THE H_3^{++} MOLECULAR SYSTEM AS A CORNER-STONE FOR BUILDING MOLECULES DURING THE BIG BANG

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The present study is devoted to the possibility that tri-atomic molecules were formed during at or shortly after the Big Bang. For this purpose we consider the ordinary H_3^+ and H_3 molecular systems and the primitive tri-atomic molecular system, H_3^{++}, for which is shown that it behaves differently. The study is carried out by comparing the topological features of these systems as they are reflected through their non-adiabatic coupling terms. Although, H_3^{++} is not known to exist as a molecule we found it to behave like that at intermediate distances. However this illusion breaks down as its asymptotic region is reached. Our study indicates that whereas H_3^+ and H_3 dissociate smoothly the H_3^{++}, is not capable to do that. Nevertheless, the fact that H_3^{++} is capable to live as a molecule on borrowed time enables it to catch an electron and form a molecule via the reaction $H_3^{++} + e \rightarrow H_3^+$ that may dissociate properly:

$$H_3^+ \rightarrow \begin{cases} H^+ + H_2 \\ H + H_2^+ \end{cases}$$
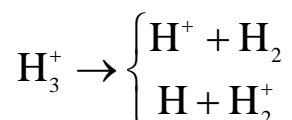
Thus, the two unique features acquired by H_3^{++}, namely, being the most primitive system formed by three protons and *one* electron and topologically, still be, for an instant a molecule may make it the sole candidate for becoming the *cornerstone* for creating the molecules.

QUANTUM NONADIABATIC DYNAMICS IN THE MOVING CRUDE ADIABATC REPRESENTATION

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On-the-fly quantum nonadiabatic dynamics for large systems greatly benefits from the adiabatic representation readily available from electronic structure programs. However, conical intersections frequently occurring in this representation introduce nontrivial geometric or Berry phases, which require a special treatment for adequate modeling of the nuclear dynamics. I analyze two approaches for nonadiabatic dynamics using the time-dependent variational principle and the adiabatic representation. The first approach, the global adiabatic representation, employs adiabatic electronic functions with global parametric dependence on the nuclear coordinates. The second approach, the moving crude adiabatic representation, uses adiabatic electronic functions obtained only at the centers of moving localized nuclear basis functions (e.g., frozen-width Gaussians). Unless a gauge transformation is used to enforce single-valued boundary conditions, the global adiabatic representation fails to capture the geometric phase. In contrast, the moving crude adiabatic representation accounts for the geometric phase naturally because of the absence of the global nuclear coordinate dependence in the electronic functions. In addition, the moving crude adiabatic representation does not suffer from appearance of the second order nonadiabatic couplings and allows us to avoid approximate Taylor series expansions of potential energy surfaces for wave-packet dynamics.

JAHN-TELLER EFFECT AMONG ELECTRONIC RESONANT STATES OF H3

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The electronic bound states of H_3 are known to exhibit a Jahn-Teller conical intersection. These states have previously been carefully studied using quantum chemistry calculations and Jahn-Teller parameters for the Rydberg series of states have been extracted [1]. We here study electronic resonant states of H3 with energies above the potential energy surface of the H_3^+ ground states. These states are important for dissociative recombination of H_3^+ at higher collision energies (E > 5 eV). Previous studies of these states have indicated that also these states exhibit a conical intersection at the D_{3h} geometry [2,3].

We have here performed electron scattering calculations on the lowest lying resonant states of 2A' symmetry using the Complex-Kohn variational method to compute the potential energies and the autoionization widths of the resonant states. These parameters are extracted by analyzing both the eigenphase sum of the fixed-nuclei scattering matrix and corresponding time-delay. Since these resonant states are high enough in energy, the local complex approximation can be applied and the autoionization from the adiabatic resonant state can be described using an imaginary term added to the potential energy surface. Following the ideas of Feuerbacher et al., the local complex potentials of the adiabatic resonant states are fitted to the eigenvalues of the complex Jahn-Teller Hamiltonian described in [4,5]. We investigate the importance of inclusion of higher order terms in the Jahn-Teller Hamiltonian. From the fitted Jahn-Teller Hamiltonian, the non-adiabatic couplings are computed and by integrating the non-adiabatic coupling around the conical intersection, we study the effect of autoionization upon the Berry phase.

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NUCLEAR VELOCITY PERTURBATION THEORY WITHIN THE EXACT FACTORIZATION: A NEW WAY OF TREATING NON-ADIABATIC EFFECTS

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The starting point of essentially all modern electronic-structure techniques is the Born-Oppenheimer (BO) approximation. It not only makes calculations feasible, the motion of nuclear wave packets on the lowest BO potential energy surface often provides us with an intuitive picture of chemical reactions. To go beyond this limit is notoriously difficult. Here we present a novel approach to non-adiabatic effects that is based on the exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The variational principle leads to two equations of motion., one for the nuclear wave function and one for the electronic conditional amplitude. The equation for the nuclear factor is a standard Schrödinger equation which describes the molecular motion –formally exactly- on a single time-dependent potential energy surface. When there is a splitting of the nuclear wave packet in the vicinity of an avoided crossing of BO surfaces, this exact time-dependent surface shows a nearly discontinuous step [2] connecting different BO surfaces, thus incorporating the influence of multiple adiabatic surfaces. The electronic equation of motion is not a standard Schrödinger equation: In addition to the usual BO Hamiltonian it contains terms which are non-linear, non-local and non-Hermitian. These terms are responsible for the proper description of decoherence [3,4]. Here we treat these additional terms by perturbation theory, the small parameter turns out to be the nuclear velocity (in the classical limit). This provides a successful description of electronic flux densities [5] and vibrational circular dichroism [6]. Furthermore, we use the approach to deduce an ab-initio electron-phonon interaction, and we explore the possibility of describing non-adiabatic effects in, e.g., proton transfer by R-dependent nuclear masses [7].

