports on the OLEDs prepared on the quinoxaline derivatives revealed their potential in the field of emissive layers for materials of organic electronics.

In the current work new push-pull luminescent chromophores containing quinoxalinone core as electron-withdrawing fragment have been comprehensively studied both experimentally and theoretically. Their photophysical properties were reliably described with the use of TD-DFT approach. Novel recently introduced quantum-mechanical parameters based on attachment/detachment methodology and NTO analysis[3] have been utilized to assess ICT nature of the electronic transitions.

Acknowledgements

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Photodynamics of Tin-Oxo Photoresists

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Abstract

Tin-oxo cages belong to a class of organometallic compounds which were recently recognized as promising photoresist materials for the extreme ultraviolet (EUV) lithography. The EUV exposure of tin-oxo cages causes significant structural changes; however, the molecular mechanism of these changes is to a large extent unknown. In the present work, we focus on the photoionization dynamics of the small tin-oxo molecules: the trimethyltin hydroxide (TMTH) and trihydroxymethyl stannane (THMS) molecules. We employed the surface hopping (SH) dynamics on the *Floating Occupation Molecular Orbital Complete Active Space Configuration Interaction* (FOMO-CASSI) potential energy surfaces. After the ionization of both molecules, we observed an ultrafast relaxation into the ground and first excited electronic states followed by a rapid dissociation yielding the neutral CH₃ and OH radicals. However, the dissociation dynamic does not occur solely on the hot ground electronic state and reaction outcome partially depends on initially ionized state. We also demonstrate that the SH+FOMO-CASSI dynamics is suitable for electron-rich open-shell systems.

PPES 2018 Abstract Submission

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Affiliation: Department of Materials, Imperial College London, U.K.

Supervisors: Prof Peter Haynes & Dr Andrew Horsfield

Title: Implicit and explicit host effects on excitons in pentacene derivatives

Abstract:

Masers (microwave lasers) have long been restricted in their applications by the impracticality of their operating conditions. For instance, solid state masers require cryogenic freezing and strong magnetic fields. In 2012, the first room-temperature maser was demonstrated using a *p*-terphenyl crystal doped with pentacene [1]. We seek to understand the importance of the *p*-terphenyl host on the excitonic properties of pentacene.

An ab initio study of the effects of implicit and explicit hosts on the excited state properties of pentacene and its nitrogen-based derivatives has been performed using ground state density functional theory (DFT), time-dependent DFT and Δ SCF [2]. We observe a significant solvatochromic redshift in the excitation energy of the lowest singlet state (S1) of pentacene from inclusion in a *p*-terphenyl host compared to vacuum; for an explicit host consisting of six nearest neighbour *p*-terphenyls, we obtain a redshift of 65 meV while a conductor-like polarisable continuum model (CPCM) yields a 78 meV redshift. Comparison is made between the excitonic properties of pentacene and four of its nitrogen-based analogues, 1,8-, 2,9-, 5,12-, and 6,13-diazapentacene with the latter found to be the most distinct due to local distortions in the ground state electronic structure. We observe that a CPCM is insufficient to fully understand the impact of the host due to the presence of a mild charge-transfer (CT) coupling between the chromophore and neighbouring *p*-terphenyls, a phenomenon which can only be captured using an explicit model. The strength of this CT interaction increases as the nitrogens are brought closer to the central acene ring of pentacene.

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Nanocomposites based on graphene oxide-titanium dioxide as a possible photoelectrochemical ion sensors

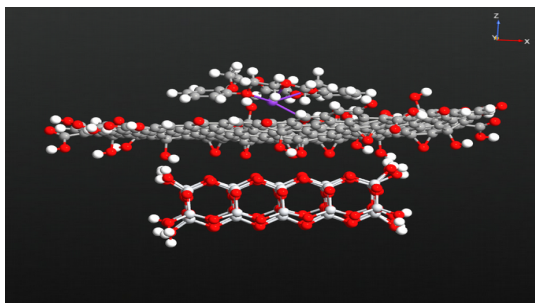
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Wide-bandgap semiconductors are widely used for its efficient absorption in the UV and visible light range. When modified with carbon nanostructure, they make a nanocomposite which upon synthesis with a molecular receptor makes a good platform for a photosensitive chemo and bio sensors.¹ Particularly useful are nanocomposites with graphene oxide (GO) due to the presence of various functional groups (hydroxyl and carbonyl) in GO that utilize the non-covalent bonding with the aromatic group of the receptor. The electronic structure of such a nanocomposite results in modified electronic and optical properties of base semiconductor facilitating the charge and energy transfer processes for desirable application purposes.

Here we present the investigation of a hybrid material based on titanium dioxide nanoparticles modified with graphene oxide and a benzannulated crown ether as a possible sensor for potassium ion. We performed the ab initio DFT based calculations. First, we obtained the electronic structure of the components of the system which showed the existence of GO states below the conduction band of TiO₂. Further, we determined the optimized geometry of the system with the crown ether and investigated the change of the structure upon absorption of potassium ion. Based on these results we discuss the possible mechanisms² for photocurrent generation at different substrate potentials and different potassium concentrations which prove the possibility of using a material as an ion sensor.



Model of benzannulated crown ether loaded onto GO modified TiO₂

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Acknowledgements

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Computing the proton momentum distribution of water through path integral molecular dynamics

It is very important to account for nuclear quantum effects in determining the static and dynamical properties of materials containing light nuclei. In particular, these affect the momentum distribution which differs from the classical Maxwell-Boltzmann form. Thanks to the link between potential energy surface and quantum kinetic energy, the momentum distribution is a sensitive probe of the local environment and, therefore, provides information complementary to the distribution in configuration space. The case of water is particularly interesting, as the large presence of light nuclei (hydrogens) strongly affects the properties of the system. For this reason, we can use the momentum distribution to understand the form of the effective potential the proton sees as the hydrogen bond network changes or viceversa as a test for the potential used to simulate the system.

It is possible to directly access momentum-dependent quantities from the off-diagonal elements of the density matrix, that can be computed through simulations of open path integral molecular dynamics. Here, we implemented open path dynamics [1] in i-Pi, a python interface for performing path integral calculations, and used this technique to study the momentum distribution of water in combination with an empirical point-charge potential (qtip4pf). By comparing with the momentum distribution obtained in deep inelastic neutron scattering experiments, we determined the important features that influence the momentum distribution and assessed the performance of the qtip4p model against another point-charge potential (SPC/F2) employed in previous path integral simulations [2].

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Low numerical scaling quantum Monte Carlo to model photo-excitations in oligothiophenes

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We investigate the use of highly-correlated quantum Monte Carlo methods for the accurate description of the electronic excitations of thiophene and its oligomers, which constitute a prototypical backbone of an optically-active component (e.g. poly-3-hexylthiophene or P3HT) in organic solar cells. For these systems, we identify a robust recipe to construct compact and accurate many-body wave functions based on orbitals localized on a single thiophene unit and a limited class of electronic excitations in the determinantal expansion. The complexity of these wave functions scales linearly with the size of the system. Our calculations on short oligothiophenes demonstrate the ability of our theoretical framework to robustly predict their excited-state energies and structures. This investigation represents a first step before addressing the nature of electronic excitations in realistic stretches of P3HT.

Perturbative Monte Carlo for Excitation Energies

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The major rearrangements of the electronic density which accompany electronic excitations makes such processes very sensitive to the intricate interplay of interactions between solute and solvent molecules as well as among the solvent molecules in the near vicinity of the solute. Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) methods are one of the available and widely used approaches which account for this effect of the environment. Nevertheless, the computational costs of the underlying self-consistent field algorithm, which requires many steps to obtain accurate and converged results, allows for an exhaustive exploration of the configurational space only with considerable computational resources at hand. Therefore, sequential approaches are favored which generate the configurations at a lower level and attempt to correct the energies and properties on a limited set of configurations with a higher level of theory. This raises the question to which degree this bias in the exploration of the configurational space affects the final results and if more accurate results can be recovered in such a sequential scheme.

We are aiming at increasing the accuracy already at the stage of the sampling with the recently developed perturbative Metropolis Monte Carlo scheme (PMC) for molecular simulations with only moderate computational costs. This is achieved by applying perturbation theory to account for the instantaneous electrostatic interaction between the QM and MM system which is in itself very efficient and additionally allows to sample the large amount of degrees of freedom in the environment independent of the degrees of freedom in the QM system. This leads to a hugely increased efficiency with computational costs reduced by several orders of magnitude. The accuracy is controlled in a transparent manner with a single parameter controlling the number of quantum mechanical calculations during a simulation. Recently, this approach has been extended to compute vertical (de-)excitation energies for multiple states on the fly which allows simulating electronic absorption and emission spectra in solution without having to resort to empirical fitting to describe the band shape due to the environment.

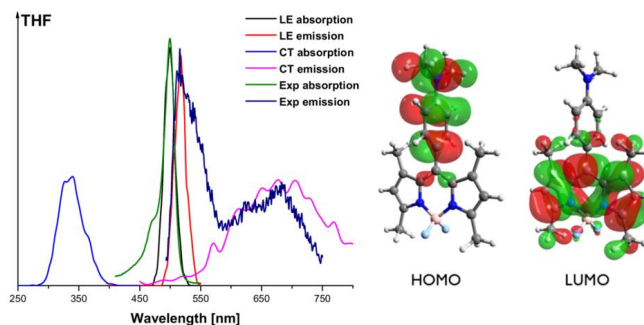
MODELLING ABSORPTION AND EMISSION OF A MESO-ANILINE-BODIPY BASED DYE WITH MOLECULAR MECHANICS

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Absorption and emission spectra of 8-(4-dimethylaminophenyl)-1,3,5,7-tetramethyl-BODIPY have been calculated using Coupled Cluster (CC) approaches, Time-Dependent Density Functional Theory (TD-DFT) and a QM-informed MM approach. In the case of TD-DFT calculations solvent effects were included using the linear-response (LR), corrected linear response (cLR) and state specific (SS) Polarizable Continuum Model (PCM). We show that range-separated functionals give results in reasonable agreement with coupled cluster methods but both tend to overestimate excitation energies. Furthermore, we show that the SS-PCM approach is unable to provide a quantitative description of solvent effects in these systems, especially for the highly challenging charge-separated charge-transfer state. In contrast, the QM-informed MM approach gives results in good agreement with experiment and we propose a scheme which can be used to directly compare theoretically obtained spectra with experimental ones.



