

Fritz Haber Center  
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# Poster Abstracts

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# Abstracts of Posters

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**THE XMS-CASPT2 EXCITED STATE MOLECULAR DYNAMICS OF THE TRUNCATED RETINAL MODEL**

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The Complete Active Space Perturbation Theory (CASPT2) method is well known to be a “gold standard” of computational photochemistry. Until recently, due to its computational cost this method had been used for a single-point energy correction only. Only a few number of excited state dynamics studies exist so far.[1,2] However, the CASPT2 analytical energy gradients and non-adiabatic coupling are now available for the resolution-of-the-identity formulation and with the efficient internal contraction via SMITH3 automatic code generator, implemented in BAGEL program package.[3,4]

However, the impact of XMS extension has not been tested for dynamics yet. Here we assess the performance of the XMS-CASPT2 in comparison to widely used CASSCF, semiempirical OM2-MRCI, and TD-DFT methods in description of the excited stated molecular dynamics of the PSB3 a truncated retinal model commonly used to study the photoisomerization.[5]

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## COUPLED-TRAJECTORY MIXED QUANTUM CLASSICAL MOLECULAR DYNAMICS FOR CHARGE TRANSPORT IN ORGANIC MATERIALS

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Accurate working simulations of charge transport in large pi-conjugated systems are extremely useful tools to guide development of promising low-cost opto-electronics.[1] Variations on the original surface hopping and Ehrenfest methods are probably the most widely used in this field. However, they both suffer from major flaws which a large amount of their literature has been dedicated to solving. These are over-coherence and unphysical nuclear dynamics due to the lack of branching along different paths in configuration space respectively. Coupled-trajectory mixed quantum classical molecular dynamics (CT-MQC) is a technique proposed to fix these problems. This is based on the exact factorisation of the molecular wavefunction into nuclear and electronic components [2] and allows for close monitoring of assumptions to avoid the aforementioned common pitfalls of other methods. However, the implementation to a model problem reported by Agostini et al [3] involved expensive ab initio electronic structure calculations limiting the usefulness of the technique to small systems. In this work, a more efficient, fragment orbital-based,[4] method will be used for the electronic structure description allowing the application of CT-MQC to larger systems of hundreds or thousands of molecules. The fragment orbital-based method involves expanding the charge carrier wavefunction and constructing the electronic Hamiltonian in a set of singly occupied molecular orbitals; negating the need to calculate full charge transfer determinants. This approximation has been scrutinized and verified before for  $\pi$ -conjugated systems.[5] In this poster I will present initial results of the new FOB-CTMQC algorithm for a small model system paying close attention to fundamental constraints such as energy conservation, detailed balance and internal consistency with the aim of scaling the system size considerably in the near future.

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**OBSERVATION OF ANOMALOUSLY SLOW VIBRATIONAL RELAXATION DURING MOLECULAR ADSORPTION AND DESORPTION ON A METAL SURFACE**

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The most common mechanism of catalytic surface chemistry is that of Langmuir and Hinshelwood (LH). In the LH mechanism, reactants adsorb, become thermalized with the surface and subsequently react [1]. At the same time, molecular vibration is well known to enhance the rates of gas-phase chemical reactions as the motion associated with vibration – for example, bond stretching may guide the atoms of the reactant molecule efficiently to the transition state. However, the measured vibrational lifetimes for molecules adsorbed at metal surfaces are in the range of a few picoseconds which is attributed to electronically nonadiabatic coupling of molecular vibration to electron-hole pairs in the metal [2-4]. As a consequence, vibrational promotion of LH chemistry is rarely observed – an exception is LH reactions occurring via a molecular physisorbed intermediate. In this work, we have directly detected adsorption and subsequent desorption of vibrationally excited CO molecules from a Au(111) surface [5]. Our results show that CO ( $v = 1$ ) survives on a Au(111) surface for  $\sim 10$ -10 sec. Such long vibrational lifetimes for adsorbates on metal surfaces are unexpected and pose an interesting challenge to the current understanding of vibrational energy dissipation on metal surfaces. They also suggest that vibrational promotion of surface chemistry might be more common than is generally believed.

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## A BEYOND BORN-OPPENHEIMER TREATMENT OF FIVE STATE MOLECULAR SYSTEM NO<sub>3</sub> AND ITS PHOTOELECTRON SPECTRA

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The nitrate radical, NO<sub>3</sub>, is considered to be one of the most complicated molecules in chemical physics in terms of its electronic structure.[1] The lowest five electronic states of this radical are: X<sup>2</sup>A<sub>2</sub>' (1<sup>2</sup>B<sub>2</sub>), A<sup>2</sup>E" (1<sup>2</sup>A<sub>2</sub> and 1<sup>2</sup>B<sub>1</sub>) and B<sup>2</sup>E' (1<sup>2</sup>A<sub>1</sub> and 2<sup>2</sup>B<sub>2</sub>). There are extensive non-adiabatic interactions among the five electronic states which we have investigated thoroughly as function of pairwise normal modes. The NO<sub>3</sub> molecule has six such modes out of which the two-fold degenerate in-plane asymmetric stretching modes and the non-planer umbrella bending mode contribute maximum to the overall non-adiabaticities of the molecule. The prominent Conical Interactions (CIs) occur due to Jahn-Teller (JT) interactions within A<sup>2</sup>E" as well as B<sup>2</sup>E' states, whereas strong Pseudo-Jahn-Teller (PJT) interactions among the ground state (X<sup>2</sup>A<sub>2</sub>') and the upper B<sup>2</sup>E' (1<sup>2</sup>A<sub>1</sub> and 2<sup>2</sup>B<sub>2</sub>) states. Along with the JT and PJT interactions, accidental CIs at several C<sub>2v</sub> geometries of the molecule exist due to the coupling between 3<sup>rd</sup>, 4<sup>th</sup> (1<sup>2</sup>B<sub>1</sub> and 1<sup>2</sup>A<sub>1</sub>) and 4<sup>th</sup>, 5<sup>th</sup> (1<sup>2</sup>A<sub>1</sub> and 2<sup>2</sup>B<sub>2</sub>) electronic states.<sup>1</sup> We have calculated *ab initio* adiabatic PESs and non-Adiabatic Coupling Terms, and solved the Adiabatic-to-diabatic (ADT) transformation equation for five electronic states on the normal mode planes to obtain the ADT angles and thereby, constructed five-sheeted smooth, continuous and symmetric diabatic PESs. Accurate dynamical calculations are carried out to simulate experimentally observed photodetachment spectra of NO<sub>3</sub><sup>-</sup> anion.[2]

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**MODELLING OF ELECTRONIC EXCITATION AS A PART OF MULTIPLE CLONING DYNAMICS**

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The Ab Initio Multiple Cloning (AIMC) method [1,2] is a powerful tool for non-adiabatic dynamics simulations, which combines some best features of Multiple Spawning [3] and Ehrenfest approaches [4]. The method was successfully applied, in particular, to simulate the nonradiative decay of the first excited state of ethylene<sup>1</sup>, to calculate the TKER spectra and VMI image for pyrrole photodissociation [5,6], and to study the mechanism of the energy transfer in dendrimers [7]. The photoexcitation in these calculations was approximated simply by Franck–Condon lifting of the ground state wave-packet to the excited state. This works well for many systems, however the fine details of the initial photoexcited wave-packet are not completely accounted for in this approximation, especially in the case of symmetry-forbidden transitions that only occurs due to the coordinate dependence of the transition dipole moment.

