Les Houches School 2023:

Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems

Book of Abstracts

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Lectures

Les Houches 2023 Numerical Practical: Quantum dynamics

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This numerical practical will illustrate the setup and interpretation of excited state quantum dynamical simulations in order to provide attendees with the knowledge of a standard workflow to conduct these calculations. All calculations will be done in Python within a provided split-operator scheme.

Starting with a one-state system with one vibrational degree of freedom, the definition of the grid, potential and initial wavefunction is followed by the analysis of the corresponding propagation in terms of energy and norm conservation as well as grid end populations to gain insight on numerical robustness. Position expectation values are extracted and compared to expected behaviour.
Following propagation in real time, students will learn about propagation in negative imaginary time ("relaxation") to generate initial conditions.
After this the focus will shift from a one-state to a two-state model with a single vibrational degree of freedom that is based on work by Pavel Maly and will also be used in the second numerical practical. Students will learn about state populations and coherences and compare the system with and without coupling between the two states.
Finally, the linear absorption spectrum of the model system is estimated based on the results to bridge the two numerical practicals.
Throughout, students are encouraged to play with the code and parameters to get a feel for the influence of, e.g., the coupling strength or grid definition. Visual feedback is given by plotting the time dependent wavefunction as well as the expectation values.

The numerical practical will have connections to the lectures, in particular those of David Picconi, Tobias Kramer and Guilio Cerullo, as well as to the second numerical practical.

Selected Topic II: Organic photovoltaics – Excitons at work

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This lecture addresses the elementary steps that determine the conversion of excitons into free charge carriers in organic photovoltaics. Similarly to biological light-harvesting systems, coherent effects play a non-negligible role, as evidenced by time-resolved spectroscopic observations. To understand how these coherent transients influence the transfer dynamics, and to what extent they are robust against static and dynamic disorder, quantum dynamical approaches are the method of choice. In this lecture, we present a protocol that combines first-principles parametrized lattice Hamiltonians [1] with accurate quantum dynamics simulations using advanced multiconfigurational methods [2], notably the Multi-Layer Multi-Configuration Time-Dependent Hartree (ML-MCTDH) technique [3]. We show that this approach permits to resolve the subtle interplay of site-to-site transport, exciton and charge delocalization, and vibronic effects. An overview will be given including exciton transport and dissociation in regioregular donor-acceptor assemblies [1,4] and singlet fission [5]. We further address the elementary mechanism of exciton migration in J-, H-, and HJ-aggregate models of poly(3-hexylthiophene) and related materials [1,6,7]. Particular emphasis is placed on the cooperation between trapping due to high-frequency modes and thermal activation due to low-frequency soft modes which drive a diffusive dynamics. These features are highlighted in simulations of 2D electronic spectroscopy (2DES) signals [8], implemented using the Equation-of-Motion Phase-Matching Approach (EOM-PMA) [9].

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Ultrashort pulse generation, manipulation, and characterization

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This lecture aims to provide the basic knowledge necessary to understand the femtosecond laser pulse generation techniques, their propagation in linear and nonlinear optical media, and the techniques available for their temporal characterization. These concepts are the «bread and butter» required for developing and applying ultrafast optical spectroscopy techniques used for the study of dynamical processes in physics, chemistry and biology. The lecture will cover the following topics:
Properties of ultrashort laser pulses: linear propagation equation for ultrashort pulses; dispersion and techniques for its compensation; nonlinear ultrashort pulse propagation in second order media; three-fields coupled equations; second harmonic generation, sum and difference frequency generation; optical parametric amplification; nonlinear ultrashort pulse propagation in third order media; Kerr effect; nonlinear Schrödinger equation ; self-phase-modulation.
Ultrashort pulse generation techniques: mode-locked lasers and passive mode-locking techniques, including Kerr lens mode locking; ultrashort pulse amplification techniques, including chirped pulse amplification.
Ultrashort pulse characterization techniques: non-collinear and interferometric second harmonic autocorrelation, frequency resolved optical gating (FROG), spectral phase interferometry for direct electric field reconstruction (SPIDER).

Les Houches 2023 Numerical Practical: Spectroscopy

James Green[1] and Dominik Brey[1]

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This numerical practical will illustrate how non-linear spectral signals, such as those from transient absorption and 2D electronic spectroscopy measurements, can be computed and used to interpret experimental results. At a basic level, the practical will highlight the necessary components of a numerical model to describe a molecular system studied in a spectroscopy experiment. These components include the choice of site energies, couplings, and dipole moments, as well as the interaction with light through the definition of electric fields, e.g. optical pulses at various delay times. Then, the polarization induced in the molecule by the electric field of the laser pulses will be computed, and used to predict spectra. The theoretical understanding of 2D spectroscopies in terms of Feynman diagrams will also be demonstrated, through generation of diagrams corresponding to specific phase matching conditions. The importance of time-ordering of the pulses will be demonstrated, and connection of the diagrams to specific parts of the spectral signal, such as ground state bleach, excited state absorption and stimulated emission, will be illustrated. Finally, inclusion of dissipation to an environment and its effect on the spectrum will be exemplified by coupling the system with a Markovian bath. The numerical practical will have connections to the lectures, in particular those of Pavel Malý and Tobias Kramer.

Exciton dynamics probed with time-dependent spectroscopy

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We discuss the computation of the excitonic energy transfer in quantum systems and how it is connected to time- and frequency- resolved spectroscopy within the Frenkel exciton model. This model provides an example of an open quantum system where observable system degrees of freedom (the optical spectra of the excitonic energies) are strongly influenced by an environment (the vibrational degrees of freedom of the proteins). Using numerically exact methods (HEOM) and approximate treatments we discuss how the coupling to vibrational modes affects the exciton dynamics and is reflected in the spectra. The influence of temperature, disorder and orientational ensemble averages, as well as the effect of different polarization sequences are worked out in examples. All data can be reproduced using the publicly available HEOM tools.

Coherently- and fluorescence-detected ultrafast spectroscopy

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Ultrafast nonlinear laser spectroscopy is an indispensable tool for observation of electronic excitation dynamics, state structure and charge transfer. While traditionally a coherent nonlinear polarization response is measured, over the recent years an alternative way of signal detection using an incoherent observable such as fluorescence has gained popularity. In this tutorial, we discuss the principles of designing an ultrafast spectroscopy experiment, including excitation pulse sequences and methods of nonlinear signal isolation. From transient absorption to two-dimensional electronic spectroscopy, we directly compare and contrast the coherent and fluorescence detection under as identical experimental conditions as possible. Despite the close correspondence in the measured nonlinear response, there are differences between the two approaches of both fundamental and practical nature. On a particular example of a coupled electronic heterodimer of squaraine molecules, we illustrate how the spectra reflect effects such as exciton delocalization, energy transfer or annihilation. Focusing on the correspondence and complementarity of the two means of detection, we review their selected applications.

Photoinduced molecular quantum dynamics: Theory and computational methods

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Abstract

The theoretical framework to model molecular photochemistry and photophysics is presented. The focus is on the quantum dynamical description of processes beyond the Born-Oppenheimer approximation, i.e. nonadiabatic photochemistry. To this end, diabatic vibronic coupling models are introduced, and their construction is illustrated for the processes of internal conversion, charge and excitation energy transfer. The motion of molecular wave packets created by the interaction with a laser field is presented using time-dependent perturbation theory. In particular, it is shown how the linear polarization induced by light absorption is related to the dipole-dipole autocorrelation function. An overview is then given over different computational approaches to model the dynamics of nonadiabatic processes in molecules and materials, treated as closed systems. The starting point are the fully quantum mechanical methods based on tensor decomposition, such as the multi-configurational time-dependent Hartree (MCTDH) and related techniques that use Gaussian wave packets. In a second step computationally cheaper approximations, such as those based on surface hopping or the Meyer-Miller-Stock-Thoss mapping, are introduced in the framework of the quantum-classical Liouville equation.
The different levels of approximation are critically compared on different aspects: computational scaling, use of on-the-fly vs. precalculated Hamiltonians, and the accuracy in predicting the rate of non-radiative transitions, as well as the behaviour of electronic, vibrational and vibronic coherences.