Fully Ab-Initio Modeling of the First Singlet Excitation Energy in Molecular Crystals

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Photon-induced electronic excitations in crystalline organic chromophores have received much recent attention due to potential applications in organic electronics, optics, and biomedicine. Specific examples include organic light-emitting diodes (OLEDs), lasers and fluorescent sensors. Theoretical modeling can aid our understanding of the excitation processes and is necessary for screening potential candidate materials for the said applications. The quantum mechanics/molecular mechanics (QM/MM) method, where time-dependent density-functional theory (TDDFT) is typically used as the QM method, is currently predominant in modeling excitation energies in molecular crystals. Full-scale application of ab initio excited-state methods to molecular crystals is hampered by significant difficulties such as the rapid scaling of computational cost under the periodic-boundary conditions. We herein present a study in which we model the first singlet excitation energy in a series of crystalline polymorphs using a novel, fully ab-initio method based on ground-state density-functional theory (DFT). We use Becke's correlated first singlet-triplet gap model to obtain the first singlet excitation energy for the crystals from their first triplet excitation energy. The intermolecular interactions within the crystalline environment have been experimentally observed to play a vital role in polymorphism-dependent photoluminescence. For their accurate modeling, we use the exchange-hole dipole moment (XDM) dispersion model paired with the B86bPBE exchange-correlation functional, which has been shown to yield optimal results for molecular crystals.

Absorption Spectroscopy and Photophysics of $[\text{Re}(\text{CO})_3(\text{dppz})(\text{pyr})]^+$ considering Environment Effects by Means of Different Models

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Transition metal complexes fulfill the requirements for being active probes of charge transport (CT) in biological context (1). The coordination complexes of the type $[\text{Re}(\text{CO})_3(\text{N,N})(\text{L})]^n$ (N,N: alpha-diimine, L: axial ligand) are common probes where the variation of the N,N and L ligands allows to control the excited-state character and energetics (2). Moreover, the strong environmental dependence of their excited-state properties makes them excellent candidates to be used as biochemical probes (3,4). In recent experiments, photo-excited $[\text{Re}(\text{CO})_3(\text{dppz})(\text{pyr})]^+$ (dppz: dipyridophenazine, pyr: pyridine) was used to promote CT when intercalated in guanine enriched DNA (5). In contrast, long lived emission is observed in acetonitrile while no emission is detected in water. (6) The response of the complex to various environments is controlled by the relative position of the low-lying triplet excited states, namely intra-ligand (IL) and metal-to-ligand-charge-transfer (MLCT), as well as by their character in terms of electronic density localization on the phen part (phen: phenantroline) of the dppz (7). In this work we present a detailed analysis of the absorbing and emissive properties of $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$ in acetonitrile, water and DNA by means of DFT, TD-DFT/conductor-like screening model (COSMO) supplemented with molecular dynamics (MD) calculations. The reliability of COSMO model to simulate specific nitrogen-hydrogen interactions in polar protic solvents is discussed and the contribution of various conformers to the absorption spectrum is analyzed on the basis of MD simulations. Finally the excited state properties of an intercalated $[\text{Re}(\text{CO})_3(\text{dppz})(\text{py})]^+$ -DNA system built for probing photo-induced CT in Re(I)-DNA assemblies is performed via TD-DFT calculations.

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Studying the Photochemical Properties of Firefly Oxyluciferin and its Analogues by QM/MM methods

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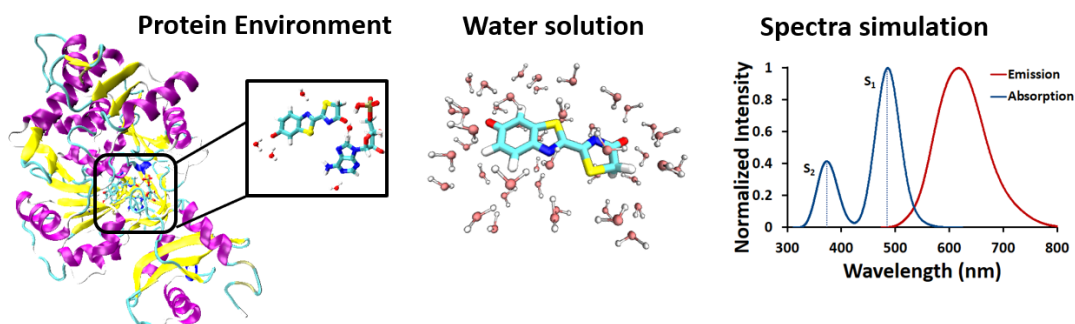
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Light emission in fireflies is an amazing bioluminescent process. Although the chemical reaction is widely accepted, still fundamental properties have to be further investigated. For instance, the chemical nature of the light emitter (so-called oxyluciferin) is a topic of debate among scientist, as it can coexist in six different chemical forms due to inter-exchange reactions (deprotonation and keto/enol tautomerization). Concerning this debate, computational studies, in particular the use of quantum mechanical/molecular mechanical (QM/MM) methods, play a key role as it is possible to study independently the different forms of oxyluciferin in diverse environments [1,2].

The aim of this work is to simulate the absorption and emission spectra of the oxyluciferin forms and some synthetic analogues (designed to block the inter-exchange reactions) in water solution and inside the protein. This way we can note the effect of the environment on the photochemical properties and also, the suitability of using the analogues to mimic the natural forms. Starting with the study of oxyluciferin in water solution [3], three novelties should be remarked: *i*) consideration of both the dynamical information and the interactions between the solute and explicit water molecules; *ii*) detailed analysis of the electronic nature of the vertical transitions to the first singlet excited state and to upper-lying excited states and *iii*) comparison of each natural oxyluciferin form with the corresponding analogues.

Regarding the methodology, MD simulations of oxyluciferin in explicit water have been performed to sample both the ground and the first singlet excited state minima. Then, the absorption and emission spectra have been simulated as a convolution of the excitation and emission energies computed at the QM/MM level of theory using the coupling of the programs G09 (DFT) and TINKER (AMBER force field).

In addition, the emission spectra of some of the oxyluciferin forms have been simulated inside the protein by using QM/MM methods. These results could get insight into the chemical nature of the light emitter in fireflies bioluminescence.



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Crossover from Hopping to Band-Like Charge Transport in an Organic Semiconductor Model: Atomistic Non-Adiabatic Molecular Dynamics Simulation

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Understanding charge transport in organic semiconductors is challenging because the parameters determining the dynamics are typically outside the regime of validity of existing theories. Here we employ atomistic non-adiabatic molecular dynamics simulation, via our decoherence-corrected fragment orbital-based surface hopping (FOB-SH), to obtain mechanistic insight into electron hole transport along chains of ethylene-like molecules [1, 2]. This method relies on ultrafast calculation of Hamiltonian and forces allowing us to treat fundamental charge transfer properties in large molecular assemblies without assuming any specific charge transport model. The simulations benefit from newly implemented algorithms that solve the problem of spurious long-range charge transfer hampering normal surface hopping codes.

We find that the CT mechanism changes from slow hopping of a fully localized electron hole to fast diffusion of a polaron delocalized over several molecules, as electronic coupling between the molecules exceeds the critical threshold $V \geq \lambda/2$ (λ the reorganization energy). With increasing temperature the polaron becomes more localized and the mobility exhibits a “band-like” power law decay, $\mu \propto T^{-1.2}$. We demonstrate that polaron localization and mobility decay in this regime are primarily due to site energy fluctuations (local electron-phonon coupling). Electronic coupling fluctuations (non-local electron-phonon coupling) enhance these effects, but do not change the qualitative picture [3]. The results of present atomistic non-adiabatic MD simulations are in line with experimental observations on systems in similar CT regimes, and they confirm the trends reported previously at the level of coarse model Hamiltonians [4, 5]. Our work reinforces the view that, in addition to high electronic couplings, small thermal fluctuations of site energy and electronic couplings are important target properties in the search for new organic materials with high room temperature mobilities.

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Optical properties of molecules interacting with their environment and light: non-equilibrium local field effects

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The electronic and optical properties of a molecule embedded in a dielectric environment can be substantially different from those of its gas-phase counterpart. The presence of the molecule induces a polarization in the surrounding (the so-called reaction field) that in turn interacts with the molecule itself. Additionally, if the molecule is subjected to an external electric field, the effective field acting locally on the molecule (namely, the local field) contains another polarization contribution of the environment due to the applied field [1]. Both reaction and local field effects can be accounted for in quantum-mechanical calculations of molecules within the Polarizable Continuum Model (PCM) framework [2,3]. Recently, a computationally convenient time-dependent extension of PCM (TD-PCM) has made possible to study the real-time evolution of the molecular density subject to time-dependent perturbations, such as electromagnetic radiation, and the polarization of the external media [4]. Such a TD-PCM scheme introduces polarization fields that are history-dependent and not instantaneously in equilibrium with the molecule or the applied fields. These non-equilibrium polarization effects arise ultimately from the frequency-dependent dielectric function describing the environment, and they are physically linked to the fact the environment takes a finite amount of time to adapt to the electrostatic perturbations. The latter TD-PCM has been formulated for the reaction and local field in the case of gas-phase molecules nearby a metallic nanoparticle [5], while by now it has been only developed for the reaction field in the case of solvated molecules [4].

It is the purpose of this contribution to present an extension of TD-PCM to consider local field effects for molecules surrounded by a uniform dielectric medium, such as a solvent. To reveal the potential of our methodology, we perform real-time real-space Time-Dependent Density Functional Theory (TDDFT) simulations of solvated molecules departing from spherical symmetry to assess the influence of the local field in the absorption spectrum and time-dependent properties.

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Absorption properties of natural dyes: a multi-scale computational approach for anthocyanins

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Anthocyanins are among the most abundant natural pigments, which, depending on the chemical environment (such as acidity and copigmentation), give rise to a variety of colors and shades in the red-purple-blue gamut. In spite of the ubiquity and potential applications of anthocyanins, the mechanisms underlying their exceptional photophysical versatility are not yet fully understood.

In this work we introduce a new multiscale modeling protocol to study the optical properties of complex molecular species in solution and apply it to the photophysics of anthocyanins in a broad pH range (1-9). Our protocol is based on enhanced sampling from classical force-fields based molecular dynamics (MD), advanced statistical analysis to identify the relevant molecular conformers, ab-initio MD in explicit solvent to accurately sample thermal fluctuations within individual conformers, and time-dependent density-functional theory to compute absorption spectra on selected molecular frames ¹.

Our simulations reveal that the broad range of colors expressed by anthocyanins crucially depend on a subtle combination of different structural and electronic traits, as determined by thermal fluctuations and/or molecular distortions impacting on the electronic conjugation. This finding allowed us to rationalize the spectroscopic behaviour of anthocyanins in terms of factors such as the overall molecular charge (modulated by pH) affecting the relative character and energy of frontier orbitals; the bond-order between the aromatic moieties of the chromophore as coupled to the corresponding dihedral angle; the fluctuations of other slow degrees of freedom and the role of the solvent ¹.