In order to improve the initial sampling, we have modified the AIMC method to include the interaction between the molecule and the laser field into the calculations. This allows us to simulate the process of photo-excitation during the laser pulse simultaneously with non-adiabatic dynamics, which often occurs on the same time-scale. In these calculations, we accurately take into account the coordinate dependences of electronic energies and transition momenta, which are provided by electronic structure calculations. The method is applied to simulate the dynamics of pyrrole photodissociation.

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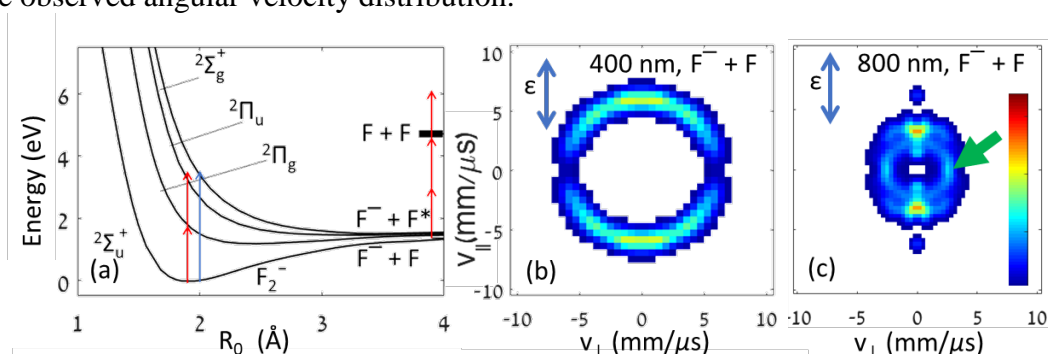
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## LINEAR & NON-LINEAR PHOTODISSOCIATION OF $F_2^-$ BY INTENSE LASER PULSES

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We present the time-resolved coincidence imaging of  $F_2^-$  photodissociation by ultrafast low-field 400nm and intense 800nm pulses.[1] We use fast beam fragment imaging technique that allows detecting the neutral, cations and anions fragments simultaneously.[2-4] Low-lying dissociative states, shown in figure (a), and its 3.08 eV detachment energy make the  $F_2^-$  anion a suitable candidate for intense field studies.[5] The low field 400nm pulses can access  $2\Sigma_g^+$  state of  $F_2^-$  anion that leads dissociation in  $F^-$  and F fragments. The corresponding angular velocity distribution is parallel to laser polarization at  $\sim 6.0$  mm/ $\mu$ s, shown in figure (b). The measured  $1.794 \pm 0.005$  eV kinetic energy release(KER) indicates a dissociation energy of  $D_0(F_2^-) = 1.256 \pm 0.005$  eV.[1] With intense field 800nm pulses, the dissociation on  $2\Pi_g$  state results a low-velocity contribution ( $\sim 2.5$  mm/ $\mu$ s) which distributed perpendicular to the laser polarization, shown by the green arrow in figure (c). The two photons can access the  $2\Pi_u$  state, forbidden transition by single photon, results a higher velocity contribution ( $\sim 6.0$  mm/ $\mu$ s) that are parallel to the laser polarization.[1] In addition, we observe velocity distribution at  $\sim 3.5$  mm/ $\mu$ s, characterized by a structured angular dependence, must arise from a different non-linear mechanism that allows the dissociating molecule to gain additional energy from the intense laser field. Further theoretical work is needed to explain the possible mechanisms such as dynamical stark shift of the potential curves or resonant Raman excitation that could account for the observed angular velocity distribution.



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## CHARGE TRANSPORT IN ORGANIC MATERIALS: DEVELOPMENT OF FRAGMENT ORBITAL-BASED SURFACE HOPPING

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Simulations of charge transport in large pi-conjugated systems (e.g. organic semiconductors or biological molecules) are paramount to a better understanding of their carrier mobilities and to improve the performance of low-cost and promising opto-electronic devices. Since hopping and wide band theories have proved inappropriate to study this kind of systems in most situations, [1, 2] the development of direct charge propagation schemes, such as non-adiabatic molecular dynamics is of great importance. In this respect, Tully's surface hopping approach [3] can aid to deal with these large and complex systems. Within this strategy, the nuclei evolve on a single potential energy surface and nonadiabatic effects are included by allowing hopping from one surface to another. Nevertheless, this method requires the calculation of the Hamiltonian and the nonadiabatic coupling elements at each time step, making the procedure still computationally very demanding.

Our fragment-orbital based surface hopping method (FOB-SH) has been specifically designed to overcome this difficulty. In particular, the ultrafast calculation of Hamiltonian and forces of the system allows us to treat fundamental charge transfer properties in large molecular assemblies without assuming any specific charge transport model [4].

Here, we present the results obtained by applying different flavours of this strategy to chains of organic molecules. We consider fundamental requirements (e.g. total energy conservation, detailed balance and internal consistency) that the surface hopping algorithm should fulfil. We show how solving well-known limitations of the SH approach for instance the overcoherence of the electronic wavefunction, the trivial crossing problem and the rescaling of the velocities after a successful hop, improves the quality of our simulations. [5] Such improvements have proved essential to recover the correct charge carrier mobility crossover between thermally activate and band-like transport in these systems. We present the temperature dependence for the hole mobility in chains of organic molecules. Focussing on both size and time step convergence for this quantity and onto the underlying charge carrier mechanism. The results presented in this work will serve as starting point for studying real application relevant organic semiconductors.

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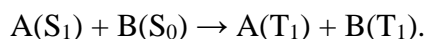
**MUTUAL NEUTRALIZATION IN  $Cl^- + C^+$  COLLISIONS**Patrik Hedvall<sup>1</sup>, Ann E. Orel<sup>2</sup> and Åsa Larson<sup>1</sup><sup>1</sup>*Department of Physics, Stockholm University, Stockholm, Sweden*<sup>2</sup>*Department of Chemical Engineering, University of California, Davis, USA*

Mutual neutralization of oppositely charged ions is a reaction driven by non-adiabatic couplings. Here the mutual neutralization reaction of  $Cl^- + C^+ \rightarrow Cl + C$  is studied at low collision energies. The 5 lowest electronic states of  $^2\Sigma^+$  symmetry and 7 lowest electronic states of  $^2\Pi$  symmetry together with the associated non-adiabatic couplings have been calculated at internuclear distance between 1.5 to 10  $a_0$  using the multi reference configuration interaction method. The potential energy curves describing the electronic states are transformed into a strictly diabatic basis, resulting in a set of coupled differential equations describing the motion of the nuclei. These are solved numerically and the cross section for neutralization into C + Cl fragments is obtained.

**COVALENT DIMERS FOR SINGLET FISSION: DESIGN STRATEGY AND SUITABILITY TEST.**

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



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

The efficiency of singlet fission depends on the interaction between the two chromophores, which in turn is highly sensitive to their relative orientation. The difficulty in engineering molecular crystals with favourable interchromophore electronic coupling motivated the idea of intramolecular singlet fission, i.e. to have the process occur within a molecule consisting of two covalently linked chromophore units. In covalent dimers the geometry and strength of interchromophore coupling can be tuned through chemical synthesis with an high degree of control, difficult to achieve in crystals of monomers. Moreover, for applications of singlet fission in photovoltaics covalent dimers offer potential practical implementations; in fact, they can be adsorbed on the surface of a semiconductor material as individual units.