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GEOMETRIC PHASE EFFECTS IN NONADIABATIC TUNNELING

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When tunneling is affected by a conical intersection, the associated geometric phase can have a significant impact on the nonadiabatic tunneling dynamics, manifesting in both lifetimes and product state distributions. It is shown in the S_1 photodissociation of phenol, which is affected by conical intersections, the neglect of the geometric phase in an adiabatic treatment results in a two-orders-of-magnitude increase of the tunneling lifetime.[1] This is apparently due to the destructive interference between tunneling trajectories traveling on the two sides of the conical intersection, which carry different phases due to their topologically different paths. An adiabatic model with the vector potential reinstitutes the geometric phase and recovers the nonadiabatic tunneling lifetime.[2] Furthermore, constructive interference can also stem from the initial phase differences in the predissociative resonances.[3] Finally, it is demonstrated that product state distributions bear signature of the geometric phase in unimolecular dissociation in the presence of a conical intersection.[4]

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RIGOROUS TRAJECTORY-BASED METHODS FOR SIMULATING NONADIABATIC DYNAMICS

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In this talk, we discuss the quantum-classical dynamics of nonadiabatic transitions from the perspective of trajectory surface hopping. Our approach builds on the semiclassical Liouville formalism for describing the dynamics of generalized phase space distributions representing elements of the electronic density matrix. Particular attention is given to the nonclassical dynamics and nature of energy conservation in molecular processes with nonadiabatic transitions. The result is a new method for trajectory surface hopping "by consensus", where individual trajectories do not carry the burden of acting as "lone wolves" in deciding by themselves the probability of transition between quantum states, but rather interact and influence each other in a way that captures the underlying features of exact quantum dynamics. Decoherence appears naturally as an ensemble level effect, avoiding the ad hoc dephasing corrections of existing approaches. Additionally, the quantum-classical energy budget of the nonadiabatic dynamics emerges rigorously from the formalism, eliminating the ad hoc momentum rescaling and accompanying "frustrated hops" of standard surface hopping algorithms. Finally, additional approximations that disentangle the consensus dynamics are described, which yields an independent trajectory surface hopping method which incorporates the insights gained from the consensus formalism while retaining the numerical efficiency of the current methods.

NEW ELECTRONIC STRUCTURE TOOLS FOR MODELING NON-ADIABATIC PROCESSES

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Modeling of non-adiabatic processes begins with electronic structure: one needs to obtain accurate potential energy surfaces of multiple electronic states and electronic couplings (non-adiabatic couplings, NACs) that governs non-adiabatic transitions. I will discuss general theory behind NACSs and present recent theoretical developments within equation-of-motion coupled-cluster framework.

A QM/MM STUDY OF THE INITIAL EXCITED STATE DYNAMICS OF GREEN-ABSORBING PROTEORHODOPSIN

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The primary photochemical reaction of the green-absorbing Proteorhodopsin is studied by means of a hybrid quantum mechanics/molecular mechanics (QM/MM) approach. The simulations are based on a homology model derived from the blue-absorbing Proteorhodopsin crystal structure. The geometry of retinal and the surrounding sidechains in the protein binding pocket were optimized using the QM/MM method. Starting from this geometry the isomerization was studied with a relaxed scan along the $C_{13}=C_{14}$ dihedral. It revealed an "aborted bicycle pedal" mechanism of isomerization that was originally proposed by Warshel for bovine rhodopsin and bacteriorhodopsin. However, the isomerization involved the concerted rotation about $C_{13}=C_{14}$ and $C_{15}=N$, with the latter being highly twisted but not isomerized. Further, the simulation showed an increased steric interaction between the hydrogen at the C_{14} of the isomerizing bond and the hydroxyl group at the neighbouring tyrosine 200. In addition, we have simulated a nonadiabatic trajectory which showed the timing of the isomerization. In the first 20 fs upon excitation the order of the conjugated double and single bonds is inverted, consecutively the $C_{13}=C_{14}$ rotation is activated for 200 fs until the S_1-S_0 transition is detected. However, the isomerization is reverted due to the specific interaction with the tyrosine as observed along the relaxed scan calculation. Our simulations indicate that the retinal - tyrosine 200 interaction plays an important role in the outcome of the photoisomerization.[1]

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CASPT2 NON-ADIABATIC DYNAMICS

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In this talk I will present our recent development of theory and programs for analytical CASPT2 nuclear gradients [1,2] and derivative couplings [3] for sizable molecules. The program is efficient and well parallelized. As a numerical example, I present the optimization of the ground- and excited-state geometries and minimum-energy conical intersections of retinal protonated Schiff base (RPSB) models [4]. The largest RPSB model we studied consists of 54 atoms, for which we used the full-π active space, i.e., CAS(12e,12o). Furthermore, I will show the use of analytical CASPT2 gradients in on-the-fly surface hopping non-adiabatic dynamics. Numerical examples will be presented for the non-radiative decay of adenine and a GFP model chromophore [5].

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TIME EVOLUTION OF THE LANDAU-ZENER PROBLEM UNDER WEAK MEASUREMENT

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The time evolution and the asymptotic outcome of a Landau-Zener-Stueckelberg-Majorana (LZ) process under continuous weak non-selective measurement is analyzed. We compare two measurement protocols in which the populations of either the adiabatic or the non-adiabatic levels are (continuously and weakly) monitored. The weak measurement formalism, described using a Gaussian Kraus operator, leads to a time evolution characterized by a Markovian dephasing process, which, in the non-adiabatic measurement protocol is similar to earlier studies of LZ dynamics in a dephasing environment. Casting the problem in the language of measurement theory makes it possible for us to compare diabatic and adiabatic measurement scenarios, to consider engineered dephasing as a control device and to examine the manifestation of the Zeno effect under the different measurement protocols. In particular, under measurement of the non-adiabatic populations, the Zeno effect is manifested not as a freezing of the measured system in its initial state, but rather as an approach to equal asymptotic populations of the two diabatic states. This behavior can be traced to the way by which the weak measurement formalism behaves in the strong measurement limit, with a built-in relationship between measurement time and strength.

NON-EQUILIBRIUM THERMODYNAMICS IN OPEN QUANTUM SYSTEMS VIA THE DRIVEN LIOUVILLE VON NEUMANN (DLvN) APPROACH

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In my talk I will present the Driven Liouville von Neumann (DLvN) approach for simulating electron dynamics in open quantum systems. I will demonstrate its performance for the problem of time-dependent electronic transport in simple tight-binding model systems as well as in more elaborate molecular junctions described by an extended Hückel Hamiltonian. I will further present preliminary results of density functional theory based calculations using the DLvN methodology. Finally, I will analyze the out-of-equilibrium thermodynamic properties of the driven resonant level model studied within the DLvN scheme.

DESCRIBING POTENTIAL ENERGY SURFACES AROUND CONICAL INTERSECTIONS VIA SYMMETRY BREAKING AND RESTORATION TECHNIQUES

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We have recently studied the behavior of Hartree-Fock (HF) in the vicinity of conical intersections and observed the appearance of intersecting solutions with broken symmetries, typically spin, point group, and complex conjugation.[1] These HF solutions are non-orthogonal at the degeneracy point and are usually noncollinear.[2] Symmetry restoration techniques[3,4] applied to this particular situation produce orthogonal states that preserve the wave function degeneracy observed at the HF level. Thus Projected HF can qualitatively describe the molecular potential energy surface near conical intersections in a blackbox manner, without the computational expense of CAS or multireference approaches. The low cost of our approach makes it applicable to very large molecules.