Light Harvesting in Photosynthesis: From Structure to Function

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The high quantum efficiency (>90 %) of photosynthetic light-harvesting antennae has been stimulating interdisciplinary research on the building principles of these systems. In this special topic lecture I will introduce a Frenkel exciton/charge transfer Hamiltonian and discuss its parametrization by multiscale methods, combining quantum chemical, electrostatic, molecular mechanics methods. This Hamiltonian will be applied in approximate theories of optical lineshapes and excitation energy transfer. We will discuss semiclassical limits of these approximate theories and the relevance of quantum effects of nuclear motion for the light-harvesting function. Different light-harvesting strategies realized in nature are summarized. A recent application of the present methodology to light harvesting and primary charge transfer in Fenna-Matthews-Olson protein/ reaction center complex supercomplexes is discussed, revealing the decisive factor for a high light-harvesting efficiency in this system.

Single Slide Presentations

Can strange sets arise out of quantum dynamics?

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We explore this question using the quantum analog of a classical impact oscillator, which consists of a forced spring-mass-damper system, with a wall it may collide against. The classical impact oscillator is known to undergo a sudden transition to chaos when the mass grazes the wall. We numerically compute the evolution of the wave function in the equivalent quantum system and investigate the dynamical signatures. The entropy of the probability density and the L_1 norm are used to generate real-valued time series, which are then subjected to diagnostic tests. Even though closed quantum systems with unitary evolution are incapable of showing chaotic behavior, we observe the characteristic features of strange nonchaotic dynamics in the forced system.

*The work is done in collboration with Arnab Acharya, Soumitro Banerjee of Department of Physical Sciences, Indian Institute of Science Education and Research Kolkata

A Sagnac-based Experiment for ultrafast Anisotropy dynamics

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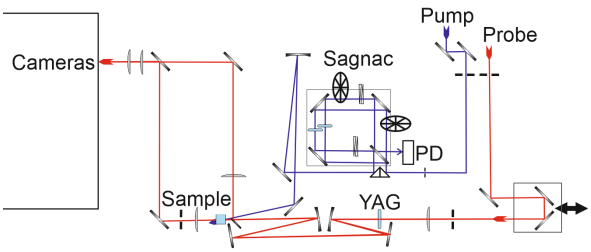
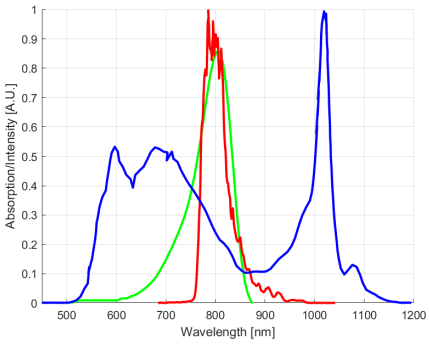
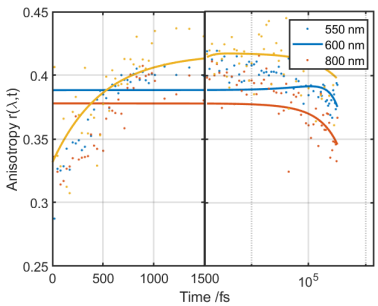




The blue graph shows the spectrum of the whitelight used to probe for anisotropy. The red graph shows the NOPA spectrum used for the pumping of the sample. The green curve shows the absorption of the IR140 laser dye.



Anisotropy Measurement Example of IR140: The moleculs orientate themselves with the pump pulse, so that the anisotropy (r) reaches the maxium value of r = 0.4 over a broad wavelength range λ and stays there for longer than 300 ps.

This setup can be used to measure the polarization dependence in Transient Absorption signals over a broad wavelength range and time resolution of up to 20 p fs at a repetition rate of up to 5 kHz. The pump beam is generated by a Non-linear Optical Parametric Amplifier [1] allowing to freely choose a central wavelength between 400 nm and 950 nm and spectrally broad pulses that can be compressed via a prism compressor to sub 20 femtoseconds. A Sagnac-interferometer is used to generate two phase stable pulses propagating collinearly after the interferometer. At the same time each beam can be fine-tuned inside the interferometer to change its relative polarization and delay as well as be chopped. The same 1030 nm beam that pumps the NOPA also is used to generate whitelight in a 3mm YAG-crystal for the probe beam, allowing to look at dynamics over a broad wavelength range. The setup was validated by a measuring the anisotropy $r(\lambda,t) = \frac{I_{\parallel}(\lambda,t)-I_{\perp}(\lambda,t)}{I_{\parallel}(\lambda,t)+2I_{\perp}(\lambda,t)}$ of a laser dye (IR140) in ethanol. In order to check the capabilities to measure short dynamics the pulse length was minimized to 25 fs and further measurements with 2,3-Naphthalocyanin are planned to jugde the accuracy for short term dynamics. Further plans include the measurement setup also being used for 2D-measurements without any physical changes to the setup. This is planned to be tested on LH2.

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Modelling the molecular motion in aggregates Nanomaterials for photothermal therapy

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Photothermal therapy (PTT) uses photosensitizing agents that accumulate in the tumor site to generate heat from light, causing the ablation of tumor cells by rapidly increasing the local temperature [1]. Photothermal effects (i.e., heat generation) generally arise as the result of nonradiative relaxation processes. Various inorganic materials have been used as photothermal agents, including golden nanorods, graphene, and MoS2 nanosheet. Interestingly, the supramolecular assembly of organic dyes can also be applied as PTT materials, offering the advantages of low long-term biosafety risk and high biocompatibility. The unique and adjustable optoelectronic characteristics of perylene diimide (PDI)-based dyes, combined with their relatively affordable production costs, have garnered significant interest[2]. Furthermore, aside from the option to connect PDI monomers using different linkers, it has been demonstrated that PDIs can undergo spontaneous self-assembly in H-aggregates into ordered one-dimensional nanostructures and diverse solutions, resulting in the formation of sizeable aggregates. In this scenario, the self-assembling process is influenced by a delicate balance of non-bonded interactions, including hydrophilic, hydrophobic, and π-stacking. This balance can be easily disrupted by modifying factors such as the substitution patterns of PDIs at the imide position. The side chains can also optimize the molecular packing conformation, thereby influencing the solubility, color, and other physicochemical properties of the PDI aggregates.
Therefore, this study is centered on giving a physical description of the self-assembling behavior of PDI layers in classical approaches through Molecular Dynamic simulations. The self-assembling analyses are crucial to the future extension of a mixed quantum-classical method (AdMD—gLVC)[3] to larger PDI aggregates, starting with 3,4 monomers. The idea is to work on a system that we already know, then extend the approach to real PTT systems.

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Nonadiabatic Molecular Dynamics Simulation of Energy Transfer Process in the Light Harvesting Complex.

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Efficient energy transfer is essential for the conversion of light energy into a chemically usable form. Over the past decades, extensive research efforts have focused on exploring the intricate mechanisms underlying highly efficient energy transfer within the light harvesting complex for natural photosynthesis. Current advances in theoretical simulation techniques have enabled the inclusion of vibrational degrees of freedom (DoF) in studying energy transfer process. Such theoretical approaches based on the coupled harmonic oscillator have highlighted the pivotal role of the intramolecular vibrations. However, establishing a connection between such theoretical models and real molecular aggregates still poses significant challenges. Moreover, the impact of vibrational anharmonicity remains largely unexplored. Here, we employ nonadiabatic molecular dynamics simulation to investigate the energy transfer processes within the Light Harvesting 2 (LH2) complex. With potential energy surface (PES) interpolation method, we investigate the influence of the intramolecular vibrations with DFT level of accuracy. Within LH2 complex, we simulate the exciton transfer between 27 bacteriochlorophylls (Bchls). Furthermore, we monitor the energy transfer between electronic DoF and intramolecular vibrations. This analysis highlights the crucial role of vibrations as temporal heat buffers that facilitate energy transfer by promoting the heat dissipation. This comprehensive simulation approach has the potential to provides molecular-level insights into the mechanisms underlying efficient energy transfer in the LH2 complex. In addition, we anticipate that further exploration of the influence of vibrational anharmonicity could contribute to advancing our understanding.