We propose here a computational strategy to design new covalent dimers for singlet fission and to test their suitability. The procedure includes the following steps: (i) search for new candidate singlet fission chromophores by designing small molecules and computing the excitation energies for their low-lying electronic states; (ii) identification of the most favorable dimeric geometries for singlet fission by evaluating the interchromophore electronic coupling; (iii) selection of a way to covalently connect two molecules of the candidate chromophore and tuning their relative orientation; (iv) simulation of the excited state dynamics for the covalent dimer, first in vacuum and then adsorbed on a semiconductor material, using a trajectory surface hopping approach [3].

The excited state dynamics simulation is particularly important not only to determine the singlet fission quantum yield, but also to identify competing processes and other deficiencies of the selected chromophore [4].

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**FAST(ER) AND (MORE) ACCURATE EXCITED-STATE CALCULATIONS WITH SEMIEMPIRICAL QM AND MACHINE LEARNING METHODS**Pavlo O. Dral<sup>a</sup>, Mario Barbatti<sup>b</sup>, and Walter Thiel<sup>a</sup><sup>a</sup>Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,  
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We are currently developing next-generation semiempirical quantum mechanics (SQM) methods for fast and more accurate calculation of quantum mechanical (QM) properties, which are called orthogonalization- and dispersion-corrected methods (ODM<sub>x</sub>)[1]. They are based on the OM<sub>x</sub> methods[2] and include explicit D3 dispersion corrections throughout. The OM<sub>x</sub> methods are already among the most accurate SQM methods for calculating various ground- and excited-state properties[2–5]; with proper *a posteriori* dispersion corrections, they also describe noncovalent interactions well[2,4]. Furthermore, they have often been applied successfully in computationally efficient nonadiabatic excited-state dynamics studies[3]. Improvements in the ODM<sub>x</sub> methods include the integrated treatment of dispersion, changes in the formalism towards making it more universal, and a parameterization using state-of-the-art reference data, with emphasis on enhancing the description of excited states. The ODM<sub>x</sub> methods are thus expected to complement existing SQM methods as a useful tool for performing nonadiabatic dynamics.

We also explore how nonadiabatic excited-state molecular dynamics can be made more efficient with machine learning (ML) techniques[6]. The general idea is to reduce the number of demanding QM calculations required for nonadiabatic dynamics by using computationally efficient ML methods[6].

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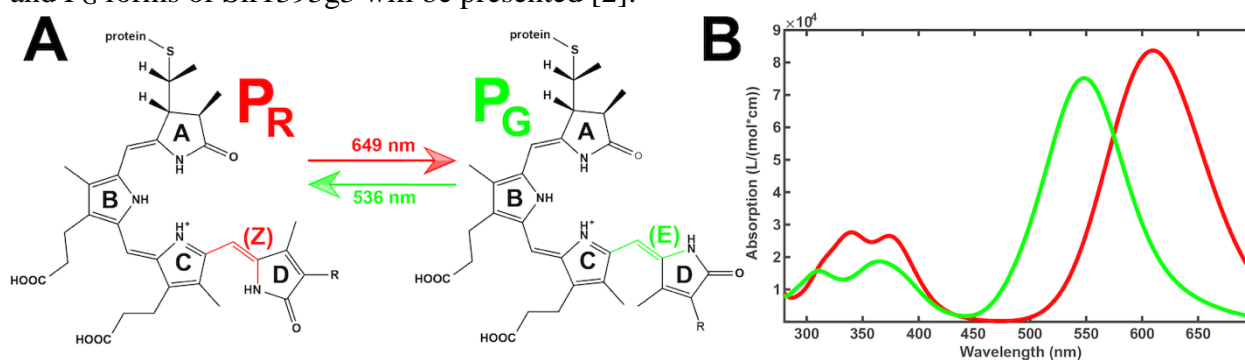
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## MULTISCALE MODELLING OF THE PHOTOPRODUCT TUNING PRESENT IN THE PROTOTYPICAL RED/GREEN CYANOBACTERIOCHROME PROTEIN SLR 1393g3

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Cyanobacteriochromes (CBCRs) are promising candidates for the use as photoswitches in biotechnological applications, owing to their photochromism, compactness and spectral diversity. In case of the CBCR Slr1393g3, the dark state absorbs red light ( $P_R$ ), whereas the photoproduct green light ( $P_G$ ) (Fig. 1 B) [1]. This hypsochromic shift of absorption from  $P_R$  to  $P_G$  is termed photoproduct tuning. The two forms can be interconverted into each other by light illumination. Slr1393 binds phycocyanobilin (PCB) as chromophore and crystal structures of both forms have been obtained recently. Comparing PCB from both structures shows that one double bond isomerization occurs during photoconversion (Fig. 1 A). In this contribution, results of hybrid quantum mechanics/ molecular mechanics (QM/MM) calculations of the  $P_R$  and  $P_G$  forms of Slr1393g3 will be presented [2].



**Figure 1:** (A) Reaction scheme of PCB photoisomerization, the wavelengths refer to the experimental lowest energy absorption maxima; (B) Simulated absorption for the  $P_R$  (red) and  $P_G$  (green) forms of PCB based on 100 snapshots for each form from DFTB2+D/AMBER molecular dynamics and computed with RI-ADC(2)/cc-pVDZ

In order to understand the photophysical properties and in particular the blue-shifted absorption of  $P_G$  relative to  $P_R$ , thorough QM/MM studies starting from the crystal structures were performed. Firstly, the structures are optimized, followed by classical molecular dynamics (MD) for thermalization and backbone relaxation. The snapshots for the excited state calculations are then generated via DFTB2+D/AMBER MD and the final spectrum is an average of the spectra from the different conformations of each form. The results of this approach are complemented with wave function and conformational analysis to understand the spectral tuning on the molecular level.

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**LOW-LYING ELECTRONIC TERMS OF THE DIATOMIC MOLECULES  
AB ((A = Sc – Ni, B = Cu/Ag/Au)**

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Diatomic molecules formed by atoms of d-block elements are building blocks for catalytically and photochemically active systems, for nanostructured materials, and for electronic devices that receive considerable attention in both fundamental and applied research, see e. g. [1] and references therein. Therefore, the detailed study of the electronic structure of such diatomic molecules, in both ground and low-lying excited states, is of great importance. We present a systematic study of low-lying electronic terms of heteronuclear diatomic molecules AB (A = Sc – Ni, B = Cu/Ag/Au, see figure below) [2]. Our approach is based on a scalar relativistic description using the Douglas-Kroll-Hess (DKH) Hamiltonian [3]. Subsequently, the Breit- Pauli Hamiltonian [4] is used for the perturbative inclusion of spin-orbit coupling. In Russell- Saunders coupling, the molecular electronic terms included in our study result from the lowest asymptote(s)  $A(^{2S+1}L) + B(^2S)$ , where the integer  $2S + 1$  ranges from 2 to 7 and L is either S, or D, or F. Complete potential energy curves (PEC) for several low-lying electronic terms of these molecules (both  $\Lambda - S$  and  $\Omega$  terms) have been obtained at the complete active space self-consistent field (CASSCF) and the multi-reference configuration interaction (MRCI) levels of theory. Standard sets of spectroscopic constants as well as dipole moment curves are also available. A group-theoretical method [5] has been used to determine all relevant molecular  $\Lambda - S$  or  $\Omega$  terms.