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Derivative Couplings, Line Integrals, Fit Coupled Potential Energy Surfaces and the Molecular Aharanov Bohm Effect Revisited

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In 1979 Mead and Truhlar observed that energetically inaccessible conical intersections could influence single surface nonadiabatic dynamics through the geometric phase. This effect, which for example eliminates the standard connection between barrier topography and tunneling rate, was referred to as the Molecular Aharanov Bohm Effect(MAB).[1] Recently we have shown, using diabatic representations of accurate ab initio data, that the MAB effect has large impact on nonadiabatic tunneling.[2]

In this talk we explain how accurate fit diabatic representations based on ab initio derivative couplings and line integrals[3]of derivative couplings can be used to derive a generally applicable formulation of single state nonadiabatic dynamics.[4] The detrimental effects of linked conical intersections are deduced and illustrated.[5]

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TOWARDS QUANTUM SIMULATIONS FOR ELECTRONIC DYNAMICS FOR SMALL MOLECULES WITH MULTI-CONFIGURATION TIME-DEPENDENT HARTREE (MCTDH) RELATED METHODS

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With the advent of attospectroscopy, it becomes possible to follow and guide not only the nuclear but also the electronic dynamics in molecular processes opening the field of attochemistry. It makes necessary the development of theoretical tools to describe these dynamics quantum mechanically. We will present simulations on small molecules based on related Multi-Configuration Time-Dependent Hartree[1] (MCTDH) methods. Two strategies are presented: if the pump pulse is not very short a small number of electronic states are populated: nuclear wavepackets are propagated on the corresponding potential energy surfaces. In this context, simulations explaining experimental few-Femtosecond electronic Wave Packet Revivals in Ozone are presented. For shorter pump pulses, many electronic states are populated and it becomes necessary to introduce explicitly the dynamics of the electrons
In this context, we present preliminary results using the Multi-Configuration Time-Dependent Hartree Fock (MCTDHF) method developed by Daniel Haxton[2] to predict and explain experiments that probe the nonlinear interaction between H2 molecules with strong, ultrafast, pulsed laser fields. For these problems, involving the interaction with strong short pulses of light, the Born-Oppenheimer expansion of the wave function in terms of electronic eigenstates breaks down due to the number of excitations driven by the nonlinear interaction. Instead an explicitly time-dependent electronic wave function provides the most efficient and general representation, one that accounts for arbitrary electronic excitation and ionization of the molecule.

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NON-ADIABATIC COUPLING IN THE OZONE MOLECULE

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The question whether a Berry phase should be included in the calculation of rovibronic states of the ozone molecule in its electronic ground state has been addressed in the present work. Since several conical intersections connect the three lowest singlet states, a phase of π generated by a symmetry-demanded conical intersection between states 2 and 3 might be present, or it might be compensated by further conical intersections. Hyperspherical coordinates were employed here as they provide a natural choice for the cyclic coordinate that is needed to investigate the presence or absence of such a topological phase. On a hyperspherical grid, we have computed the electronic energies of the three lowest singlet states using a multi-reference configuration interaction (MRCI) procedure. Non-adiabatic coupling terms along the cyclic variable were evaluated numerically. Investigation of the behaviour of the adiabatic-to-diabatic transformation angles, using the quantization criterion of the non-adiabatic coupling terms (Baer and Alijah, Chem. Phys. Lett. 319, 489 (2000)), shows that a geometrical phase is retained. This phase has no practical effect on the well-established energy values of the rovibrational states located deeply in the three equivalent C_{2v} potential wells, but will come into action as highly excited states reach the dissociation region.

NESTED FUNNELS AND NONADIABATIC DYNAMICS IN PHOTOSYNTHESIS

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The remarkable efficiency of photosynthetic energy transfer processes has been a mystery for over 75 years.[1] Recent two-dimensional (2D) spectroscopy experiments have found quantum beats with unexpectedly large amplitude from a coherence that persists for longer than the apparent energy transfer timescale. We have shown that intramolecular vibrations that become delocalized over the donor and acceptor can drive electronic energy transfer beyond the Born-Oppenheimer framework developed by Forster.[2] The nested funnels that drive energy transfer are not necessarily conical, but are deeply nonadiabatic and closely related to the pseudo Jahn-Teller effect.[3] An associated nonadiabatic Raman process drives delocalized vibrations on the ground electronic state of the antenna, in which no pigments are electronically excited. These generate all of the reported 2D signatures and their properties indicate some new design principles for light harvesting based on vibrational-electronic resonance. For a model photosynthetic dimer, the figure shows the uncoupled diabatic states in the site basis (a), the electronically delocalized adiabatic exciton states (b), and a colored exact factorization of the nonadiabatic eigenstates (c). The nonadiabatic states and dynamics in photosynthetic nested funnels will be discussed.
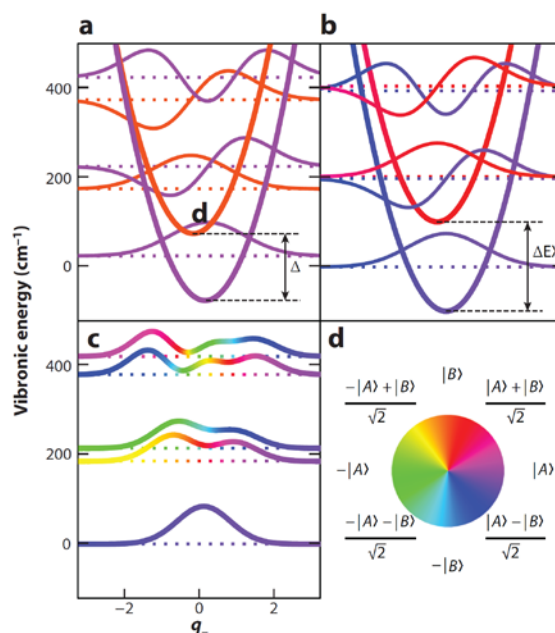
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UNDERSTANDING AND ENGINEERING THE VIBRATIONAL COHERENCE OF VISION