Investigation on the influence of the local H-bonding network on vibronic couplings within the Photoactive Yellow Protein (PYP) Chromophore using vibrationally resolved absorption spectra

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Advances in genetic engineering, especially for medical purposes have increasingly attracted the attention of researchers for a better understanding of the functionality and induction of biochemical processes. The signaling processes are normally caused by structural changes in molecules after interaction with the environment. In this context, photoactive molecules, i.e. chromophores, play an important role, because their signal transduction can be directly triggered by light excitation. For the small size, solubility in water and reversibility of its signaling process (photocycle), the Photoactive-Yellow-Protein (PYP) constitutes a good example of photoreceptors. The chromophore in PYP consists of the anionic thioester of p-coumaric acid embedded in 125 amino acids. Its active site comprises the residues Glu46, Tyr42 and Cys69. The presence or absence of the H-bonds between the chromophore and those residues, which occurs within different conformers in the ground state of the chromophore, is of importance for the photocycle triggered by the initial isomerisation [1,2]. The H-bonding potentially influences the strength of the respective vibronic couplings as well. The role of the vibronic interactions and their sensitivity to H-bondings can be probed by Vibrationally Promoted Electronic Resonance (VIPER) spectroscopy experiments, a mixed vibrational and electronic excitation scheme, where an initial IR pulse vibrationally pre-excites the system followed by an off-resonant actinic pulse. Only the combination of both pulses enables the electronic excitation, which provides a very selective excitation scheme.[3]
Hence, in this work we present the simulation of vibrationally resolved electronic spectra of the chromophore for six possible H-bond scenarios. Aiming to focus on the role of the H-bonds in the systems, the amino acids were substituted by water molecules in a first instance following Ref. [2]. The electronic structure parameters for ground and excited states were obtained by DFT and TDDFT calculations respectively and excited-state gradients were computed to parametrise a Linear Vibronic Coupling (LVC) Hamiltonian. Vibronic spectra were estimated by using the time-dependent method implemented in FCclasses [4]. This uses a Fourier transformation of the time-dependent analytical correlation function to obtain the linear absorption spectrum.

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Unveiling Ultrafast Electronic and Nuclear Dynamics in Biomolecules with Femtosecond soft–X–Ray absorption spectroscopy

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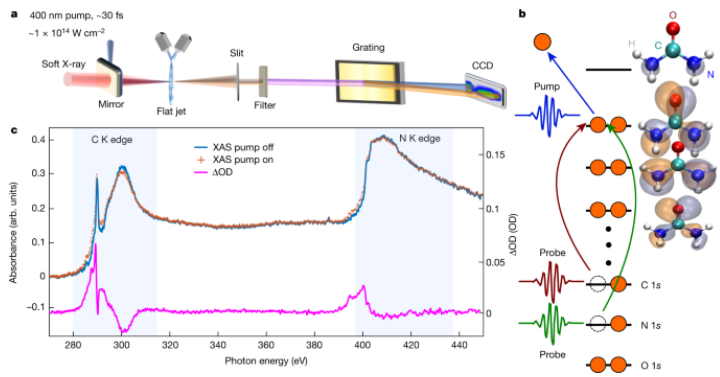
Photoinduced excitation and ionization of matter is critical for a wide range of bio-chemical phenomena. Multiphoton ionization can lead to nuclear rearrangement, an ultrafast mechanism, that is challenging to follow in real time due to to the lack of sufficient time resolution. We present time-resolved X-ray absorption spectroscopy (XAS) of liquid and gaseous samples utilizing a state-of-the-art table-top driven HHG source for the water-window regime [1,2,3]. Using this system, we present experimental evidence for charge transfer and nuclear dynamics of biomolecule solutions in water. These measurements are enabled by merging the water-window soft X-ray transient absorption beamline driven by 1.8 μm post-compressed pulses and the liquid flat-jet sample delivery system that provides sub-μm thickness [4]. As an example, we present time-resolved measurements of photoionized aqueous urea at the carbon and nitrogen K-edges and identify spectral features that are attributed to ultrafast proton transfer within urea dimers [4]. The inherently broadband HHG pulse allows to probe both edges simultaneously and is therefore ideal for XAS [2]. XAS is unique as an element and site-specific method to access the electronic and structural properties of matter simultaneously [3]. The primary spectral features are well reproduced by theoretical simulation and XAS calculations of various urea dimer and urea-water geometries, supporting the experimental results. Theoretical findings further show that charge dynamics alter structural organization and leave geometrically distinct spectral fingerprints.



(a) Schematic of the experimental setup. **(b)** Schematic molecular-orbital diagram illustrating ionization by a pump pulse, followed by probing of the system with a SXR pulse. **(c)** XAS spectrum of a 10 M urea solution covering the carbon and nitrogen K edges and the time-averaged ΔOD signal.

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Photoisomerization dynamics of spiropyrans

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Spiropyrans are a broad class of compounds widely used in materials science due to their pronounced photochromic properties. The excitation of spiropyrans in the UV range converts them into the open and colored merocyanine form. Despite the large use of these molecular switches, the exact mechanism of the photoisomerization reaction is not fully understood and appears to be strongly dependent on the substituents and the environment [1]. For these reasons, we want to study the excited-state dynamics of two spiropyrans labeled as BIPS and nitro-BIPS (Figure 1) through "on the fly" surface hopping nonadiabatic dynamics simulations using the FOMO-CI method in a semiempirical AM1 framework [2,3].
We considered the modifications of the lowest-lying excited state PESs of BIPS induced by nitro substitutions, and their impact on the nonadiabatic dynamics. Furthermore, to bring the solvent effects out on the BIPS excited state dynamics, we ran simulations in three different environments (chloroform, methanol, and ethylene glycol) and we compared these results with previous simulations carried out in vacuo [4].

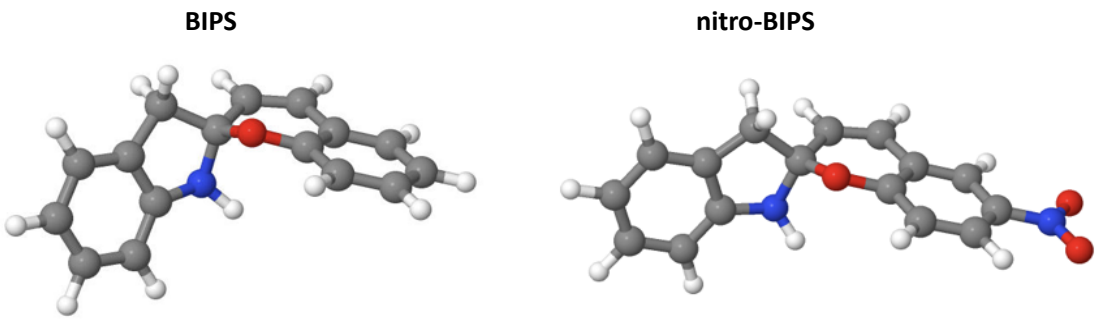

Figure 1. Spiropyrans labeled BIPS and nitro-BIPS

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Ultrafast energy transfer and diffusion in dye-doped organic nanoparticles studied by fluorescence up-conversion

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The exploration of electronic excitation energy transport mechanisms in molecular systems has garnered significant interest due to its wide range of applications in light-harvesting and optoelectronic devices [1, 2]. These processes centrally rely on exciton diffusion dynamics [3]. Natural photosynthetic organisms, for example, utilize networks of interacting chromophores called Light Harvesting Complexes (LHCs) to efficiently absorb and convert light energy [4]. In this work, we investigate the photophysical properties of dye-loaded, polymeric, organic nanoparticles (ONPs), which replicate the function of LHCs. These ONPs, specifically designed for biosensing and imaging applications, have demonstrated a remarkable "giant" antenna effect, primarily resulting from the highly efficient diffusion of excitons within the nanoparticles [5]. Here, we employ fluorescence up-conversion spectroscopy (FLUPS) with a time resolution of ∼200 fs, to unravel the dynamics of energy transfer and diffusion that underlie this giant antenna effect.

Firstly, we observe the timescale of exciton hopping to the nearest neighbors, by using FLUPS with a polarization-resolved excitation and detection to measure the decay kinetics of fluorescence anisotropy. The analysis reveals a multiexponential decay with a shortest resolved temporal component of ∼300 fs, along with an unresolved decay time (< 200 fs), indicating an ultrafast energy transfer. This multi-component decay reflects on the inter-dye distance distribution within the ONPs. In such a disordered system, a stretched exponential is commonly used to fit the anisotropy decay [6, 7]. By doing so, we retrieve an energy transfer time of 90 fs and a diffusion constant of 1.56 nm^2/ps for ONPs of 0.36 M dye concentration. Secondly, we investigate the population decay kinetics in the presence of a fluorescent acceptor at low concentration inside the ONPs. We observe a fast decay of the donors' fluorescence. The donor-acceptor energy transfer is measured to occur after a few picoseconds from excitation on a timescale of ∼100 ps for ONPs loaded with 100w% donors and 1w% acceptors. This suggests that the diffusive energy transfer dominates the direct transfer to the acceptor. These findings underscore the efficient energy diffusion within the nanoparticle, corroborating the above mentioned high antenna effect.

