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Quantum Dynamics and Spectroscopy of Functional Molecular Materials and Biological Photosystems

Book of Abstracts

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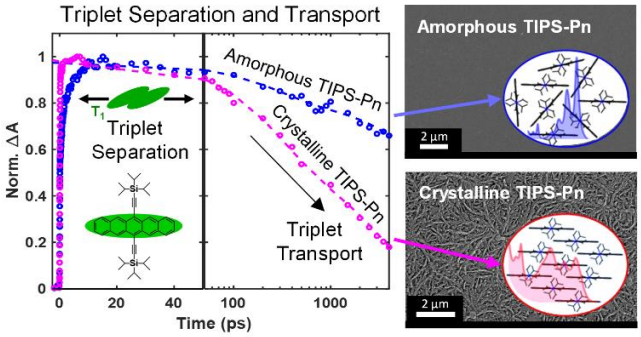
Invited Talks

Separation and Trapping of Triplet Pair Intermediates in Amorphous Singlet Fission Materials Measured with Ultrafast Infrared Spectroscopy

John B. Asbury

Department of Chemistry
The Pennsylvania State University, University Park, PA 16802

This talk will focus on the use of ultrafast infrared spectroscopy as a probe of correlated triplet pair dynamics and separation following singlet fission in pentacene derivatives. The method can be used to probe the spatial separation of triplet pair intermediates on ultrafast time scales through two types of transitions that provide complementary information. When triplet pair states overlap neighboring molecules, they exhibit broad electronic transitions that arise from mixing of singlet exciton and net singlet spin correlated triplet pair states. As the triplet pair states dissociate on the picosecond to nanosecond time scale, their coupling to the singlet exciton states is diminished, which leads to loss of the broad electronic transition. In this way, triplet pair separation can be probed directly on ultrafast time scales. Simultaneously, triplet excitons exhibit distinct vibrational frequencies that are perturbed by the change in symmetry and electronic spatial distribution as they transition from singlet to triplet spin states. The dynamics of triplet pair separation measured through their vibrational features is compared in crystalline and amorphous TIPS-Pentacene films are compared quantitatively. Surprisingly, triplet separation occurs on similar time scales in both environments. However, triplet transport is markedly slower in amorphous environments, indicating the presence of triplet traps. The findings suggest that it may be possible to nanostructure amorphous or polymeric singlet fission sensitizers to allow ultrafast triplet pair separation and harvesting despite their low triplet exciton diffusivity.



Spin cross-over dynamics in photoexcited haem proteins

M. Chergui
Laboratoire de Spectroscopie Ultrarapide and Lausanne Centre for Ultrafast Science, ISIC, Faculté des Sciences de Base, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Probing the detachment and binding of diatomic ligands to the Fe centre in haem proteins has been of high interest since the birth of ultrafast spectroscopy.
Detachment of the ligand can be triggered by photoexcitation of the π–π* transitions of the haem and monitoring of the ensuing dynamics was carried out using visible-UV (sensitive to the porphyrin π–π* transitions), IR (sensitive to the ligand stretch) or Raman studies. All agree on a prompt ligand detachment, but two interpretations have emerged to explain the ensuing dynamics: a) the newly formed deoxy haem is in a vibrationally hot ground state; b) it relaxes via intermediate electronic states. None of the above-mentioned used methods can distinguish thermal, electronic and spin relaxation, nor are they probes of structure, and therefore the debate was still not been settled.
We combined femtosecond optical transient absorption[1–3] and ultrafast optical fluorescence[4,5] studies with picosecond/femtosecond Fe K-edge X-ray absorption (XAS)[6,7] and X-ray emission spectroscopy (XES)[7,8] that are sensitive to the electronic and spin structure of the metal as well as the local structure around it. Our study of ferrous Myoglobin-NO[8] shows that upon excitation, prompt ligand dissociation occurs, flowed by a relaxation of the penta-coordinated haem via an intermediate spin (S=1) state to the deoxy HS (S=2) State (Fig. 2). The latter goes back to the low spin (LS) planar state after ligand binding. Thus, the entire ligand detachment and binding cycle is a spin cross-over (SCO) and back-SCO process. Extending these studies to the case of ferric cytochrome c, for which no ligand detachment is known to occur, we find that the photocycle of its haem is also characterised by an SCO followed by a back SCO step.[7] By comparing several porphyrin and haem systems, we conclude that regardless of the oxidation state of the Fe atom, the type of ligand or whether it dissociates or not, the haem photocycles are governed by SCO.

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How the environment can tune the energy, the coupling, and the ultrafast dynamics of interacting chromophores: the effect of hydrogen-bonds

Elisabetta Collini

Department of Chemical Sciences, University of Padova, via Marzolo 1, 35131 Padova (Italy)

The role of hydrogen bonds (H-bonds) is central to understanding microscopic structures and functions in many functional biological and artificial materials. H-bonds stabilize and determine the 3D structure of biological macromolecules such as proteins and DNA and can play an essential role in determining the reactivity of the active site of enzymes. The directional nature of H-bonds has important implications not only for the final geometry of the complexes but also for their electronic properties.
In this work, we compared a biological pigment-protein complex, the Water-Soluble Chlorophyll-binding Protein (WSCP), and an artificial H-bonded BODIPY dimer, in order to verify how the presence of H-bond could affect the ultrafast dynamic relaxation in the excited state. 2D Electronic Spectroscopy is applied for this purpose since it allows to follow the ultrafast dynamics of complex systems, providing information on the temporal evolution of both coherent and non-coherent processes with a time resolution in the order of femtoseconds.
For both the systems, the directional nature of H-bonds has important implications for the electronic properties. In WSCP, it has been found that the transition dipole moments, the electronic coupling and the excitonic energy gaps are tuned by the presence of specific and directional interactions between the protein backbone and the formyl group on the Chl *b* moiety.[1] In the BODIPY dimer, the H-bonds activate new ultrafast dynamic channels in the relaxation dynamics of the dimer involving intra- and inter-molecular mechanisms.[2]
These findings suggest that the design of H-bonded structures is a particularly powerful tool to drive the ultrafast dynamics in complex materials since it implies the possibility of tuning the photophysics and the transport properties of complex systems by engineering specific interactions with the surroundings.

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In Silico Photochemical Experiments with Non-Born-Oppenheimer Molecular Dynamics

Basile F. E. Curchod

Department of Chemistry, Durham University, Durham DH1 3LE, UK

What happens to a molecule once it has absorbed UV or visible light? How does the molecule release or convert the extra energy it just received? Answering these questions clearly goes beyond a pure theoretical curiosity, as photochemical and photophysical processes are central to numerous domains like energy conversion and storage, radiation damages in DNA, or atmospheric chemistry. Different theoretical tools have been developed to address these questions by simulating the excited-state dynamics of molecules [1]. Two examples of such methods include ab initio multiple spawning (AIMS) and trajectory surface hopping (TSH). AIMS describes the dynamics of nuclear wavepackets using adaptive linear combinations of traveling frozen Gaussians [2]. TSH portrays the nuclear dynamics with a swarm of independent classical trajectories that can hop between potential energy surfaces for this task [3].

In this talk, I intend to survey some of our recent work aiming at understanding the approximations underlying AIMS [4] and developing new approximate techniques based on the multiple spawning framework [5]. I will also discuss the application of nonadiabatic methods to unravel the photochemistry of molecules in gas phase, focusing on (i) the calculation of photolysis rate constants for transient atmospheric molecules [6] and (ii) the investigation of athermal ground-state dynamics following the passage through a conical intersection [7].

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Light-induced ultrafast coherent exciton-phonon dynamics in functional materials

Antonietta De Sio
Institut für Physik, Carl von Ossietzky Universität, 26129 Oldenburg, Germany

The ultrafast dynamics of non-equilibrium excitations upon light-matter interaction in functional materials and nanostructures are governed by the details of the electronic structure, by its coupling to the vibrational degrees of freedom, and by structural factors like the specific arrangement and possible disorder in the condensed phase. All these microscopic properties ultimately determine the flow of energy and the motion of charges upon photoexcitation. They are therefore of primary importance for the efficient application of such materials in e.g., light-harvesting, energy conversion, sensors, light-emission.

Here I will discuss examples showing the importance of strongly coupled electron-nuclear dynamics in condensed phase photoactive materials for energy conversion and how ultrafast two-dimensional electronic spectroscopy (2DES) can provide detailed new insight into these dynamics [1-5]. Specifically, we experimentally track, for the first time, ultrafast energy relaxation through an intermolecular conical intersection in molecular aggregates [3]. Combining sub-10-fs 2DES and atomistic nonadiabatic dynamics simulations, we probe the coherent motion of an optically launched vibronic wavepacket through an intermolecular conical intersection within only ~40 fs [3]. This passage drives the first step in the ultrafast energy transfer in molecular aggregates. Our results suggest that intermolecular conical intersections may effectively steer energy pathways in functional nanostructures. In a second example, using temperature-dependent 2DES in reflection, we probe coupled exciton-lattice dynamics in halide perovskite crystals [4-5]. At 20 K, our data identify the coupling of excitons to three selected persistent low-frequency phonon modes of the lead-halide lattice. Importantly, the analysis of the dynamical nonlinear optical response reveals that a purely displacive excitation of coherent phonons cannot account for our data. Instead, they are dominated by coherent oscillations of the exciton transition dipole moment governed by the phonon modes [5]. Our results suggest new strategies to control coherent energy transport and relaxation dynamics in functional photoactive materials by tailoring electron-phonon couplings.

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Probing singlet fission and exciton transport with femtosecond stimulated Raman spectro-microscopy

Renee Frontiera, Department of Chemistry, University of Minnesota

Singlet fission is a process in which absorption of a single photon results in the generation of two triplet states, with the potential of increasing photovoltaic efficiency beyond the Shockley-Quissar limit. Acene materials have served as excellent model compounds for studies of singlet fission, due to their excellent electronic properties, packing characteristics, and high mobilities. However, predicting how chemical modifications of these molecules impact singlet fission can be quite challenging, particularly because a single substitution can unpredictably impact packing, fission rates and yields, and exciton transport properties. Here we show how spectro-microscopy measurements have successfully guided the rational design of new singlet fission materials, leading to substantial improvements in metrics including rate and yield of triplet generation. We first used femtosecond stimulated Raman spectro-microscopy to determine the mechanism of triplet separation in crystalline rubrene, finding that separation of the correlated triplet pair is associated with a loss of electron density in the tetracene core. We then examined a series of fluorinated and methylated rubrene derivatives, which vary in the degree of charge density in the tetracene backbone. We find that the singlet fission rates and yields are dramatically improved by priming the system for triplet separation, which we achieve through chemical modifications which reduce electron density in the tetracene core in the ground state. Finally, we discuss our efforts to understand the role of phonon mode coherences in promoting triplet transport, through the development of a spatially-resolved femtosecond stimulated Raman microscope.

Exciton transport in molecular aggregates imaged by ultrafast microscopy

Libai Huang
Purdue University, West Lafayette, IN, 47907, USA
E-mail: libai-huang@purdue.edu

Long-range exciton transport is a key challenge in achieving efficient solar energy harvesting in both organic solar cells and photosynthetic systems. Exciton transport is not well understood in the intermediate regime where many molecular aggregates and photosynthetic antennas belong. Excitons are delocalized over part of the system and the exciton delocalization (coherent) length is defined by the competition between intermolecular coupling strength and disorder and transport has mixed coherent and incoherent characteristics. Within each delocalized segment the excitation energy propagates ballistically. However, there currently lacks an experimental tool to directly characterize exciton transport in space and in time to elucidate mechanisms. Here we report a direct visualization of exciton diffusion in tubular molecular aggregates by transient absorption microscopy with ~ 200 fs time resolution and ~ 50 nm spatial precision. These measurements provided exciton diffusion constants of 3−6 cm^{2-1} for these aggregates, which were 3−5 times higher than a theoretical lower bound for pure incoherent hopping. Simulation showed that the states crucial for exciton transport are delocalized over < 10 molecules, suggesting that coherent effects play a role despite relatively weak delocalization.

Observation of coherent wavepacket along the Jahn-Teller axis in a Mn-based Single Molecule Magnet

F Liedy[1], J Eng[2], R McNab[1], R Inglis[1], T J Penfold[2], E K Brechin[1], J O Johansson[1,*]

[1]School of Chemistry, University of Edinburgh, UK
[2]Chemistry - School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK
*Email address: olof.johansson@ed.ac.uk

Single-molecule magnets (SMMs) are metal complexes with two degenerate magnetic ground states[1] and are promising for future applications in data storage. We have explored the ultrafast dynamics occurring after photoexcitation of the tri-nuclear SMM $[Mn^{III}_3O(Et\text{-}sao)_3(\beta\text{-}pic)_3(ClO_4)]$ (hereafter Mn_3), whose magnetic anisotropy is related to the Jahn-Teller (JT) distortion arising from the $t_{2g}^3 e_g^1$ electronic configuration of the Mn^{III} ions. We observed a coherent modulation of the axial anisotropy on a femtosecond timescale,[2] which could provide a method towards achieving optical control of the magnetisation direction in SMMs.

Using ultrafast transient absorption spectroscopy in solution, we found oscillations superimposed on the decay traces due to a vibrational wavepacket. Based on a complementary study on the monomer $Mn(acac)_3$, we concluded that the excited state corresponds to a shift of electron density from the antibonding d_{z^2} to $d_{x^2-y^2}$ orbitals, which in turn leads to a compression of the axial bonds and an elongation of equatorial bonds *via* the formation of a vibrational wavepacket (Fig. 1). In $Mn(acac)_3$, this leads to a shift from axial to equatorial JT distortion. However, in Mn_3, equatorial expansion is not possible due to the strong bonds in the plane of the triangle provided by the μ_3-oxo and μ-oxime bridges, and the main motion of the wavepacket is a collective displacement of all three Mn ions along the z-axis. This leads to a modulation of the axial JT distortion and a significantly shorter excited state lifetime. Interestingly, the simpler reaction coordinate in the tri-nuclear Mn_3 molecule leads to a more well-defined wavepacket with longer dephasing time than in the $Mn(acac)_3$ monomer. This opens up new molecular-design challenges to control the wavepacket motion in the excited state of polynuclear transition-metal complexes.