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The light-induced double-bond isomerization of the visual pigment rhodopsin operates a molecular-level opto-mechanical energy transduction, which triggers a crucial protein structure change. In fact, rhodopsin isomerization occurs according to a unique, ultrafast mechanism that preserves mode-specific vibrational coherence all the way from the reactant excited state to the primary photoproduct ground state. In this lecture we revise recent results which have enhanced our comprehension of such non-adiabatic process through semi-classical dynamics and transient spectroscopy studies. Most importantly, we will discuss an attempt to engineering such a biological energy-funneling function in synthetic compounds potentially capable of achieving optimum light-to-mechanical energy conversion.
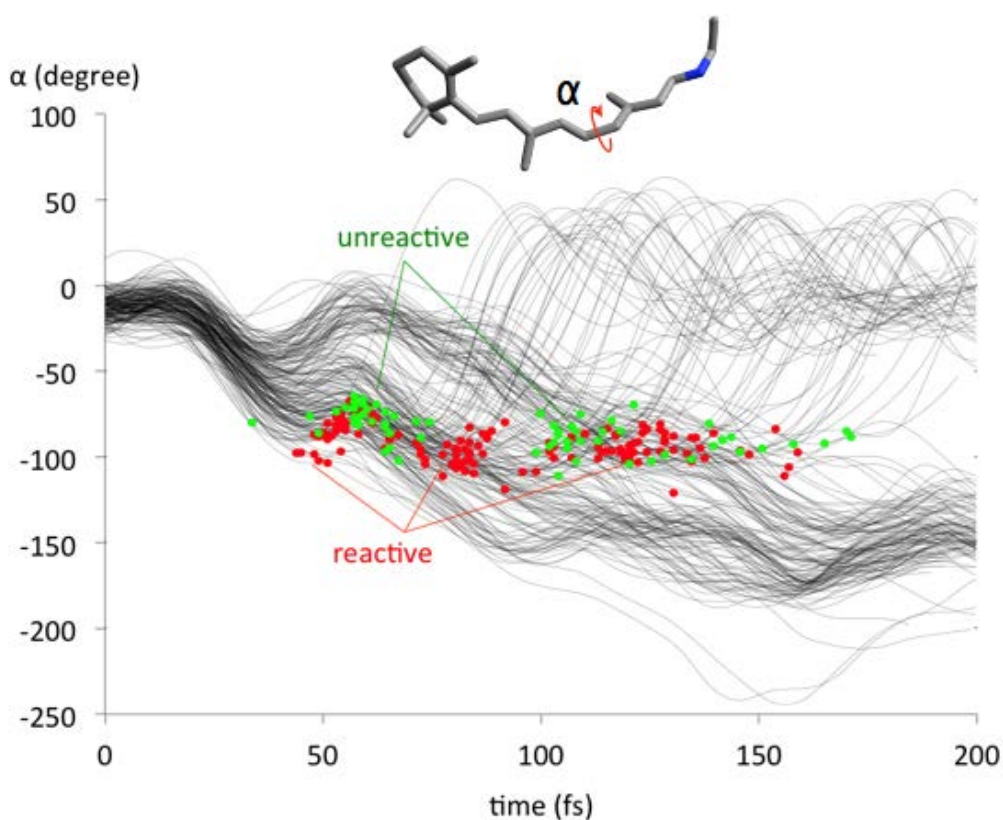
Complexity of the excited state decay pattern of a population of rhodopsin molecules at room temperature. The circles indicate points of hop from the excited to the ground state potential energy surface of single molecules. Red circles indicate hop points leading to photoproduct formation while green circles indicate internal conversion to the reactant.

NONADIABATIC ENERGY TRANSFER

Troy Van Voorhis
Massachusetts Institute of Technology

Energy transfer is an extremely important step in solar energy conversion. In order to efficiently harness absorbed light, we must guide the energy both spatially and energetically toward desired products. In this talk we will summarize some of our recent work on triplet energy transfer and the important processes of triplet fusion and singlet fission. Beginning with a diabatic picture of energy transfer, we will outline how localized, physically relevant reactant and product states can be generated using constrained DFT. These diabatic states then form the basis for both adiabatic and non-adiabatic descriptions of energy transfer, fission and fusion. Time permitting, we will illustrate some of the applications of these techniques to organic semiconductors and quantum dots.

NON-ADIABATIC INTERACTION AND THE GEOMETRIC PHASE

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After a brief presentation of the potential energy curves[1] for H_2 and H_2^- and the autodetachment in H_2^-, the properties of nonadiabatic coupling terms (NACTs) for molecular systems will be discussed. Using the behavior of NACTs and the geometric phase, conical intersections between potential energy surfaces are identified for NHH [2], CO_2^+ [3] and HeH_2^+.

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CLASSICAL MOLECULAR DYNAMICS SIMULATIONS OF ELECTRONICALLY NON-ADIABATIC PROCESSES

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A recently described symmetrical quasi-classical (SQC) windowing methodology for classical trajectory simulations has been applied to the Meyer-Miller (MM) model for the electronic degrees of freedom in electronically non-adiabatic dynamics. The approach treats nuclear and electronic degrees of freedom (DOF) equivalently (i.e., by classical mechanics, thereby retaining the simplicity of standard molecular dynamics), providing ``quantization'' of the electronic states through the symmetrical quasi-classical (SQC) windowing model. The approach is seen to be capable of treating extreme regimes of strong and weak coupling between the electronic states, as well as accurately describing coherence effects in the electronic DOF (including the de-coherence of such effects caused by coupling to the nuclear DOF). It is able to provide the full electronic density matrix from the one ensemble of trajectories, and the SQC windowing methodology correctly describes detailed balance (unlike the traditional Ehrenfest approach). Calculations can be (equivalently) carried out in the adiabatic or a diabatic representation of the electronic states, and most recently it has been shown that a modification of the canonical equations of motion in the adiabatic representation eliminates (without approximation) the need for second-derivative coupling terms.

# EXCITED-STATE DYNAMICS WITH TRAJECTORIES

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Excited-state dynamics is at the heart of Photophysics and Photochemistry. Nonadiabatic transitions are induced by the strong coupling between electronic dynamics and the ultrafast motion of the nuclei, and are observed in phenomena such as photosynthesis, photovoltaics, and exciton transport in π-conjugated complexes. An essential part of the research efforts in these fields is directed towards developing theoretical and computational approaches to describe conformational changes, energy dissipation, or quantum decoherence, i.e., the signature aspects of excited-state processes. In this context, among the most successful frameworks for molecular dynamics simulations of excited-state processes stand trajectory-based quantum-classical methods, as they give access to the study of complex molecular systems. Trajectory-based approaches combine a classical description of nuclear dynamics with a quantum-mechanical description of electronic dynamics. However, the approximations underlying quantum-classical methods are sometimes severe, and are at the origin of controversies as well as of continuous developments.