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Characterisation of vibronic couplings within the Photoactive Yellow Protein (PYP) Chromophore using vibrational pre-exctation

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Photoactive yellow protein (PYP) is a photoreceptor involved in the signal transduction pathway of the bacterium *Halorhodospira halophila* and is well suited as a model system for studying double-bond isomerisations or functional protein dynamics.[1] The reversible photocycle has been studied using a variety of different methods ranging from neutron crystallography over time-resolved spectroscopies to in detail investigations of the electronic structure. In recent years, a correlation was drawn between the selective double-bond isomerisation of PYP and the nature of the H-bonds present in the system.[2] To further understand the influence of the local protein environment on the photoexcitation and on the subsequent photocycle, the simulation of vibrationally resolved absorption spectroscopy can be used to map the strength of the respective vibronic couplings. Additionally, this serves as a prediction tool for the activity of normal modes within the Vibrationally Promoted Electronic Resonance (VIPER) spectroscopy,[1] which, as a mixed vibrational and electronic technique, would enable the selective photo-induced double-bond isomerisation of a subensemble of conformers of the PYP.

To shed light on vibronic coupling in PYP, this work presents the vibrationally resolved absorption spectra for time-dependent (TD), time-independent (TI) *FCClasses*[3] and MCTDH[4] calculations within the framework of the linear vibronic coupling model (LVC). While TD *FCClasses* and MCTDH both use a Fourier transform of the correlation function to plot the absorption spectrum, TI *FCClasses* rather employs an efficient calculation of the Franck-Condon factors of the individual transitions. Thus, 2D vibronic maps are obtained which relate directly to VIPER and to experimental two-dimensional vibrational-electronic (2D VE) spectroscopy.

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SPECTROSCOPIC ANALYSIS OF THE INTERACTION BETWEEN De Novo PROTEIN MAQUETTES AND Zinc Pheophorbide CHROMOPHORES

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Abstract

This work presents the spectroscopy study of a family of artificial proteins maquettes capable of binding chlorophyll derivate chromophores (ZnPPaOH and p-ZnP). These are single-chain proteins folding into a four-alpha-helix bundle structure, where the ligation with the chromophores is controlled by histidine amino acids (zero, two, or four, according to each design) to their metal center. Binding stoichiometries and constants were determined via equilibria modelling of data from titrations monitored by absorption spectroscopy. Moreover, circular dichroism spectra revealed excitonic interactions between chromophores attached inside the structures by the histidines, but also signals that corresponds to the chromophore aggregation outside the protein due to the saturation of the maquettes were observed. These are the first steps towards artificial photosynthetic chromophore-protein assemblies that could allow to build a new solar energy conversion system.

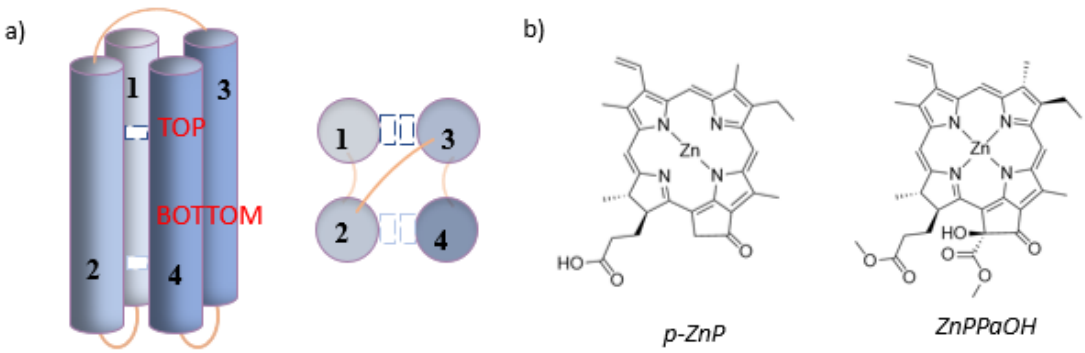

Figure 1. Protein structure scheme. a) Side and top view of the four alpha helices and the three random coils are represented by cylinders and bows, respectively. The alpha helices are labeled consecutively following the amino acids sequence and the protein folding. b) Structure of the Zinc Pheophorbide chromophores studied.

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Exciton theory of circular dichroism of proteins

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Circular dichroism (CD) of proteins is a spectroscopic approach that is widely used in different areas including biochemistry, structural biology and pharmaceutical research. However, a theory that is accurate enough to link the structures predicted from molecular dynamics (MD) simulations to the experimentally observed CD spectra is still missing. A major challenge in the description of the CD of proteins is that there are two close-lying electronic transitions of the peptide bond, where one of them is electric dipole-forbidden. In addition, a large inhomogeneous broadening is observed, which makes the widely used procedure of centering Gaussian bands around discrete transitions in exciton stick spectra inaccurate.
In our exciton approach, the charge densities and transition dipole moments of the peptide bond are calculated by applying time dependent density functional theory, including a polarizable continuum model, to a model system (N-Methylacetamide). In order to reduce the computational costs, we fit the transition densities by atomic partial charges (APCs). These APCs are then placed onto the backbone atoms of the whole protein and additional auxillary points in order to calculate the excitonic couplings between the excitations of different peptide bonds. This procedure makes the calculation efficient even for large protein complexes. Screening effects arising from the polarizability of the protein/solvent environment are described with the Poisson-TrEsp [1] method. Site energy shifts for both transitions of the peptide bond are calculated using a similar electrostatic approach. The large inhomogeneous broadening observed in the CD of proteins is explained microscopically by analyzing MD snapshots, revealing a Gaussian distributed fluctuation of the site energies. Those fluctuations are taken into account in the calculation of the spectra explicitly along the MD trajectory or implicitly via a Monte Carlo approach. Furthermore, it is shown that there are no correlations in the fluctuations of the site energies and that also the fluctuations of the excitonic couplings can be neglected. The overall agreement between theory and experiment on typical α-helices [2,3] as well as β-sheets [2,3], investigated in this work, is found to be remarkably good. The method is not only able to reproduce the spectrum of stable proteins but also reveals spectroscopic signatures of partially unfolded α-helices observed in the MD simulation and in the experiment [4].

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Impact of thermally activated charge separation with offset in non-fullerene acceptors

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Organic Solar cells have produced great excitement in the recent years with significant improvement in the power conversion efficiency (>19%) due to high charge generation yield and low voltage loss. However, the precise behaviour of charge generation and its corelation with energetic offset, in low voltage loss systems remain highly debated and questioned for numerous reasons. Here, we have studied the charge generation efficiency for wide range of donor:acceptor (D:A) system including low-offset and high-offset system. Surprisingly, we noted that charge generation is a temperature mediated process for low-offset systems and temperature-independent process for high-offset systems. The poor charge generation efficiency for low-offset system, which is further supported by **transient absorption spectroscopy**, is found to be increased by external thermal energy. Moreover, the charge generation activation energy (Ea) is also calculated and found that for an efficient charge generation at room temperature, the Ea should be less than the room temperature thermal energy, corelating well with the energetic offset between the donor and acceptor. The study also reveals that an increase in electrostatic dipole is the way forward to achieve the efficient charge generation without compromising on the voltage loss.

Ultrafast Mapping of Solar Energy Conversion

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The efficiency of single junction solar cells reaches its theoretical maximum at 33%, known as the Shockley-Queisser limit. There is however a possibility of circumventing this limit by making use of a mechanism known as singlet fission. Singlet fission is able to convert an excited singlet state on a chromophore to two triplet states on two chromophores via a correlated triplet pair state formed across the two chromophores. This makes two electrons available for conduction, even though only a single electron was initially excited [1][2]. The underlying mechanism of this process is however not well-understood, which complicates development of functional singlet fission materials. The struggle to determine this mechanism is largely related to the complex nature of the interplay of electron movement and geometry rearrangement of the molecules in question as singlet fission takes place [3].

We aim to shed light on this interplay by experimentally tracking observables with different dependence on the structural and electronic configurations as the sample is excited and undergoes singlet fission, using hard x-ray ultrafast X-ray Raman Spectroscopy (XRS) and Wide Angle X-ray Scattering (WAXS). This is compared to theoretical modelling of the system in question, including a large number of degrees of freedom coupled to many different electronic states. As this model must fit both experiments simultaneously, this will guide the untangling of the electronic and structural parameters.