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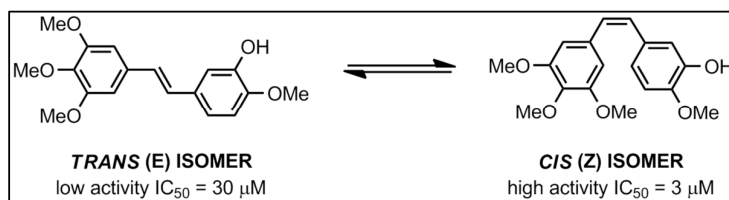
Influence of Charge Transfer on the Photoinduced Isomerisation of Stilbene Derivatives for Application in Cancer Therapy

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First isolated in 1982 from the bark of the African bush willow by Pettit^[1], combretastatins are promising anti-cancer drugs targeting microtubule assembly. While the naturally occurring *cis* (Z-) isomers of these stilbene-based compounds show high cytotoxicity, their *trans* (E-) analogs are considerably less toxic. Photoisomerisation from the *trans* to the *cis* isomers can be achieved by both one- and two-photon excitation, the latter enabling the use of tissue penetrating wavelengths in the red or near-infrared region^[2].



Substitution of functional groups by electron pushing and electron pulling moieties has been carried out to introduce a charge-transfer character in these compounds. This results in significant changes in the spectroscopic properties. In particular, fluorescence spectra exhibit enhanced red shifts with respect to non-charge transfer combretastatins and enhanced sensitivity in solvents of increasing polarity. An increase in the two-photon absorption cross section has also been observed, which suggests that charge transfer combretastatins are potential drug molecules for *in-vivo* two-photon isomerisations^[3].

Using TDDFT methods we explore the isomerisation coordinate and the spectroscopic properties of several charge transfer and non-charge transfer stilbene derivatives. Based on our calculations we aim to predict new and enhanced synthetic targets for application in photodynamic cancer therapy^[4,5].

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Exploring the photochemistry of an ethyl sinapate dimer: A step towards a better ultraviolet filter

In recent years several artificial sunscreens have come under scrutiny due to concerns about their safety. Alongside this “sunscreens controversy”, incidences of skin cancer are on the rise, even with the increasing use of artificial sunscreens. This highlights the need for not only improved education on how to use artificial sunscreens and general sun exposure, but a requisite for new generations of artificial sunscreens that provide enhanced photoprotection as well as being non-toxic.

One approach has been to use photoprotective molecules found throughout nature, which has had a few billion years head start in UV photoprotection, as starting points for the new generation of sunscreens. To this means, the photoprotective molecules found in plants have garnered interest as a starting point and one of these sunscreens found in plants is the sinapate ester: sinapoyl malate. The photoprotective nature of sinapoyl malate has been elucidated, as well as related sinapate esters, and is due to a highly efficient photoisomerization pathway. These sinapate esters also possess strong broad absorptions in the UVA (400 – 315 nm) and UVB regions (315 – 280 nm) and act as highly potent antioxidants. However, they are not perfect, their UVA absorption does not cover the entire region. Therefore, if the sinapate esters could be functionalized in such a way that the UVA absorption is broadened to cover the whole UVA region, while maintaining the efficient photoisomerization pathway and their photoprotective nature, they would produce a superior sunscreens agent.

The broadening of the UVA absorption of these sinapate esters was achieved *via* dimerization, both the absorption spectrum and structures is shown in Figure 1. Here we aim to determine whether this new dimer, dehydrodiethylsinapate (DHDES), possesses the same photostability as the sinapate ester it is derived from and if not, why? We achieve this by using a combination of femtosecond transient electronic absorption spectroscopy to observe the initial photochemistry after absorption of a UV photon and steady-state irradiation to observe the dimers long-term stability.

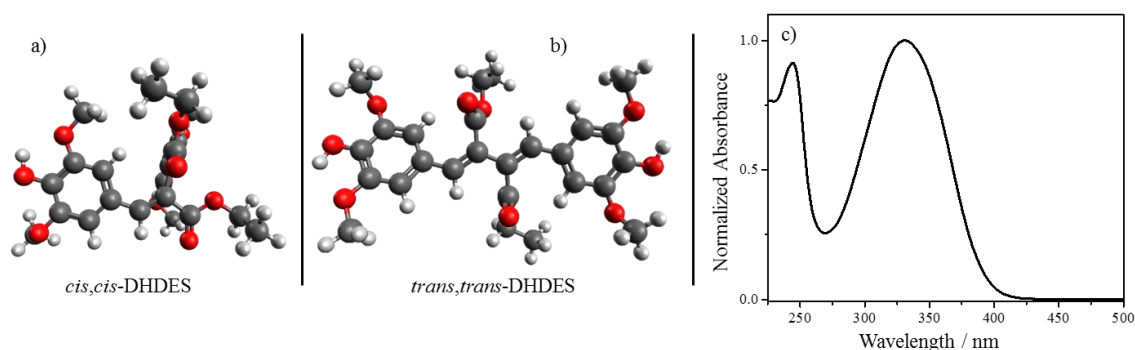


Figure 1: The calculated structures of the two lowest energy isomers of DHDES, a) *cis,cis*-DHDES is lower in energy than b) *trans,trans*-DHDES. c) The UV/visible absorption spectrum of $\sim 1 \mu\text{M}$ of DHDES in ethanol. Geometries calculated using: density functional theory geometry optimization with a cc-pVTZ basis set and PBE0 functional, using the NWChem software.

Cysteine linkages accelerate electron flow through tetra-heme protein STC

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Bacteria like *Shewanella* and *Geobacter* are species that have multi-heme proteins which enable them to respire and survive without oxygen by reduction of extracellular solid substrates[1]. Multi-heme proteins have attracted much attention recently due to their prominent role in mediating extracellular electron transport (ET), but one of their key fundamental properties, the rate constants for ET between the constituent heme groups, have so far evaded experimental determination.

For the modelling of the electron transfer reactions between the hemes, we need to compute the diabatic state coupling matrix element, which is an important parameter in calculating heme-heme electron transfer(ET) rates. The coupling matrix elements are calculated for ET between the heme pairs in a small tetraheme cytochrome[3] (STC) from the bacterium *Shewanella oneidensis* using the projector-operator diabatization approach[2]. Several quantum models are tested by systematically including more side chains of the heme porphyrin. Finally the calculation is done in a reasonably big model and averaged over 25 snapshots from a molecular dynamics trajectory. Rather surprisingly, we find that electronic coupling between the hemes is significantly enhanced by the cysteine linkages for two terminal hemes[4].

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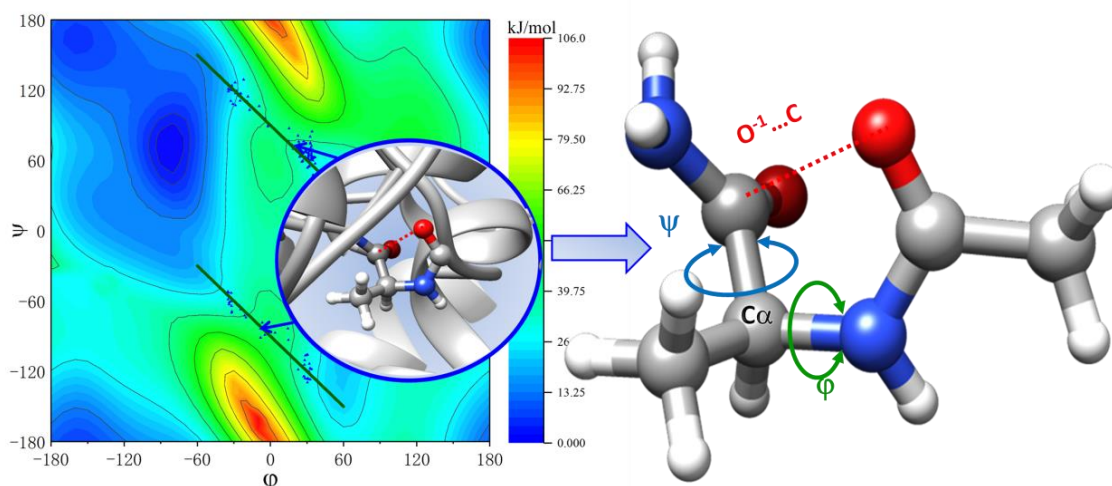
Polypeptide models as tools for detailed analysis of unusual local arrangements in proteins

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In the process of structural changes, proteins often need to pass through some high-energy regions. However, there are also cases of stable structures with some residues belonging to these non-typical high-energy conformations. If the “standard tools” are used to refine the proteins in that transition region, it is likely to provide misleading results, because these tools have been defined based on the most-stable/populated parts of the Ramachandran plot. At variance, quantum mechanical computations with the small polypeptide as a molecular model, allow analyzing and matching the local structural parameters of residues for any (ψ, ϕ) combination. For example, the B3LYP-D3 and B2PLYP-D3 calculations for small peptide (AcAlaNH₂), lead to the very good agreement with high-resolution experimental protein structure X-ray data ($\leq 1.5\text{\AA}$) in the $\phi \sim 0$ “mountain pass” regions. Whereas, Amber FF99SB and “standard tools” predict the non-bonded $O^{-1}\dots C$ distance, as too long or too close, respectively. These results confirm that quantum chemistry computations add valuable support for detailed analysis of local structural arrangements in proteins, providing improved or missing data for less understood high-energy or unusual regions.



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Molecular modeling of supramolecular photochromic actuators : from solution to stimuli responsive polymers

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Supramolecular chemistry is one of the most challenging field of research as illustrated by the Nobel Prize in Chemistry awarded in 2016 for the design of efficient molecular machines. The weak reversible interactions that are involved in such assemblies, along with the use of stimuli-sensitive entities as building blocks, can lead to the formation of larger structures with tunable macroscopic properties. Hydrogen bonds, due to their directionality and their easily strength adaptability, are one of the key building blocks and, in the midst of the wide variety of external stimuli, light is probably the easiest one to set up and consider. In this context, a photochromic compound, a dithienylethene (DTE) fonctionnalized by ureidopyrimidinone (Upy) moieties (Figure 1.a), which enable the formation of a block of 4 hydrogen bonds (Figure 1.b), has been studied. DTE-Upy molecules exist in an open form (OF) that can be isomerized into a closed form (CF) upon UV light excitation (the cycloreversion reaction being triggered by visible light). It has been demonstrated that only CF can form supramolecular assemblies (involving Upy-Upy interactions) in solution. Moreover, for CF isomers embedded in a polymer matrix (Figure 1.c), the morphology of the film is modified upon visible light irradiation (Figure 1.d). This macroscopic optomechanical effect is attributed to a molecular-scale phenomenon, i.e the photochromic reaction. We aim here to rationalize, thanks to Molecular Dynamics (MD) and TD(DFT), the behavior of DTE-Upy molecules :

- i) in solution, to investigate the properties of both OF and CF that can justify the supramolecular assembly for CF only
- ii) in a polymer matrix, to explore the interactions between both DTE-Upy and polymer chains that can justify the optomechanical behavior. At that stage, the MD « STAMP » code developed by the CEA-DAM will allow us to perform *in situ* polymerization around the photochromic molecule.