In this talk I will present a recently-developed trajectory-based approach to nonadiabatic dynamics [1,2]. The actual numerical scheme has been derived from the exact factorization of the electron-nuclear wavefunction[3], a new framework proposed to investigate, interpret and approximate the coupled dynamics of electrons and nuclei beyond the Born-Oppenheimer approximation. The exact factorization provides a new perspective to analyze nonadiabatic processes: (i) it proposes an alternative[4] to the standard Born-Oppenheimer framework, that pictures excited-state processes in terms of wavepackets moving on and transferring between static potential energy surfaces; (ii) it suggests new interpretations[5] of molecular geometric-phase effects, related to conical intersections; (iii) it provides guidelines for developing simulation algorithms in different[6] nonadiabatic regimes. These points will be discussed during the talk and illustrated on low-dimensional models and molecular systems (oxirane is shown in the figure below).
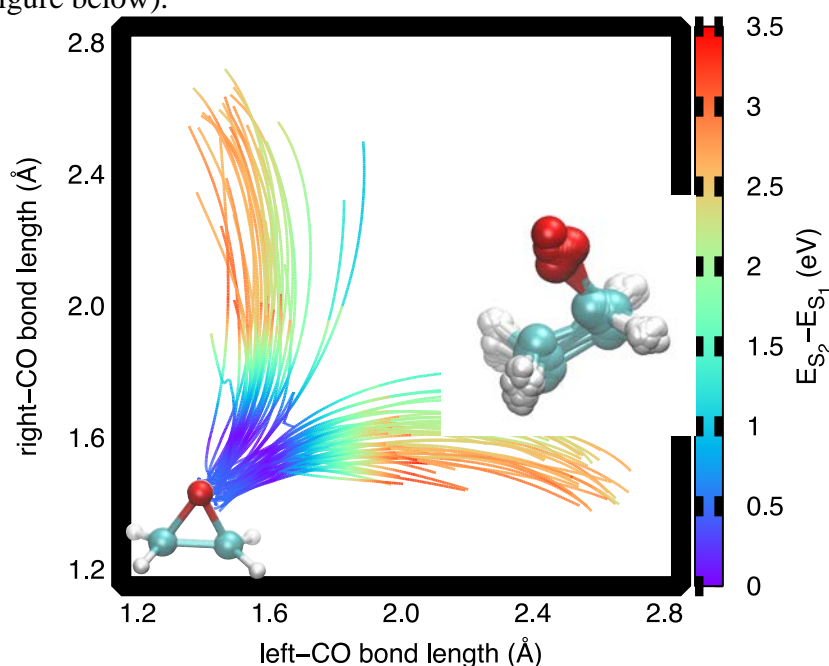
Ultrafast ring-opening process in Oxirane triggered by photo-excitation from S_0 to S_2. The energy gap S_2/S_1 along the simulated trajectories is represented as function of the reaction coordinates, i.e., the CO bonds length

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FULL QUANTUM DIRECT DYNAMICS SIMULATIONS OF NON-ADIABATIC PHOTOCHEMISTRY

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Solving the time-dependent Schrödinger Equation has a natural exponential scaling with system size. This makes it hard to achieve complete quantum mechanical results for molecules with more than a few atoms without resorting to approximations. The exponential scaling manifests itself in 2 ways. Firstly in the computer resources required for the propagation of the nuclear wavepacket and secondly, in the space to be covered when calculating the potential energy surfaces. These problems are exacerbated for systems involving excited states where couplings between potential surfaces are required and high accuracy is sometimes necessary for even qualitatively correct results.

The multi-configurational time-dependent Hartree (MCTDH) algorithm has gone a long way in solving the first problem [1]. In particular the multi-layer form (ML-MCTDH) is able to propagate multi-dimensional wavepackets with 100s of degrees of freedom. It does, however, in general require global potential surfaces which can restrict it to using model Hamiltonians rather than general, flexible molecular potentials. While this approach has been very useful in describing the initial stages of, e.g. non-adiabatic dynamics after photo-excitation [2] it is not able to describe the longer time photochemistry.

An approach to break both the exponential scaling and provide general potentials is the variational multi-configurational Gaussian (vMCG) method [3]. This uses a set of Gaussian wavepackets (GWP) as a time-dependent basis, but unlike conventional GWP methods, the GWPs follow variational rather than classical trajectories and retains the full quantum description of the system. It is also suited for direct dynamics simulations, calculating the potential on-the-fly using quantum chemistry programs and so opens up the use of flexible potentials [4]. The present state-of-the art of this method will be presented, showing its promise and highlighting the problems still to be solved.

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ISOTOPE EFFECT IN A NON ADIABATIC TRANSITION AND LONGER TIME VIBRONIC COHERENCE

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An isotope effect in the VUV high resolution spectrum and in the photodissociation of N2 is well established. We proposed that the mass dependence can be due to coupling of the initially photoexcited bound valence and Rydberg electronic states in the frequency range where there is strong mixing. To focus on this early time dynamics we here consider a time dependent point of view where the excitation is by an ultrafast pulse. The frequency broad pulse creates a coherent superposition of electronic states. Shortly thereafter the nuclei respond. But the isotope effect during this very early initial stage is modest. The valence excited state is more weakly bound that the Rydberg states and as such has a longer period. Depending on the energy, during the period of the valence state its nuclear wavepacket can significantly overlap with a faster moving wavepacket on a Rydberg state. Accurate numerical simulations show that this coincidence allows an effective transfer of population that is very mass dependent. An analytical toy model recovers the (strong) mass and energy dependence.

LIGHT-INDUCED CONICAL INTERSECTIONS

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Conical intersections are degeneracies between electronic states and are very common in nature. It has been found that they can also be created both by standing or by running laser waves [1,2]. The latter are called light-induced conical intersections. Recently, several theoretical and experimental studies have demonstrated that similarly to the natural CIs the light-induced conical intersections have also significant impact on the different dynamical properties of molecules [5-9]. Among others it can strongly modify e. g. the spectra, the alignment, the dissociation probability or fragment angular distribution of molecules. However, there are features in which the natural and light-induced CIs differ significantly. As long as the position of a natural CI and the strength of its nonadiabatic effects are inherent properties of the electronic states of a molecule and are difficult to modify, the energetic and spatial positions of the LICI can be controlled by changing the parameter settings (intensity, frequency) of the laser light. This latter can open up a new direction in the field of molecular quantum control processes [6].

It is well known that conical intersections are the sources for numerous topological effects which are manifested e.g. in the appearance of the geometric or Berry phase. In one of our former works by incorporating the diabatic-to-adiabatic transformation angle with the line-integral technique we have calculated the Berry-phase of the light-induced conical intersections [8,9].

Recently we demonstrated that by using the time dependent adiabatic approach suggested by Berry the geometric phase of the light-induced conical intersections can also be obtained and the results are very similar to those of the time-independent calculations [10].

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A New Look at Normal and Anomalous Diffusion

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By combining point transformations with ideas from super--symmetric quantum mechanics (SUSY), the Heisenberg uncertainty principle, the Central Limit Theorem of probability theory, we show that a wide range of anomalous diffusion processes are actually normal diffusion systems when described using the new canonical variables.

TIME DEPENDENT NON ADIABATIC MARKOVIAN QUANTUM MASTER EQUATION

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A quantum master equation is developed for a driven system coupled to a bath. The derivation is based on the weak coupling limit, in second order of the system bath interaction. An advantage of an explicit solution of the free driven system is taken. This solution is based on a Lie algebra which includes the time dependent Hamiltonian of the system and the system operators coupled to the bath. As a result the propagator of the system has a closed form. Under the conditions that the bath dynamics is considerably faster than the external driving time-scale we obtain a time dependent Markovian master equation. The derivation termed Non Adiabatic Master Equation (NAME) goes beyond the adiabatic approximation. The NAME is composed from time dependent rate coefficients and time dependent generators. The temporary invariants of the equation include both energy and coherence terms. The scheme is demonstrated for a time dependent Harmonic Oscillator. The NAME is compared to the adiabatic limit and to a numerical model.

