

## MO 11: Theoretical Approaches

Time: Tuesday 14:00–16:00

Location: PA 1.150

MO 11.1 Tue 14:00 PA 1.150

**Ab initio molecular dynamics of thiophene and its smaller oligomers: The interplay of internal conversion and intersystem crossing** — ●THOMAS SCHNAPPINGER<sup>1</sup>, PATRICK KÖLLE<sup>1</sup>, MARCO MARAZZI<sup>2</sup>, ANTONIO MONARI<sup>2</sup>, LETICIA GONZÁLEZ<sup>3</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department Chemie, Ludwig-Maximilians-Universität München — <sup>2</sup>TMS, SRSMC, Université de Lorraine-Nancy — <sup>3</sup>Institut für Theoretische Chemie, Universität Wien

Regarding their remarkable intrinsic properties thiophene derivatives and their oligomers are promising candidates of organic materials for technological applications for example as solar cells and light emitting diodes. A deeper understanding of the initial processes after photoexcitation and the subsequent relaxation mechanisms of oligothiophenes is an essential part to improve the performance of thiophene-based applications.

In this work we have investigated the relaxation processes after photoexcitation of thiophene, 2-2'-bithiophene and 2,2':5',2''-terthiophene. Using the SHARC ab initio surface-hopping algorithm in combination with the complete active space self-consistent field method and the time-dependent density functional theory we were able to simulate the whole relaxation including singlet and triplet states. After excitation fast ring-opening is leading the system to a degeneracy of singlet and triplet states. This situation enables fast intersystem crossing (ISC) and internal conversion (IC). The simulated relaxation pathway and the calculated time constants are in agreement with experiment.

MO 11.2 Tue 14:15 PA 1.150

**Conical Intersections and Electronic Coherence: A Novel Path to Steer Nuclear Motion** — ●CAROLINE ARNOLD<sup>1,2,3</sup>, ORIOL VENDRELL<sup>1,3,4</sup>, RALPH WELSCH<sup>1</sup>, and ROBIN SANTRA<sup>1,2,3</sup> — <sup>1</sup>Center for Free-Electron Laser Science, DESY — <sup>2</sup>Department of Physics, University of Hamburg — <sup>3</sup>The Hamburg Centre for Ultrafast Imaging — <sup>4</sup>Department of Physics and Astronomy, Aarhus University

Ultrashort pulses can be used to create coherent superpositions of electronic states in a molecule through photoexcitation. The electronic and nuclear dynamics that are triggered by the excitation are coupled in the vicinity of conical intersections (C.I.), and the Born-Oppenheimer approximation breaks down. This coupled motion provides a possibility for attochemistry, i.e., steering nuclear dynamics by controlling electronic degrees of freedom. In this work, the effect of nuclear dynamics and C.I.s on electronic coherences is investigated employing a two-state, two-mode linear vibronic coupling model. Exact quantum dynamical calculations are performed using the multi-configuration time-dependent Hartree method (MCTDH). It is found that the presence of a C.I. close to the Franck-Condon point can preserve electronic coherence to some extent. Additionally, the possibility of steering the nuclear degrees of freedom by imprinting a relative phase between the electronic states during the photoexcitation process is discussed. It is found that steering the nuclear wavepacket is possible given that a coherent electronic wavepacket embodying the phase difference passes through a C.I. A C.I. close to the Franck-Condon point is thus a necessary prerequisite for attochemistry.

MO 11.3 Tue 14:30 PA 1.150

**Non-adiabatic molecular dynamics with long-range corrected tight-binding DFT** — ●ALEXANDER HUMENIUK and ROLAND MITRIĆ — Julius-Maximilians-Universität Würzburg

The efficiency of tight-binding DFT permits non-adiabatic molecular dynamics simulation on larger systems as would be possible with full TD-DFT. However, large molecular assemblies pose new problems to DFT(B) and surface hopping, which are absent in smaller molecules: For weakly coupled chromophores, DFT with a local exchange-correlation-functional predicts unphysically low charge-transfer states. Also many degenerate electronic states appear due to excitations localized on the various identical subunits, which renders the adiabatic picture partly useless and causes numerical instabilities.

We present a software package which provides the electronic structure needed for running non-adiabatic molecular dynamics simulations at the level of charge-consistent tight-binding DFT. A long-range correction is incorporated to avoid spurious charge transfer states. Excited state energies, their analytic gradients and scalar non-adiabatic

couplings are computed using tight-binding TD-DFT. These quantities are fed into a molecular dynamics code, which integrates Newton's equations of motion for the nuclei together with the electronic Schrödinger equation. Non-adiabatic effects are included by surface hopping.

As an example, the program is applied to the optimization of excited states and non-adiabatic dynamics of polyfluorene.

MO 11.4 Tue 14:45 PA 1.150

**Improved virtual orbitals for charge transfer excitations in time dependent DFT** — ●ROLF WÜRDEMANN<sup>1</sup> and MICHAEL WALTER<sup>2,3</sup> — <sup>1</sup>FMF, Universität Freiburg, Freiburg, Germany — <sup>2</sup>FIT, Universität Freiburg, Freiburg, Germany — <sup>3</sup>IWM, Freiburg, Germany

Charge transfer excitations (CTE) are of high importance in photovoltaics, organic electronics and molecular and organic magnetism. Range separated functionals (RSF) can be used to correctly determine the energetics of CTEs within linear response time dependent density functional theory (TDDFT).

TDDFT becomes numerically very demanding on grids if hybrid or RSF are used due to the inclusion of exact exchange derived from Hartree-Fock theory.