Group	3	4	5	6	7	8	9	10	11
	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu
									47 Ag
									79 Au

Figure 1: The elements involved in the present study of heteronuclear diatomic molecules AB.

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**A STOCHASTIC APPROACH TO THERMAL DENSITY FUNCTIONAL THEORY**

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Warm dense matter (WDM) is a phase characterized by temperatures of the order of 10,000 K and high nuclei densities. WDM is of high interest in many fields of physics, chemistry, planetary sciences and even industry: from giant gas planets, the earth's core, laser-heated solids and surfaces, and up to ignition of inertial confinement fusion capsules. Nowadays, using intense lasers, WDM properties can be investigated in the laboratory, thus requiring attention to theoretical research for interpretation and understanding of the results. In terms of tools for theoretical description it is considered a complex regime, being the intermediate between condensed matter physics (i.e., quantum description) and plasma physics (classic thermodynamics). WDM is often described theoretically using finite-temperature Kohn-Sham (KS) density functional theory (DFT) calculations with reasonably good agreement to experiments. These calculations in finite (non-zero) temperatures are, however, extremely expensive due to the large number of fractionally occupied KS orbitals involved in them. In fact, the computational cost exhibits exponential scaling with temperature. Orbital-free DFT is often considered a solution to this problem as it uses non-interacting kinetic energy approximations that depends directly on the electronic density, thus avoiding the use of KS orbitals. This approximation, however, has been known to be less accurate than the KS single particle wave function approach.

Stochastic methods, developed recently [1] appear to be a fitting approach to this scaling problem, since it is somewhat of an orbital free KS method. It uses the states occupation operator to calculate the energy, but skips the step of finding the orbitals and finds the electronic density by taking the trace of it using random orbitals. We introduce stochastic calculations of the canonical free energy. We further demonstrate our ability to calculate the zero pressure lattice constant (first order derivative) and the bulk modulus (second order derivative) of bulk silicon in different temperatures, despite the noise associated with the calculations. I will discuss the calculations' convergence as a function of temperature and system size as well as the computational effort that is required for it.

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**SINGLE-PHOTON COULOMB EXPLOSION OF METHANOL USING BROAD BANDWIDTH  
ULTRAFAST EUV PULSES**

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Experiment of Single Photon Coulomb Explosion (SPCE) of methanol using broad bandwidth ultrafast EUV pulses generated by high order harmonics generation was performed. SPCE channels breaking either C-O or C-H bonds were found.

As the SPCE occurs under low field conditions, it is valuable to neglect the ionizing field and perform *ab initio* calculations of Born Oppenheimer Potential Energy Curves(PECs) of C-O dissociation channel of doubly ionized  $\text{CH}_3\text{OH}^{2+}$ . We found that C-O breaking channel that was observed at the experiment is a result of coulomb explosion that begin at high excited state of methanol di cation.

## MULTICONFIGURATIONAL GAUSSIAN WAVEPACKET AND EHRENFEST SIMULATIONS OF ULTRAFast CHARGE SEPARATION IN DONOR-ACCEPTOR COMPLEXES

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Two different – but potentially complementary – approaches are generally followed for the theoretical simulation of non-adiabatic processes. On the one hand, the quantum dynamics community focuses on highly accurate simulations using advanced multiconfigurational techniques. However, most of this work is done for model Hamiltonians, including the coupling to vibrations that often relies on standard linear vibronic coupling models. Conversely, researchers from the electronic structure community tend to adopt a more accurate description of the potential surfaces using first-principles methodologies. These methods, though, are often interfaced with simple heuristic approaches for the description of nuclear dynamics, such as surface hopping and Ehrenfest dynamics, and are not able to properly describe coherence effects.

Against this background, we aim to develop and test variational Gaussian wavepacket based quantum dynamical methodologies that are compatible with the *on-the-fly* computation of the potential and its derivatives [1], and permit introducing different levels of approximation. Here, we report on two such methods that are designed to have an advantageous scaling with the dimensionality of the system.

The first technique is a novel two-layer extension of the Gaussian-based Multi-Configuration Time-Dependent Hartree (G-MCTDH) method, hence denoted 2L-G-MCTDH [2,3]. Here, the first layer is composed of flexible single particle functions, which are in turn expanded as combinations of low-dimensional frozen Gaussians. The second methodology is Multiconfigurational Ehrenfest (MCE), which is constructed by combining ensembles of classically moving Ehrenfest configurations with variational quantum coefficients. This method is thus capable to – at least partially – capture quantum coherence. This type of method was first proposed by Shalashilin [4,5] and later rederived as the semi-classical limit of the G-MCTDH method [6].

To assess the accuracy of these methods, we have tested both on a non-adiabatic model system, representing the dissociation of an exciton in an oligothiophene-fullerene complex [7,8]. Accurate quantum dynamical results showed that the charge dissociation process is ultrafast and is characterized by oscillatory features during a period of about 100 fs, which are due to electronic coherence [8]. In the present work, we compare the MCE and 2L-G-MCTDH dynamics with the benchmark results of Ref. [8], in order to establish the rate of convergence, scaling and accuracy of the methods for this model system. In the case of MCE, we also “measure” the level of coherence that is accounted for by the method as compared with the standard statistical Ehrenfest approach. Further, we carefully analyzed the algorithmic aspects of the different methods and optimized them so that both – at different levels of accuracy – are promising candidates for the study of high-dimensional non-adiabatic problems.

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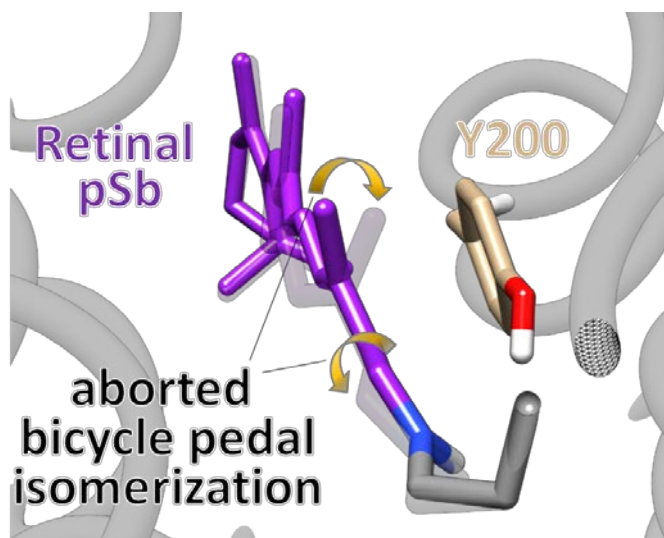
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**QM/MM EXCITED STATE DYNAMICS OF GREEN ABSORBING PROTEORHODOPSIN**

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The primary photochemical reaction of the green absorbing Proteorhodopsin is investigated by means of a hybrid quantum mechanics/molecular mechanics (QM/MM) approach. The homology model for the green absorbing Proteorhodopsin was derived from the crystal structure of blue-absorbing variant.[1] The nonadiabatic molecular dynamics was initiated from a ground state sampled trajectory. In the FC region the C13=C14 rotation is activated for 200 fs until the S<sub>1</sub>-S<sub>0</sub> transition occurs.[2] An “aborted bicycle pedal” mechanism of isomerization was observed involving a concerted rotation about C13=C14 and C15=N, with the latter being highly twisted but not isomerized. Further, the simulation showed an increased steric interaction between the hydrogen at the C14 of the isomerizing bond and the hydroxyl group at the neighbouring tyrosine Y200. Our simulations indicate that the retinal-Y200 interaction plays an important role in the overall outcome of the photoisomerization.