NONADIABATIC DYNAMICS VIA THE GENERALIZED QUANTUM MASTER EQUATION

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The generalized quantum Master equation (GQME) can provide a useful framework for simulating electronically nonadiabatic dynamics. Within this framework, a memory kernel super-operator contains all the information needed in order to account for the impact of the nuclear degrees of freedom on the dynamics of the electronic degrees of freedom. By avoiding commonly employed assumptions, such as weak coupling between electronic and nuclear degrees of freedom, harmonic potentials energy surfaces and the Condon approximation, this framework allows one to validate and go beyond currently available methods, which rely on the validity of those assumptions. The fact that the memory kernel is often short-lived also implies that it can be calculated via semi-classical, mixed quantum-classical and quasi-classical methods, whose accuracy and/or efficiency is often limited to short times. As a result, the applicability of those methods can be extended to longer time scales compared with those accessible via direct application. Previous GQME-based methodologies required one to start out with the overall Hamiltonian cast is a system-bath form (system term + bath term + system-bath coupling term). This requirement can lead to ambiguity since such a decomposition is not unique in a system involving multiple electronic states, where each electronic state is associated with a different potential energy surface. I will present a new formalism for calculating the memory kernel that avoids this ambiguity by not requiring one to cast the overall Hamiltonian in a system-bath form. The applicability of the new formalism will be demonstrated on a benchmark model where the short-time inputs are calculated via the Ehrenfest mean-field mixed quantum-classical method.

DOES ELECTRONIC NON-ADIABATICITY INFLUENCE RATES OF SURFACE REACTIONS?

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In 1929, Nobel Laureate Paul Dirac set the direction of research for computational chemistry that persists to the present day, writing that with the advent of quantum mechanics "The underlying physical laws necessary for the mathematical theory of… …the whole of chemistry are… …completely known…". He went on to say: "the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." Despite electrifying advances in computational power since that time, Dirac is still right. The theory of chemistry requires approximations before theoretical descriptions and predictions of chemical reactions can be made.

The advent of the Born-Oppenheimer Approximation led to the development of the standard model of chemical reactivity where quantum motion of nuclei on an electronically adiabatic potential energy surface is calculated. For surface chemistry, additional approximations are often needed: 1) classical mechanics for describing nuclear motion, 2) density functional theory (usually at the generalized gradient level) for calculating electronic states, and 3) reduced dimensionality approximations. I call this collection of approximations, the provisional model for surface chemistry. In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will present examples from our recent work using full dimensional potential energy surfaces including nuclear coupling to electronic degrees of freedoms. We perform complementary scattering experiments using nearly mono-energetic H-atom beams in combination with Rydberg atom tagging detection of the H atoms final speed and direction to test the validity of the dynamical simulations. For hydrogen atom adsorption at metal surfaces, we find that adsorption cannot occur without Born-Oppenheimer failure and that adsorption occurs by a penetration/resurfacing mechanism. For H adsorption at a graphene surface, transient C-H chemical bond formation results in efficient energy loss even on the 30-fs time scale.

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COOLING AND MECHANICAL STABILIZATION OF MOLECULAR RESONANT TUNNELING DEVICES

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The promise for future realization of single molecule-based electronic devices relies, to a large extent, on the ability to mechanically stabilize the molecular bonds, while making use of efficient resonant charge transport through the molecules. In single molecule junctions, resonant charge transport involves excessive charging of the molecule (transiently, at least). For most organic molecules this is likely to lead to vibrational heating, conformation changes or bond rupture, which hinder the mechanical stability of the junction. Accounting for vibronic coupling during resonant charge transport is therefore essential for the realization of single molecule devices. In the talk we shall mention several mechanisms for transport induced mechanical instability in molecular junction, and focus in particular on vibrational heating due to inelastic charge transport through the molecule, and on the analysis of the phenomenon of vibrational instability. This analysis will lead to new strategies for overcoming the excessive vibrational heating during resonant transport, including counter-intuitive effects, such as high-voltage assisted mechanical stabilization[1], and high temperature stabilization ("cooling by heating"[2]). These results are explained using an analytical model and are demonstrated to hold beyond the model limitations using numerical simulations. This work provides some guidelines for cooling nano-scale conductors operating in the resonant tunneling regime, as well as some practical suggestions with respect to experimentally controlled parameters that can be tuned in order to enhance the mechanical stability of nano-electronic devices.

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MEAN FIELD VS STOCHASTIC APPROACHES TO NONADIABATIC DYNAMICS

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In this talk, I will present some theoretical and some practical results regarding nonadiabatic dynamics. By comparing both mean-field and surface-hopping approaches, focusing on both short and long time dynamics, I will highlight how much we now understand about running these dynamics—decoherence, detailed balance, entropy production, etc. For the most part, my intention is to discuss dynamics in solution rather than at metal surfaces.

ELECTRONIC EXCITED STATES FROM PAIRING MATRIX FLUCTUATIONS AND PARTICLE-PARTICLE RANDOM PHASE APPROXIMATION

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We developed the particle-particle Random Phase Approximation to describe the pairing matrix fluctuation and then determine ground and excited state energies by the differences of two-electron addition/removal energies. This approach can be viewed as combining the accurate many-body description of two-electron subsystems with the DFT description for the remaining (N-2) electrons.

This approach captures many types of interesting excitations: single and double excitations are described accurately, Rydberg excitations are in good agreement with experimental data and CT excitations display correct 1/R dependence. Applications to the singlet-triplet energy gaps of diradicals and poly-acenes and conical intersections will be featured.

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STOCHASTIC GW FOR THOUSANDS OF ELECTRONS AND MORE

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Stochastic Quantum Chemistry (SQC) is a new paradigm we developed for electronic structure and dynamics, which rewrites traditional quantum chemistry as stochastic averages, avoiding the steep power law scaling of traditional methods. As an example I will discuss Stochastic GW (SGW). The GW technique is known to achieve high accuracy, with only a 0.1-0.3 eV experiment-theory deviation for affinities and ionization energies. SGW reproduces the results of traditional deterministic GW for small systems, but also handles very large systems; as an example, we easily calculated affinities, charging energies, and photoelectron spectroscopy for Si clusters and Si and P platelets with up to 5000 valence electrons, for clusters with 40 thiophene molecules, and for periodic systems. These systems are significantly bigger than any calculable in existing approaches, so that SGW makes a quantum jump in the ability to calculate accurate electronic affinities and potential energies for large molecules. We will specifically discuss recent improvements in the algorithm and implementation which makes SGW superior to traditional techniques already for systems with 100 electrons, and reduces experiment-theory deviations to ~0.1eV.