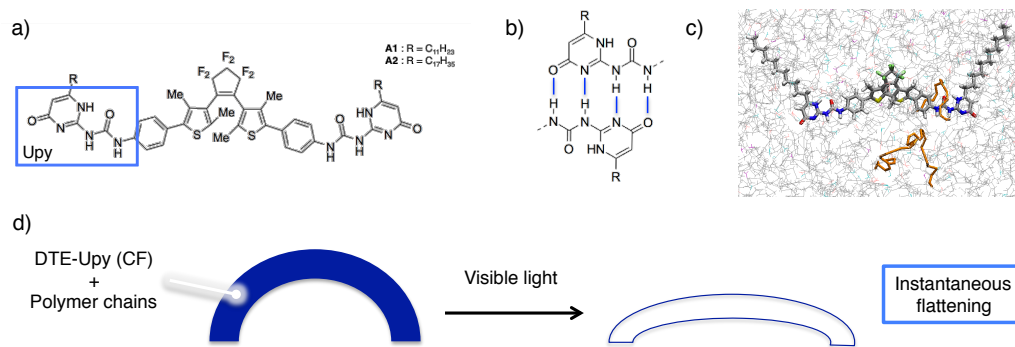


Figure 1. Structure representations of a) DTE-Upy and b) Upy-Upy interaction. A representation of c) a DTE-Upy molecule embedded in a polymer matrix is also provided along with d) a schematic representation of the optomechanical effect.

Hybrid QM/MM Molecular Dynamics with AMOEBA Polarizable Embedding

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In recent years lots of efforts have been devoted in the field of classical molecular dynamics (MD) for the development of force fields that explicitly account for polarization, but still efficient for the study of large systems. They include many-body effects, improving, in principle, flexibility and accuracy. Such improvement is still not enough for the description of many important phenomena in molecular science, such as chemical reactivity and photoinduced processes, due to their intrinsic quantum nature. In that respect, Hybrid Quantum Mechanics/Classical methods represents a very promising strategy as they combines the computational efficiency of a classical model with the required quantum description of the subsystem of interest.

In the last years we developed a Born-Oppenheimer (BO) hybrid QM/MM MD strategy, based on the coupling[1,2] of Density Functional Theory (DFT) and the polarizable AMOEBA[3] force field. This approach involves the interplay between the Gaussian and Tinker suite of programs through a variational formalism allowing for a self-consistent relaxation of both the AMOEBA induced dipoles and the DFT electronic density at each MD step.

In this contribution we will present some new advances in the implementation of the code, and some recent applications in the field of computational spectroscopy of molecular dyes embedded in complex environments (DNA or proteins).

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Preparation of Initial Conditions for Flexible Transition Metal Complexes in Solution

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Initial condition generation is one of the most critical steps in carrying out nonadiabatic dynamics simulations. The two most popular approaches for this task are sampling from a Wigner distribution—based on harmonic frequencies and linear normal modes—and sampling from a molecular dynamics (MD) trajectory.^{1,2} The first approach works very well for small, rigid molecules with few energetic minima and delivers a good representation of the ground state vibrational wave function. The second approach is required for extended, flexible, or solvated systems, due to its ability to deal with anharmonic potentials, non-linear vibrational modes, and a large number of local energetic minima. Unfortunately, sampling from MD trajectories comes at the price of an inferior description of vibrational zero-point energy and usually underestimates the total vibrational energy of the molecule,¹ leading to too narrow spectra and too slow dynamics.² Furthermore, sampling using general force fields might lead to deviations of the distribution from the ab initio equilibrium geometries. Here, we present some novel approaches to remedy these two shortcomings of MD sampling. Examples are shown for $[\text{Re}(\text{ImH})(\text{CO})_3(\text{Phen})]^+$ (Figure 1), a transition metal complex where the imidazole ligand can almost freely rotate.³

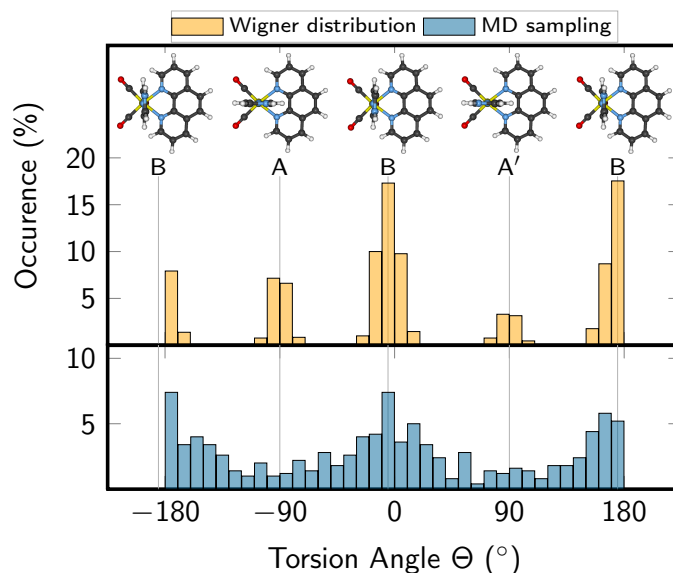


Figure 1: Distribution of imidazole torsion angles in $[\text{Re}(\text{ImH})(\text{CO})_3(\text{Phen})]^+$, based on sampling from either a Wigner distribution or an MD trajectory.

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DNA PHOTSENSITIZATION BY ORGANIC DYES: FROM NON-COVALENT BINDING TO IRREVERSIBLE LESIONS

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Although diverse DNA photostability mechanisms exist, organic dyes in the vicinity of DNA can induce damages through indirect light absorption. Hence, understanding the underlying mechanisms involved in photosensitized DNA damage is crucial to describe and possibly anticipate photobiological risks, as well as to design anticancer phototherapies.¹

Here, we present the results concerning our latest studies on different reactivities induced by common organic dyes, through multiscale molecular modeling techniques coupled to spectroscopy experiments. Especially, the photochemistry of benzophenone – a paradigmatic DNA photosensitizer – and its implications in the competitive processes of hydrogen abstraction² and energy transfer to DNA^{3,4} will be described. The results will be compared with structurally related compounds of pharmaceutical interest, *i.e.* the non-steroidal 2-arylpropionic acids ibuprofen and ketoprofen, which photosensitization activity was properly assessed by computational and experimental studies.⁵

Electron transfer is also considered by the interaction of DNA with two fluorescent dyes widely used in cellular biology: nile blue and nile red.⁶ Finally, the potentialities of a recently synthesized novel carbazole in photosensitizing DNA through two-photon absorption will be reported. Especially, it will be shown how it can induce DNA strand break upon photoionization with the production of a solvated electron.⁷ The main advantage is the low-energy (infra-red) irradiation required also in the absence of molecular oxygen, *i.e.* a prodrug of great interest for the potential treatment of solid tumors.

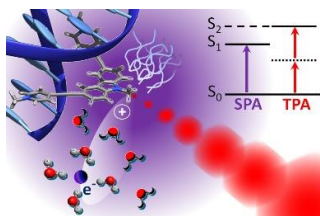


Figure. Artwork showing the two-photon absorption (TPA) of infra-red light by the BMEMC sensitizer interacting with DNA, followed by the generation of a cation and a solvated electron.⁷

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Effects of Mutations on the Excited State Dynamics of Anabaena Sensory Rhodopsin

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Protein engineering of microbial rhodopsins with enhanced fluorescence has been successful in the generation of variants with improved properties for applications in the expanding field of optogenetics¹. These systems exhibit a significant change in the fluorescence as a consequence of action potential variation along the neuron membrane. Archaeorhodopsin 3 (Arch3) from *Halorubrum Sodomense* performs a limited temporal resolution for action potential visualization. However, the observed fluorescence is very dim. In order to overcome the limitations present in Arch3, one could look for variants with enhanced fluorescent or, alternatively, engineering other suitable microbial rhodopsins.

Here we report the discovery of a mutant (W76S/Y179F) of a sensory rhodopsin from the cyanobacterium *Anabaena* PCC7120, which displays a ten-fold increase in red-light emission already 15 fs after photoexcitation. More specifically, by combining computational multi-configurational quantum chemistry and experimental pump-probe spectroscopy studies, we show that such enhancement must be due to the formation of a region of S_2/S_1 degeneracy which is promptly accessed upon excited state relaxation and that significantly slows down progression along an isomerization coordinate². As a counter example we show that the lifting of such degeneracy in another mutant of the same rhodopsin (L83Q), reduces the fluorescence of two orders of magnitude³.

This finding opens the way to the reprogramming of highly reactive, but weakly emissive, rhodopsins in optogenetics tools for action potential visualization in live cells.

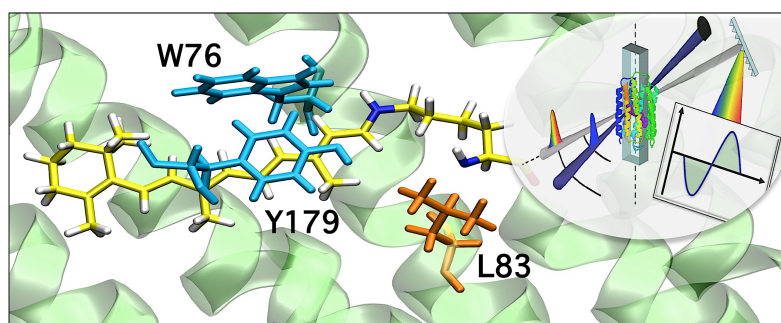


Figure 1. Molecular structure of dark-adapted ASR. The mutated residues are highlighted in orange (L83Q) and blue (W76S/Y179F). The pump-probe spectroscopy scheme is also shown.

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³ Agathangelou D. *et al.* Effect of point mutations on the ultrafast photo-isomerization of Anabaena sensory rhodopsin. *Faraday Discussions*, (2017).

Photophysics modification of the native all-*trans*-retinal protonated Schiff base through methylation: A CASPT2/MD study in gas phase and methanol

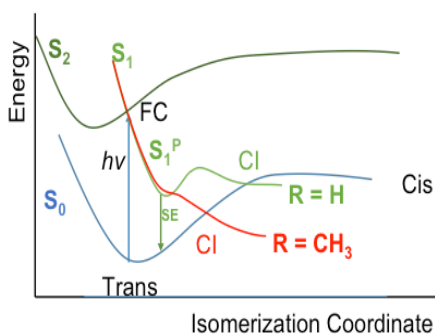
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Abstract

Despite the fact that Retinal Protonated Schiff Base (RPSB) is one of the more studied photochemical systems, there is some controversy about the details of the photoisomerization dynamics in polar solvent. Recent studies¹ have shown that the methylation at the C10 position produces important changes in the reaction dynamics. In this study we have compared, at CASPT2//CASSCF level, the S_1 free-energy surface of the native and methylated compound in gas phase and in methanol solution. Solvent effects were included using the Averaged Solvent Electrostatic Potential from Molecular Dynamics method (ASEP/MD)² that makes use of the mean field approximation.