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**DOES N<sub>2</sub>O<sub>5</sub> REACT WITH PURE WATER?**

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The N<sub>2</sub>O<sub>5</sub> molecule plays an important role in atmospheric chemistry: its concentration in the atmosphere has significant implications on the abundance of ozone. In particular, the hydrolysis reaction of N<sub>2</sub>O<sub>5</sub> is a matter of investigation since there is experimental evidence for its occurrence in pure water, yet, there are no theoretical studies supplying a molecular level description of the mechanism, nor the time scales are clear.

In our approach, we give mechanistic insights for N<sub>2</sub>O<sub>5</sub> hydrolysis in pure water by performing *ab initio* molecular dynamics starting from transition state structures of different size clusters. The results suggest ultrafast hydrolysis (dozens of fs) for some of them. On the other hand, due to the energetics, these transition states are not easy to be reached, what its traduced in the long time scale for this reaction. We analyze the transition states' structures and properties, and we examine the possibilities of the potential reaction pathways starting from different water clusters.

**MOLECULAR DYNAMICS OF PHOTOINDUCED REACTIONS OF ACRYLIC ACID: PRODUCTS, MECHANISMS AND COMPARISON WITH EXPERIMENT**

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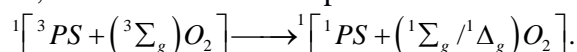
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The photochemistry of acrylic acid is of considerable atmospheric importance. However, the mechanisms and the timescales of the reactions involved are unknown. In this work, the products, yields and reaction pathways of acrylic acid photochemistry are investigated theoretically by molecular dynamics simulations on the  $\pi\pi^*$  excited state. Two methods were used to describe the excited state: the semi-empirical OM2/MRCI and the ab initio ADC(2). Over one hundred trajectories were computed with each method. A rich variety of reaction channels including mechanisms, timescales and yields, are predicted for the single potential energy surface used. Interestingly, although non-adiabatic transitions and spin-flip processes are possible, experimental results can be explained by using a single potential energy surface only. Main findings include: (1) Products predicted by the calculations are in good agreement with experiments. (2) ADC(2) seems to validate OM2/MRCI predictions on main aspects of mechanisms, but not on timescales. It is concluded that both semi-empirical and ab initio molecular dynamics simulations have useful advantages for the description of photochemical dynamics of carboxylic acids.

## A KINETIC MODEL FROM DIVIDE-TO-CONQUER PRINCIPLE TO STUDY SINGLET OXYGEN PHOTSENSITIZATION

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Thio-nucleobase derivatives have been often investigated as potential singlet oxygen photosensitizer (PS), and we have interpreted the absorption and decay to T<sub>1</sub> state of different thio-thymine derivatives using multireference quantum chemical methods,[1] and explained the intrinsic triplet decay dynamics of thio-nucleobases using a two-step mechanistic model.[2] Based on these works, now we consider the photosensitization reaction itself:



To investigate this weakly-coupled intermolecular energy-transfer process, we have built a kinetic model to calculate the reaction rates based on a divide-to-conquer principle. The complex system is splitted into sets of orthogonal coordinates, to compute diabatic couplings, activation energies, and reorganization energies at minimum computation costs.[3] Then we took 6-aza-2-thiothymine as PS, and investigated spatial factor of the reaction by calculating the rate along different directions and intermolecular distance of the PS-O<sub>2</sub> complex.[4] Based on these results, the triplet fusion mechanism of the photosensitization reaction is revealed by the interplay between charge-resonance-bridge approach, spatial factor of bimolecular system, and electronic structure of oxygen molecule during the reaction.<sup>5</sup>

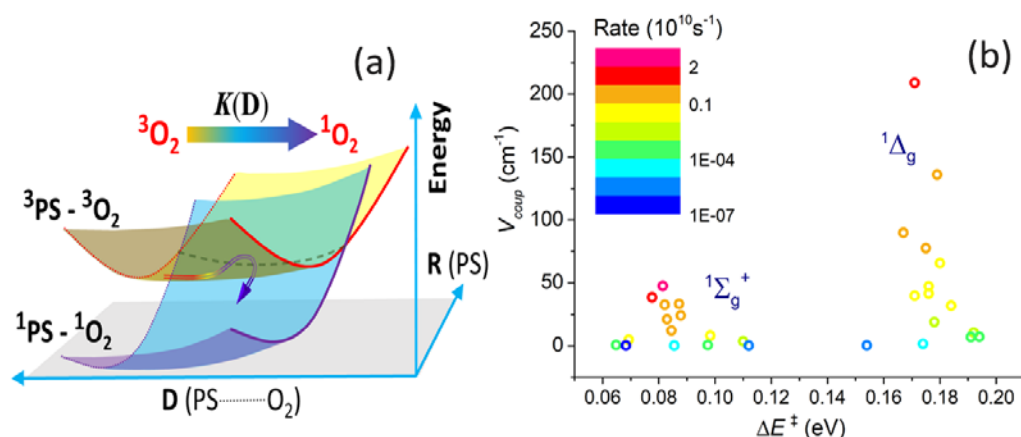


Figure 1. (a) Extension of the inverted Marcus model along the intramolecular and intermolecular coordinates in PS-O<sub>2</sub> complex; (b) Maximum reaction rates of <sup>1</sup>O<sub>2</sub> generation as a function of activation energy and diabatic coupling for all calculated directions.

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**A MIXED QUANTUM/CLASSICAL DYNAMICAL METHOD FOR NONADIABATIC  
PHOTOPHYSICS IN EXPLICIT SOLVENT MODELS.  
 $\pi\pi^*/n\pi^*$  DECAY OF THYMINE IN WATER AS A TEST CASE**

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The impact of the environment (e.g., solvent) on internal conversion (IC) processes can be quite significant, especially when the interaction of each coupled state with the solvent molecules is remarkably different. The theoretical simulation of the process, which should resort, in principle, to quantum dynamics, becomes very challenging if the solvent molecules are explicitly included in the model. In this contribution, we face such a problem, and present a novel mixed quantum classical dynamical method [1] to include solvent effects on IC processes. Concretely, in the method, all the solute degrees of freedom are propagated following nonadiabatic quantum dynamics using the multiconfigurational time-dependent Hartree (MCTDH) as implemented in Quantics code [2], while the motion of an explicit solvent model is described by an ensemble of classical trajectories, run with a molecular dynamics engine: Gromacs [3]. We account for the mutual coupling of the solute and solvent dynamics, within a mean-field framework, solving simultaneously the coupled quantum and classical equations of motions [4]. As a test case we investigate the ultrafast  $\pi\pi^* \rightarrow n\pi^*$  decay of thymine in water. The explicit treatment of the solvent allows us to identify key structural solvent rearrangements along the process, namely, the water librational motions that stabilize the most populated state. Interestingly, such effects have a remarkable impact on the IC yield already on the 50 fs time scale.