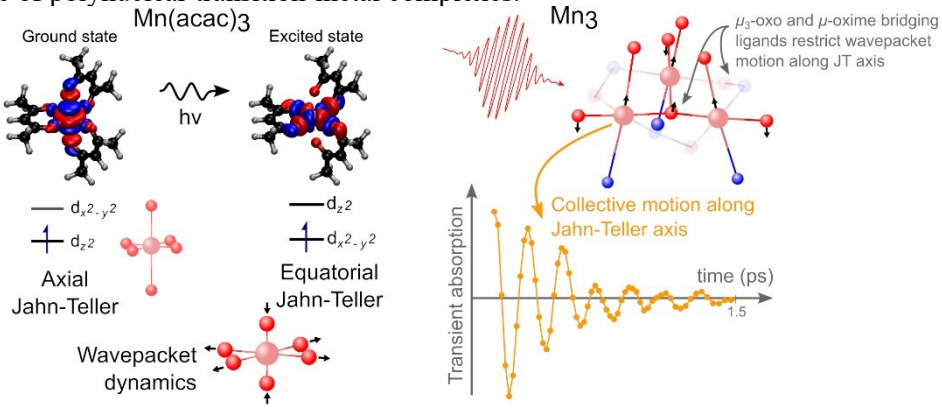

Figure 1: *Photophysics of Mn^{III} complexes. The antibonding nature of the e_g orbitals lead to a rapid switch of the JT distortion in the excited state of $Mn(acac)_3$ (left). In Mn_3, the strong bonds in the triangle prevent equatorial expansion and the Mn ions move in a collective motion along the axial JT distortion axis (right).*

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Role of coherent nuclear motions in ultrafast processes in liquid by time-resolved spectroscopies and molecular dynamics simulation

Taiha Joo

Department of Chemistry, POSTECH, Pohang 37673, Korea

Following photoexcitation to a Franck-Condon state, a molecule may undergo various processes such as internal conversion, intersystem crossing, and chemical reactions. Nuclear wave packets (NWPs) in the initial excited electronic state created by the short pump pulses will be carried over to product states. Some NWPs that are orthogonal to the reaction coordinate survive the process. For others coupled with the process, frequencies, phases, and amplitudes of the NWPs will be modified in the course of the reaction. Thus, NWPs in the product state shed light on the molecular dynamics of the process.

Oscillation of a signal in a time-resolved spectroscopy by coherent NWPs can be recorded up to 3,000 cm^{-1} to cover the entire vibrational spectrum of molecules. For molecules that undergo ultrafast photochemical processes, we recorded NWPs in the product state by using transient absorption and time-resolved fluorescence. Because the NWPs in the product was created via initial Franck-Condon state, it is non-trivial to predict NWPs in the product state, and molecular dynamics simulation will be a valuable tool to understand the NWPs and the molecular reaction dynamics. Two chemical reactions studied by NWPs in the product state will be presented. In one, we analyze the NWPs of 10-hydroxybenzo[h]quinoline (HBQ), which undergoes ultrafast excited state intramolecular proton transfer (ESIPT), in the product state by molecular dynamics simulation and normal mode projection method. The results are consistent with the NWPs observed by time-resolved fluorescence[1] including both amplitude and phase. The theory and experiement provided the shape of the potential energy surface and the role of low-frequency skeletal vibrations in the ESIPT. The other molecular system is ruthenium complexes that undergo ultrafast intersystem crossing (ISC).[2] NWPs were observed in the reactant and product states following ISC, which provide important information on the excited-state dynamics. We can identify the vibrational modes strongly coupled to the ISC, whose vibrational coherences experience attenuation after the ISC. The coupled modes contain metal-ligand stretching or symmetry breaking component.

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Finding good polarization sequences for tracking dynamics in 2DES with HEOM and machine learning

Tobias Kramer

Zuse Institute Berlin, Germany

The hierarchical equations of motions (HEOM) provide an exact solution for open quantum system dynamics [1] and have been applied to study the exciton dynamics and time-resolved spectra of larger photosynthetic complexes with DM-HEOM [2].
An important application is the description of energy transfer in photosynthetic systems from the antenna to the reaction center and the computation of the corresponding 2D time- abd frequency resolved spectra [1].
The specific excitonic energies and the orientation of transition dipole moments is revealed by varying the polarization sequence of 2D spectroscopy. We find that the “double-crossed polarization sequence” is highly susceptible to static disorder and analyze the (dis)advantages of various polarization sequences [3].
To facilitate disorder averages, we use machine learning techniques to encode the HEOM results in small neural networks [4]. The neural networks is used to perform ensemble averaging to compress the time-resolved spectra.

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Efficient and fast prediction of ultrafast spectroscopies

Jacob Krich

Department of Physics, University of Ottawa, Ottawa, ON, Canada

Nonlinear optical spectroscopies are powerful tools for probing quantum dynamics and energy transfer in molecular systems. Intuition about ultrafast spectroscopies is often built by considering infinitely short duration — impulsive — optical pulses. Actual experiments have finite-duration pulses, and finite-pulse-duration effects both can be important to interpret results and can be purposely used to distinguish electronic from vibrational coherence. I will describe a new freely available open source tool for spectroscopic modeling, called the Ultrafast Spectroscopy Suite (UFSS), available at https://github.com/peterarose/ufss. UFSS includes integrated tools for 1) automatic construction of Feynman diagrams for both phase-matching and phase-cycling spectroscopies, and 2) computationally efficient and convenient evaluation of those diagrams to predict nonlinear spectra, including treatment of arbitrary pulse shapes. UFSS efficiently treats open systems with Markovian baths and currently supports Redfield (both full and secular) and Lindblad forms. The primary computation method requires diagonalization of the system Liouvillian, and I will explain why the conventional wisdom that such diagonalizations are too costly is dramatically incorrect in many important cases. We can achieve multiple orders of magnitude speedups over common direct-propagation methods in many commonly considered cases with sufficiently small Hamiltonian size. When using a secular Redfield model, our method is more efficient than standard alternatives even for large systems, until memory becomes limiting.

UV induced femtosecond and attosecond dynamics in 2D and 3D carbon-based molecular structures

Franck Lépine

CNRS, Institut Lumière Matière, Lyon (France)

Ultrashort XUV pulses provide a new tool to have access to ultrafast processes in excited matter on the femtosecond and even attosecond timescales. In recent experiments we have studied XUV induced dynamics in carbon based molecular structures. We have shown that electron correlation drives energy deposition in so called "correlation bands" and that the energy is dissipated on few 10 fs in specific vibrational states. On even shorter timescale, we have used attosecond metrology to measure the timing of XUV induced electron ejection on few 10 as which serves as a probe of the interaction potential on the atomic length scale.

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Femtosecond Stimulated Raman Spectroscopy as a Test of Theoretical Predictions of Excited-State Structural Changes

Zachary Piontkowski and **David McCamant***
Department of Chemistry, University of Rochester, Rochester, New York, USA.
*Email: David.mccamant@rochester.edu

Much of our modern understanding of rapid photochemical events depends on theoretical predictions about the shapes of excited-state potential energy surfaces and the agreement of those predictions with experimental observations. However, there are actually very few experiments and theoretical predictions that can be directly compared to verify the excited-state nuclear motion predicted by theory. Here, we will present several studies that aim to put this comparison on firmer ground. In our recent work, we have used resonance Raman spectra collected using femtosecond stimulated Raman spectroscopy (FSRS) to corroborate excited-state potential energy surface predicted by Density Functional Theory (DFT). That corroboration can provide confidence in the theoretical method when it is subsequently used to make predictions about areas of the potential energy surface that are important for the photochemical dynamics but difficult to probe experimentally. Specifically, we are interested in the excited-state structural rearrangements in a series of rhodamine dyes used for solar hydrogen production.[1] Additionally, we have used time-resolved FSRS in conjunction with predictions from DFT to establish the particular torsional geometries of a rapidly relaxing chromophore, a chalcogenopyrylium monomethine dye, during its internal conversion process through a conical intersection.[2] These studies aim to provide more concrete, testable hypotheses that can be passed back and forth between experimentalists and theoreticians.

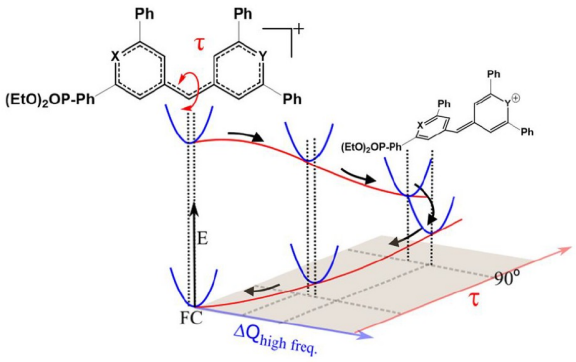

Figure 1. Photochemical torsional motion in chalcogenopyrylium dyes measured by FSRS and predicted by DFT. From ref. 2.

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Development of Theoretical/Computational Tools for Excited State Molecular Dynamics

Seung Kyu Min[1]

[1]*Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), 50, UNIST-gil, Ulsan 44919, Republic of Korea*

Excited state molecular dynamics (ESMD) is an effective theoretical/computational tool to understand photochemical/physical phenomena such as photosynthesis, vision process, photovoltaics and light-driven chemical reactions. The conventional ESMD simulation within mixed quantum-classical frameworks propagates classical nuclear trajectories on multiple electronic states, so-called Born-Oppenheimer electronic states, with nonadiabatic coupling among them. In this presentation, I would like to introduce several attempts in my research group to develop computational approaches for ESMD simulations. First, I present an efficient ESMD algorithm to take into account for decoherence in nonadiabatic situation based on the so-called exact factorization scheme. [1] Second, I present a development of efficient excited state calculations for singlet states based on the combination of spin-restricted ensemble Kohn-Sham method and density-functional tight-binding approach. [2,3] Third, I present ESMD simulations with a combined machine-learning and quantum chemical (ML/QM) calculations to consider the correct topology of conical intersections with diabatic states. [4] Finally, I cover an in-house python-based ESMD simulation program package, the so-called pyUNIxMD program. [5]

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Multispectral multidimensional spectroscopy studies of excitonic structure and charge separation in the Heliobacterial Reaction Center

Yin Song[1], Riley Sechrist[1], Hoang H. Nguyen[1], William Johnson[2], Darius Abramavicius[3], Kevin E. Redding[2,4], and Jennifer P. Ogilvie[1*]

[1]*Department of Physics, University of Michigan, Ann Arbor, MI, 48109, US*
[2]*School of Molecular Sciences, Arizona State University, Tempe, AZ, 85287, USA,*
[3]*Institute of Chemical Physics, Faculty of Physics, Vilnius University, Sauletekio 9-III, 10222 Vilnius, Lithuania*

[4]*Center for Bioenergy and Photosynthesis, Arizona State University, Tempe, AZ, 85287, USA*

Photochemical reaction centers are the engines that drive photosynthesis. The reaction center from heliobacteria (HbRC) has been proposed to most closely resemble the common ancestor of photosynthetic reaction centers, motivating a detailed understanding of its structure-function relationship. The recent elucidation of the HbRC crystal structure motivates advanced spectroscopic studies of its excitonic structure and charge separation mechanism. I will present our recent multispectral two-dimensional electronic spectroscopy studies of the HbRC and corresponding numerical simulations that resolve the electronic structure and test recent excitonic models. Through a combination of lifetime density analysis and global target analysis, we reveal that charge separation proceeds via a single pathway in which the distinct A_0 chlorophyll *a* pigment is the primary electron acceptor. In addition, we find strong delocalization of the charge separation intermediate. Our findings have general implications for the understanding of photosynthetic charge separation mechanisms, and how they might be tuned to achieve different functional goals.

Vibronic quantum dynamics and coherence in light-harvesting systems

Alexandra Olaya-Castro

University College London

There is mounting evidence that vibronic coupling and the associated quantum mechanical exchange of energy between excitonic and vibrational degrees of freedom could be at the heart of the counterintuitive long-lived coherence beating probed in ultrafast spectroscopy of photosynthetic complexes. Within this hypothesis, intramolecular vibrations influence excited-state dynamics through the formation of joint quantum states of excitonic and vibrational degrees of freedom. The exact influence such vibronic coupling on excited state dynamics is not fully understood. In this talk I will discuss implications of coherent vibronic coupling for excitation energy transfer, energy conversion and synchronisation processes in prototype light-harvesting systems as well as quantum optical signatures of such vibronic interactions.

Molecular photodynamics and its manifestation in UV-Vis and X-ray time-resolved spectra. Insights from quantum chemistry and quantum dynamics.

David Picconi

Institut für Chemie, Universität Potsdam, Germany

Time-resolved spectroscopies performed on functional molecules - with UV-Vis pump and probes from all kinds of spectral domains - can bear signatures of multimode nuclear dynamics, nonadiabatic effects and quantum mechanical coherences. Relating these observations to the underlying molecular dynamics is instrumental to the ability of designing and controlling photoactive molecules.
This talk illustrates computational strategies which combine quantum chemistry and quantum dynamics to investigate which aspects of the photochemical mechanisms can be unambiguously inferred from time-resolved spectra. Two examples will be shown.
The first one is the prototypical excited state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline. Transient absorption and fluorescence spectroscopies revealed a number of long lived multimode quantum beats due to the ultrafast reaction mechanism [1,2]. The most recent investigations regard these coherences as a signature of a nonadiabatic reaction involving two coupled states [3]. The quantum dynamical simulations of this contribution, based on ab initio potential energy surfaces, show that the dynamics initiated by the S1 ← S0 excitation actually proceed mostly on a single Born-Oppenheimer surface. The observed coherences are generated by mode mixing along the reaction path. The reaction mechanism following the S2 ← S0 excitation is instead nonadiabatic and involves a nπ* state which becomes stable at the geometries of the photoproduct.
The second example is the gas-phase photoprotection mechanism of the nucleobase analogue 2-thiouracil (2-TU), which is studied using time-resolved X-ray photoelectron spectroscopy (XPS) at the sulphur 2p edge [4]. The relaxation following the S2 (ππ*) <- S0 excitation involves the three lowest singlet and triplet states. The mechanism is disentagled by comparing the time-dependent shift of the XPS signal with the core ionization potential calculated at the coupled-cluster level for the different electronic states. The excited molecules relax from S2 to S1 and T1 on a time scale faster than 100 fs and, a 200 fs relaxation channel to S0 is found, and a coherent electronic population exchange is observed. The quantum chemical data allow us to formulate a potential model [5] to invert the observed changes in the core ionization potential to the partial charge at the probed atom.