It is found that the methyl group bonded to C10 produces noticeable changes in the solution



free-energy profile of the S_1 excited state, mainly in the relative stability of the minimum energy conical intersections (MECIs) with respect to the Franck-Condon (FC) point. In this way, the small barrier that separates the S_1 minimum from the MECI in the native chromophore disappears when the all-*trans*-RPSB is methylated at C10, and therefore, the photoisomerization becomes a nonactivated process. In addition, the conical intersections

yielding the 9-*cis* and 11-*cis* isomers become stabilized with respect to the FC point and other MECIs. These two effects combine to speed up the photoisomerization. Moreover, the interaction with the solvent brings closer the S_1 and the S_2 energy levels at the absorption FC geometry, permitting the branching of the population between the reactive and nonreactive channels.

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Ab initio molecular design for [2+2] photocycloaddition and metathesis reactions

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Well-known [2+2] photocycloaddition reactions of two olefins leading to a cyclobutane ring formation is thermally forbidden in the ground state due to Woodward-Hoffman rules and typically occurs only after sensitization to the triplet state. Direct excitation to the lowest lying singlet states requires UV light and leads to fragmentation of the system.

Compared to photocycloadditions, photocycloreversions are still a subject of ongoing reactions. The reversion is an important step in the metathesis reaction [1], which represents a viable way for transferring double bond. Photocycloreversion is particularly attractive in the context of photoredox catalysis [2], because ring cleavage can be also achieved both in a cationic or anionic state via photoredox catalysis using e.g. flavinium salts as the catalyst. [3]

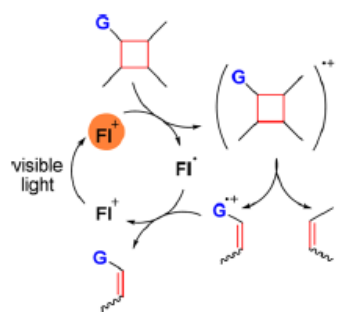


Figure 1: Flavinium salt facilitates the electron transfer from or to the cyclobutane moiety, upon which the ring cleavage can take place. [4]

Theoretical description of the photocycloreversion is, however, difficult due to complicated electronic structure of intermediates. We study the formation and fragmentation of [2+2] systems using *ab initio* molecular dynamics in ground and excited states. Using accelerated molecular dynamics approaches we evaluate the free energy profiles for the reactions and we estimate reaction barriers. We also benchmark DFT approaches against high-level multi-reference calculations. Finally, we perform a screening of the systems in the chemical space, trying to identify potential candidates for further experimental identification.

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Coherent energy transfer in Peridinin – Chlorophyll *a* – Protein

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Photosynthetic organisms, depending on their habitat, developed distinct strategies based on chlorine and bacteriochlorin derivatives, but also on carotenoids as main pigments to enhance their light-harvesting activity. The subtle details of the mechanism of energy flow from carotenoids to chlorophylls in natural antennas are still not fully understood, mainly because the peculiar optical properties of carotenoids make their spectroscopic characterization particularly challenging, especially in the ultrafast time regime.

Peridinin-chlorophyll *a*-protein (PCP) is a water-soluble external antenna system of dinoflagellates whose light-harvesting capability largely rely on its carotenoids, peridinins. PCP is well known for its remarkable efficiency of excitation energy transfer from peridinins to chlorophylls [1]. The sub-picosecond optical response of the antenna system was investigated in this work with two-dimensional electronic spectroscopy, by gradually turning on the resonance with peridinin absorption band. The third-order nonlinear response of PCP revealed multiple pathways of energy flow from the lowest states of peridinins excitonic framework (S_2). PCP dynamics of energy transfer was analyzed with a novel data-analysis tool [2], and modelled with a kinetic scheme that shows how, in contrast to general assumptions, the main channel of energy transfer from S_2 links directly to chlorophyll Q_y state, without other intermediate steps.

The mismatching results with previous literature could be explained by the presence of an ultrafast coherent transfer also detected in PCP optical response. The experiments revealed a coherent superposition of peridinin S_2 states and chlorophyll Q_y states that dephases, driving population on the final acceptor Q_y state. The process unveiled and described in this work shows how coherent phenomena can be functional for biological energy transport, and it adds an important piece to the mosaic of quantum biology.

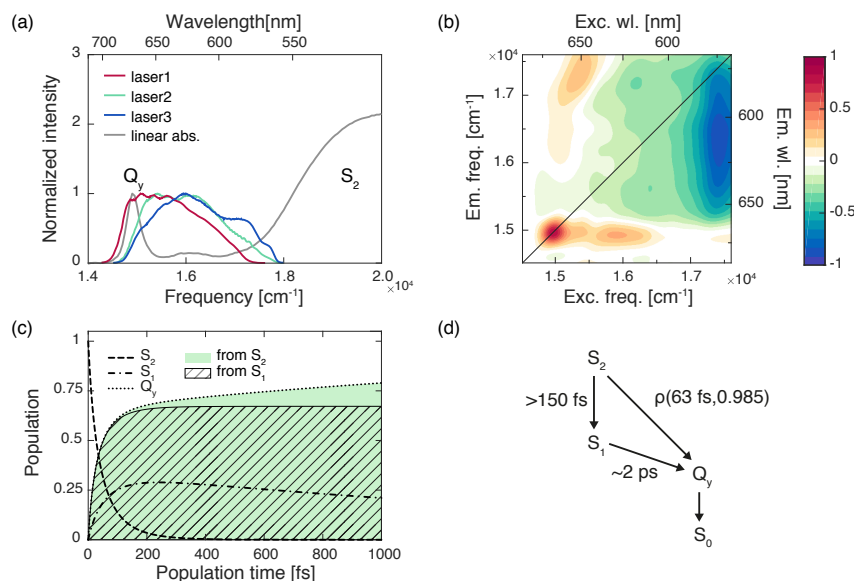


Fig. 1. (a) PCP linear absorption spectrum (gray line) and laser spectrum profiles (red, green and blue lines) used in the three 2DES experiments. (b). Experimental 2DES map at a selected value of population time (100 fs) obtained with laser 3 and normalized to 1 at its maximum. (c) Time evolution of populations according to the results of the fitting based on the kinetic model of excitation energy transfer pathways in PCP reported in scheme (d).

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Surface hopping within an exciton picture - An electronic embedding scheme

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Electronic excitation energy transfer (EET) is the fundamental process observed in biosystems and materials through which an excited chromophoric unit (the donor) nonradiatively transfers the excitation energy to another proximate unit (the acceptor). One of the most prominent examples of this process is the initial step of photosynthesis, where the excitation energy is transferred many times in and between pigment-protein complexes until the reaction center is reached.[1, 2]

The theoretical investigation of EET processes can be highly challenging due to (i) the size of the involved system, (ii) the influence of the environment and (iii) the complexity of the involved dynamics .[3]

To address these problems we developed an hybrid QM/MM exciton scheme with mechanical and electrostatic embedding for non-adiabatic molecular dynamics. Hereby we utilize the Gaussian 09 suite of codes for the electronic structure calculation and combine it with the SHARC (Surface Hopping Including arbitrary couplings) scheme [5, 6] for the surface hopping dynamics.

We apply our approach to a molecular dyad consistent of a BODIPY moiety covalently bonded to a tetrathiophene group. The results using our exciton Hamiltonian were compared with those obtained on the whole system treated at TDDFT level of theory. [4] Although covalent linked systems represent quite challenging cases for simple Frenkel exciton models, the obtained results show an excellent agreement with the full TDDFT [7].

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Poster presentation at the PPES, Pisa 23-27 June 2018

Title: *In silico* design of a photoanode for solar fuel production

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Institution: Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands

Abstract

Dye-sensitized photoelectrochemical cells (DSPECs) have attracted much interest in recent years as a promising device for converting visible light directly into molecular fuel. To fulfil the potential of DSPECs in producing clean photosynthetic fuels, more effort is required to increase their chemical stability and efficiency, which is largely governed by well-tuned and optimized components. Computational studies can provide insight into the fundamental charge separation and recombination processes and suggest design principles. In this project the focus is on the dye-semiconductor interface and the coupling with the water oxidation catalyst in an explicit solvent environment. Given the complexity of the problem, one has to find a good compromise between accuracy and computational cost. Here we use mostly Density Functional based Tight Binding (DFTB) to study (i) water adsorption dynamics on a TiO₂ anatase semiconductor slab, (ii) dynamical stability of different anchoring groups for the dye on the surface including explicit solvation. Moreover, we explore the photo-induced electron injection process and the effect of the anchoring groups on the charge recombination.

Interplay of Electronic and Structural Features in the Prediction of Organic Solar Cells Efficiency

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Abstract

In this contribution we present an approach to predict Organic Solar Cells Efficiency based on Machine Learning. We present a data set of small molecule donor-acceptor pairs gathered from the literature (between 2013 and 2017), for which equilibrium geometries and electronic properties have been computed at DFT level. We used electronic data in combination with Scharber's model to calculate photovoltaic parameters of the organic solar cells. Comparison with experimental data reveals a disappointing performance of DFT. It has been shown that DFT data can be refined through Machine Learning to improve the performance of Scharber's model to predict experimental photovoltaic parameters. In this contribution, we adopt a similar procedure to predict photovoltaic parameters from structural information only, expressed in terms of molecular fingerprints. This allows to bypass a high number of DFT calculations, obtaining similar results to those reported in the literature and based on electronic data exclusively. Finally, with a similar approach, we obtain direct predictions of solar cell efficiencies. We show that considering only electronic or structural parameters leads again to similar results, while considering both parameters at the same time results in improved predictions, allowing to obtain direct predictions of solar cells efficiency with a reasonable level of accuracy. Finally, we critically assess the usefulness of the proposed approach for the discovery of new materials that have not been synthesized yet.

Multi-faceted spectroscopic mapping of the ultrafast nonadiabatic dynamics near avoided crossings

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Avoided crossings in molecular potential-energy surfaces play the key mechanistic role in molecular spectroscopy of energy- and charge-transfer processes [1]. Electron-transfer dynamics constitutes the basic step in a majority of biological processes occurring in nature, such as in the cell metabolism and energy balance in protein complexes. The comprehensive visualization of the ultrafast electronic, vibrational and photochemical dynamics at avoided crossings is therefore an important goal of femtosecond time-resolved spectroscopy in chemistry. Established spectroscopic techniques [2] provide us with femtosecond time-resolved spectroscopic signals, which in general can be challenging to interpret. Each of these techniques provides an alternative glimpse of the photoinduced dynamics by projecting the multidimensional electronic/nuclear wave packet onto specific “reporter states”. A comprehensive mapping of the nonadiabatic wave packet calls for the application of complementary time and frequency resolved spectroscopic techniques to a given avoided crossing.