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**PHOTO-IONIZATION INDUCED FRAGMENTATION DYNAMICS OF ACETYLENE**

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Absorption of ultrashort laser pulses often induce ultrafast physical and chemical processes in molecules and ions. Acetylene, being the simplest molecule with a CC triple bond, serves as a prototypical system and has motivated many experimental and theoretical studies in recent time [1, 2, 3]. In spite of being rather small in size, its rich electronic structure has made acetylene cation even more appealing to the theorists, as accurate theoretical methods can be employed to achieve a clearer understanding of the non-adiabatic dynamics, which are otherwise not feasible for larger biomolecules. Being motivated by a recent pump-probe experiment, where acetylene is photo-ionized with a pump pulse in the extreme ultraviolet (XUV) spectral range and subsequently probed by a time-delayed infrared (IR) pulse [4], we have investigated the ultrafast fragmentation dynamics of the acetylene cation theoretically. Static PES scans at SA-CASSCF/XMS-CASPT2/cc-pVTZ level with a full-valence (9/10) active space uncover the influence of the different symmetry-adapted nuclear displacements on the PESs and provide hints on their relative importance on the overall non-adiabatic dynamics. To achieve a more complete understanding, unbiased on-the-fly molecular dynamics simulations have been performed with Tully's fewest switches surface hopping (FSSH) method, while the underlying electronic structure problem was solved at SA(3)-CASSCF/6-31G\*\* level with a (9/8) active space. Along with the already reported acetylene-vinylidene isomerization [2, 3], C-H dissociations have also been observed which occur at three distinct time scales, which correlate with the experimental C<sub>2</sub>H<sup>+</sup> ion yield as a function of the pump-probe delay. Overall, the comparison of the experimentally recorded fragmentation dynamics with the excited-state non-adiabatic dynamics simulations reveal several ultrafast nonradiative relaxation channels and have demonstrated the possibility to control the branching ratios with tailored laser pulses in a conical intersection induced dynamics, in general.

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**CHARGE TRANSFER IN *DROSOPHILA* CRYPTOCHROME:  
INVESTIGATING THE DYNAMICS OF COMPLEX DISSIPATIVE QUANTUM SYSTEMS VIA  
MACGIC-QUAPI**

Martin Richter and Benjamin P. Fingerhut

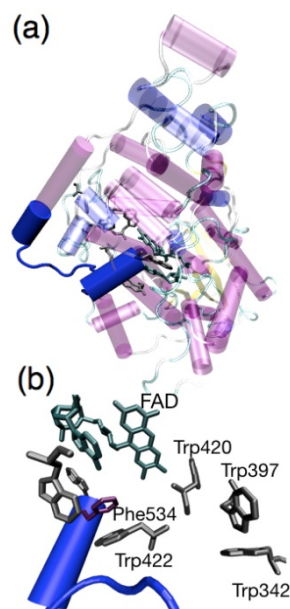
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Despite the recent growth of computational resources, the dynamics of dissipative quantum systems still presents a challenge for systems of biological relevance that typically include a large number of coupled exciton and charge transfer states. Moreover, the ‘sluggish’ protein environment imposes non-Markovian system-bath memory times of substantial length. The **quasi-adiabatic propagator path integral (QUAPI)** method [1] provides numerical efficiency due to a carefully chosen adiabatic reference Hamiltonian where non-adiabatic corrections are accounted for in the time-nonlocal influence functional. The QUAPI method allows for the numerical exact solution of quantum dissipative dynamics but is limited by the exponentially scaling with growing memory time and system size.

We present a novel approximate method that relies on **mask assisted coarse graining** of Feynman-Vernon **influence coefficients** (MACGIC-QUAPI) [2] and allows for a substantial reduction of computational effort while quickly converging to exact results. The MACGIC-QUAPI method thus provides access to the regime of biological significant long-time bath memory on the order of hundreds of propagation time steps.

The performance is demonstrated on microscopically derived model Hamiltonians of multi-step electron transfer dynamics in dCRY, a flavoprotein that undergoes ultrafast charge separation upon electronic excitation (cf. Figure inset). [3] Site energies, inter-chromophore couplings and fluctuation dynamics were parametrized by first principles QM/MM (TD-DFT(BNL)/amber ff14SB) trajectory simulations. The simulated dynamics along different charge transfer pathways is discussed and the importance of the protein electrostatic environment on pathways is elucidated upon *in silico* point mutations of key amino acid residues.



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### 3-D ELECTRONIC STRUCTURE ON THE EXCITED STATES MANIFOLD OF NORBORNADIENE-QUADRICYCLANE

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The [2+2]photo-cycloaddition of Norbornadiene is one of the most promising reactions for the purpose of stocking solar or thermal energy. The molecule is capable to store a significant amount of energy ( $\Delta H = 89$  kJ/mol) and several methods to exploit the inverse reaction have already been developed and are readily available [1,2].

Studies on computational models that statically explore the electronic structure propose different photoreaction paths [3], but the underlying dynamical mechanism still remains unknown, due to the sheer size of the computational problem: the challenge presented by the multiple electronic excited states and the several nuclear degrees of freedom that participate in the photoreaction. In this work we present the complete active space (CASSCF) electronic structure of Norbornadiene on a 3- dimensional grid along the main reaction coordinates using a manifold of 14 electronic states and an active space of 4  $\pi$ -electrons in 8 orbitals. The multiconfigurational computations show a complicate potential energy hypersurface topology, with many Rydberg/Valence states in a range of 3-4 eV that cross and interact from the Frank-Condon region all the way to the products.

The 3-D potential energy surfaces are suitable to run grid based coupled electron-nuclei quantum dynamics, to properly compute the wavepacket propagation and follow the reaction path after the excitation of the system. The aim of the work is to better understand the reaction mechanisms and to be able to control the efficiency of the cycloaddition.

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## Classical Molecular Dynamics Simulation of Electronically Nonadiabatic Processes via a Symmetrical Quasi-Classical Windowing

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A symmetrical quasiclassical (SQC) windowing model for “quantizing” the electronic harmonic oscillator degrees of freedom (DOF) in the Meyer-Miller (MM) classical vibronic (nuclear + electronic) Hamiltonian has previously been shown to be a simple yet viable approach for extending classical molecular dynamics (MD) simulation to the treatment of electronically nonadiabatic processes. The SQC/MM approach provides a fully classical treatment of the electronic DOF in nonadiabatic dynamics thereby maintaining dynamic consistency with the standard classical MD treatment of the nuclear DOF and the likely possibility of linear scaling (or better) to treat very complex molecular systems. Moreover, the accuracy of the approach has been demonstrated in a variety of application contexts—e.g., gas phase reactive scattering and photochemistry models, as well as condensed-phase spin-boson-type models of dissipative electronic dynamics—and the methodology is seen capable of quantitatively describing quantum coherence effects in regimes of extremely strong to extremely weak coupling between the electronic states, including the de-coherence of such effects as modulated by coupling to the nuclear DOF. Presented here are recent further developments in the SQC/MM approach including: (i) a new universally superior SQC windowing model which elegantly handles the limit of very weak-electronic coupling, (ii) an extension of the SQC model for extraction of the full electronic density matrix at no cost relative to a standard SQC/MM calculation, (iii) a new “kinematic” adiabatic representation of MM vibronic dynamics which totally eliminates the need to calculate second-derivative couplings (as appear in the adiabatic multi-state/channel Schrödinger Eq.) when it is desirable to use *ab initio* Born-Oppenheimer potential energy surfaces in realistic simulations, (iv) a recent SQC/MM treatment of exciton dynamics in *ab initio* parameterized models of semiconducting polymers, and (v) exploration of the issue of long-time detailed balance and equilibrium stability in classical MM vibronic dynamics.