BEYOND BORN-OPPENHEIMER THEORIES ON MOLECULAR PROCESSES AND PHASE TRANSITIONS IN SOLID STATES

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The formulation of beyond Born-Oppenheimer (BBO) methodology is briefly presented from first principle for the construction of diabatic potential energy surfaces (PESs) both for spectroscopic [1-4] (Na_3, K_3, NO_2, NO_3, $C_6H_6^+$ and $C_6H_3F_3^+$) and scattering [5,10] processes ($D^+ + H_2$). Jahn-Teller (JT) and Renner-Teller (RT) types of conical intersections (CIs) along with Psude Jahn-Teller (PJT) interactions in those systems and semi-circular CI seam [5] (rather than a CI point) between the ground and first excited states of H_3^+ system are the new interesting observations. The nuclear dynamics is performed on the diabatic PESs of Na_3 and NO2 to calculate the photoelectron spectrum, which matches quite well with the experimentally measured ones. Moreover, we carry out reactive scattering dynamics [6-10] on the adiabatic and diabatic surfaces for H_3^+ system in hyperspherical coordinates for total angular momentum zero and non-zero situation to reproduce experimental cross sections and rate coefficients for reactive non-charge and charge transfer processes. Optical spectra of $REMnO_3$ (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy) shows anomalous temperature dependence around the Neel temperature [11]. This behavior could be due to the quantum rotor orbital excitations, originated from dynamic Jahn-Teller effect [12], in both ground [13], and excited state. Such observations have been investigated [14] theoretically to explain the experimental spectra due to the excitations of the quantum rotors.

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ULTRAFAST NONADIABATIC DYNAMICS IN PHOTOVOLTAIC POLYMER MATERIALS: COHERENCE, DELOCALIZATION, AND DISORDER

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This talk addresses quantum dynamical studies of ultrafast photo-induced exciton migration and dissociation in functional organic polymer materials, in view of understanding the intricate interplay of electronic delocalization, coherent nonadiabatic dynamics, and trapping phenomena. Our approach [1] combines first-principles parametrized Hamiltonians, based on TDDFT and/or high-level electronic structure calculations, with accurate quantum dynamics simulations using the Multi-Configuration Time-Dependent Hartree (MCTDH) method [2] and its hierarchical multi-layer (ML-MCTDH) variant [3], as well as mixed quantum-classical techniques. The talk will specifically focus on the elementary mechanism of exciton migration [4] and creation of charge-transfer excitons [5] in polythiophene and poly-(p-phenylene vinylene) type materials and various donor-acceptor assemblies [1,5]. Special emphasis is placed on the influence of structural (dis)order and molecular packing, which can act as a determining factor in transfer efficiencies. Against this background, we will comment on the role of temporal and spatial coherence, along with a consistent description of the transition to a classical-statistical regime.

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COMBINED ELECTRONIC STRUCTURE AND QUANTUM DYNAMICAL ANALYSIS FOR CHARGE SEPARATION AND SINGLET FISSION

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Charge separation in organic photovoltaics [1] and singlet fission in molecular crystals [2-4] are analyzed by first principles calculations and quantum dynamics calculations. The charge and exciton dynamics are described by the linear vibronic coupling model parametrized based on diabatization of TDDFT [5] and MRMP2 adiabatic states. Quantum dynamics calculations are carried out using the MCTDH method explicitly considering intra-molecular modes and essential inter-molecular modes. In organic photovoltaics, charge separation from photo-generated exciton occurs at donor-acceptor interfaces on a time scale of few hundred second despite the small permittivity of organic materials. Our quantum dynamics calculations revealed the role of charge delocalization and hot exciton in the ultrafast charge separation [1]. In the same way, mechanisms of singlet fission in molecular crystals are analyzed using the MCTDH method [2,3]. Further, the separation rate of free triplets from a triplet pair is analyzed based on Marcus-Levich-Jortner theory in conjunction with ab initio calculations [4].
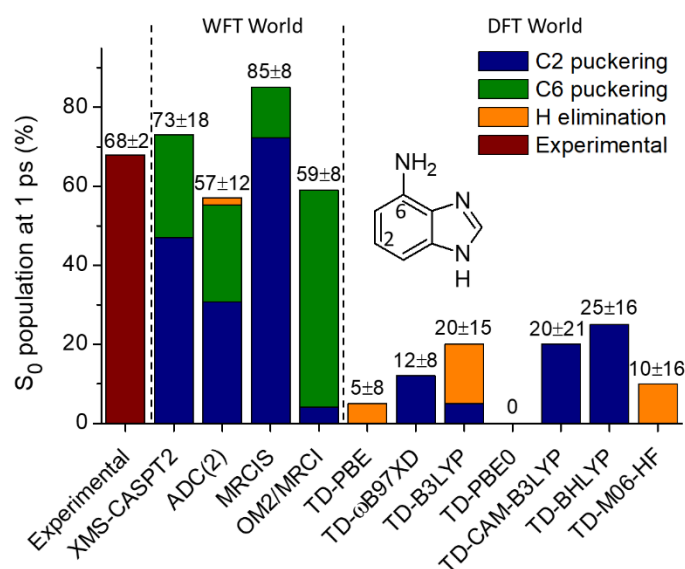
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NONADIABATIC DYNAMICS SIMULATIONS OF ORGANIC MATERIALS WITH OPTICAL ACTIVITY

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Organic materials with optical activity (OMOA) are cutting-edge components of advanced electronic and photonic applications. Diversity, plasticity and low cost make them ideal for a variety of devices, from solar cells, through sensors, to information storage and display. Photo-electronic processes in OMOA are highly complex, and nonadiabatic dynamics simulations may help by providing insights into physical-chemical phenomena and aiding to deconvolute time-resolved spectroscopic data. The use of nonadiabatic dynamics in this field faces, however, different challenges, including the development of new functionalities, reliable research protocols, efficient computational methods, and better integration with experimental analysis. In this lecture, I will discuss recent investigations by our group on nonadiabatic dynamics of OMOA.[1] I will also present recent methodological advances we have implemented [2-4] within the Newton-X platform (www.newtonx.org) and deliver a critical appraisal of the field.