In the proposed work, we will simulate with computational methods the outcome of such a concerted experimental effort. We will consider a model of a spectroscopically accessible avoided crossing formed by the lowest two excited singlet states in the vicinity of the Franck-Condon region of a polyatomic molecule, augmented with a higher excited electronic state. The considered system reaction mode is coupled to a harmonic bath, which is responsible for the relaxation dynamics. The electronic interstate-coupling is assumed strong, so that the electron-transfer dynamics deviates from the Fermi-Golden behavior, showing electronic and vibrational beatings. For this model, we compute the signals of four well-established two-pulse spectroscopic techniques: time and frequency resolved fluorescence, two-pulse photon-echo (2PE), pump-probe (PP) and femtosecond stimulated Raman (FSRS) spectroscopy. The simulations are based on an exact numerical solution of the driven time-dependent Liouville-von-Neumann equation [3]. The effects of laser pulse shape and pulse overlap are fully included. We demonstrate which features of the photoinduced dynamics, such as electronic/nuclear populations, electronic/nuclear coherences or electronic/nuclear charge transfer processes are imprinted in the spectroscopic signals. It will be shown that a fairly complete and systematic picture of the coupled electronic/nuclear dynamics at avoided crossings can be obtained in this manner.

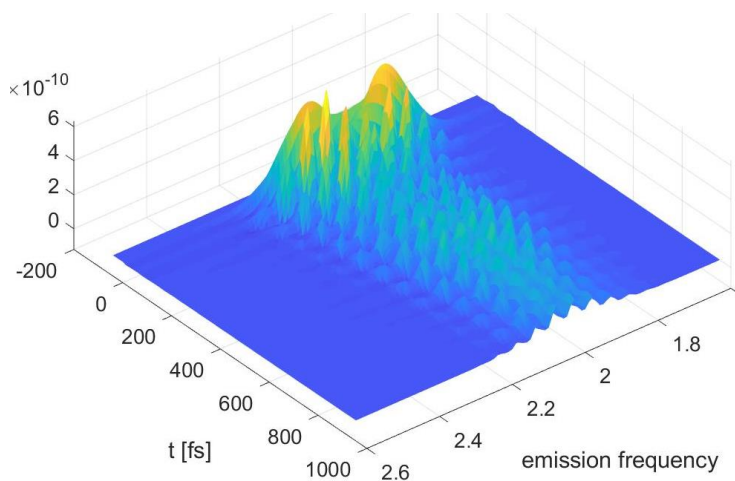


Figure 1: Ideal frequency- and time-resolved fluorescence up conversion signal excited by a short (10.0 fs) pump pulse.

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Automatic Generation of QM/MM Models of Biological Photoreceptors

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The Automatic Rhodopsin Modeling (ARM) has recently been proposed as a protocol for the automatic and parallel generation of basic QM/MM models of Wild-Type and mutant rhodopsin-like photoreceptors.[1] The only required input is a template crystallographic structure or comparative model of the protein and, additionally, the information on the protonation states of ionizable side chains and the geometry of external counterions. In the current approach (*m*-Model), the procedure for adding these information consist of a series of manual steps including visualization of the structure, execution of external software (i.e. PROPKA[2]) and manual modification of the initial file, thus creating a execution bottleneck long several hours. Such bottleneck represents, presently, one of the limits to the full automation of the protocol.

In this work we push the automation of our protocol a step further by linking the ARM protocol to a program avoiding the time-consuming manual generation of the external counterion set (*a*-Model). The performance of this approach, that speeds up the model construction time of several hours, has been tested on a set of 7 Wild-Type Rhodopsins (including vertebrate, invertebrate and microbial) to examine the suitability of their ARM *a*-Models for the prediction of Vertical Excitation Energies (ΔE_{S1-S0}) and Maximum Absorption Wavelengths (λ_{max}). Moreover, the protocol[1] is implemented in a Web interface to ARM (WARM).[3] A first remarkable finding is that the experimental trend in ΔE_{S1-S0} , is reproduced by the new *a*-Model protocol better than when using the original *m*-Model. The agreement with experimental data is reflected by an overall mean absolute error of 1.1 kcal mol⁻¹ and a maximum absolute deviation of 1.7 kcal mol⁻¹. One of the most appealing features of the new protocol is that the ARM *a*-Models, whose execution time is reduced from 3 hours to less than 5 minutes, are reproducible regardless of the user.

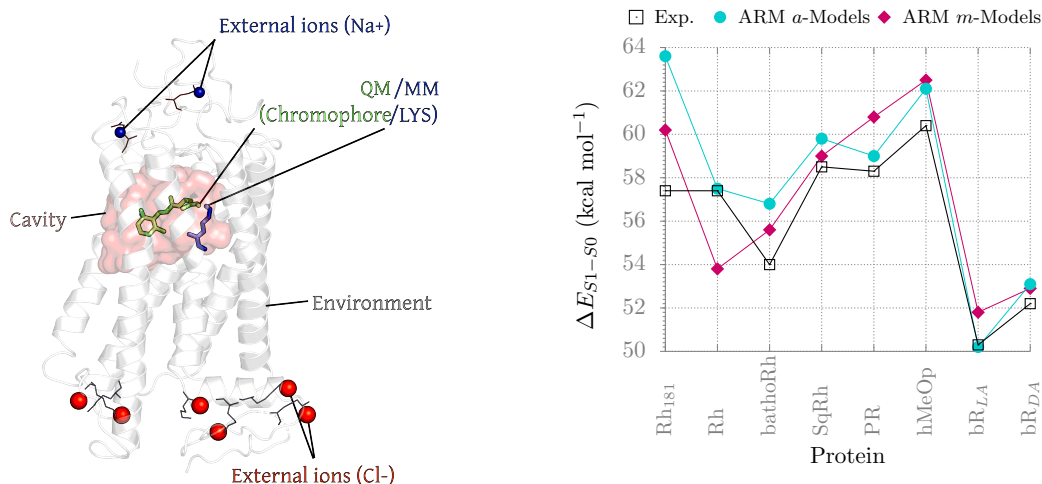


Figure 1: General structure of a QM/MM model constructed using the new ARM *a*-Model approach (left). Vertical Excitation Energies (ΔE_{S1-S0}) calculated using the new *a*-Model and the original *m*-Model, along with experimental data (right)

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Photo-Induced Electronic Transitions and Spectroscopic Signatures of Localized Defects in Nanodiamonds

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The presence of mid-gap states introduced by localized defects in doped wide-band-gap semiconductors can strongly affect the electronic structure and optical properties of materials. Diamond presents a large optical band gap (~ 5.5 eV for bulk), and has a very dense lattice that both restricts defect diffusion and phase transitions at high temperatures. Thus, interest in the manipulation and characterization of isolated defects in diamonds has been generated from the wide range of applications for these systems, such as quantum computing, sensing, and cryptography.¹⁻³

Substitutional nitrogen and nitrogen-vacancy (NV) centers are common defects in diamond and have received attention for their sensitive optical and spin properties.⁴⁻⁶ Similar applications in quantum cryptography have been proposed for the negatively-charged silicon-vacancy (SiV) center due to its short fluorescent lifetime, narrow emission line-width, and high percentage of photons ($>95\%$) emitted through its zero-phonon line.⁷⁻⁹ Despite their importance, carbon K-edge X-ray and vibrational transitions for the characterization of defects in nanodiamond, along with the effects of the defect location in the crystal lattice (i.e. surface effects, symmetry breaking) and system size (i.e. quantum confinement) on these transitions, have not been well studied.

In this work, theoretical investigations with a finite cluster approach of both the electronic and vibrational properties are carried out using density functional theory (DFT) and linear-response time-dependent density functional theory (LR-TDDFT) in defect containing nanodiamonds of different sizes. Using group theory, the molecular origin of mid-gap states, zero phonon line splitting, Carbon K edge X-ray and Raman vibrational absorption, and the size dependence of the electronic transitions are investigated for the SiV system and compared with the NV center.

This work presents an important analysis of the photo-induced transitions of localized defects embedded in complex matrices, such as nanosized semi-conductors, providing new insights into possible mechanisms for modulating their optical properties.

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Photodynamics and spectroscopy of halogens embedded in rare gas solids: Quantum dynamical description of the $I_2 : Kr$ system

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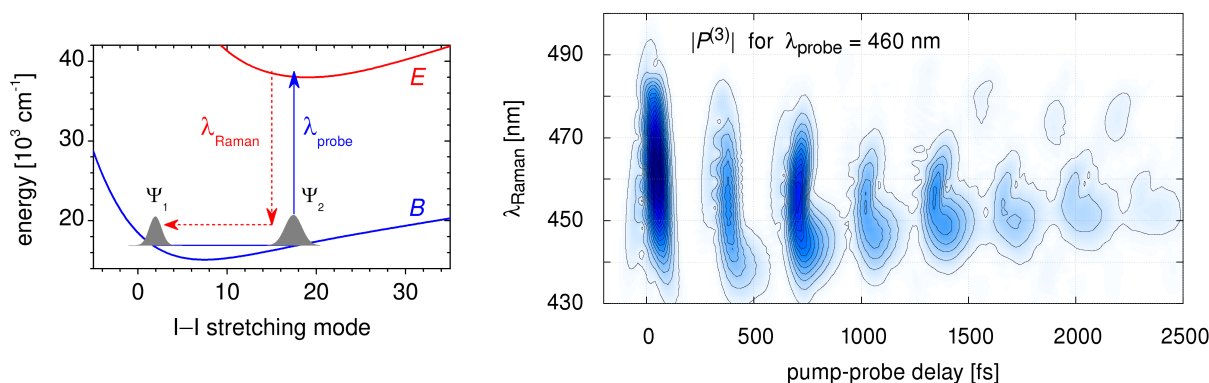
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Diatomic halogen molecules embedded in rare gas crystals provide prototypes for the investigation of condensed phase chemical dynamics.^{1,2} Nonlinear spectroscopy experiments performed on these systems reveal strong guest-host interactions and manifestations of quantum effects such as entanglement between system and environment, non-local correlations, and the transition to classicality through decoherence.³

Such pronounced quantum behaviour is also ideally suited for testing novel computational approaches to describe the dynamics of open quantum systems.⁵ In this contribution, we study cluster models of I_2 in a fcc Kr crystal, by comparing two wave packet propagation methods: (i) the numerically exact multiconfigurational time-dependent Hartree (MCTDH) approach,⁶ and (ii) the G-MCTDH variant,⁷ in which the rare gas cage coordinates are treated with Gaussian wave packets. Due to anharmonicities, non-trivial molecule-cage correlations are generated. Vibrational coherences last for several vibrational periods of the embedded I_2 , despite extensive dissipation to the Kr lattice.