Acknowledgments
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Self-trapping in LH2 energy transfer and its biological relevance

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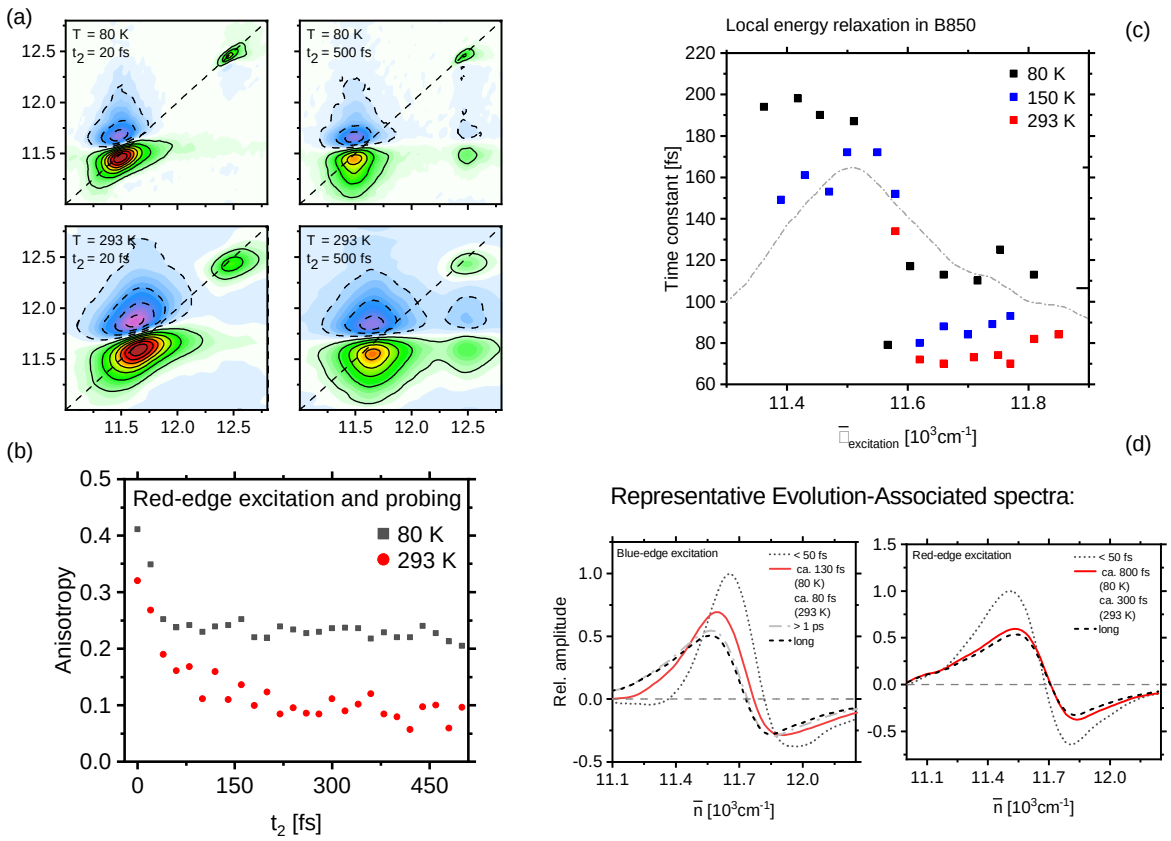
Energy transport in the light-harvesting antenna of phototrophic organisms can be remarkably fast and efficient at biological conditions, often proceeding on timescales well below a picosecond. In stark contrast to this picture of fast and efficient transport, recent experiments[1–3] on the purple bacteria antenna complex LH2 indicated self-trapping of excitons due to strong coupling to phonons in parts of the excited-state manifold. This interaction's direct consequence can be seen as substantially reduced exciton mobility. Notably, however, these experiments were performed at cryogenic temperatures, as is common in spectroscopy of photosynthetic complexes. Thus, it remains unclear whether such effects contribute at biologically relevant temperatures.
Our work here investigates the ultrafast relaxation dynamics in LH2 from the purple bacterium *Rps. acidophila*, using coherent two-dimensional electronic spectroscopy. Results are shown in Fig. (a). Crucially, we rely on control of temperature, field polarization, and excitation intensity to elucidate the intricate relationship between energy relaxation and spatial exciton motion in the disordered potential energy landscape of LH2.
While our observations at 80 K are consistent with earlier claims of local exciton trapping and thus severely limited transport, we find that this trapping becomes negligible at temperatures above only 150 K (Fig. b-d). As such, our work suggests that LH2 at cryogenic temperatures may be a good system for detailed studies of exciton-phonon interactions in soft matter, but it also simultaneously highlights that observations made in high-resolution spectroscopies at low temperatures do not necessarily generalize to biological function.



(a) 2DES data for Rps. acidophila at different temperatures and population times; (b) anisotropy traces show that at the red edge, the depolarization is slower at low temperatures, indicating inhibited transport; (c) dependency of the time constant associated with local relaxation on excitation wavelength and temperature; at higher temperatures, the relaxation is faster; (d) representative EAS for blue- end red-edge excitation, showing faster local relaxation (red) at higher temperatures.

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X-Ray induced Electron Transfer using Real-Time DFT with Explicit Electromagnetic Field

$$i\frac{\mathrm{d}}{\mathrm{d}t}\left|\Psi^i_{VG}(t)\right\rangle = \left[\hat{H}_{KS}(t) - i\hat{\boldsymbol{\nabla}}\cdot\boldsymbol{A}(t) - \frac{1}{2}\left|\boldsymbol{A}(t)\right|^2\right]\left|\Psi^i_{VG}(t)\right\rangle$$

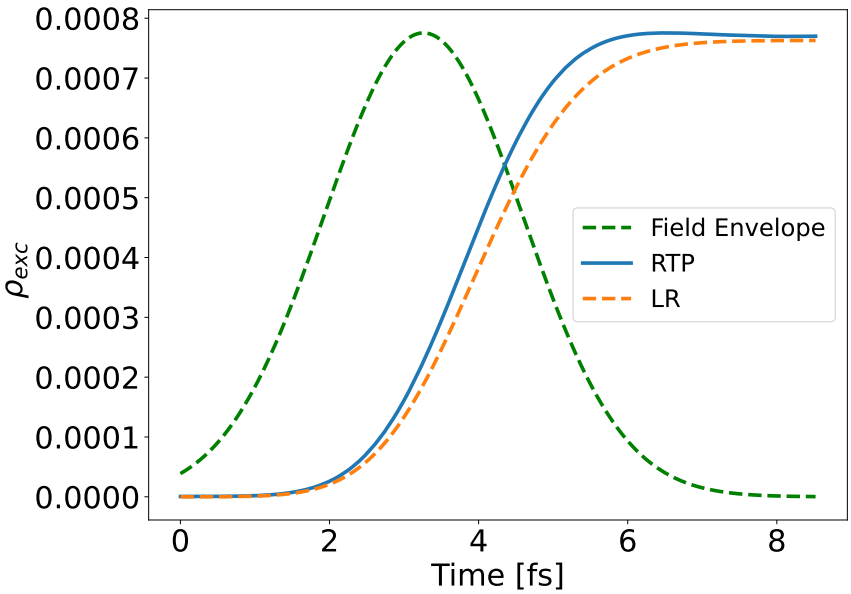

Figure: Evolution of the first available excited state population of Solvated cysteine under Sulfur K-edge field

Dr. Guillaume Le Breton

Towards realistic simulations of strongly correlated open quantum systems in steady-state

Anqi Li and Michael Galperin

We discuss the applicability of theoretical Green's function methods to open quantum systems out of equilibrium, in particular, to single molecule junctions. Two characteristic energy scales governing the physics are many-body interactions within junctions and molecule–contacts couplings. Both weak interactions and weak coupling cases can be treated within diagrammatic expansions. However, lacking small parameter, the intermediate regime, where these two scales are comparable, can mostly be treated efficiently within the nonequilibrium dual approaches. We discuss the recently developed auxiliary quantum master equation dual-fermion and dual-boson approaches. Applications of both approaches in realistic simulations are limited by heavy numerical cost, which grows exponentially with system size when solving the auxiliary quantum master equation. Therefore, we explore the possibility of employing the flow equation renormalization group and low-order many-body Green's function techniques as inexpensive solvers capable of providing single- and two-particle Green's functions of the auxiliary problem. This will be a valuable addition to the theoretical toolbox by itself and as a part of a divide-and-conquer type of approach to study the response of strongly correlated open quantum systems to external perturbations in the field of spintronics, optoelectronics, and energy harvesting.