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Hunting Electronic States in Two-Dimensional Electronic Spectra

Ivan Rivalta

Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Bologna, Italy
Laboratoire de Chimie UMR 5182, École Normale Supérieure de Lyon, CNRS, Lyon, France

Two-dimensional electronic spectroscopy (2DES) is a developing multidimensional technique based on ultrashort laser pulses used to track electronic transitions in complex systems with femtosecond spectral and time resolution. 2DES in the ultraviolet (2DUV) can be used to investigate structure, conformation dynamics, energy transfer, and chemical/photochemical reactivity in a wide range of systems in physical chemistry, energy sciences and biophysics. The interpretation of 2D electronic spectra is challenging and computational modeling is required to disentangle the congested information contained in the nonlinear optical response of the sample. In this presentation, the 2DES technique is briefly introduced and the computational tools/protocols developed to perform first-principles simulations of 2DES spectra are illustrated.[1] The methodology has been so far applied to the study of structure and dynamics of various biological systems, including proteic systems [2], organic fluorescent probes, [3] DNA/RNA nucleobases [4] and complex organic polymers (lignin). The presentation will focus on the characterization of high-lying electronic states by means of wavefunctions methods and time-dependent density functional theory within hybrid QM/MM schemes. Recent developments to assess environmental and conformational effects that shape the 2D electronic spectra [5] will be also presented.

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Insight into the Spectral Tuning and Photoisomerization of Proteorhodopsin

Igor Schapiro
Institute of Chemsitry, The Hebrew University of Jerusalem, Israel

Proteorhodopsin (PR) is a photoactive proton pump found within marine bacteria which was first discovered in 2000. PR has been suggested to play a large role in marine photoactivated processes due to their wide presence in marine life and their unique ability to absorb sunlight. PR has two major variants which exhibit an environmental adaptation in their absorption maximum to the ocean's depth. The green-absorbing PR (GPR, λ_{max} = 520 nm) is mainly found in microbes at the surface of water whereas the blue-absorbing PR (BPR, λ_{max} = 490 nm) is distributed at the deeper region in the ocean. The amino acid at position 105 controls the color tuning of the two variants, where an L to Q substitution causes a ~25 nm green to blue color-shift in addition to affecting the geometric properties of the retinal chromophore. In this work the green-blue shift was investigated with QM/MM simulations using a polarizable embedding scheme. The L to Q mutation produces a positive electrostatic interaction near C_{14}-C_{15} of retinal, which in turn destabilizes the S_1 state leading to the observed green to blue shift.

Upon light absorption the protein embedded retinal protonated Schiff base (rpSb) of PR undergoes an ultrafast all-*trans* to 13-*cis* isomerization that constitutes the first step of its photocycle. We have simulated a few hundreds of nonadiabatic excited state molecular dynamics (MD) trajectories to investigate the photoisomerization rpSb in GPR. We have found that the electrostatic interaction between positively charged rpSb and its counterion aspartate controls the overall outcome of the isomerization process in addition to the intrinsic retinal coordinates.

Exciton Dynamics in Biological Rings

Erling Thyrhaug
Department of Chemistry, Technical University of Munich,
Lichtenbergstrasse 4, 85748 Garching b. München, Germany
E-mail: erling.thyrhaug@tum.de

Abstract

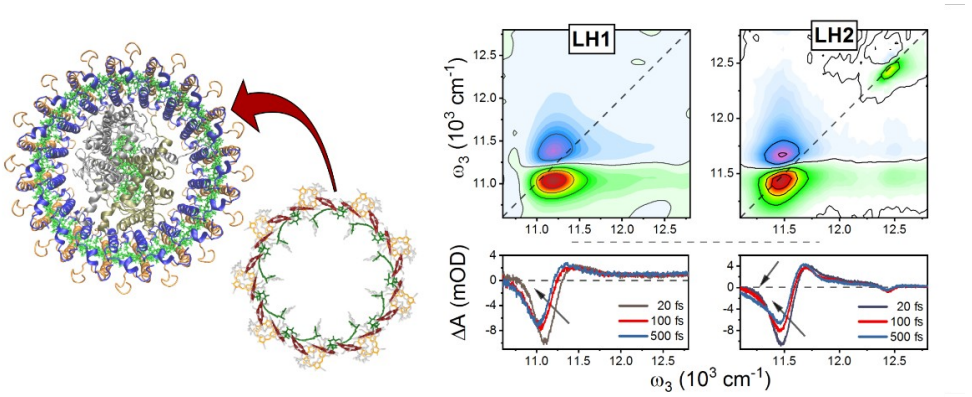

Figure 1: Left: Structures of the purple bacteria light-harvesting protein complexes LH1 (*r rubrum*) and LH2 (*r acidophila*). Right: Absorptive two-dimensional spectra of LH1 and LH2 at 100 fs population time, and corresponding transient absorption spectra at selected probe delays.

The photosynthetic apparatus of purple phototrophic bacteria has been the target of a wide range of spectroscopic studies over the last several decades. In particular, the light-harvesting antennae of these organisms have been popular model systems in both the context of biological function and in the fundamental study of excitons in soft-matter systems.
This extensive family of protein complexes are all built on similar structural motifs: essentially being moderately large assemblies of so-called αβ polypeptide subunits. Each of these subunits bind pairs of bacteriochlorophyll a pigment (as well as a variety of carotenoids), resulting in characteristic well-ordered ring-like assemblies of electronically coupled pigments. While the optical spectra resulting from these assemblies are deceptively simple, the photophysics are relatively complex – in large part due to involvement of a number of sub-ps relaxation processes.

Here, I outline recent work where we revisit the early-time photoinduced dynamics in these complexes. We present a comparative study of the relaxation in three superficially similar ring systems: the weakly coupled B800 ring in LH2 extracted from *r acidophila*, the moderately strongly coupled B850 ring from the same organism, and the significantly larger B880 ring found in reconstituted reaction-center-free LH1 from *r rubrum*. Using polarization controlled 2D electronic spectroscopy at cryogenic temperatures, we compare the exciton energy-relaxation and mobility in the three structures. In all systems we find the dynamics to be dominated by sub-ps processes. However – although energy-relaxation remains ultrafast at low temperatures – the exciton mobility appear to be severely inhibited even in the B850 and B880 rings at low temperatures.

Ligth-driven electron dynamics in molecules and nanostructures

Jean Christophe Tremblay

CNRS-Université de Lorraine, LPCT, Metz (France)

In this contribution, I will present an overview of our newest results in the field of ultrafast many-electron dynamics. I will first introduce a many-body wave-function simulation method, the Time-Dependent Determinantal Configuration Interaction (TD-detCI), to study light-induced ultrafast charge migration dynamics in rigid molecules and nanostructures. I will show how recasting the equations in hydrodynamics terms can provide an intuitive understanding of the processes. Selected applications will focus on the generation of charge migration and circular currents in oriented molecules using short laser pulses, on the measurement of the ultrafast charge carrier dynamics using time-resolved X-ray diffraction, and on exciton transfer in weakly bound complexes.

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Invited contribution

Light-matter interactions: from ab initio molecular dynamics and machine learning to x-ray spectroscopy

Morgane Vacher [a]

a) *Laboratoire CEISAM, Université de Nantes - CNRS, Nantes, France*
morgane.vacher@univ-nantes.fr

Computer simulations are a key complement to experiments in the laboratory, providing much greater details of a molecular process than can be observed experimentally. For instance, ab initio molecular dynamics simulations are often key to the understanding of the mechanism, rate and yield of chemical reactions [1,2,3]. One current challenge is the in-depth analysis of the large amount of data produced by the simulations, in order to produce valuable insight and general trends. In the first part of my talk, I will present recent machine learning analysis tools used to extract relevant information from ab initio molecular dynamics simulations without a priori knowledge on chemical reactions [4,5]. It is demonstrated that, in order to make accurate predictions, the models evidence empirical rules that are, today, part of the common chemical knowledge. This opens the way for conceptual breakthroughs in chemistry where machine analysis would provide a source of inspiration to humans. In the second part of my talk, I will show recent experimental and theoretical results on the photo-induced dynamics of an iron photosensitizer. Coherent structural dynamics in the excited state of an iron photosensitizer was observed through oscillations in the intensity of Kalpha x-ray emission spectroscopy (XES). Using multiconfigurational wavefunction calculations, we explain the origin of the unexpected sensitivity of core-to-core transitions to structural dynamics [6,7].

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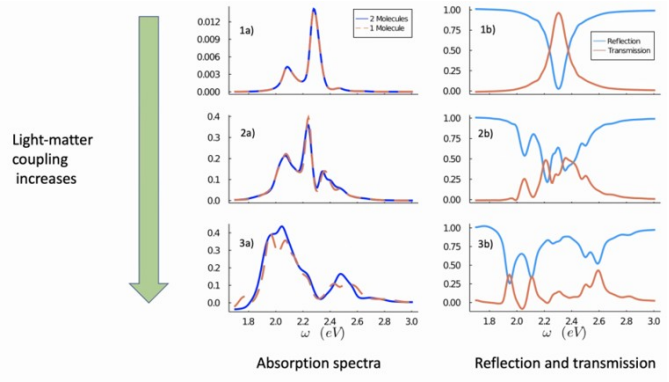
Optical spectroscopy of molecular polaritons

Joel Yuen-Zhou

University of California San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Dr MC 0340, La Jolla, CA 92093, United States



In quantum optics, strongly-coupled light-matter systems are typically described in terms of multilevel quantum models that are weakly coupled to Markovian baths. However, the description of recent spectroscopic experiments with molecular polaritons, where the material degrees of freedom give rise to dense spectra in the UV-visible range, begs for a more intuitive time-dependent formalism in terms of correlation functions of light and matter degrees of freedom. Here, we provide compact expressions and model calculations for linear spectroscopy of vibronic polaritons in terms of Fourier transforms of such functions. Time-resolved emission spectra are also discussed in relation to the latter development. Importantly, the definitions and expections of what “strong” light-matter coupling means is clarified for molecular systems.

The Hierarchical Stochastic Schrödinger Equations: Theory and Applications

Yi Zhao

State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, Fujian Provincial Key Lab of Theoretical and Computational Chemistry, and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
Email: yizhao@xmu.edu.cn

The hierarchical stochastic Schrödinger equations (HSSE) are a kind of numerically exact wavefunction-based approaches suitable for the quantum dynamics simulations in a relatively large system coupled to a bosonic bath. Starting from the influence-functional description of open quantum systems, this talk outlines the general theoretical framework of HSSEs and their concrete forms in different situations. The applicability and efficiency of HSSEs are exemplified by the simulations of ultrafast excitation energy transfer processes in large-scale systems.

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Contributed Talks

Monitoring molecular coherences by time-resolved x-ray Raman spectroscopy and diffraction with stochastic free-electron-laser pulses

Stefano M. Cavaletto, Daniel Keefer, and Shaul Mukamel
Department of Chemistry and Department of Physics & Astronomy, University of California, Irvine, CA 92697, USA

X-ray free-electron lasers (FELs) relying on the self-amplified spontaneous emission (SASE) mechanism generate stochastic x-ray pulses lacking phase control. This has represented a major bottleneck, since most time-resolved multidimensional nonlinear x-ray spectroscopy schemes are based on sequences of coherent, phase-controlled pulses. We show that suitable *correlation signals* averaged over independent realizations of stochastic FEL pulses can retrieve the same joint temporal and spectral resolutions of signals with phase-controlled pulses [1, 2]. This is demonstrated both for Raman spectroscopy [1] and diffraction [2] signals, and can be extended to additional complex multidimensional nonlinear x-ray spectroscopy experiments.

We apply this approach to TRUECARS, a spectroscopy technique which was recently put forward for probing molecular coherences with high temporal and spectral resolutions. TRUECARS can provide direct evidence of conical intersections (CoIns), as presented for the RNA base uracil [3], but its experimental implementation has thus far been hindered by the lack of reproducible, coherent x-ray pulses. We show that, by exploiting the correlations between the spectral components of stochastic FEL pulses, the TRUECARS technique can be implemented at existing FELs [1].

We further present time-resolved x-ray diffraction, which provides a movie of the transient molecular charge density. The technique is applied to monitor the femtosecond isomerization of azobenzene, a textbook photochemical process [4]. Again, the coherence contribution to the signal emerges during the CoIn passage, and is captured by inelastic scattering using stochastic FEL pulses. Correlation signals can help disentangle the coherence inelastic contributions to the diffraction signal from the background terms arising from the populations [2].

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Controlling photochemical reactions through strong light-molecule coupling

Jacopo Fregoni,* Giovanni Granucci,[c] Maurizio Persico,[c] Stefano Corni[b,d]

(*a) Dipartimento di Scienze Fisiche, Informatiche, Matematiche, Università di Modena e Reggio Emilia, 41125 Modena, Italy*
(b) Istituto di Nanoscienze, Consiglio Nazionale delle Ricerche CNR-Nano, 41125 Modena, Italy
(c) Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124, Pisa, Italy
(d) Dipartimento di Scienze Chimiche, Università di Padova,35131, Padova, Italy

* jacopo.fregoni@unimore.it, jacopofregoni@gmail.com

Strong coupling between molecules and light can be achieved in resonant cavities[1], giving rise to hybrid light-molecule states (polaritons). In these systems, light does not act only as an external driving to trigger photochemical processes, but it is actively involved in modifying photochemical properties[2]. As such, polaritonic chemistry[3] is emerging as a compelling and non-conventional approach to manipulate photochemical reactions. To provide the conceptual tools for interpreting polaritonic chemistry results, we firstly introduce the basic features of strong coupling applied to quenching of photochemical processes[4], also leading to efficient photoprotection[5].

By relying on accurate quantum chemistry multiscale simulations, we find that strong coupling can also lead to an enhancement of the photoisomerization quantum yield of azobenzene in a realistic nanoplasmonic setup[6]. We recognise that the strong coupling regime acts as a quencher of non-reactive pathways, typically responsible for the low trans-cis photoisomerization quantum yield of azobenzene[7]. Through our results, we show the potential of polaritonic chemistry to control photochemical reactions at the nanoscale.