The computationally cheaper G-MCTDH approach is able to reproduce the detailed features of the absorption spectrum, autocorrelation function and subsystem density of the I_2Kr_n system, providing therefore a correct description of the dissipation mechanism.⁸ The method is implemented in in-house codes, and is used to simulate and interpret nonlinear optical signals of high-dimensional dihalogen/host models from first principles. In the example of the figure, the I_2 chromophore is prepared in a ‘Schrödinger’s cat’ superposition of two wave packets in the electronic B state; the time-resolved resonance Raman signal is calculated and used to monitor vibrational decoherence.^{4,5,8}



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Investigating the pH-Dependency of Proteins UV Absorption Spectrum using a multiscale QM/MM Approach

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The Anabaena Sensory Rhodopsin microbial protein (ASR) owns particularly interesting photophysical and photochemical features, such as a photochromism that involves different structural configurations of his chromophore, the retinal^[1,2]. In this work, we seek to highlight the parameters that govern the pH-dependency of the UV absorption spectrum of this protein, where the pH value is known to induce a weak but significant shift in its spectroscopic signature^[3,4].

The modeling of such a phenomenon is a real challenge due to the impressive size of both the conformational (~41000 atoms when the protein is embedded in a biological membrane) and protonation state space (up to 37 titratable residues under physiological conditions); we wish to achieve this study by developing new models and applying them through large simulations taking into account explicitly all the important degrees of freedom, including the states of protonation of all ionizable amino acids. For this purpose, we combined Constant pH Molecular Dynamics (CpHMD) techniques with Quantum Chemistry methods.

In this work, we applied the CpHMD method to ASR in order to obtain informations on the protonation states population; 20000 snapshots were taken from the trajectories at pH 3.5, 5.5 and 7.5, coupled with the protonation microstate information and used to calculate the absorption spectrum of retinal at a given pH value.

The results (Fig. 1) show a qualitative agreement with the experimental data, highlighting a small redshift going from pH 3.5 to 5.5 and a relevant blueshift at a higher pH value. Moreover, this approach provides a remarkable amount of information, that can be analyzed with advanced statistical techniques in order to investigate the role of the key ionizable residues and elucidate the mechanism behind the pH-dependence of the absorption spectrum.

As pH is also known to affect the photochemical behavior of retinal in ASR, tentative investigations of retinal excited states dynamics will be presented.

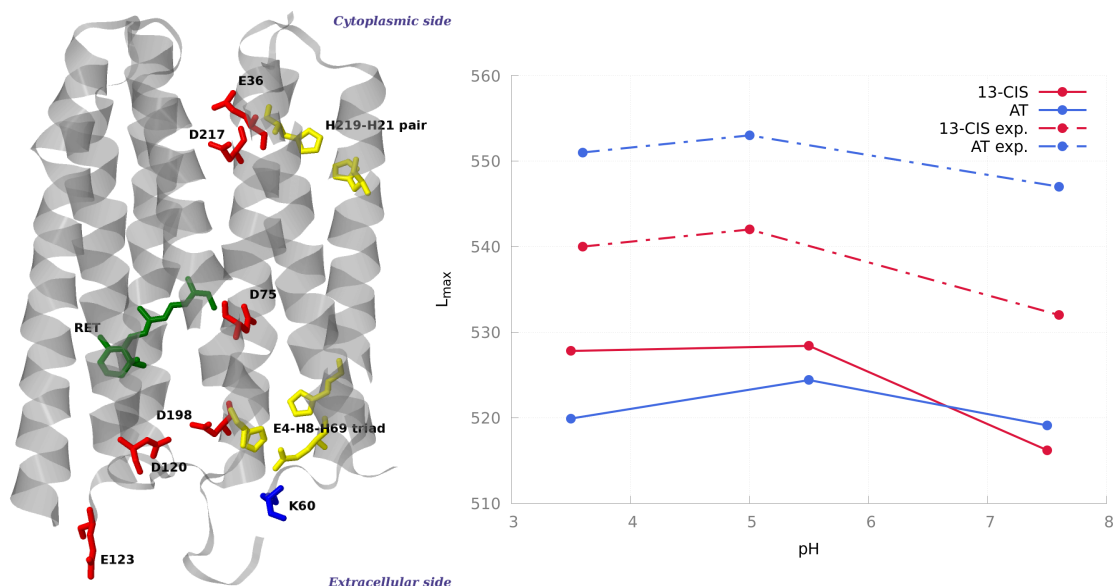


Figure 1: Calculated absorption maximum of ASR (retinal fragment, in green) at different pH values.

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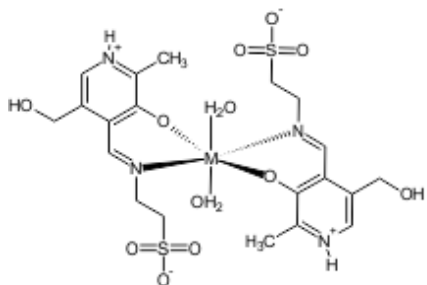
Vibrational spectra of transition metal complexes: An anharmonic approach

Martin Pižl,^{1,2} Marco Fuse³, Nicola Tasinato³, Vincenzo Barone³, Antonín Vlček^{1,4}, Stanislav Zális¹

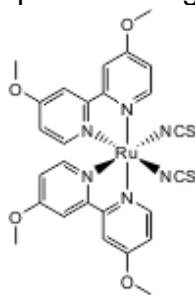
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Vibrational properties of coordination compounds are often used for their characterization. Harmonic approximation is a standard approach for description of vibrational properties like infrared or Raman spectra. On the other hand, anharmonic calculation is important for better understanding of spectra and detailed description of experimental data by calculated results. Vibrational second-order theory (VPT2) is widely used for estimation of anharmonic frequencies. All calculations were performed by Gaussian 16 program package.

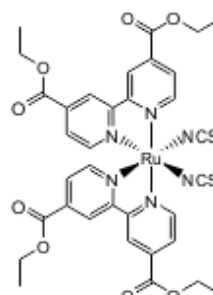
In this study, we focused on anharmonic effects on Raman spectrum of Co (1), Ni (2) and Cu (3) complexes derived from vitamin B6. This work also contains application of anharmonic approach for estimating of diagonal and off-diagonal anharmonicities in 2DIR spectra of Ru complexes – [Ru(4,4'-di-R-2,2'-bipyridine)₂(NCS)₂] (R = OMe (4) and CO₂Et (5)). Structures of complexes 1-5 are depicted on Fig.1.



M = Co (1), Ni (2) or Cu (3)

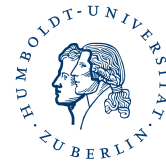


[Ru(MeObpy)₂(NCS)₂] (4)



[Ru(EtCOObpy)₂(NCS)₂] (5)

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Simulation of Light-Induced Charge Separation at a Nano-Hybrid *para*-sexiphenyl/ZnO Interface

Thomas Plehn and Volkhard May

Abstract:

Charge separation kinetics at a realistic organic/inorganic hybrid interface system are reported. A vertical stacking of 20 *para*-sexiphenyl molecules is physisorbed on a ZnO nanocluster of about 3900 atoms. Energy transfer within the organic body is induced by laser-pulse excitation and leads to an electron transfer process from the molecules to the ZnO cluster. The exciton, injected electron and remaining hole are simulated in atomic resolution. The system Hamiltonian is based on (time-dependent) density functional theory and density functional based tight-binding approaches, where the latter copes with the expansive ZnO cluster. The proper inspection of the charge separation process relies on rather extended ranges. Regarding the essential nano-scale of the system, a stochastic Schrödinger equation approach becomes highly advantageous and takes heed of electron-vibration interactions [1].

The report brings the initial system kinetics in response to the fs laser-pulse into focus. The charge separation dynamics are monitored in dependence on the strength of charge transfer across the interface and the hole transfer coupling within the molecular body. The results highlight the importance of direct laser-pulse excitation in comparison with conventional initial state preparation techniques [2].

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Wavefunction Frozen Density Embedding: an analysis of the errors in excitation energies.

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Frozen Density Embedding Theory (FDET)¹ is a multi-level method which describes the effect of a frozen electron density of the environment, $\rho_B(\mathbf{r})$, on the wavefunction of the system of interest (Ψ_A). FDET exhibits large flexibility: any choice of methods for the subsystems A and B is possible, including for instance the generation of $\rho_B(\mathbf{r})$ as a superposition of densities. Additionally, the multi-level approach of this formalism can be further extended by combination with other environment models (e.g. PCM, MM).

Contrary to conventional FDET, which requires macrocycles to calculate the embedding potential self consistently, linearised FDET³⁾ relies on a single calculation of the embedding potential, considerably speeding up the procedure with no significant loss in accuracy. Furthermore, while conventional FDET leads to a different embedding potential for each state, linearised FDET leads to a state-independent embedding potential resulting in orthogonal states.

Our group implemented a combination of linearised FDET with the Algebraic Diagrammatic Construction scheme for the polarisation propagator, the latter being a promising high - performance excited state method.

In our research, we aim at assessing the scope and limitations of such protocol by investigating the relation between the theoretical approximations of the model and chemical properties. Factors such as the overlap of $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ and the delocalisation of the excitation have been analysed on a dataset of 52 supermolecular clusters. The distance dependence of the error and of said factors has been investigated in order to discern different error components. Furthermore, the relation between the error on the one hand, and the dipole moment and polarisability of the two subsystems on the other, has been investigated in order to better understand the influence of induction on the performance of the method.

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Analytic second derivatives of the QM-MM energy with Kohn-Sham DFT and Electrostatic Potential Fitting Method

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Chemical reactions often occur in complex media. Mixed quantum-classical mechanics (QM-MM) approaches play an important role in understanding the influence of the environment. This generally requires detailed characterization of the potential energy surface, including first and second derivatives. Here we present the derivation and implementation of analytic second derivatives of the Kohn-Sham DFT QM-MM energy with respect to the nuclear coordinates. The interaction energy is described by the Electrostatic Potential Fitting (ESPF) method.¹ The ESPF method uses a classical electrostatic-like expression where the QM charge density is represented by distributed multipole operators fitted to the electrostatic potential. This allows the efficient computation of the QM-MM Hessian matrix which is essential for the search of minima and conical intersections, as well as for characterizing the vibrational motions.

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Predicting solvent effects on the photoelectron spectra of halide ions with WFT-in-DFT embedding

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Photoelectron spectroscopy is a powerful approach to determine the electron binding energies in molecular species and materials. These, together with electron affinities, are essential quantities for understanding reactivity in gas phase and in solution, as well as the structure of the solvent around a solute [1]. In this contribution we aim to present a protocol for obtaining the photoelectron spectra in the valence region, which can yield accurate information on both the solvent and solute binding energies at a reasonable computational cost while accounting for specific interactions such as hydrogen bonding. The protocol is based on a combination of classical molecular dynamics (CMD) with polarizable force fields [2] and electronic structure calculations employing the frozen density embedding (FDE) approach in combination with the single electron detachment (EOM-IP-CCSD) variant of the equation of motion coupled cluster method for the solute and the SAOP model potential for the solvent.