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Near-field scanning optical microscopy of topologically protected excitons in molecular aggregates

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Delocalized excitonic eignestates of molecular aggregates are responsible for the energy transfer from an incoming radiation into the aggregate. Static disorder, which can arise from an imperfect environment of each molecule, reduces the exciton transport and large disorders can even localize the exciton. It has been shown theoretically that a two-dimensional periodic array of tilted and interacting molecules in a homogeneous magnetic field shows topologically protected edge states [1]. With a scattering scanning near-field optical microscope setup, one can not only record position dependent absorption spectra [2] but also reconstruct the wavefunctions from these specta [3]. We study theoretically the near field spectra of the aforementioned 2D aggregates in which the molecules experience a disordered environment because of the probing metallic tip. Due to the topological protection, the edge states are robust even in the presence of the metallic nanopar- ticle, such that the spectrum shows clear signatures of these states.

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Hidden Phase of the Spin-Boson Model

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A quantum two-level system immersed in a sub-Ohmic harmonic bath experiences enhanced low-frequency quantum statistical fluctuations which render the nonequilibrium quantum dynamics highly non-Markovian.

Upon using the numerically exact time-evolving matrix product operator approach [1], we investigate the phase diagram of the polarization dynamics. In addition to the known phases of damped coherent oscillatory dynamics and overdamped decay, we identify a new third region in the phase diagram for strong coupling showing an aperiodic behavior.

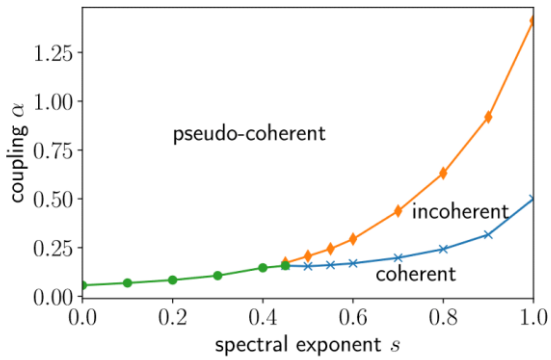

Fig. 1 Phase diagram of the (sub-)Ohmic spin-boson model at T=0

We determine the corresponding phase boundaries. The dynamics of the quantum two-state system herein is not coherent by itself but slaved to the oscillatory bath dynamics.

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Application of Density Matrix Wigner Transforms for Ultrafast X-ray Crystallography

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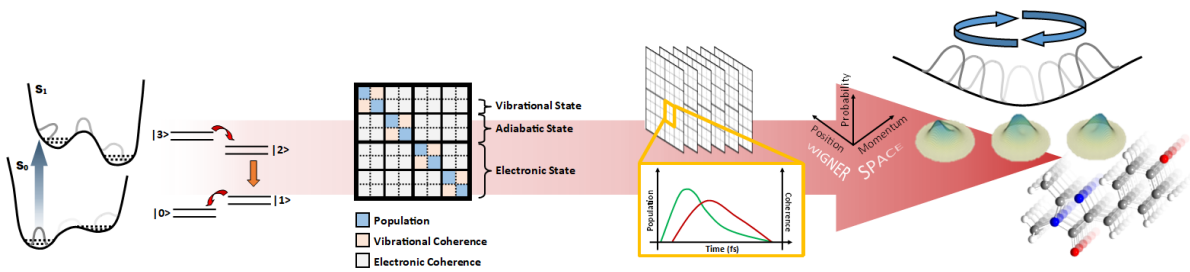
With the advent of 4th generation light sources (XFELs), Time-Resolved Serial Femtosecond Crystallography (TR-SFX) has been a powerful tool in capturing structural molecular movies of many light-initiated processes.(1) Femtosecond optical pump, X-ray probe has allowed a new regime of coherent dynamics to be explored. The difference electron density obtained from pump-probe TR-SFX contains contributions from both ground and excited states and are not separable as in spectroscopy. Additionally, in the sub-picosecond regime, it is known from the Raman literature that coherent motion is generated in both ground and excited states, upon excitation in the Franck-Condon regime. The extent to which this vibrational coherent motion is observed in difference electron density maps is unclear. (2)

Here we present a theoretical work, to model the various population and coherent dynamics of a system. The non-perturbative density matrix simulation describes the response of a system upon excitation. It is tuneable according to the parameters of the system (energy levels, dephasing, population decay...) and the conditions of the excitation (carrier frequency, pulse energy…). Temperature dependence of the coherent and population amplitude following excitation has been implemented as per Kumar *et al.* (3) unique to this time dependant density matrix simulation. A Wigner Transform of the time-dependant density matrix evolving under the Liouville-von Neuman equation converts to a phase space distribution (position and momentum) showing the coherent dynamics. These phase space Wigner distributions are analogous to the difference electron density maps obtained by SFX and thus can be used to describe the experimentally observed signals.

A series of TR-SFX in the sub-picosecond regime experiments in a Tannor-Rice (pump-dump) control scheme, were used to investigate excited and ground state coherence contributions in the difference electron density maps of a fluorescent protein.(4) It was found that a stimulated emission dumping interaction within the vibrational dephasing time drastically increased the observed signals. A density matrix simulation using the proteins experimentally measured parameters, assigned the observed signals to ground state coherence enhanced by the stimulated emission dumping. Further multi-pulse excitation conditions are explored including the structural equivalent of Impulsive Stimulated Raman and Stimulated Raman Adiabatic Passage Spectroscopy.

Shorter optical and X-ray pulse durations (<50 fs) and increasingly more exotic pulse regimes are becoming available at FELs. Combined with high repetition of the latest FELs, improving the signal-to-noise-ratio will allow vibronic motion to be observed on the sub-Angstrom level. Wigner transforms of the density matrix will allow analysis and assignment of the complex motion observable with developing capabilities of XFEL instruments.



Theoretical investigations on 2D electronic spectroscopy of the Water-Soluble Chlorophyll-Binding Protein (WSCP)

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We explore the connection between electronic excitations, dissipative dynamics, and features observed in experimental data of the "Water Soluble Chlorophyll-Binding Protein"(WSCP) using a theoretical model of 2D electronic spectroscopy (2DES). To this end we employ third-order response functions derived from a second-order perturbative treatment of an open quantum system, incorporating the partial ordering prescription (POP) and considering a fast nuclear relaxation in potential energy surfaces of exciton states. The third-order polarizations are obtained as a solution to a system of differential equations coupled via different orders of the system-field interaction. The tetrameric structure of WSCP, modeled as 2 dimeric subunits with weak excitonic coupling between them, exhibits different characteristics in terms of linear absorption and circular dichroism (CD), depending on the chlorophyll variants present, Chl-a or Chl-b. Although the model for Chl-a agrees with the experimental data [1], in the case of Chl-b the substantial difference cannot be explained by the same modeling procedure as used for Chl-a. For Chl-b, the authors of the experimental study [1] suggest a model with a changed energy structure of the tetramer, resulting from an increased dipole moment caused by an H bond. We suggest an alternative model where a percentage of Chl-b dimers are chemically altered into Chl-b derivates [2] with decreased electronic excitation energies, but the same excitonic coupling as the original Chl-b dimers. Both models were investigated using linear absorption, CD, and 2DES with the finding that the existence of such derivates is a plausible explanation for the origin of the enhancement of peaks in the energetically lower region of linear absorption and 2D-spectra. The change in the energy structure caused by the H-bond would be too severe, as shown by the linear absorption, CD, and 2DES.

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Differential Shannon entropies characterizing electron-nuclear dynamics and correlation: Momentum-space versus coordinate-space wave packet motion

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We extend our previous work [1] and calculate differential Shannon entropies derived from time-dependent coordinate-space and momentum-space probability densities. This is done for a prototype system of a coupled electron-nuclear motion. Two situations are considered, where one is a Born-Oppenheimer adiabatic dynamics, and the other is a diabatic motion involving strong non-adiabatic transitions. The information about coordinate- and momentum-space dynamics derived from the total and single particle entropies is discussed and interpreted with the help of analytical models. From the entropies, we derive mutual informations which are a measure for the electron-nuclear correlation. In the adiabatic case it is found that such correlations are manifested differently in coordinate- and momentum space (Figure 1). We argue that the mutual information in momentum space is related to the nodal structure of the wave function. For the diabatic dynamics we show that it is possible to decompose the entropies into state specific contributions, which reveal and quantify details on the transition between the adiabatic states.