We discuss a way to circumvent this problem by utilizing Huzinagas improved virtual orbitals (IVOs) that form an improved basis for this type of calculations. The CTE energetics may be even obtained by means of DFT ground-state calculations using IVOs.

MO 11.5 Tue 15:00 PA 1.150

**Comparison of theoretical methods for solving one-dimensional three-body problems** — ●LUCAS HAPP<sup>1</sup>, MAXIM A EFREMOV<sup>1</sup>, and WOLFGANG P SCHLEICH<sup>1,2</sup> — <sup>1</sup>Institut für Quantenphysik and Center for Integrated Quantum Science and Technology (IQ<sup>ST</sup>), Universität Ulm, D-89069 Ulm — <sup>2</sup>Hagler Institute for Advanced Study, Institute for Quantum Science and Engineering (IQSE), and Texas A&M AgriLife Research, Texas A&M University, College Station, TX 77843-4242, USA.

The well-known Born-Oppenheimer(BO) approach relies on the approximate separation of the dynamics of the light particles from that of the heavy ones which makes it suitable for systems with large mass-imbalance. On the other hand, the integral equation of Skorniakov and Ter-Martirosian (STM) provides in principle an exact description of a three-body system for any mass ratio.

In this presentation we compare both methods by solving one-dimensional three-body problems. We analyze a system of three particles with a *s*-wave resonant two-body interaction and compare the spectrum obtained via the STM method with well-known results for identical particles. In the case of a large mass-imbalance we contrast the spectrum with results of the BO approach. Finally, we extend this analysis to systems with a *p*-wave resonant two-particle interaction.

MO 11.6 Tue 15:15 PA 1.150

**Phase control of a complex Fano resonance** — ●NICOLA MAYER, MISHA IVANOV, and OLEG KORNILOV — Max Born Institut, Max-Born-Straße 2A, 12489 Berlin, Germany

A complex Fano resonance is a generic quantum mechanical system consisting of two or more autoionizing states coupled to a common continuum. This system may exhibit a counterintuitive quantum effect: an increase of the lifetime of one of these states for increasing strength of coupling to the continuum. Commonly known as interference stabilization, the effect was first proposed for laser-dressed Rydberg states [1]. In our previous work we showed that the effect takes place in the autoionization of a complex resonance in N<sub>2</sub> [2,3]. Here, we explore possibility of controlling such autoionization dynamics by changing the relative phase of two discrete states via laser-induced couplings to a third one. In particular, we show how, by inducing a phase shift of the coherent wavepacket of the two discrete states, one can control the resulting interference and selectively excite the long- or short-lived components of a complex resonance. We present theoretical calculations for transient absorption and photoelectron signals for this model system.

Reference:

[1] M.V. Fedorov, Atomic and free electrons in a strong light field.

Word Scientific, 1998. [2] M. Eckstein, N. Mayer et al., Faraday Discuss., DOI: 10.1039/C6FD00093B, 2016. [3] M. Eckstein, et al., Phys. Rev. Lett., 116, 153003, 2016.

MO 11.7 Tue 15:30 PA 1.150

**A simplified derivation of the reversal time for classical single domain ferromagnetic particles** — DECLAN BYRNE<sup>1</sup>, ●WILLIAM COFFEY<sup>1</sup>, YURI KALMYKOV<sup>2</sup>, and SERGEY TITOV<sup>3</sup> — <sup>1</sup>Department of Electronic and Electrical Engineering, Trinity College Dublin, Dublin 2, Ireland — <sup>2</sup>Laboratoire de Mathématiques et Physique (EA 4217), Université de Perpignan Via Domitia, F-66860, Perpignan, France — <sup>3</sup>Kotel'nikov Institute of Radio Engineering and Electronics of the Russian Academy of Sciences, Vvedenskii Square 1, Fryazino, Moscow Region 141120, Russia

It is shown, by exactly following the procedure of Kramers (H.A. Kramers, Physica 7, 284 (1940)) for escape of particles over potential barriers due to the shuttling action of the Brownian movement, how his original approach can be simply generalized to calculate the magnetization relaxation time of thermally agitated classical magnetic nanoparticles. His approach as generalized avoids the mathematical complexities associated with previous derivations. Moreover it leads to a simplified derivation of the magnetization reversal time in the

presence of spin-torque transfer.

MO 11.8 Tue 15:45 PA 1.150

**Effect of a magnetic field on molecule-solvent angular momentum transfer** — ●WOJCIECH RZADKOWSKI and MIKHAIL LEMESHKO — IST Austria (Institute of Science and Technology Austria), Am Campus 1, 3400 Klosterneuburg, Austria

Recently it has been shown that a molecule exchanging angular momentum with the surrounding bosonic solvent can be described in terms of the ‘angulon’ quasiparticle [1]. We now extended the angulon theory to the case of molecules possessing an additional spin-1/2 degree of freedom and studied the behavior of the system in the presence of a static magnetic field [2]. We showed that the exchange of angular momentum between the molecule and the bath can be altered by the field, even though the bath itself is not susceptible to the latter. In particular, we observed the possibility to control resonant emission of phonons with a given orbital angular momentum using a magnetic field.

[1] M. Lemeshko, Quasiparticle Approach to Molecules Interacting with Quantum Solvents, Phys. Rev. Lett. 118, 095301 (2017)

[2] W. Rzadkowski and M. Lemeshko, Effect of a magnetic field on molecule-solvent angular momentum transfer, arXiv:1711.09904