**DOUBLE PHOTOIONIZATION OF  $\text{H}_2\text{O} + \text{F}^-$  IN A STRONG LASER FIELD: AN AB INITIO  
EXPLORATION OF EXCITED STATE DISSOCIATION PATHWAYS**

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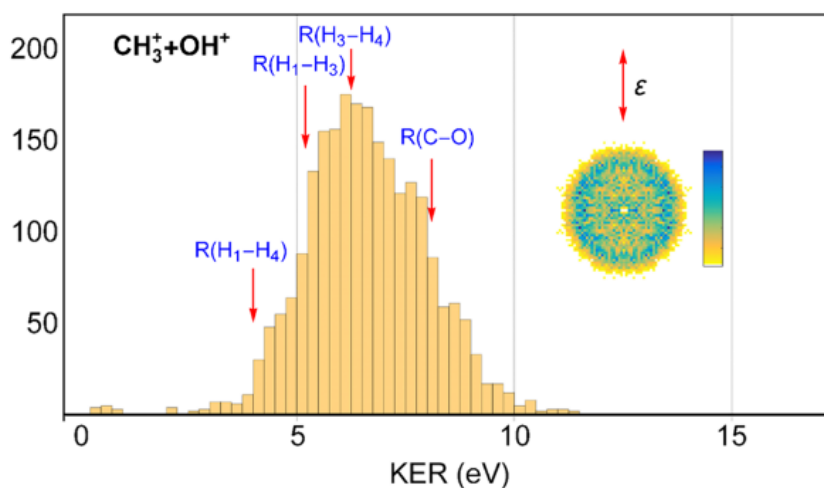
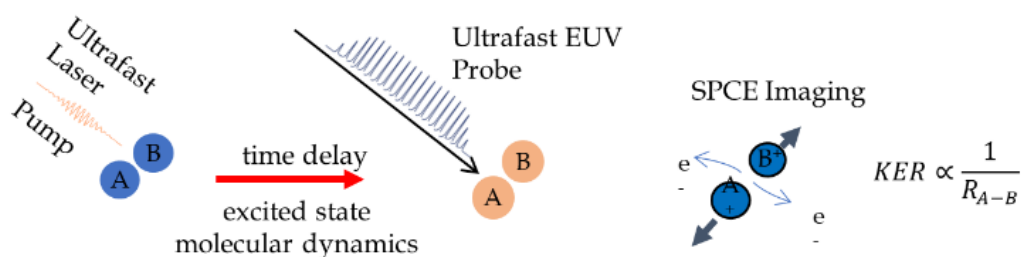
The interaction of exotic ions with water is of great importance due to its implications in combustion, atmospheric, and environmental processes. These computational studies are motivated by collaborative experimental work with Prof. Daniel Strasser's research group. Experimentally,  $\text{H}_2\text{O} + \text{F}^-$  is doubly ionized in an intense laser field ( $\sim 10^{14}$  W/cm<sup>2</sup>) to form  $\text{H}_2\text{O} + \text{F}^+$ , which dissociates into the following product pairs:  $\text{H}_2\text{O}/\text{F}^+$ ,  $\text{H}_2\text{O}^+/\text{F}$ ,  $\text{OH}/\text{FH}^+$ ,  $\text{OH}^+/\text{FH}$ ,  $\text{H}_2\text{F}/\text{O}^+$ , and  $\text{H}_2\text{F}^+/\text{O}$ . The presence of  $\text{FH}$ ,  $\text{FH}^+$ ,  $\text{H}_2\text{F}$ , and  $\text{H}_2\text{F}^+$  products indicate a rearrangement of geometry to form H-F bonds after electron detachment. Here we present a computational and theoretical study to better understand the geometric rearrangement and dissociation pathways in these processes. Early studies of the system using ab initio molecular dynamics (AIMD) with on-the-fly density functional theory (B3LYP/cc-pVDZ) in the singlet ground state indicate that much of the dissociation processes occur in excited states of the system, as the dissociation product distribution was quite different from that which was found experimentally. Explorations into the excited states of the system show an "electronic soup" of states, indicating an extremely challenging system to understand. Here we present high-level ab initio excited state calculations (EOM-EE-CCSD(dT)/cc-pVTZ) along four approximate dissociation coordinates. We find that each of these one-dimensional slices through the "electronic soup" gives rise to a band structure in the dissociation limit representing the ground and excited states of the dissociation products. The density of states and relative energies for each product predict a product distribution that compares favorably with the experimental results. The computational results have also proven useful for understanding the Franck Condon region and its connections to the dissociation products. In the future we aim to pursue AIMD in excited states with the inclusion of surface hopping.

## SINGLE PHOTON COULOMB EXPLOSION OF METHANOL USING ULTRAFAST EUV PULSES

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Ultrafast EUV pulses, produced by high-order harmonics generation (HHG), are used to induce single photon Coulomb explosion (SPCE) of isolated methanol molecules. Using 3D coincidence fragment imaging, SPCE channels are disentangled from the dissociative ionization background, providing angularly resolved kinetic energy release (KER) measurements of the different SPCE channels.<sup>1</sup> The most dominant channel: CH<sub>3</sub><sup>+</sup> + OH<sup>+</sup>, exhibits prompt dissociation of the C-O bond. Also observed are structural rearrangement of the parent dication, producing H<sub>3</sub><sup>+</sup> + COH<sup>+</sup> and H<sub>2</sub><sup>+</sup> + HCOH<sup>+</sup> channels. Furthermore, a proton migration channel producing CH<sub>2</sub><sup>+</sup> + H<sub>2</sub>O<sup>+</sup> is reported.

Our experimental data is directly compared with previous intense field coulomb explosion (IFCE) studies of methanol using intense near-IR pulses<sup>2</sup>, as well as with ab-initio calculations.<sup>1</sup> Furthermore, we will present time resolved measurements revealing how the SPCE dynamics are modulated by a time delayed intense near IR pulse in a pump-probe experiment.



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## Stochastic Basis Set Approach to Density Functional Theory

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Although density functional theory (DFT) is routinely used to study the properties of a wide range of molecular and crystal systems, its utility for studying large systems in materials science and biology is limited. This is due to the fact that the DFT computational effort, in terms of memory and CPU time, typically scales quadratically with system-size. While linear-scaling methods have been developed by several groups, these are often of limited applicability due to the non-locality of the density matrix in many types of large systems. An alternative approach has been developed which circumvents the calculation of the density matrix and the Kohn-Sham (KS) orbitals using stochastic orbitals. These stochastic orbital methods are useful for orthogonal basis-sets, such as plane-waves and grids. In this work we extend the methods to non-orthogonal basis sets which are common in quantum chemistry. The greatest hurdle is to bypass the need to invert the overlap matrix and this we accomplish by using the preconditioned conjugate gradient method. The projection of orbitals on the occupied space is carried out using Chebyshev propagators. Various observables are treated as random variables with mean equal to the deterministic KS values and variance which drops when the number of random orbitals is increased in accordance with the central limit theorem. Results for the calculation of silicon clusters are shown.