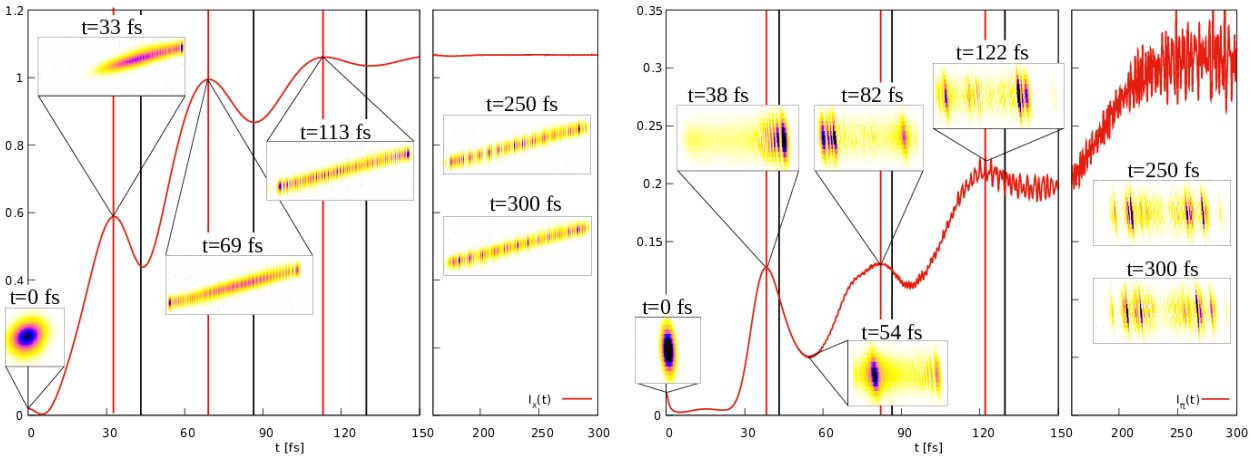

Figure 1: Mutual Information in coordinate (left) and momentum space (right).

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Enhanced Excitation Transport under Strong Light-Matter Coupling: Insights from Molecular Dynamics Simulations

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Transfer of excitation energy is a key step in light harvesting and, therefore, of high technological relevance for solar energy conversion. In bare organic materials, energy transfer proceeds via incoherent hops, which restrict propagation lengths to the nanoscale[1]. This imposes a limitation on the thickness of the active layer of organic solar cells and, as a consequence, on their efficiency. In contrast, energy transport over several micrometers has been observed in the strong coupling regime where excitations hybridise with confined light modes to form polaritons[2-9]. Here, we study this polariton-enhanced energy transport by means of atomistic multiscale molecular dynamics simulations of organic molecules in a Fabry-Perot cavity. Our results suggest that polariton propagation is limited by the cavity lifetime and appears diffusive due to reversible population transfers between bright polaritonic states that propagate ballistically at their group velocities, and dark states without group velocity. In addition, we qualitatively reproduce recent experimental results of Pandya et.al.[6] on the unexpected dependency of the polariton group velocity on the cavity quality factor and suggest an explanation of this phenomenon in terms of cavity decay and non-adiabatic population transfers into dark states. Finally, we propose an approach aiming at representing experimentally relevant large molecular ensembles with a computationally tractable number of effective molecules and discuss the validity and limitations of this method on the example of polariton transport.

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Unraveling the photophysics of nature-inspired molecular light-to-heat converters

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One major challenge in the twenty-first century is to increase global food production while the quality and quantity of arable land are diminishing. Central to this problem is the necessity to increase the yield of numerous crop species and to find ways to extend geographical locations suitable for agriculture. One environmental constraint which hinders plant growth and development is cold stress. To protect plants from cold stress, we propose using molecular heaters, molecules which can absorb light at specific wavelengths and convert it into heat. Combining efforts from synthesis, spectroscopy, toxicology, and computational chemistry, we present a series of suitable candidates to be used as molecular heaters for crop yield improvement.[1-3]

To elucidate the photophysics of these molecules, we combine different strategies such as TDDFT, DFT/MRCI, CASSCF/CASPT2, and surface hopping simulations. The target chromophores are inspired by sinapoyl malate, a naturally occurring molecule identified as an efficient photoprotective plant sunscreen.[4] Our sinapoyl malate derivatives present a fast and efficient relaxation mechanism that involves population transfer from an initially populated bright $^1\pi\pi^*$ state to a dark twisted intramolecular charge transfer state. This intermediate state mediates an efficient internal conversion to the ground state through a conical intersection. The photoisomer formation is naturally prevented due to a symmetric substitution in one of the sp2 carbons, ensuring almost complete recovery of the initial ground state. After the internal conversion to the ground state, vibrational cooling to the solvent can release the excess energy as heat, increasing the temperature on the plant surface.

In summary, we present a new class of nature-inspired molecules with suitable photophysics to be used as molecular heaters. They present an efficient nonradiative energy dissipation mechanism allowing the absorbed light to be converted into heat with minimal implication for photosynthesis. Considering their green synthesis, impressive photostability, and lack of critical toxicity, these molecules are promising molecular heaters for applications in agriculture, phototherapy and where photothermal conversion is desirable.

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Histamine sensing by Boron and Silicon doped Fullerenes: A first principles investigation

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Abstract

The present communication reports the interaction of histamine neurotransmitters on the surfaces of pure, boron, and silicon-doped fullerenes. The interaction of histamine with pure, boron, and silicon-doped fullerenes has been investigated with the help of density functional theory calculations in terms of stabilities, geometry, work function, electronic properties, and density of state. The magnitude of adsorption energies has been computed to be -1.664, -35.287, and -37.426kcal/mol for histamine, corresponding to the most favorable adsorption configurations, respectively. The band gap analysis revealed that pure fullerene's electrical conductivity remains nearly the same even after histamine adsorption. However, the doping of boron and silicon leads to the reduction in the band gap after histamine interaction, resulting in an increment in the electrical conductivity, which infers that boron and silicon doped fullerenes are more sensitive towards histamine than pure fullerene. The NBO calculations showed charge transfer of 0.008, 0.409, and 0.272*e* from histamine to pure, boron, and silicon-doped fullerenes in the most favorable adsorption configurations, respectively.

Keywords: DFT, Fullerene nanocages, Adsorption Energy, NBO, Electronic properties.

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Bimolecular Symmetry Breaking Charge Separation in Concentrated Perylene Solutions

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Symmetry-breaking charge separation (SB-CS) enables the conversion of solar energy into charge carriers by photoinduced electron transfer between identical molecules.[1] Typically, SB-CS is studied in systems where the two chromophoric moieties undergoing SB are covalently linked.[2] On the other hand, examples of bimolecular SB-CS of organic chromophores yielding free ions remain scarce due to solubility or aggregation issues of the organic dyes at the high concentrations needed to study this diffusion-assisted process.

In this study, we investigate the excited state dynamics of Perylene (Pe) in solution at high chromophore concentration solvents of varying polarity. By mapping out the excited state dynamics from subnanosecond to microsecond timescales, using transient absorption spectroscopy, we demonstrate that the locally excited (LE) state undergoes quenching through excimer formation[3] in concentrated solutions in all solvents used. Furthermore, we detect the generation of ions[4] ($Pe^* + Pe \rightarrow Pe^{\bullet+} + Pe^{\bullet-}$) through dissociation of the excimer in polar solvents, providing evidence for the occurrence of bimolecular SB-CS (see Figure 1).

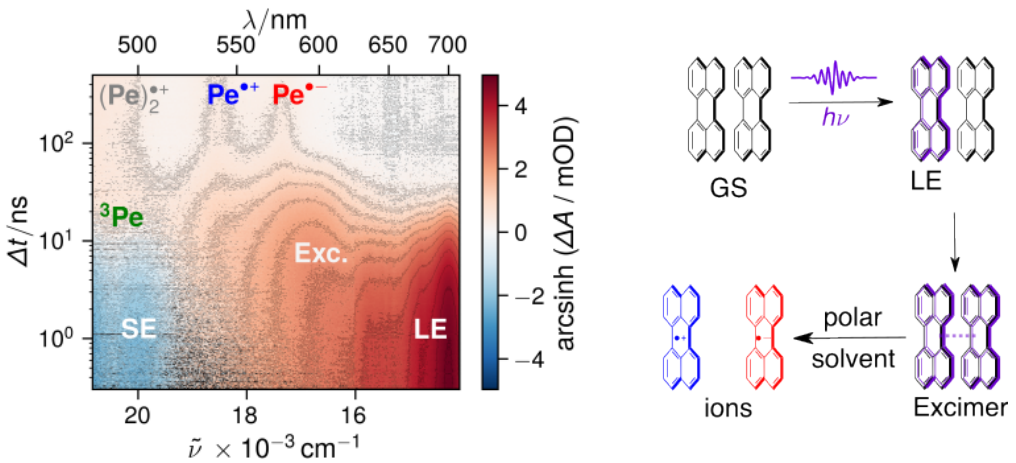

Figure 1: Nanosecond-microsecond visible transient absorption spectrum of Pe (1.5 mM) in acetonitrile showcasing bimolecular SB-CS as well as excimer formation.