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UV Photoresponse of the Green Fluorescent Protein Chromophore

William J. Glover[1,2,*], Wutthinan Thongyod[1,3], Chutintorn Punwong[3,4]

[1]*NYU Shanghai, China*
[2]*Department of Chemistry, New York University, New York, USA*
[3]*Department of Physics, Prince of Songkla University, Thailand*
[4]*Department of Chemistry, Stanford University, California, USA*

[*] e-mail: william.glover@nyu.edu

Green Fluorescent Protein (GFP) has revolutionized many fields of biology due its use in imaging organisms at the sub-cellular level. However, upon exposure to UV or intense visible light, GFP undergoes an irreversible reaction, altering its photocycle. A detailed understanding of the pathways that lead to GFP's irreversible damage following excitation to high-energy states will aid greatly in the development of new FPs with improved imaging and lifetime characteristics. Yet the mechanism of GFP's UV-initiated photodamage is currently the subject of controversy, with competing interpretations of photoelectron experiments on the isolated chromophore arguing for either nonadiabatic decay [1] or autoionization [2] from the initial S_3 excited state being dominant.

To address the controversy in GFP's UV-initiated excited-state decay pathways, we performed ab initio multiple spawning excited-state dynamics simulations on the GFP chromophore with on-the-fly multiconfigurational electronic structure using our recently developed dynamically-weighted complete active space self-consistent field (DW-CASSCF) method [3]. In addition, we computed Time-Resolved Photoelectron Spectroscopic observables, to make direct comparison to experiment. Our simulations of the GFP chromophore reveal that ultrafast non-adiabatic decay of the initial excited state outcompetes autoionization, in agreement with photoelectron experiments[1].

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Imaging electron currents in molecules and clusters

with ultrafast resonant x-ray scattering

D. Gorelova

I. Institute for Theoretical Physics, Universität Hamburg, Hamburg, Germany

We study how ultrashort x-ray pulses can be employed to image dynamical properties of nonstationary electron systems with (sub-)femtosecond temporal and sub-nanometer spatial resolutions. Using a rigorous theoretical analysis based on a framework of quantum electrodynamics, we accurately describe time-resolved signals taking into account all transitions that a broadband probe pulse can induce in a nonstationary electron system. Although individual spectral lines cannot be resolved in this case, it turns out that signals still encode valuable time- and space-resolved information about electron dynamics. Comparing various imaging techniques, namely, ultrafast resonant x-ray scattering[1,2], nonresonant x-ray scattering (Compton scattering) [3] and time-angle-resolved photoelectron spectroscopy (trARPES)[4], we could identify a common procedure to reveal charge and electron current distributions from the time- and momentum-resolved signals [5].

In my talk, I will focus on the ultrafast resonant x-ray scattering technique for imaging coherent electron dynamics in molecules [1] and clusters [2], and show our method to reconstruct interatomic electron currents based on our finding above.

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Femtosecond vibrational coherence spectroscopy reveals excited branching in Fe(II)-NHC complexes for photo-sensitizing applications

F. Hainer[1], N. Alagna[1], Li Liu[2], M. Darari[3], P. Gros[3], T. J. Penfold[4], T. Buckup[1], S. Haacke[2]
[1] Institute of Physical Chemistry, Ruprecht-Karls University Heidelberg, Germany
[2] University of Strasbourg – CNRS, IPCMS, Strasbourg, France
[3] University of Lorraine – CNRS, L2CM, Nancy, France
[4] Chemistry-School of Nat. & Env. Sci., Newcastle University, Newcastle Upon-Tyne, UK

One recent development in the realm of sustainable, green chemistry is to explore the replacement of rare transition metals like Ir, Pt and Pd in metalorganic complexes by more abundant elements like Fe, Cu or Cr. Coordination of Fe(II) with electron-rich carbene bonds can considerably enhance the ligand field splitting energy (LFSE) and ^{3}MCLT lifetimes, up to ≈2 ns, were reported [1]. Indeed, if the LFSE is high enough, the metal-centred (MC) states would be higher in energy than the ^{3}MLCT states, as in the noble metal congeners, thus preventing ultrafast internal conversion, and rendering the Fe(II) complexes luminescent and amenable to photo-voltaic or -catalytic applications.
Our work addresses the ultrafast photophysics of such Fe(II)-NHC (N-heterocyclic carbene) compounds with four carbene bonds [2]. Here, it appears quickly that the ligand field splitting argument applies only to the energy level ordering in the Franck-Condon region. Indeed, the excited state relaxation involves vibrational dynamics, leading to a possible crossing of MLCT's into metal-centered (MC) potential energy surfaces and a progressive change in the nature of the long-lived excited state. Parallel population of the ^{3}MC and ^{3}MLCT states may also occur [3], as was recently shown forthe prototypical $[Fe(bmip)_2]^{2+}$ complex, where bmip= 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine [4], which potentially limits the benefit of a purely MLCT-driven excited state photo-chemistry (e.g. electron transfer).
The double-carboxylated form of $[Fe(bmip)_2]^{2+}$, termed $[Fe(bmipc)_2]^{2+}$, is a decent photo-sensitizer, with an 18-20 ps excited state lifetime, recently used in solar cell sensitised by Fe(II) complexes and displaying, for the first time, a power conversion efficiency > 1 % [5]. What is the excited state reaction scheme for this complex, and how can the ^{3}MLCT and ^{3}MC states be distinguished spectroscopically?
Since for Ru complexes, both states display similar excited state absorption [6], we used femtosecond fluorescence spectroscopy to evaluate the radiative rate of the long-lived excited state and found for $[Fe(bmipc)_2]^{2+}$ in acetonitrile a radiative rate 500-1000 times smaller than the one of the ^{1}MLCT fluorescence [7], in agreement with a dominant ^{3}MLCT character, decaying with the above 18ps lifetime. In addition, femtosecond impulsive vibrational spectroscopy (pump-IVS) was performed with 15 fs pulses to obtain the excited state Raman spectrum ($\nu \leq 800$ cm^{-1}). Two major features are observed: (I) A strong low frequency Raman activity (~110cm^{-1}) decays completely within the first picosecond after initial excitation. (II) A ≈150 cm^{-1} mode can be reinduced by the push pulse on time scales equal to the ^{3}MLCT lifetime. Normal mode and Raman activity calculations show that these modes are related to global Fe-L breathing modes, in the ^{3}MC and ^{3}MLCT electronic state, respectively [8]. Feature (I) thus clearly demonstrates that excited state ^{3}MLCT/^{3}MC branching occurs also in $[Fe(bmipc)_2]^{2+}$. A detailed analysis of fs TAS and fs-IVS is ongoing in order to determine the branching ratio.
In summary, the present combined experimental and computational study highlights the importance of ultrafast excited state branching in the MLCT/MC manifold for these 4-carbene coordinated Fe(II) complexes with moderate LFSE. The design of novel Fe-based sensitizers

needs to take into account, in addition to the LSFE, the dynamic aspects and as much as possible, the excited state energetics along the most prominent reaction coordinates, such as Fe-L bond length changes.

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Controlled Ultrafast Charge Transfer Dynamics in Peptides with Tailored Micro-environment

Marius Hervé, Alexie Boyer, Richard Brédy, Isabelle Compagnon, Abdul-Rahman Allouche, Franck Lépine

University of Lyon, Université Claude Bernard Lyon 1, CNRS, Institut Lumière Matière, F-69622 Villeurbanne, France

Corresponding Author E-mail Adress: marius.herve@univ-rennes1.fr

Ultrafast charge and energy dynamics in molecules are driven by the topology of the multidimensional potential energy surfaces, that determines the coordinated electronic and nuclear motion. These quantum processes, whose description is made more complex in larger biomolecules, are also strongly influenced by the interaction with the molecular environment, thus challenging the precise understanding of the underlying mechanisms. In particular, charge transfer dynamics play a significant role in the relaxation of UV-excited peptides and proteins [1], where the natural bioenvironment is crucial to regulate the molecule's properties.

In this context, we investigated the UV-induced charge transfer dynamics in tryptophan-containing peptides that bear a charged atomic adduct. This was achieved by performing UV-IR time-resolved mass spectrometry measurements on isolated peptides and amino acids bearing an H^+ or Na^+ adduct ($TrpH^+$, $TrpNa^+$, $GlyTrpNa^+$, $AlaTrpNa^+$), produced by electrospray technology [2]. We show that the charge transfer timescale can be controlled on more than one order of magnitude by replacing the adduct atom only (Fig. 1.a-b), and is further affected by changes in the peptide chain for sodiated species. Excited-state potential energy surfaces are calculated to rationalize the process, understood as a non-adiabatic coupling between the ππ* and πσ* states [3] (Fig 1.c). A model is further proposed to rationalize the observed femtosecond-to-picosecond timescales, based on the local and global effects of the adduct and micro-environment on the ππ* and πσ* states [4]. These results open new control strategies of fundamental processes in complex biomolecules, based on atomic length scale designed micro-environment, that can be further used in the context of XUV-induced attosecond molecular chemistry [5,6].

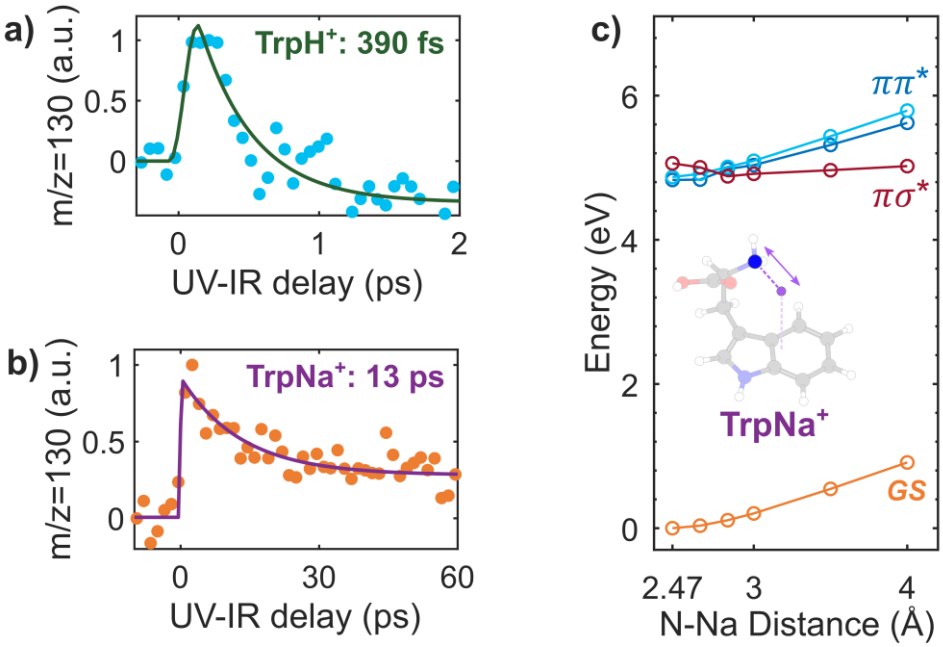

Figure 1. a) Time-dependent fragmentation yield for protonated tryptophan, $TrpH^+$, following 267 nm excitation. b) Same measurement for sodiated tryptophan, $TrpNa^+$, showing an increase of the timescale by a factor of 30. c) Potential energy surfaces for $TrpNa^+$ along the reactive N-Na coordinate (obtained by RICC2 calculations): the increase of the timescale and its modulation for dipeptides is explained by the relative tuning of the excited states by the micro-environment.

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Electronic relaxation of aqueous aminoazobenzenes studied by time-resolved photoelectron spectroscopy and surface hopping TDDFT dynamics calculations

Evgenii Titov,[1] Johan Hummert,[2] Evgenii Ikonnikov,[2] Roland Mitrić,[1] and Oleg Kornilov[2*]
[1]*Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Emil-Fischer-Straße 42, 97074 Würzburg, Germany*
[2]*Max Born Institute, Max-Born-Straße 2A, 12489 Berlin, Germany*

Electronic relaxation of molecular chromophores upon photoexcitation plays an important role in many biological processes, such as vision, photosynthesis and stability of DNA against the sunlight. Many experimental and theoretical studies have been conducted to unravel these dynamics, which often involve fast passages through conical intersections. These studies are complicated by the fact that most chromophores of biological importance are rather large molecules and strongly affected by environment, either solvent or a protein cage. Thus, experimental approaches are necessary, which can deliver direct and analytical information for the state-of-the-art first-principles methods. Photoelectron spectroscopy has traditionally been one of the most direct methods to analyze electronic structure. Recently, we extended the method of XUV time-resolved photoelectron spectroscopy to solvated organic molecules [1]. We employed an HHG source for production of femtosecond XUV pulses and combined it with the microliquid jet technology. Recently we applied this method to look at the relaxation dynamics of two derivative aminoazobenzenes: Methyl Orange and Metanil Yellow solvated in water [2]. Typical for azobenzenes, these molecules undergo ultrafast relaxation via conical intersections, which may involve cis-trans-isomerization. The ππ* and nπ* are almost overlapping making the molecules challenging targets for modern ab initio theories. We used a surface hopping TDDFT approach [3] employing B3LYP+D3 and ωB97X-D functionals and demonstrated that the method is suitable for description of these ultrafast dynamics and can recover absolute binding energies observed in the experiment. Our results pave the way towards quantitative understanding of evolving electronic structure in photoinduced relaxation processes.