Here we apply our protocol to the determination of the photoelectron spectra in the valence region of halide ions (X^- , $X = F-At$) in aqueous solution, which show a rather large solvent effect that can not be captured with implicit models [3]. The CMD simulations are made for a droplet model with 50 water molecules and the halogen ions [4], which reproduce the radial distributions obtained from periodic calculations [2]. As relativistic effects [5] become increasingly important along the series—notably due to the increased strength of spin-orbit coupling that splits the partially filled p orbitals of the halogens—we employ the two-component molecular mean-field (X2Cmmf) Hamiltonian available in the Dirac program [6] for the EOM-IP-CCSD calculations.

We show our fully quantum mechanical treatment of the electronic structure for the droplet does indeed yield accurate results while considering only the halide as the solute, with the exception of F^- , whose valence p orbitals strongly mix with those of the closest water molecules. It was nevertheless important to relax (in the FDE treatment) the densities of the water molecules in both first and second solvation shells, due to the long-range influence of the charged halide species.

This work has been supported by the French national agency for research, contract ANR-11-LABX-0005 chemical and physical properties of the atmosphere (CaPPA).

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First principles calculation of fluorographene optical and excitation transfer properties

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Recently, increasing attention has been focused on artificial light harvesting systems which would possess properties such as photo-stability, fast excitation energy transfer, high energy yield and tunability in frequency range. One class of possible candidates are bio-inspired fluorographene based systems [1]. Fluorographene is a two-dimensional (2D) material which has been recently intensively studied as one of the derivatives of graphene. Perfectly fluorinated fluorographene, is an insulator with energy gap wide enough to make it transparent to almost complete solar spectrum. However, when only partial fluorination of graphene is achieved, π -conjugated impurities can be formed, which can serve as centers, quantum dots, for excitation energy transfer (Fig 1) [1]. Quantum chemistry calculation of fluorographene sheet with these impurities revealed localization of π -molecular orbitals and transition densities for the lowest optical transitions in the area of the impurity. These impurities can be hence treated as individual molecules embedded in fluorographene environment, same as pigments in photosynthetic complexes, rather than by solid state techniques as defects in periodic structure. Covalent bonds between impurities and the rest of the fluorographene sheet, the resulting short distance between “molecules” and the environment, and the 2D nature of these systems, require different theoretical treatment than natural pigment-protein light harvesting complexes for which most of the current methods were developed.

In this contribution we propose new approach for calculation of site energy shifts and interaction energy changes induced by the environment, which is based on perturbation expansion of interaction between impurity and fluorographene environment, and results in terms similar to the polarizable QM/MM model [2]. This approach is then used for the first principles calculation of properties of fluorographene systems with impurities, starting from calculation of site and interaction energies between individual impurities, calculation of spectral densities from normal mode analysis [3], all the way to the calculation of optical spectra and simulation of excitation energy transfer. This approach can be applied to systems with different scales, from small clusters to large sheets. Particular results such as site energy shifts and interaction energies were compared with full quantum chemistry calculation on small clusters yielding good quantitative agreement for different impurity sizes and shapes.

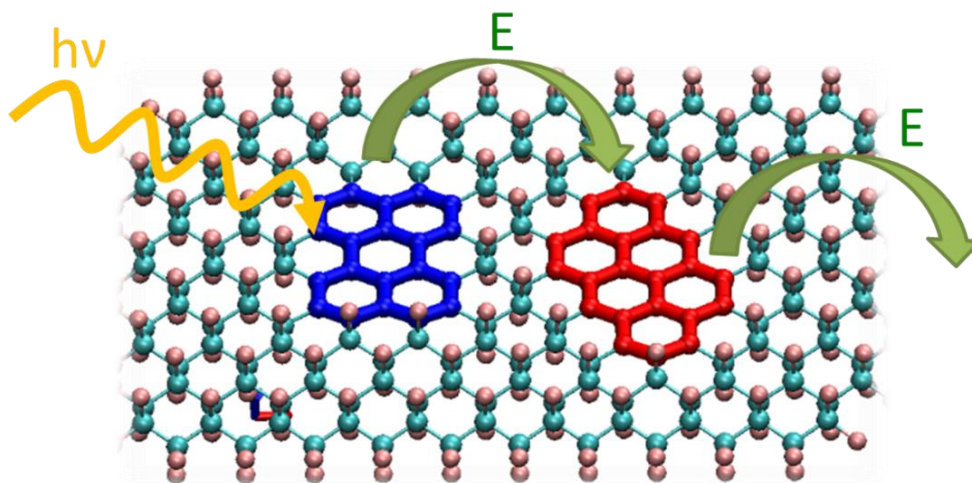


Fig. 1. Representation of fluorographene based artificial light harvesting antenna with π -conjugated impurities.

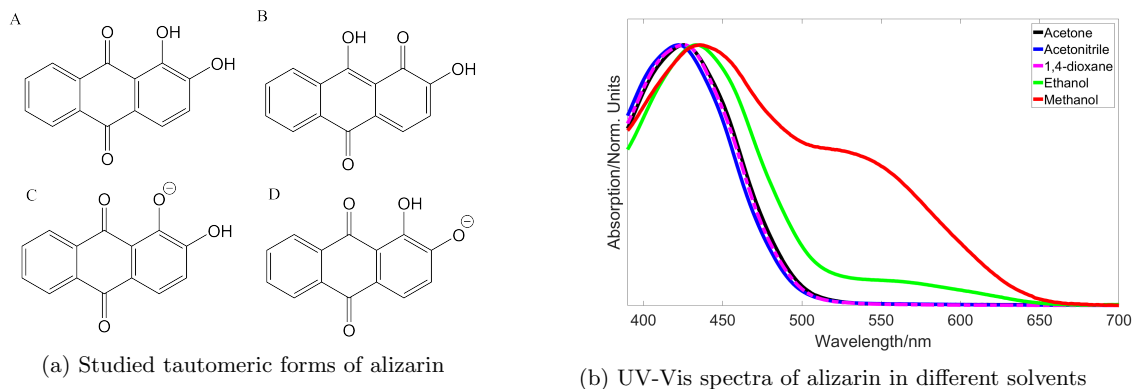
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Determination of secondary species in solution through pump-selective transient absorption spectroscopy and explicit-solvent TDDFT

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The optical absorption spectrum of a molecule in solution often comprises of a superposition of spectra arising from several different species in equilibrium. The secondary species may result in unwanted effects, for instance in medicine where potentially dangerous side products may be formed, or in dyes or paints whose colour may be affected by properties which influence the equilibrium, such as solvent, pH, or temperature. Determining the identity of the various species present is the first step to controlling them, but is currently rather challenging both for experimental and theoretical methods. In this work we apply a combination of state-of-the-art experimental and theoretical techniques to deconvolve the spectrum of a widely studied exemplar dye: Alizarin, figure a[A]. Alizarin displays a solvent dependent secondary excitation, see figure b. Owing to temperature and pH dependent UV-Vis scans it was determined that this excitation was due to another form of alizarin in solution. This alternative form of alizarin was likely formed through deprotonation or tautomerisation, see figure a. Within this work we aim to identify this secondary species.



Two complementary features are required for an unambiguous species determination: high-accuracy theoretical spectroscopy on each candidate species and species-selective ‘fingerprinting’ via time-resolved spectroscopy.

We achieve the necessary accuracy in theoretical spectroscopy by using a newly-emerging combination of methodologies: linear-scaling time-dependent DFT and spectral warping[1]. The reduced scaling of the computational effort associated with linear-scaling forms of linear-response TDDFT enables calculations on an ensemble of model systems each incorporating a large solvent cluster.

In the current work this method can be used to predict the excitation energies from each species in a given solvent, which can be compared to experimental spectra to determine the likely concentration of each of the candidate molecules.

To enable even greater confidence in the identity of equilibrium species giving rise to specific absorption peaks, we also examine their excited state properties. We were able to selectively examine electronic properties of alizarin and the secondary species in equilibrium. This was achieved through use of transient electronic absorption spectroscopy, following photoexcitation of a specific species in equilibrium. The resulting transient absorption spectra were compared to known transient absorption spectrum of potential secondary equilibrium species. This evidence, along with that from the computational studies, suggested that the excitation at 540 nm arises from a monoanionic form of alizarin, figure a[D].

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Resolving the singlet fission dynamics at QM/MM levelMEILANI WIBOWO^{1,2}, GIOVANNI GRANUCCI², AND MAURIZIO PERSICO²¹*Theoretical Chemistry, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands*²*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy*meilani.wibowo@hotmail.com

Singlet fission (SF) is an ultrafast process whereby a photogenerated excited singlet state transfers part of its energy to a neighbouring ground state chromophore to form singlet coupled triplet pairs (¹TT) [1]. This process is of current interest in the application of organic solar cells to overcome the Shockley-Queisser limit [2] because it exploits a high-energy photon to generate multiple charge carriers that are capable for charge separation. For an efficient SF process, the energetic condition of $E(T_2) > E(S_1) > 2E(T_1)$ for a SF chromophore has to be met, as, for instance, in some alternant hydrocarbons and biradicaloids [1]. Moreover, insight about SF mechanism can be gained by performing excited state dynamics simulations of (at least) a pair of SF molecules in molecular crystals or in covalently linked dimers. Here, we present the excited state dynamics simulations based on surface hopping approach with quantum decoherence corrections [3] applied to pair of SF molecules of 2,5-bis(flourene-9-ylidene)-2,5-dihydrothiophene (ThBF) [4] embedded in the crystal environment (Figure 1). In this approach, the electronic wave functions and energies are computed on the fly based on the semiempirical FOMO-CI method in its QM/MM version [5].

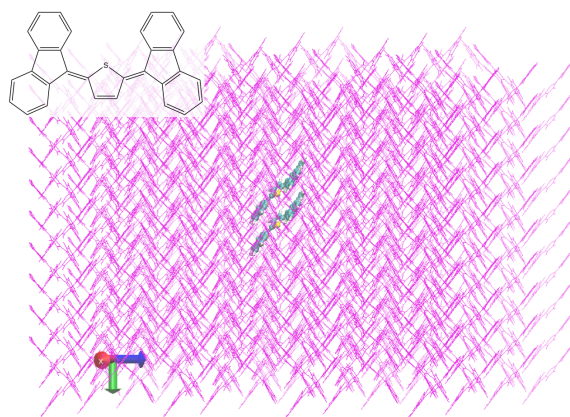


Figure 1. The crystal structure of 2,5-bis(flourene-9-ylidene)-2,5-dihydrothiophene (ThBF).

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