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RECENT ADVANCES IN NONADIABATIC DYNAMICS AND APPLICATIONS TO NANOSCALE MATERIALS

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Motivated by time-resolved experiments, we develop suitable non-adiabatic molecular dynamics (NAMD) techniques [1], implement them within time-dependent density functional theory [2,3], and apply them to modern condensed phase systems [4-19]. Nanoscale systems create new challenges to NAMD, associated with large system size and long-range transfer (super-exchange, trivial "unavoided" crossings, decoherence), while at the same time allowing additional simplifications (classical path approximation). Having reviewed the recent NAMD challenges and advances, we will discuss photo-initiated charge and energy transfer in several classes of materials, include semiconducting and metallic quantum dots [4-7], hybrid perovskites [8-10], graphene, MoS2 and related two dimensional materials [11-13], sensitized TiO2 [14,15], etc. [16-19]. Our studies on realistic aspects (defects, dopants, boundaries) and provide a unifying description of quantum dynamics on the nanoscale, bridging molecular and bulk points-of-view.
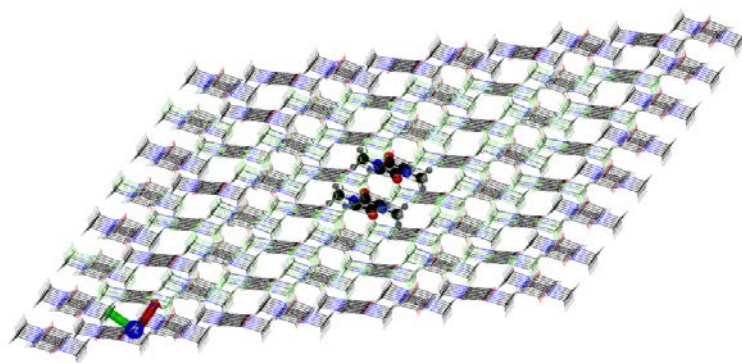
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PROBING CHROMOPHORES FOR SINGLET FISSION BY SURFACE HOPPING SIMULATIONS.

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Singlet fission is a process in which a molecule, excited to the S1 state, transfers part of its energy to another molecule, whereby populating the singlet combination of the lowest triplets of both molecules, 1TT. Since the system remains within the singlet manifold, the spin-orbit coupling is not primarily involved. The process can be exploited in photovoltaics, to produce two electron-hole pairs with one photon: in this way, one improves the solar energy conversion efficiency in the short wavelength part of the solar spectrum. Of course one needs molecules where the excitation energies of S1 and T1 are in a ratio at least [2-1]. This requirement is satisfied, for instance, by several biradicaloids or by large conjugated π systems[1]. However, at computational level the only way to assess with good confidence the suitability of a chromophore for singlet fission is to simulate the excited state dynamics of (at least) a pair of molecules. In this talk we outline a strategy to carry out such simulations, either in molecular crystals or in covalently bound dimers. The approach is based on surface hopping with quantum decoherence corrections.[2] The electronic energies and wavefunctions are computed on the fly by the semiempirical FOMO-CI method in its QM/MM version.[3] We shall see that a simulation, besides providing an assessment of the singlet fission mechanism and quantum yield, can also reveal competing decay processes and other drawbacks of the selected compound.[4] This information is valuable in planning changes of the molecular structure and of its environment, in order to improve its efficiency.

A pair of QM molecules embedded in a MM crystal structure.

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QUANTUM TRANSITIONS WITH CLASSICAL TRAJECTORIES: A SIMPLE AND RIGOROUS DERIVATION

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Many important electronic processes, such as electron transfer, energy transfer, quenching of electronic excitation and radiationless transitions inherently involve the breakdown of the Born-Oppenheimer (BO) approximation. To describe these processes accurately one has to take into account the non-adiabatic coupling between BO potential energy surfaces. Since the early 1970s, a wide variety of methods have been developed that generalize the classical trajectory motion of nuclei to include electronically nonadiabatic processes, the most popular of these being Ehrenfest dynamics and surface hopping. We present a novel trajectory method for treating quantum transitions with classical trajectories, with a simple derivation from the Schroedinger equation. Each trajectory evolves on a single surface according to Newton's laws but with complex positions and momenta. The trajectories affect their counterparts on the other surface(s) via the difference in their complex phase. The method leads to different trajectory dynamics on the different surfaces (non-Ehrenfest dynamics). It allows not only the calculation of asymptotic probabilities, but also the reconstruction of the time-dependent wavepacket. We present results for the three benchmark systems introduced by Tully, where there is generally excellent agreement of the method with exact quantum calculations. The method is also applicable to ultrafast optical spectroscopy. In contrast with most classical-based methods, the present approach is applicable in both the weak field and strong field regimes and automatically takes into account the amplitude as well as the phase of the excitation pulse.

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ELECTRON AND NUCLEAR DYNAMICS DRIVEN BY A COHERENT SUPERPOSITION OF ELECTRONIC WAVEFUNCTIONS (IMPLICATIONS FOR ATTOSECOND SPECTROSCOPY)

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Attosecond spectroscopy has opened up the possibility of observing the motion of electrons on their natural timescale (few attoseconds). We have been studying such electron dynamics together with coupled nuclear motion, using our implementation of the Ehrenfest method and Gaussian Wavepacket methods. The initial electronic wavepacket is chosen as a superposition of eigenstates to model the effects seen in attosecond spectroscopy. We will discuss two types of application with some examples: 1) pure electron dynamics , and its subsequent decoherence driven by nuclear motion and the natural zero point distribution in geometries, and 2) the electronic control of nuclear dynamics.

(a) t = 0

(b) t = 2.4 fs
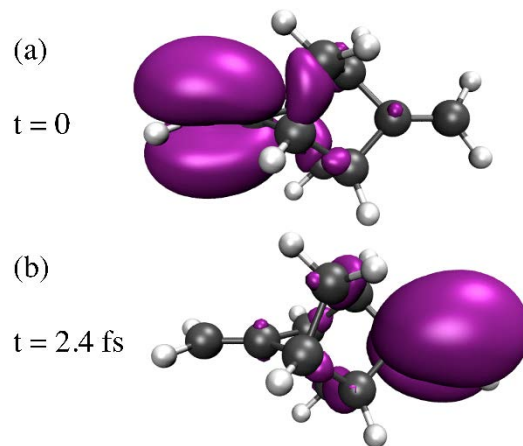
TIME-DOMAIN QUANTUM CHEMISTRY

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We have been developing a theory of nonadiabatic electron wavepacket dynamics, which I refer to as "Time-domain quantum chemistry" in an analogy to time-domain spectroscopy, which was termed to contrast to frequency-domain (or energy-domain) spectroscopy in 1970s to 1980s. Our main interests are in chemical phenomena beyond the Born-Oppenheimer realm. [1,2] After a short description about the basic theory I report our recent applications of the theory, which include;

(1) Symmetry breaking in chemical reactions due to nonadiabatic interactions of essentially multi-dimensional nature like conical intersections. [3,4,5]

(2) Nonadiabatic electron dynamics in molecular photoionization and autoionization, which are represented in complex natural orbitals. [6,7,8]

(3) Coupled proton electron-wavepacket transfer in water splitting dynamics. [9,10]

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TUNNELING FLIGHT TIME IN NONADIABATIC TRANSITIONS

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Time has been an enigma in non-relativistic quantum mechanics. Already Pauli noted that there is a difficulty in defining a quantum time operator obeying an $i\hbar$ commutation relation. This led to the question – how long does it take to tunnel through a barrier? In this talk, we introduce the concept of a transition path time distribution and use it to determine a tunneling flight time. We show that it leads to a vanishing time for tunneling through a parabolic barrier, Eckart barriers, square barriers and via a non-adiabatic transition. The implications of these observations on time of flight experiments as well as approximate quantum theories are discussed.