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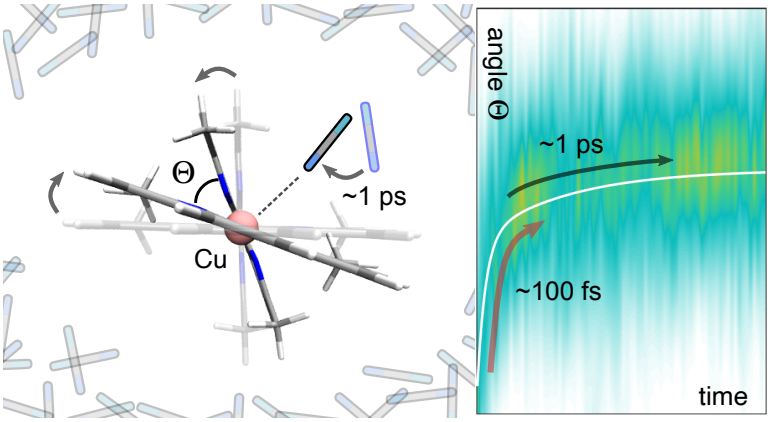
Exploring excited-state and solvation dynamics through multi-scale atomistic simulations

Gianluca Levi
Science Institute and Faculty of Physical Sciences, University of Iceland, 107 Reykjavík
E-mail: giale@hi.is

Modern time-resolved spectroscopy and X-ray scattering techniques provide a means to observe photoinduced ultrafast electronic and nuclear dynamics in solvated functional molecules. The interpretation and analysis of such experiments is often complicated, requiring the support of molecular dynamics simulations. We are developing a methodology to accurately and robustly characterize the interplay between electronic-nuclear dynamics and nonequilibrium solvation effects by combining variational density functional calculations of excited states with QM/MM explicit solvent models. Examples of applications using the Born-Oppenheimer approximation include modelling the light-induced bond-formation dynamics in a photocatalytic diplatinum complex to interpret femtosecond X-ray solution scattering measurements[1,2], and predicting the influence of the orientational response of a polar solvent on the excited-state flattening in a copper photosensitizer[3] (see figure below). In order to extend the methodology to nonadiabatic dynamics simulations, we have developed novel algorithms for variational excited-state calculations within density functional theory based on direct energy optimization[4,5]. Contrary to standard self-consistent field methods, the new approach can robustly converge where potential energy surfaces cross and nonadiabatic effects are important, as demonstrated by the calculation of potential energy curves of several excited states of an iron molecular photosensitizer[5]. This paves the way to efficient nonadiabatic dynamics simulations in the condensed phase.



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Non-conservative circular dichroism of photosystem II reaction centers: Is there an enhancement by a coupling with charge transfer states?

Dominik Lindorfer[1], Frank Müh[1], Robin Purchase[2], Elmars Krausz[2], Thomas Renger[1]

1. Institute for Theoretical Physics, Johannes Kepler University, Linz, Altenbergerstrasse 69, 4040 Linz, Austria.
2. Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

Abstract

The non-conservative nature of the circular dichroism (CD) spectrum of the Q_y spectral region of the D1/D2/cytb_{559} reaction center complexes of photosystem II is investigated. Our theory, in addition to the usual excitonic couplings between the low-energy Q_y transitions of the chlorophyll and pheophytin pigments, takes into account the coupling of the Q_y with the higher-energy B_x, B_y and N_{x+xy} transitions of these pigments and with $S_0 \rightarrow S_2$ transitions of the two β-carotene pigments in the complex. The higher-energy transitions are parameterized by using quantum chemical calculations and an analysis of the experimental oscillator strength of the isolated pigments. The Poisson-TrEsp method is used to obtain the excitonic couplings between pigments, whereas the coupling between exciton and charge transfer states in the central P_{D1}-P_{D2} pigments is implicitly taken into account by a scaling factor of the obtained excitonic coupling of the dimer. It is shown that the observed non-conservativity of the Q_y CD spectrum can be qualitatively understood by the above described mixing of Q_y and higher-energy transitions and the analysis further suggests, that the non-conservativity may be enhanced by coupling to charge transfer states.

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Modelling absorption and emission spectra taking into account the dynamic environment: example of firefly bioluminescent systems

Cristina Garcia-Iriepa , Madjid Zemmouche, Romain Berraud-Pache, and Isabelle Navizet,

MSME, Univ Gustave Eiffel, CNRS UMR 8208, Univ Paris Est Creteil, F-77454 Marne-la-Vallée, France
Email: Isabelle.navizet@univ-eiffel.fr

The emitting light in fireflies or other bioluminescent species arises from the electronic relaxation of oxyluciferin, an organic compound resulting from the oxidation of the D-luciferin substrate inside an enzyme called luciferase. In order to have insight of the mechanism of the light emission, both experimental and theoretical joint studies have been performed. Absorption and fluorescence spectra of the products of the bioluminescence are obtained by a combination of molecular dynamics (MD) followed by calculation of the electronic transitions by hybrid (QM/MM) methods. The emission and absorption spectra are accurately reproduced compared to the experimental ones when the dynamic of the system is taking into account. Taking rovibrational structures to explain the shape of the spectra will also be presented.

I will present briefly the used methodology and examples of theoretical studies that can give complementary insights to the experimental results.

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Quantum parallelism by coherent excitonic dynamics of an ensemble CdSe quantum dots with size dispersion

F. Remacle

Theoretical Physical Chemistry, University of Liège, Allée du 6 Août 11, B4000 Liège, Belgium

The ultrafast femto-second (fs) electronic coherences can be experimentally characterized in semi-conducting colloidal quantum dot (QD) assemblies at room temperature by two-dimensional electronic spectroscopy (2DES).[1, 2] These electronic coherences exhibit a wide range of beating periods and provide a versatile basis for parallel quantum information processing on a fs time scale at room temperature.

We report on the exploitation of the electronic coherences as they are probed in 2DES to design a quantum emulator of several types of non equilibrium vibrational dynamics of a linear triatomic molecule.[3, 4] The implementation is based on the underlying Lie algebraic structure of the hardware system: the N quantum levels of the QD dimers provide N^2-1 observables, the $N(N\text{-}1)$ electronic coherences and N-1 populations, which allows for processing N^2-1 logic variables in parallel at the level of the ensemble.[5] Furthermore, the use of the classical ensemble allows a simultaneous reading of the observables.

The quantum dynamics are computed using an excitonic model Hamiltonian based on the effective mass approximation.[6] The Hamiltonian includes the Coulomb, spin-orbit and crystal field interactions that give rise to the fine structure splittings. In the dimers studied, the interdot distance is sufficiently small to allow for efficient interdot coupling and delocalization of the excitons over the two QDs of the dimer. To account for the inherent few percent size dispersion of colloidal QDs, the optical response is modeled by averaging over an ensemble of 2000 dimers.[5] The size dispersion is responsible for an inhomogeneous broadening that limits the lifetimes of the excitonic coherences that can be probed to about 150-200fs.

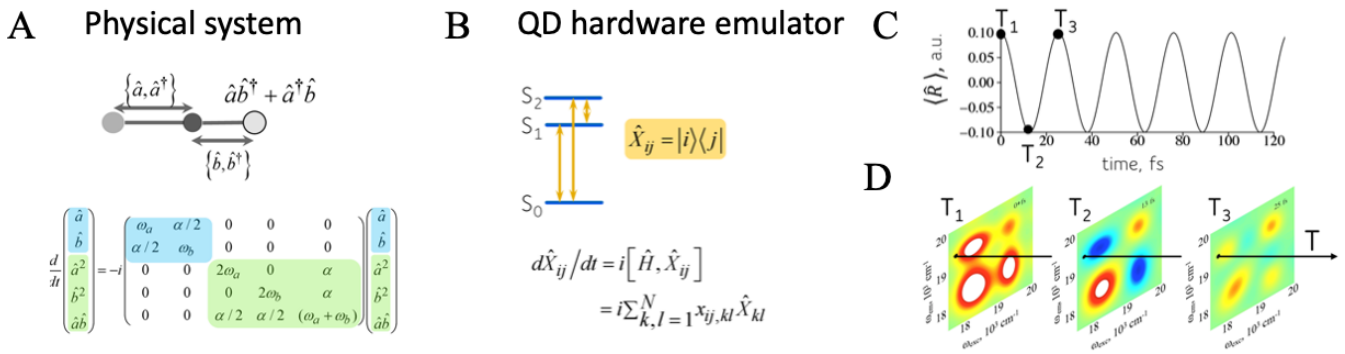

Figure. A: The algebra of the physical system. B: The algebra of the QD hardware used to emulate it. C. The time evolution of the mean bond displacement. D. The time dependence of the hardware observable used to emulate the mean bond displacement as measured in 2DES. Adapted from ref.[3].

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Photoinduced Charge Transfer Dynamics via Semiclassical Methods

Xiang Sun [1]

[1] **New York University Shanghai, 1555 Century Ave, Shanghai, 200122, China**

Photoinduced charge transfer (CT) plays a key role in the conversion of solar energy. In this talk, we introduce a hierarchy of post-Marcus rate methods for calculating the CT rates in organic photovoltaic materials. In particular, we derived the linearized semiclassical photoinduced CT rates within the framework of nonequilibrium Fermi's golden rule. The semiclassical theory provides a flexible, rigorous and self-consistent framework for developing computationally feasible methods, capable of capturing important quantum effects in complex many-body systems. We showcase the feasibility, accuracy, and robustness of these rate calculation methods within the context of a realistic molecular application to the carotenoid-porphyrin-C_{60} molecular triad in explicit tetrahydrofuran solvent described in terms of anharmonic force fields. Our results show that accounting for the nonequilibrium nature of the initial ground state significantly enhances the transition rate of the porphyrin-to-C_{60} CT process. We also derived the instantaneous Marcus theory (IMT), which casts the CT rate coefficients in terms of a Marcus-like expression, with explicitly time-dependent reorganization energy and reaction free energy. IMT is found to reproduce the CT rates in the system under consideration remarkably well.

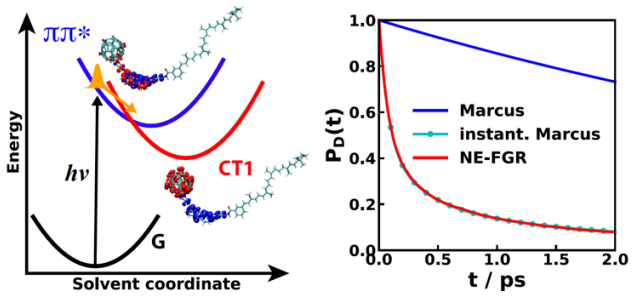

Fig. 1 Photoinduced charge transfer in carotenoid-porphyrin-C_{60} triad dissolved in THF

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Single Slide Presentations

Nonradiative deactivation mechanisms of bio-relevant systems
Document the **basic phenomena** controlling the **lifetime of the excited states**

A multi-level and -step theoretical approach

1. **Qualitative exploration** with **nonadiabatic dynamics** (**NA-TDDFT**) and **optimization of CI** (TDDFT, CC2)
2. **Quantitative investigation** of the deactivation mechannisms at the "**Coupled Cluster**" level (CC2)

Benchmarks:

Adiabatic exitation energies
IR signature

Medium-sized systems:
Models of phenyalalanine **protein**
Capped peptides

❒ **TD-DFT vs CC2 & Experiment**
(submitted)

❒ **CC2 vs MRCI & Experiment**
(J. Chem. Phys. 148, 184105 (2018) & Accepted (2020); JCTC, 16, 601 (2020))

TD-DFT: ***Long-range corrected hybrid functionnals***

CC2: ***RI&Aug(N,O, π)cc-PVDZ***

MRCI: **CAS-DDCI & GAS-DDCI**

⇨ ***Toward NA-ADC(2) around CI***

Toward larger systems:
Composite CC2/TD-DFT protocols

V. Brenner - LIDYL ERL9000

Quantum dynamics of electron-hole separation in stacked perylene diimide (PDI) based self-assembled nanostructures

Dominik Brey, Wjatscheslaw Popp, Rainer Hegger, and Irene Burghardt

Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

The recent shortage of silicon based chips has highlighted the importance of research on alternatives to silicon, notably organic electronics. Here, we focus on organic photovoltaics, where so-called non-fullerene acceptor materials have recently attracted much attention, as exemplified by perylene diimides (PDIs). These have desirable properties like ease of functionalization and cheap cost in comparison to fullerene derivatives.[1]

In this work, we present high-dimensional quantum dynamical simulations of electron-hole separation in self-assembled mesomorphic nanostructures composed of donor-acceptor conjugated co-oligomers. The latter are based on PDIs combined with bisthiophene–fluorene donor units, which form highly ordered, stacked structural motifs upon self-assembly.[2] Simulations are shown for a first-principles parametrized model lattice of 20 stacked PDI units under the effects of an applied external field and temperature. The simulations are carried out with the Multilayer Multiconfiguration Time-Dependent Hartree (ML-MCTDH) method[3] with nearly 800 vibrational degrees of freedom and 20 electronic states. Temperature effects are included using the Thermofield Dynamics (TFD) approach of Ref. [4]. The results for electron-hole separation rates are employed as a benchmark to calibrate the parametrization of Kinetic Monte Carlo (KMC) simulations applied to much larger lattice sizes.

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Quantum dynamics of exciton transport in semiconducting polymer chains: Coherent or diffusive?

R. Binder, F. Di Maiolo, D. Brey, I. Burghardt

Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Max-von-Laue Str. 7, 60438 Frankfurt, Germany

Intra-chain exciton transport in organic molecular materials is often described by the Frenkel-Holstein (FH) Hamiltonian that admits incoherent hopping or coherent transport dynamics in different parameter regimes. To bridge the gap to a molecular-level description, we describe a protocol that generates a one-to-one mapping of supermolecular oligomer potential energy surfaces onto a generalized FH Hamiltonian [1,2]. When combined with efficient quantum dynamical simulations using the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method [3], this approach provides unbiased insight into the elementary mechanism of exciton migration. This presentation addresses case studies of polythiophene and poly(*para*-phenylene vinylene) type materials [1,2,4,5] where a coherent transport regime is observed, showing that "*excitons surf along conjugated polymer chains*" [6]. The dynamics acquires partial hopping character if static disorder becomes prominent and Anderson localization sets in [7]. Special emphasis is placed on the interplay of delocalization, trapping, and thermal activation due to soft modes such as ring torsions.

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Unraveling the Nature of Unusual Quantum Properties in the $H_2O@C_{60}$ Endofullerene

O. Carrillo-Bohórquez[1,3], Á. Valdés[2] and R. Prosmiti[3]*

[1]Departamento de Física, Universidad Nacional de Colombia, Calle 26, Cra. 39, E 404, Bogotá, Colombia.
[2]Escuela de Física, Universidad Nacional de Colombia, Cra. 65 Nº 59A – 110, Bloque 21, Medellín, Colombia.
[3]Institute of Fundamental Physics, IFF-CSIC, Serrano 123, 28006 Madrid, Spain.

[*]ocarrillob@unal.edu.co

Encapsulated molecules in cage compounds offer a unique opportunity to study the fundamental characteristics of such guest-host systems, with potential applications in nanoscience and nanotechnology. Recent experiments have shown interesting, uncommon quantum properties of the nanoconfined guest molecules, that motivates us to develop a systematic computational protocol to treat the full-dimensional and fully-coupled quantum problem within the MCTDH framework for any triatomic molecule in a embedded or confined environment [1,2].