**TIME AUTOCORRELATION OF ELECTRONIC WAVEFUNCTIONS: A NEW CONCEPT FOR DESCRIBING THE EVOLUTION OF ELECTRONIC STRUCTURE IN THE COURSE OF MOLECULAR DYNAMICS**

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We propose a new concept for analyzing changes in electronic structure in the course of ab initio molecular dynamics (AIMD) simulations using time autocorrelation functions of individual orbitals as well as the many-body electronic wavefunction. The approach offers new insights for the interpretation of dynamical events that arise in classical trajectories, which may not be easily revealed by consideration of nuclear snapshots alone. We apply the method to the shared proton vibration in the  $F\cdots(H_2O)$  complex, the reversible proton transfer in the water dimer cation and to the chemical reaction  $F + H_2O \rightarrow HF + OH$ . In all cases, we observe distinct features in the time autocorrelation functions when chemical changes occur. Future work will consider this approach in the context of nonadiabatic dynamics.

**POSSIBILITIES OF NON-ADIABATIC DYNAMICS USING COUPLED-CLUSTER**

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In this work, we enquire into the possibilities of formulating and implementing non-adiabatic dynamics using coupled-cluster (CC) wave-functions. The CC theory has been a well-established and most-popular electron-correlation method in quantum chemistry for description of ground and excited-electronic states [1]. Description of electronically excited states in and around the Franck-Condon region using a variety of CC methods has been deemed to be reasonably accurate for ionized, electron-attached and singly-excited states [2]. Currently, there exist methods and formulas to compute non-adiabatic couplings (NACs) in CC theory [3,4]. Here, we present arguments as to why these NACs are not entirely suitable to be employed within different methods of non-adiabatic dynamics. The key conceptual requirements of all CC theories, i.e., biorthogonality, non-hermiticity and its not-so-easily normalizable electronic wave-functions, are not accommodated in currently existing formulation of non-adiabatic dynamics. Our approach avoids focusing on computation of NACs as purely a problem of electronic structure, instead tries to obtain a more general and consistent formulation of non-adiabatic dynamics where all requirements of CC methods are properly built into this.

We show that this is easily achieved by altering the gauge transformation requirements of the non-adiabatic dynamics [5]. The consequences of this reformulation on computational procedures of electronic structure and non-adiabatic dynamics are assessed. A single-state biorthogonal formulation using gauge-theoretic principles is presented. This not only yields general gauge-invariant expressions for the diagonal Born-Oppenheimer correction [6,7], but allows one to identify restrictions placed by CC theory on adiabatic-to-diabatic transformation procedure. Our recent work on a thorough analysis of two-state case will also be presented.

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**NON-EQUILIBRIUM ELECTRON DYNAMICS ON-THE-FLY: ATTOSECOND EXCITATION IN LiH**

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We examine an effective way to formulate and perform quantum dynamical computations when the coherently excited electronic states are not in equilibrium with the nuclei. We describe the coupled nuclear wave packets, one on each adiabatic electronic state, on a grid of equidistant points with non-adiabatic coupling terms explicitly taken into account. Computing is on the fly as if we are running a classical trajectory while retaining full quantum coherence. We are able to do so by introducing a Hamiltonian that only couples near neighboring grid points. One can propagate only along few grid points relevant at this particular time and extend the grid by a finite number of points when the wave packets approach the edge of the grid. Thereby the very time demanding quantum chemical computations for each grid point are used only for the physically relevant regions of the internuclear distances. We use as an example the case of short-time (100fs) dynamics in LiH following the attosecond IR-pulse

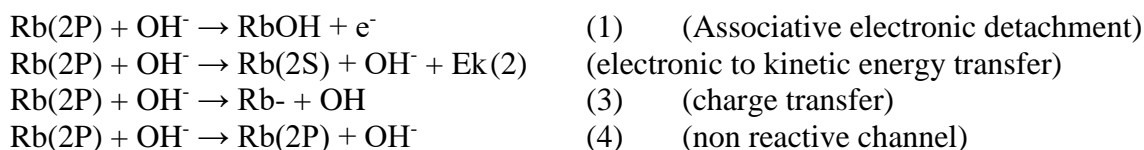
**THEORETICAL STUDY OF EXCITED STATE DYNAMICS IN A HYBRID TRAP: Rb(2P) + OH<sup>-</sup>**

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Sympathetic cooling of molecular ions using ultracold atoms is one of the possible way to reach the ultracold regime for molecular species. The co-trapping experiment of OH<sup>-</sup> and Rb is currently under investigation by the HAITrap team of the university of Heidelberg. Their experimental setup consist of a radio frequency ion trap with a magneto optical trap (MOT) that allows the OH<sup>-</sup> cloud to be immersed in a ultracold Rb cloud. In such environment, elastic and inelastic (including reactive) collisions can occur. In our previous work [1], we showed that the associative detachment channel Rb(2S)+OH<sup>-</sup> → RbOH+e<sup>-</sup> is energetically accessible and lead to a loss of OH<sup>-</sup> ions. Our results agrees with the first obtained experimental value [2]. In addition, we have also investigate the excited state channel Rb(2P)+OH<sup>-</sup> for which loss is to be expected [1,3]. Comparison between theoretical and experimental rate constant are under investigation for the Rb+OH<sup>-</sup> system [4].

Experimental evidences of interesting collision processes via excited channels in hybrid traps have been pointed out by several groups [5,6]. In the present study we extend our previous work [1] and investigate the potential energy surfaces (PES) of the low lying states of the RbOH<sup>-</sup> molecular anions. Several reaction are energetically accessible:



We used conventional ab initio approaches (MCSF/MRCI) to compute the relativistic PES of both the neutral and anionic low lying states. The PES exhibit numerous crossings and avoided crossings between anionic states. We carefully investigate the autodetachment region i.e the region where  $E_{\text{neutral}} < E_{\text{anion}}$  which leads to reaction (1). Using a capture model that takes into account appropriate long range interaction and Landau-Zener transition probabilities, we discuss the branching ratio between the different exit channels.

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**UNRAVELING OPEN-SYSTEM QUANTUM DYNAMICS OF NON-INTERACTING FERMIONS**

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The Lindblad equation is commonly used for studying quantum dynamics in open systems that cannot be completely isolated from an environment, relevant to a broad variety of research fields, such as atomic physics, materials science, quantum biology and quantum information and computing. For electrons in condensed matter systems, the Lindblad dynamics is intractable even if their mutual Coulomb repulsion could somehow be switched off. This is because they would still be able to affect each other by interacting with the bath. Here, we develop an approximate approach, based on the Hubbard-Stratonovich transformation, which allows to evolve non-interacting Fermions in open quantum systems. We have shown that this approach allows for accurate reconstruction of the dynamics of non-interacting Fermions in a Harmonic oscillator potential well, coupled to a bath through a specific Lindblad operator. We have also studied the dynamics of such Fermions in a double-well system, where a non-monotonic behavior of the energy can be seen when starting from an excited eigenstate of the Hamiltonian.

This development has the potential of technically enabling a time-dependent density functional approach for electron dynamics in open systems. And the combination of the present development with stochastic orbital methods for electronic structure is an exciting venue.