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Coherent vibronic exciton dynamics and 2DES signals in a reduced-dimensional conjugated polymer model

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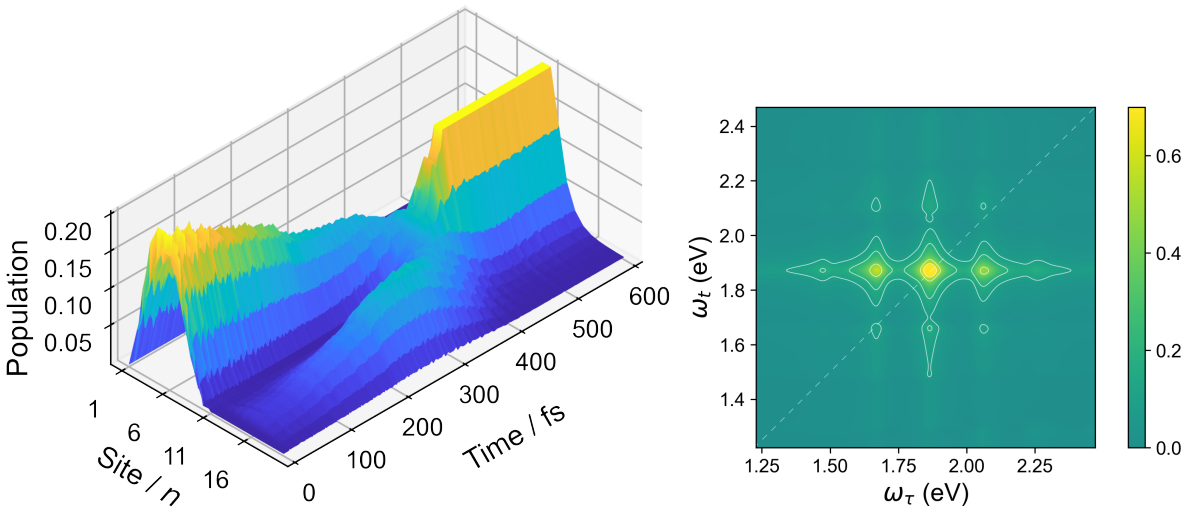
Understanding exciton transport in organic semiconductors is crucial to gain insight into technologies such as organic solar cells. In this work, two-dimensional electronic spectroscopy (2DES) signals associated with exciton migration in the donor material eicosathiophene are simulated using an in-house Fortran code.[1] To reduce the number of required degrees of freedom, only a single collective lattice mode and a torsional mode are introduced. The latter is treated within a mean-field Ehrenfest description. The Equation-of-Motion Phase-Matching Approach (EOM-PMA) within a wave function description[2] is employed to calculate the 2DES spectra.

The dynamics simulations start with a defect geometry ("conjugation break") that separates the system into two subunits of the same size. The initial exciton is trapped in the bright state of one of the subunits, which corresponds to a superposition of the S_1 and S_2 states of the lattice. Upon planarization, the exciton can then move towards the center of the lattice. These dynamics are driven by the torsional mode and the polaronic mode: The energy gap between the lowest adiabatic states is modulated and leads to near adiabatic exciton migration.
The evolving quantum dynamics are linked to the spectroscopic features of the system. Due to the polaronic mode, dominant fine structures are visible in the spectra. These fine structures are likely related to the S_1 state. The spectra strongly depend on the population time T due to the dynamics.



(a) **(b)**

Figure 1: **(a)** Calculations of time-dependent excitonic site populations of the model system including a single collective lattice mode and a torsional mode. **(b)** Absolute value of the 2DES spectrum of the system with a population time $T = 0$ fs.

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Widefield Detection of Single Molecule Absorption Spectra through Fourier Transform Spectroscopy

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The detection and identification of single molecules over large fields of view makes both individual and group statistics available simultaneously. Through Fourier transform spectroscopy, the absorption spectrum of both single and clustered molecules can be resolved in one measurement and differentiated from other species in the same image. This method demonstrates fast identification of different species at single-molecule concentrations, while also offering a pathway towards single molecule 2 dimensional electronic spectroscopy.

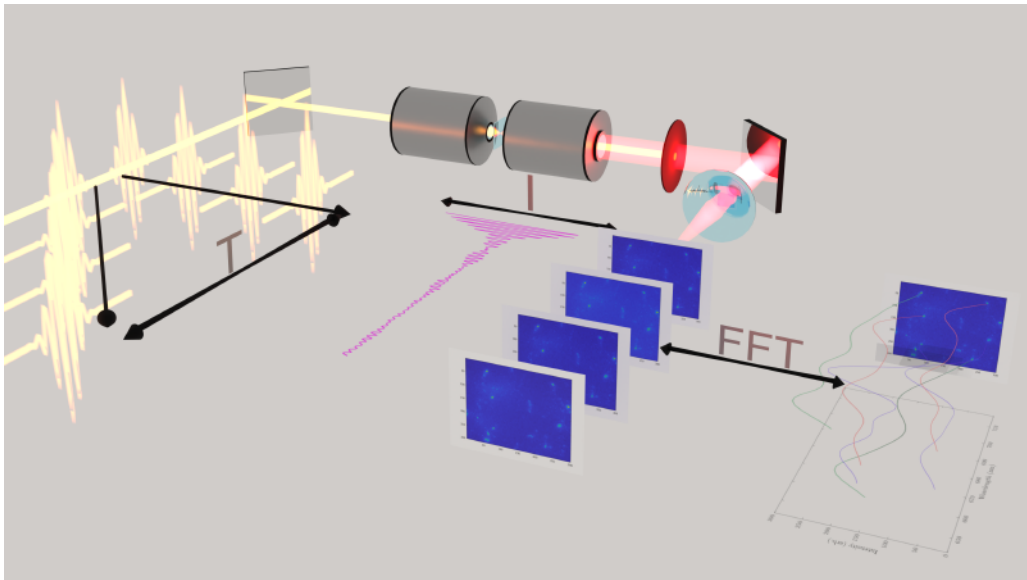

Figure 1: Visual representation of the experimental set up. The scheme can be readily adapted to a two dimensional spectroscopic approach.

As seen in Figure 1, the response correlating to scanned delays between two pump pulses is used to reveal the absorption spectra of several discrete molecules simultaneously. Pulse pairs were generated using an amplitude mask on a spatial light modulator, through which both the relative delay and phase of the pulses can be controlled. The subject of the poster/SSP would be this preliminary work with a view to expansion into the two dimensional. Expanding the scheme to incorporate two pulse pairs would allow the two dimensional spectra of such molecules to be determined. The proposed scheme, building on previous investigation into 2D charge dynamics (1), would have the capability of spectroscopically probing exciton dynamics in materials from the femtosecond to the picosecond timescale.

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Bipolar organics for photovoltaics

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Organic photovoltaics (OPVs) hold the potential to deliver cost-effective and flexible solar energy solutions. Unlike silicon photovoltaics that directly generate free charges, OPVs necessitate the use of electron-donating and -accepting materials to divide excitons into charges. Recent advancements have seen Y6 and its derivatives significantly boost the efficiency of organic solar cells by serving as electron acceptors. However, their capacity to act as electron donors remains unexplored.

This study introduces a bipolar molecule, A6, designed through the strategic modulation of the end group on Y6-based acceptors. Our findings demonstrate that A6 can effectively function as either an electron donor or acceptor, achieving an unprecedented quantum efficiency exceeding 50% in charge generation in both scenarios. Remarkably, when A6 operates as an electron-donating material, a rapid charge transfer process within 100 femtoseconds is observed.

These results underscore the pivotal role of end group modulation in adjusting the electron-donating and -accepting properties of organic semiconductors. This new understanding offers a fresh perspective in the molecular design of materials for organic photovoltaics, paving the way for future advancements in this field.