A 9-dimensional model for the $H_2O@C_{60}$ system, where the water molecule was described through Radau coordinates, with the C_{60} cage considered rigid, is presented as an efficient way to calculate its rotational-translational-vibrational levels and energies. In turn, we investigate vibrational frequency shifts, as well as the nature of anomalous splitting of rotational ortho- and para-H_2O levels, reported experimentally for such light-molecule endofullerene [3], through different models [4], in order to provide insights and physical interpretations of the observed symmetry breaking.

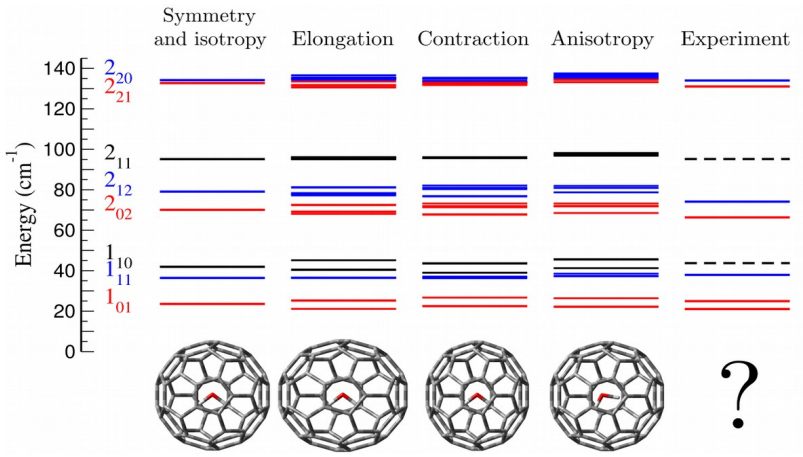

Figure 1: Water-C_{60} models developed for exploring the energy splitting on the 1_{01} levels of the $H_2O@C_{60}$ complex.

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Cooperation between Excitation Energy Transfer and Anti-synchronously Coupled Vibrations

Kwang Hyun Cho and Young Min Rhee

Department of Chemistry, KAIST, Daejeon 34141, Korea

Here, we present our recent analysis about relation between the environment and the energy transfer system. We investigate how the energy transfer and the emergence of vibrational correlations cooperate with each other based on simulations with a few numerically approximate mixed quantum classical (MQC) methods. By adopting a two-state system with locally coupled underdamped vibrations that are resonant with the electronic energy gap, we observe prominent energy dissipations from the electronic system to the vibrations, re-highlighting the role of underdamped vibrations as a temporal electronic energy buffer. More importantly, this energy dissipation generates specific phase relations between the two vibrations. Namely, the vibrations become anti-correlated right after the initiation of the energy transfer but then synchronized as the transfer completes. These phase relations are interpreted as a selective activation of an anti-correlated motion of the vibrations and a subsequent deactivation by thermal energy redistribution. Furthermore, we show that a single vibration simultaneously coupled to the two electronic states with opposite phases induces a completely equivalent energy transfer dynamics as the two localized vibrations, hinting the emergence of a delocalized vibration from the localized ones. Finally, we discuss how the vibrational energy dissipation dynamics is affected by the adopted MQC approaches and warn about the increased subtlety toward properly treating dissipation effects over having reliable population dynamics.

Theoretical Approaches to Quantum Molecular Dynamics in Out of Equilibrium Environments

F. Di Maiolo[1] and I. Burghardt[1]

[1]Goethe Universitaet, Frankfurt am Main, Germany
E-mail: dimaiolo@chemie.uni-frankfurt.de

The description of quantum molecular dynamics as influenced by a polarizable and dynamically evolving environment is critical to understand the nature of various physical processes, from solvation phenomena to photobiological processes in protein environments, and transport of charge carriers and excitons in nanostructures. Indeed, experimental molecular systems, S, are not closed systems due to the interaction with the surrounding environment, generically denoted the bath, B. Large effects on S dynamics can be expected depending on the nature of the environment as well as on the SB interaction strength. The typically used dielectric continuum picture for B is likely to fail when dealing with nonequilibrium solvation effects. On the other hand, fully atomistic first principles quantum calculations are hardly feasible due to the large number of environmental degrees of freedom.

Against this background, we present the effect of a dynamic environment on a time-evolving molecular system, using the Quantum-Classical Reduced Hydrodynamic (QCRH) approach [1]. In particular, the hydrodynamic formalism naturally describes density, current and heat transport phenomena. Accordingly, the QCRH theory can describe molecular relaxation in condensed dynamic phases, complementing typically used dielectric continuum models for the environment. At present, we have extended the QCRH approach in order to deal with orientational solvation processes in charge-transfer phenomena, using a Maxwellian closure for the hydrodynamic hierarchy.

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Dark state spectral signatures in Methylene blue: A tensor network approach

Using powerful tensor network methods, we are able to compute absorption spectra for real molecules in a solvent environment. The calculated spectra are exact within a description based on a linear vibronic coupling Hamiltonian and may be computed at any temperature at a modest computational cost thanks to a recently introduced technique which allows one to obtain finite temperature open system dynamics from a single, pure state wave-function simulation at 0K. These methods are applied to the investigation of the absorption spectrum of the widely used dye and medication, Methylene blue (MB). By performing simulations on models parameterized using Density Functional Theory (DFT) and molecular dynamics (MD) we are able to demonstrate that the characteristic shoulder in the MB absorption spectrum arises from the presence of a previously overlooked dark excited state that is vibronically coupled to the lowest excited singlet state. Furthermore, we find that the shape of this shoulder is highly sensitive to the presence of correlations between the environment-induced fluctuations of the bright and dark state energies, and that by introducing such correlations into our model we are able to obtain an excellent fit with experimental data. As well as providing microscopic insight into the spectral signatures of optical dark states in organic systems, this work also provides a means of comparing different levels of theory in DFT and MD in terms of their ability to reproduce experimentally observed spectra.

Tunnelling splittings of vibrationally excited states via instanton approach

Mihael Eraković, Marko T. Cvitaš
Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia

In molecules that possess several symmetry-related minima separated by potential energy barriers, tunnelling gives rise to the splittings of energy levels. The magnitude of the splitting encodes the timescales of molecular rearrangements at low temperatures, and can be determined experimentally. Tunnelling splittings are generally much smaller than the barrier heights and are extremely sensitive to its width and shape. The exact quantum mechanical calculation of tunnelling splitting requires basis sets that span large configurational space and are therefore limited to small molecules, inexpensive electronic potentials or reduced-dimensional models. The semiclassical instanton method circumvents the above deficiencies and is known to give excellent tunnelling splittings for the ground vibrational states of molecules, especially in the deep tunnelling regime. The method is full-dimensional and can be used with on-the-fly computation of the electronic energies, with the orders of magnitude smaller number of potential evaluations in comparison to the quantum-mechanical methods. However, instanton methods for the excited vibrational states have so far only been developed for the systems with symmetric instanton paths[1].

In this presentation, we generalize the instanton method for the low-lying vibrationally excited states to systems with general paths[2]. The method can thus be used to compute tunnelling splittings in systems with multiple symmetry-related minima that regularly feature asymmetric instanton paths, while it also gives improved splitting estimates in systems with symmetric paths. The method is used to compute the splittings in malonaldehyde and in the water dimer. The results are compared with the benchmark calculations and experimental data.

Instanton method obtains the splittings from the semiclassical wavefunction constructed in the harmonic neighbourhood of the instanton path. One can, therefore, envisage development of similar wavefunction-based generalization schemes for calculating molecular tunnelling rates (adiabatic and nonadiabatic) with similar efficiency gains and broad applicability.

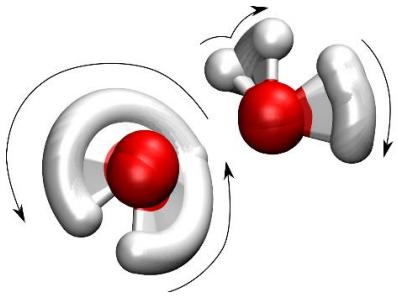

Figure 1. Instanton path for donor exchange in water dimer.

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Title:

Comparison of non-adiabatic excited states methodologies

Author:

Victor M. Freixas (vmfreixas@gmail.com)

Abstract:

Direct atomistic simulation of nonadiabatic molecular dynamics is a challenging goal that allows important insights into fundamental physical phenomena. A variety of frameworks, ranging from fully quantum treatment of nuclei to semiclassical and mixed quantum−classical approaches, were developed. These algorithms are then coupled to specific electronic structure techniques. Such diversity and lack of standardized implementation make it difficult to compare the performance of different methodologies when treating realistic systems. Here, we compare three popular methods for large chromophores: Ehrenfest, surface hopping, and multiconfigurational Ehrenfest with ab initio multiple cloning (MCE-AIMC). These approaches were implemented in the NEXMD software, which features a common computational chemistry model. The resulting comparisons reveal the method performance for population relaxation and coherent vibronic dynamics. Our results provide helpful reference data for selecting an optimal methodology for simulating excited-state molecular dynamics.

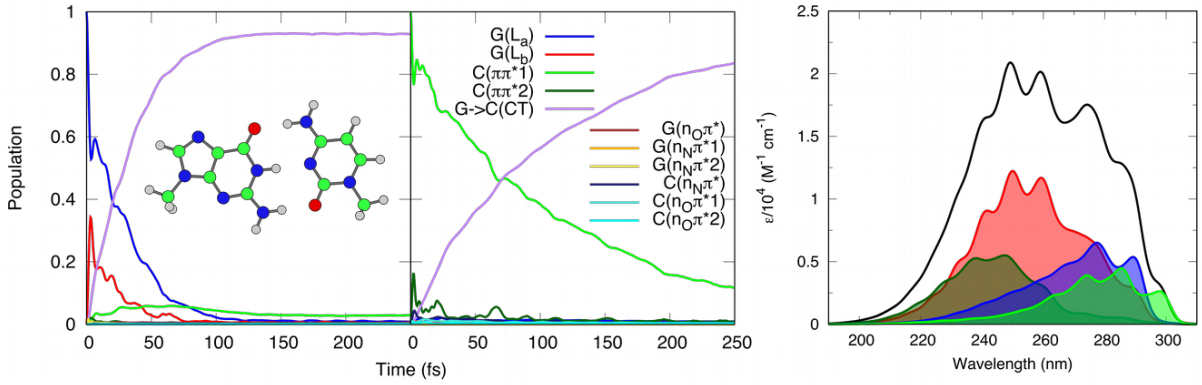
Les Houches, 3-7 May 2021 | Abstract

A Fragment Based Approach to the Quantum Dynamics of Multichromophoric Systems: Application to the GC DNA Base Pair

James Green,*[a] Martha Yaghoubi Jouybari,[b] Haritha Asha,[a] Fabrizio Santoro,[b] and Roberto Improta[a]

a) CNR-IBB, via Mezzocannone 16, 80134, Naples, Italy.
b) CNR-ICCOM, Area della Ricerca, via G. Moruzzi 1, I-56124, Pisa, Italy
** james.green@ibb.cnr.it*

A fragment diabatisation scheme is described, based on recent works,[1-3] that can parameterise a linear vibronic coupling (LVC) Hamiltonian in a relatively automated fashion, for use with quantum dynamics calculations. The scheme takes as reference states local excitations (LEs) on individual fragments (such as bright ππ* or dark nπ* states) and one orbital transitions between fragments to describe charge transfer (CT) states. These reference states are then projected onto the multi-fragment species to obtain the energies and couplings necessary for the LVC model, and any arbitrary number of states and fragments may be considered. This is described within the framework of TD-DFT, so that large systems may be tractably considered. As an initial test, the method is applied to the guanine-cytosine (GC) Watson-Crick DNA base pair, an archetypal example of a multichromophoric species with individual LE structure. We compute the dynamics with ML-MCTDH and illustrate how strong electronic coupling of the ππ* states on G and C to the G→C CT state, combined with the large vibrational reorganisation energy of the G→C CT state leads to its efficient ultrafast population. We also show how formation of the GC pair leads to suppression of the population of the nπ* states. Furthermore, the absorption spectrum of GC is calculated, demonstrating the contribution of each ππ* state and the role of ultrafast internal conversion on the broadening of the spectrum. We believe the method can be useful in aiding interpretation of time-resolved spectroscopic signals, and we will soon expand the approach to include the effect of solvent/environment.



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Exploring the Role of Excitonic Coupling in Melanin's Broadband Absorption Spectrum

Alex T. Hanes* and Bern Kohler
The Ohio State University
e-mail: hanes.104@osu.edu

Abstract: Melanin is a ubiquitous natural pigment characterized by broadband absorption, ultrafast nonradiative deactivation (sunscreening), and radical scavenging abilities. These origins of these functions are obscure because the precise structure of any melanin is still unknown. Transient spectral hole burning experiments from our laboratory indicate that a melanin polymer contains many subensembles of distinct chromophores that are likely differentiated by size and redox state. To better understand melanin's electronic absorption spectrum, we have begun model calculations of Frenkel excitonic materials characterized by distributions of coupled chromophores. Preliminary results are clarifying how excitonic coupling contributes to melanin's unusual absorption spectrum, which decreases monotonically from UV to near-IR wavelengths.

Measurements and theoretical simulation of Vibrationally Promoted Electronic Resonance (VIPER) spectra using two-photon excitation

H. Masood[1,*], M. Horz[2,*], H. Brunst[1], H. Vormann[2], M. N. Shyam[2], D. Picconi[2], F. Santoro[3], J. Bredenbeck[1], I. Burghardt[2]

[1]Institute of Biophysics, Goethe University Frankfurt, Max-von-Laue-Str. 1, 60438 Frankfurt am Main, Germany
[2]Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany
[3]Consiglio Nazionale delle Ricerche-CNR, Istituto di Chimica dei Composti Organo Metallici (ICCOM-CNR), UOS di Pisa, Via G. Moruzzi 1, I-56124 Pisa, Italy

* These authors contributed equally to this work.

In recent years, combined electronic-vibrational nonlinear spectroscopies have gained increased attention. In this context, the versatile Vibrationally Promoted Electronic Resonance (VIPER) experiment [1,2] has been employed, e.g., to induce a selective cleavage of photolabile protecting groups (PPGs). In particular, selectivity could be achieved for PPGs that are chemically identical but differ in isotopic composition [3]. One of the key aspects of the VIPER experiment is that the UV/VIS pulse alone is not able to induce an electronic transition since it is by design slightly off-resonant. In order to bridge the energy gap, the UV/VIS pulse is preceded by vibrational excitation via a narrow-band infrared (IR) pulse. Furthermore the usage of a two-photon (2P) excitation pulse instead of the UV/VIS pulse is desirable since the former provides an intrisic 3D resolution, a lower noise level, an increased penetration depth and minimized photodamage. This makes 2P excitation highly attractive for biological systems, among a wide range of possible applications [4].
In this work, we present experimental results and simulations of 2P-VIPER measurements of the laser dye coumarin 6. Coumarin-based PPGs are widely used due to their favourable experimental properties such as a high quantum yield and fast photorelease rates [5]. In our theoretical investigation, vibrationally resolved electronic spectra including vibrational pre-excitation are computed using the *FCclasses* program [6], which is based on the efficient evaluation of Franck-Condon overlap integrals. Franck-Condon as well as Herzberg-Teller contributions are considered, which are compared with previously computed one-photon VIPER results [2]. Additionally, the role of interference terms in the total spectrum is evaluated in detail.

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Applying non-linear spectroscopic techniques with a 100 kHz OPCPA laser system

Gabriel Karras, Greg Greetham, Gourab Chatterjee, Emma Springate, Paul Donaldson, Igor Sazanovich, Mike Towrie

[1]*Central Laser Facility, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK*

The Ultra facility in Rutherford Appleton Laboratory was recently equipped with a new laser system based on Yb:YAG technology which pumps an infrared optical parametric chirped pulse amplifier (OPCPA). The repetition rate of the system is 100 kHz accommodating multiple outputs in the near-IR regime with the femtosecond and picosecond pulse duration. It will be used for static and time resolved studies in liquid and condensed matter samples. Some of the techniques we are envisaging to develop around this system are: surface sum-frequency generation, two-dimensional infra-red spectroscopy and kerr-gated Raman spectroscopy [1]. The superior stability and higher repetition rate of the new system could provide the means to attain higher signal to noise ratios [2] and perform the experiments in a less time consuming manner avoiding long term acquisitions. In addition, exploiting the wide wavelength range tunability of the new laser, preliminary results on supercontinuum generation in the molecular fingerprint region will also be presented, assessing the wavelength coverage and other critical characteristics e.g. stability, chirp, pulse durations.

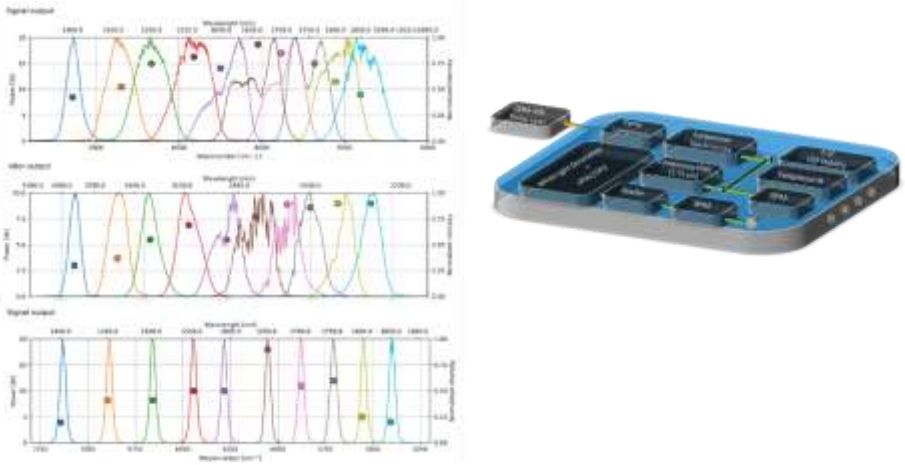

Fig. 1 Layout of the new 100 kHz OPCPA system and some of the characteristics of the system in the tunable femtosecond and picosecond modes.

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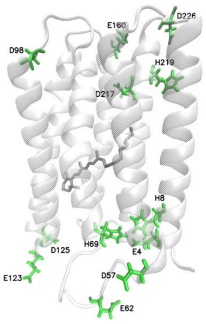
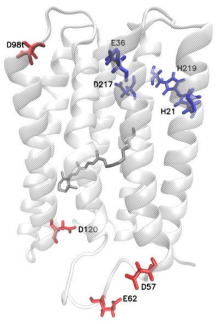
Effect of pH on the retinal isomerization reaction of *A*SR unveiled by fs time-resolved spectroscopy and semi-classical non-adiabatic MD simulations

Oskar Kefer,[1,2] Elisa Pieri,[3] Oliver Weingart,[4] Rei Abe-Yoshizumi,[5] Marco Garavelli,[6] Hideki Kandori,[7] Nicolas Ferré,[8] Tiago Buckup.[1,2]

Titrations - pH 5



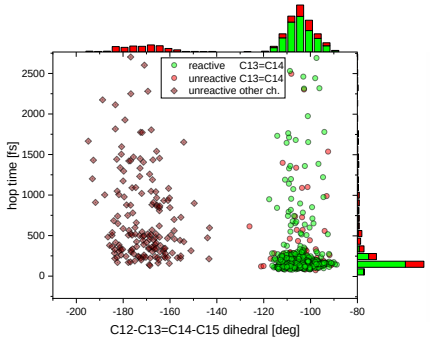
Titrations - pH 3

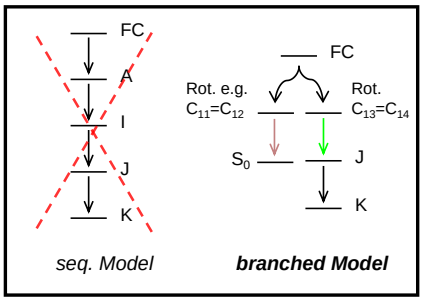


- Rhodopsins powerful tool in Optogenetics
- Control of isomerization reaction via protein modification ➔ pH-variations as first step
- Combination of experiment and theory to understand mechanism and influence of protonation states

1 Physikalisch-Chemisches Institut, Ruprecht-Karls Universität, D-69120 Heidelberg, Germany
2 Centre for Advanced Materials, Ruprecht-Karls Universität, D-69120 Heidelberg, Germany
3 Department of Biotechnology, Chemistry and Pharmacy, University of Siena, via Aldo Moro, 2, Siena 53100, Italy
4 Institut für Theoretische Chemie und Computerchemie, Heinrich Heine Universität, Universitätsstr. 1, D-40225 Düsseldorf, Germany.
5 Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan
6 Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale del Risorgimento 4, Bologna I-40136, Italy
7 OptoBioTechnology Research Center, Nagoya Institute of Technology, Showa-ku, Nagoya 466-8555, Japan
8 Aix Marseille Univ, CNRS, ICR, 13397 Marseille, France

Sequential mechanism problematic



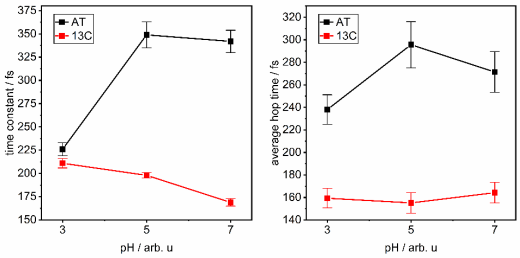


(Theory) At least two channels:
- C_{13}=C_{14} – reactive/non-reactive
- Non C_{13}=C_{14} – non-reactive

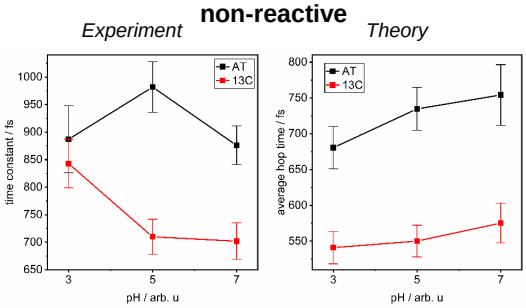
(Exp.) Two rate-const. for S_1-decay

Influence of pH

reactive



non-reactive



- Reactive channel – fast
- Non-reactive channel – slow
- Dynamics pH 5 ≈ pH 7
- Fast AT and slow 13C at pH 3

Two-oscillator Mapping Basis Approximations of the Quantum-classical Liouville Equation and Their Comparisons to the Forward and Backward Trajectory Solution

Hyun Woo Kim[1] and Young Min Rhee[2]

[1]Center for Molecular Modeling and Simulation, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Korea
[2]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

Mapping basis solutions provide efficient ways for simulating mixed quantum-classical (MQC) dynamics in complex systems by matching multiple quantum states of interest to some fictitious physical states. Recently, various MQC methods that employ double mapping basis with two harmonic oscillators representing one electronic state were devised, showing improvements over methods with one-to-one mapping constructions. Here, we introduce and analyze double mapping basis approximations of the quantum-classical Liouville equation (QCLE). With the double mapping basis, we design two separate mapping relationships that we can adopt toward simulating dynamics and computing expectation values. Two MQC methods can be constructed, one of which actually reproduces the population dynamics of the forward and backward trajectory solution (FBTS) of QCLE. By applying the methods to spin-boson systems with a range of parameters, we find out that the choice of mapping relationships greatly affects the simulation results. Our findings with the double mapping basis will be helpful in constructing improved MQC methods in the future.

Normal mode analysis of spectral density of FMO trimers: Intra- and intermonomer energy transfer

Alexander Klinger, Dominik Lindorfer, Frank Müh, and Thomas Renger
Department for Theoretical Biophysics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria

Abstract

Intra- and intermonomer excitation energy transfer (EET) of the homotrimeric Fenna–Matthews–Olson (FMO) light-harvesting protein of green sulfur bacteria *P. aestuarii* is studied[1]. We employ the charge density coupling method for the calculation of local transition energies of the pigments combined with a normal mode analysis (NMA) of the protein for intermolecular contribution to the spectral density of the exciton-vibrational coupling. The high-frequency intrapigment part of the spectral density is extracted from fluorescence line-narrowing spectra.
Correlations in site energy fluctuations across the whole FMO trimer are found at low vibrational frequencies, however, EET is not influenced by these correlations. We find the main contributions to the intramonomer EET originates from the high-frequency part of the spectral density, whereas intermonomer EET is dominated by the low-frequency intermolecular contributions to the spectral density.
At room temperature, the intermonomer transfer in the FMO protein occurs on a 10 ps time scale, whereas intramonomer exciton equilibration is roughly two orders of magnitude faster. At cryogenic temperatures, intermonomer transfer limits the lifetimes of the lowest exciton band. The lifetimes are found to increase between 20 ps in the center of this band up to 100 ps towards lower energies, which is in very good agreement with the estimates from hole burning data[2].

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Origin of the High Quantum Efficiency of Rhodopsin

Xuchun Yang[1], Madushanka Manathunga[1], Samer Gozem[2], Jérémie Léonard[3], Tadeusz Andruniów,[4,] Massimo Olivucci[1,5,6]

[1]Department of Chemistry, Bowling Green State University, Bowling Green, OH 43403, United States
[2]Department of Chemistry, Georgia State University, Atlanta, GA 30303, United States
[3] Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, F-67034 Strasbourg, France
[4]Department of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland
[5]Dipartimento di Biotecnologie, Chimica e Farmacia, Università di Siena, Italy
[6]University of Strasbourg Institute for Advanced Studies, F-67083 Strasbourg, France

The ultrafast C=C double bond photoisomerization of the protonated Schiff base of retinal (PSBR) inside the cavity of the dim-light receptor Rhodopsin protein is described to be "vibrationally coherent". Indeed, the vibrational wavepacket created in the Franck-Condon region by an actinic coherent laser pulse propagates on the excited state potential energy surface (PES), through a conical intersection, and further on the ground state surface where it is eventually observed in the form of oscillating transient absorption signals detected in the photoproduct absorption band. [1–3]

We propose here to model this (a priori quantum) dynamics by adopting a semi-classical limit: we sample the Boltzmann distribution in the ground state phase space as initial Franck-Condon geometries and velocities for an ensemble of non-interacting trajectories propagated by Newton's law on a unique excited state PES defined by the Tully surface hop method and a 3-state QM/MM model of the chromophore and its protein environment computed on the fly. The set of trajectories is seen to remain largely correlated in a bundle which soon splits in sub bundles in the region of proximity between S1 and S2 PES's.

We observe that such a model correctly predicts the absorption spectrum, the excited state lifetime and the photoisomerization quantum yield.[3, 4] The later appears as the sum of fractional contributions from the subpopulations and we predict that it can be increased by reducing the population splitting upon tuning the electrostatic protein environment. We propose[4] that (i) within such a model the observed vibrational coherence is interpreted as a force-field induced, classical coherence in a statistical ensemble and (ii) the optimum PES topography must also minimize the ground state isomerization in addition to improving the photochemical reaction yield, in order to optimize the rhodopsin light-sensitivity function, which would explain why the QY does not exceed 67%.

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Excited-state Many-Body Expansion: formalism and application to the solvatochromism of Brooker's Merocyanine Dye

Xingpin Li[1, 2, 3], William J. Glover[1, 2, 3]

[1]*NYU Shanghai, 1555 Century Avenue, Shanghai, 200122, China*
[2]*NYU-ECNU Center for Computational Chemistry at NYU Shanghai, Shanghai, 200062, China*
[3]*Department of Chemistry, New York University, New York, New York, 10003, USA*

Electronic excited states play an important role in a variety of systems including fluorescent proteins, DNA damage, molecular switches and solvatochromic dyes. However, the computational cost of calculating excited states with standard quantum chemical methods scales steeply with the number of atoms. Molecular fragmentation is an increasingly popular way to reduce the scaling of electronic structure calculations; however, there has been little exploration of fragmentation approaches to electronic excited states. Thus, in this study, we examine the convergence of the Many Body Expansion (MBE), upon which many fragmentation schemes are based, for the excitation energies of Brooker's merocyanine dye (MOED) in a variety of condensed-phase environments at the Time-Dependent Density Functional Theory level. We find the resulting Excited-State Many Body Expansion (ES-MBE) converges at second order and reproduces relative solvatochromic shifts of MOED with near quantitative accuracy compared to experiment.

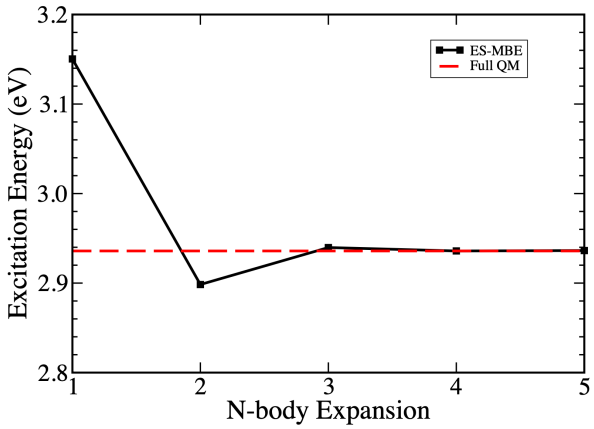

Fig. 1: Convergence of excitation energy of MOED($CHCl_{3(l)}$) with expansion order of ES-MBE at the TD-ωB97X/6-31G* level. The full system QM result is shown as the dashed red line.

A novel quantum-classical approach to electronic nonlinear spectroscopy

Jonathan Mannouch[1,a], **Jeremy Richardson**[1]
[1]ETH Zurich, Switzerland

Nonlinear spectroscopy offers a powerful tool for investigating microscopic quantum dynamics. However such quantities are often challenging to obtain theoretically for complex condensed phase systems, due to the large number of degrees of freedom.

For nonadiabatic systems, computationally cheap semiclassical approximations for the full electron-nuclear dynamics can be derived with the use of mapping variables [1, 2]. Within these approaches the electronic subsystem is mapped exactly onto a fictitious system, which has a well-defined classical limit. The dynamics associated with the mapped system is then described by an ensemble of classical trajectories. In particular, we have recently developed a new classical-trajectory mapping-based technique, called spin-PLDM [3], which is able to obtain the relatively short time quantum dynamics extremely accurately, does not suffer from over-damped coherences and can be applied to calculate both single and multi-time correlation functions. These characteristics make it ideally suited for obtaining optical response functions.

In this talk, we will show how spin-PLDM can be applied to accurately and efficiently compute the various optical response functions that contribute to the nonlinear electronic spectra of nonadiabatic condensed phase systems, such as a Frenkel biexciton model and the Fenna-Matthews-Olsen complex. Because each optical response function is calculated independently within our approach, contributions from different dynamical pathways can be separated from the full signal, giving further insight beyond what can be achieved directly from experiment.

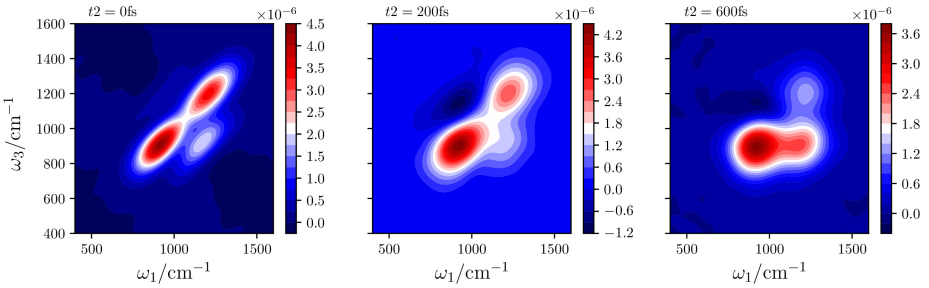

Figure 1: Pump-probe spectra for a Frenkel biexciton model calculated using spin-PLDM

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[a]jonathan.mannouch@phys.chem.ethz.ch

Molecular Nonadiabatic Dynamics Simulations by Quantum Wavepacket and Semiclassical Trajectory Methods

M. Pápai[1,2], M. Abedi[2], G. Levi[2], G. Vankó[1]
M. M. Nielsen[3], T. J. Penfold[4], T. Rozgonyi[1,5], K. B. Møller[2]

[1] Wigner Research Centre for Physics, Hungarian Academy of Sciences,
P.O. Box 49, H-1525 Budapest, Hungary
[2] Department of Chemistry, Technical University of Denmark,
DK-2800 Kongens Lyngby, Denmark
[3] Department of Physics, Technical University of Denmark,
DK-2800 Kongens Lyngby, Denmark
[4] School of Chemistry, Newcastle University,
Newcastle upon Tyne, NE1 7RU, United Kingdom
[5] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences,
Hungarian Academy of Sciences, P.O. Box 286, H-1519 Budapest, Hungary

Understanding, and subsequently being able to manipulate, the excited-state decay pathways of functional molecules is of utmost importance in order to solve grand challenges in new technologies, such as solar energy conversion and molecular data storage. Herein, we exploit the complementary character of quantum wavepacket dynamics (exact solution to the time-dependent Schrödinger equation) and trajectory surface hopping (access to full-dimensional simulations) to address the coupled nuclear-electronic (nonadiabatic) dynamics in functional molecules. The presented theoretical investigations lead to a detailed understanding on the chemical control of photophysics in Fe-carbene photosensitizers [1−4], and excited-state mechanisms of photochemical reactions [5,6]. These results, alongside with the related ultrafast spectroscopic and scattering experiments, will contribute to the improved design of novel high-efficiency functional molecules.

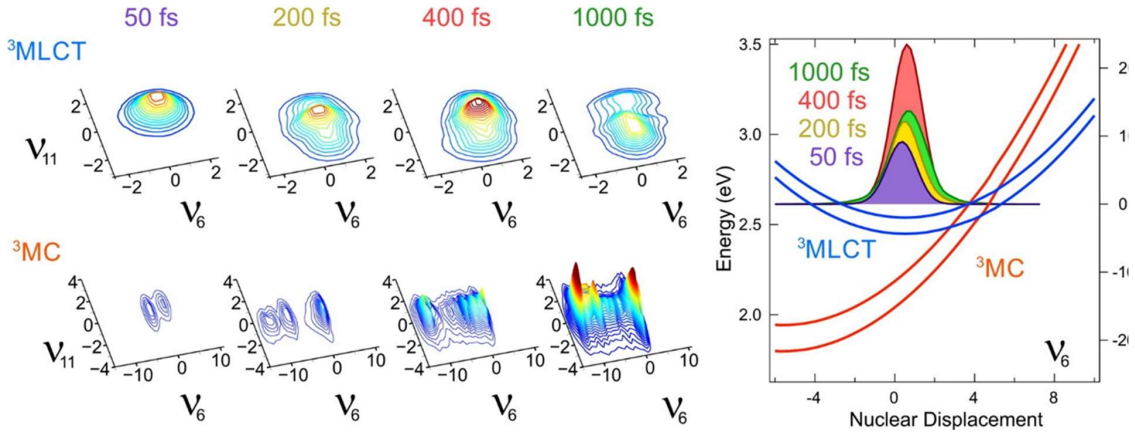

Figure 1: Graphical illustration of wavepacket dynamics in excited triplet metal-to-ligand charge transfer (^{3}MLCT) and metal-centered (^{3}MC) states. ν_6 and ν_{11} denote the nuclear (vibrational) degrees of freedom dominant for the excited-state dynamics; nuclear displacements are given in dimensionless mass-frequency weighted normal coordinates.

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Automatic Orbital Selection for Multiconfigurational Self-Consistent Field

Amiel S. P. Paz[a,b,c], William J. Glover[a,b,c]

[a]NYU Shanghai, 1555 Century Avenue, Shanghai 200122, China
[b]NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshang Road North, Shanghai 200062, China
[c]Department of Chemistry, New York University, New York, New York 10003, USA

We present an algorithm for the automatic determination of an orbital active space guess to help preserve active space consistency for a photoactive molecule in different nuclear configurations and embedded in different chemical environments. The algorithm relies on the singular value decomposition (SVD) of the overlap matrix between a subsystem's reference active space orbitals and the full system's molecular orbitals, yielding orbitals with maximum overlap with the reference space. Our approach avoids the need to manually choose orbitals for an active space guess over every geometry in an ensemble, allowing for high-throughput electronic structure calculations over many geometries and different solvent environments with CASSCF. We apply this technology, which we call the Automatic Orbital Selection for Multiconfigurational Self-Consistent Field (AOS-MCSCF), to constructing a linear absorption spectrum for the solvated GFP chromophore, with a particular focus on the states relevant to GFP photoexcitation from UV radiation, and find excellent agreement with recent experiments. The technology presented herein provides systematically improvable approaches to obtaining highly accurate absorption and emission spectra with the inclusion of dynamic correlation through CASPT2.

Attosecond imaging of coupled electron-hole dynamics in fundamental compounds of organic semiconductors

Marvin Reuner, Daria Popova-Gorelova

I. Institute for Theoretical Physics, University of Hamburg, Germany

We theoretically study how to reveal coupled electron-hole dynamics in molecules by means of time- and angle-resolved photoelectron spectroscopy (tr-ARPES). We consider experiments in which a pump pulse creates a coherent superposition of singlet states of molecules that are fundamental compounds of organic semiconductors. An attosecond soft x-ray pulse probes the dynamics by ionizing a molecule. We calculate photoelectron momentum distributions taking into account all transitions that a broadband probe pulse can induce. We demonstrate that simulated excited state properties of the isolated molecule map onto unique features of momentum maps. This approach provides a powerful method of following excited state dynamics on few-femtosecond time scales with atomic resolution.

1

The linear acetylenic carbon chain (or carbyne) is the simplest example of a 1D carbon system and the prototype of a charge-density wave (CDW). As a matter of fact, at sufficiently low temperatures, it undergoes a Landau-Peierls phase transition from an orderered metallic phase (cumulene) to a distorted insulating phase (polyyne) due to the insurgence of an unstable phonon mode with momentum $2k_F$ (where k_F is the Fermi momentum) [1-2].

Nevertheless, experimentally, only the insulating phase has been observed even at high temperatures: indeed it is possible to obtain carbyne either as relative small sized chains (~40 atoms) stabilized by end-capping [3] or as ultra long chains (~6000 atoms) encapsulated in single- [4] or multi-walled carbon nanotubes [5].

We therefore investigate the optical and excitonic properties of a free-standing linear carbon chain taking also into account quantum anharmonicity of the lattice [6], which play a fundamental role in renormalizing optical observables such as the optical band gap.

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Spin-mapping approach to exciton dynamics in light-harvesting complexes

Johan E. Runeson, Jeremy O. Richardson*

April 15, 2021

Abstract

We present a recently developed simulation approach to describe light-induced reactions found in biological processes such as photosynthesis, vision, and DNA repair, as well as light-harvesting compounds relevant for future energy technology. For two-level systems, the method can be thought of as a mapping to a spin in a magnetic field [1], and for N-level systems we use its generalization to the Lie group $SU(N)$ [2]. This leads to a set of classical equations of motion of N harmonic oscillators that are able to describe complex quantum problems. As an example, we have simulated electron transfer in photosynthetic green sulphur bacteria with state-of-the-art accuracy (see figure). For arbitrary environments, the absorption spectrum can be calculated through correlation functions of off-diagonal elements of the density matrix. The method outperforms conventional Ehrenfest calculations, scales linearly with system size, and opens the path towards nonadiabatic extensions of path-integral-based methods that include nuclear zero-point energy, which could make it a powerful tool for computing rates in general nonadiabatic reactions.

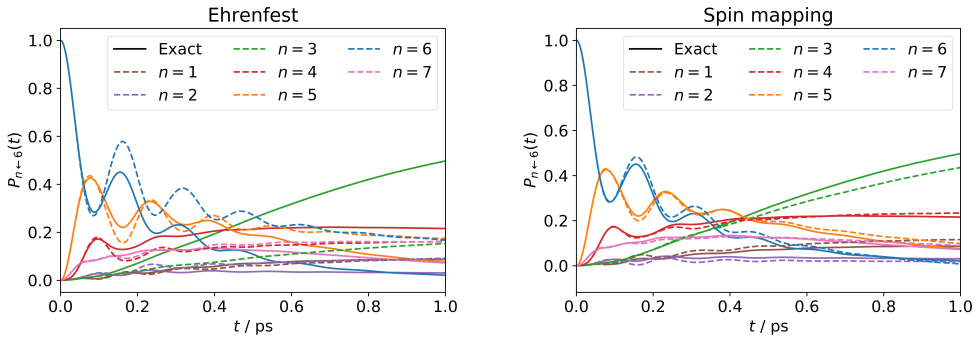

Figure: Electron population dynamics in a seven-state model of the Fenna–Matthews–Olsen complex, where solid lines indicate the exact benchmark. Our spin-mapping dynamics (right) outperforms conventional Ehrenfest dynamics (left) for comparable computational effort.

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Adaptive Boundary Layer using Exchange for solution-phase QM/MM molecular dynamics

Zhuofan Shen[a,b] and William J. Glover[a,b,c]

[a]NYU Shanghai, 1555 Century Ave., Shanghai, 200122, China
[b]NYU-ECNU Center for Computational Chemistry at NYU Shanghai, 3663 Zhongshan Road North, Shanghai, 200062, China
[c]Department of Chemistry, New York University, New York, NY, 10003, USA

QM/MM is a powerful computational chemistry approach to exploring the electronic structure and reaction dynamics of complex systems wherein a chemically active region can be defined and treated at a quantum mechanical (QM) level while the remainder of the system is treated with cheaper molecular mechanics (MM). A challenge arises when trying to apply QM/MM methodology to solvated systems if some of the solvent must be included in the QM region, for example in the description of solvent-supported electronic states or reactions involving Proton Transfer or Charge-Transfer-To-Solvent: the boundary between QM- and MM-treated solvent molecules must dynamically adapt in the course of the simulation to avoid mixing of QM and MM regions. We have developed a new method called Adaptive Boundary Layer using Exchange (ABLE) that solves the problem by adding a biasing potential to the system that maintains QM and MM separation while leaving ensemble averages unaltered. With a careful choice of biasing potential, we demonstrate ABLE on the hydrated electron and show that dynamics is conservative (total energy and momentum) and remarkably, dynamical quantities in the QM region are unaffected by the applied bias. This opens the door to studying a wide range of solution-phase chemical reactions with ABLE-QM/MM methodology.