

MO 4: Theory 1: Molecular Dynamics

Time: Monday 14:00–16:00

Location: BEBEL SR144

Invited Talk

MO 4.1 Mon 14:00 BEBEL SR144

Ultracold Rydberg plasma formation in intense laser-cluster interactions: resolving the mystery of highly charged ions — ●THOMAS FENNEL — Institute of Physics, University of Rostock, Rostock, Germany

Many strong-field cluster experiments have demonstrated the emission of atomic ions in extreme ionization stages of $q \geq 20$, e.g. in Ref [1]. This observation is commonly interpreted as a proof for ultraefficient light absorption in laser-induced nanoplasmas, e.g. through transient resonant plasmonic heating in near-infrared pulses. However, it can be shown that electron removal from the cluster during the laser pulse - this outer ionization is what one would intuitively require for ionization - is insufficient to explain observed average charge states [2]. Striking evidence for this apparent contradiction is given by recent FEL experiments on large Xe clusters [3]. Via molecular dynamics (MD) simulations we show that (i) large clusters are only weakly outer ionized during laser excitation and (ii) relax to finite, ultracold Rydberg plasmas. Our explicit MD analysis reveals that DC-field induced frustrated recombination, i.e. field ionization of this peculiar cluster state in weak static external fields, is key to explaining the observed highly charged ions [4]. Routes for identifying Rydberg plasmas in clusters experimentally via electron spectroscopy will be proposed.

- [1] T. Döppner *et al.*, Phys. Rev. Lett. **105**, 053401 (2010)
- [2] T. Fennel *et al.*, Phys. Rev. Lett. **99**, 233401 (2010)
- [3] T. Gorkhover *et al.*, Phys. Rev. Lett. **108**, 245005 (2012)
- [4] C. Peltz, in preparation

MO 4.2 Mon 14:30 BEBEL SR144

A ring-polymer approach to electronically nonadiabatic dynamics within the mapping representation — ●JEREMY O. RICHARDSON and MICHAEL THOSS — Institut für Theoretische Physik und Interdisziplinäres Zentrum für Molekulare Materialien, Friedrich-Alexander-Universität Erlangen-Nürnberg

A new method [1] based on an extension of ring-polymer molecular dynamics is proposed for the calculation of thermal correlation functions in electronically nonadiabatic systems for which the Born-Oppenheimer approximation is not valid. The ring-polymer dynamics are performed using a continuous-variable representation of the electronic states within the mapping approach, such that the electronic and nuclear degrees of freedom are treated on an equal footing. Illustrative applications of the method to models for nonadiabatic processes with two electronic states coupled strongly to a nuclear mode show good agreement with exact quantum results for the dynamics over short to moderate times and reveal a systematic improvement over the classical implementation of the mapping approach (single-bead limit). Being based on trajectories, the method scales well with the number of degrees of freedom and will be applicable to simulate certain nonadiabatic processes in complex molecular systems.

- [1] J. O. Richardson and M. Thoss. *J. Chem. Phys.* **139**, 031102 (2013).

MO 4.3 Mon 14:45 BEBEL SR144

Coherent electron hole dynamics near a conical intersection — HENRY TIMMERS¹, ●ZHENG LI^{2,3}, NIRANJAN SHIVARAM¹, ROBIN SANTRA^{2,3}, ORIOL VENDRELL², and ARVINDER SANDHU¹ — ¹Department of Physics, University of Arizona, Tucson, AZ, 85721 USA — ²Center for Free Electron Laser Science, DESY, Notkestraße. 85, D-22607 Hamburg, Germany — ³Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

The motion of an electron hole (positive charge) across a molecule is vital for many chemical and biological phenomena. These quantum mechanical charge dynamics are mediated through complex electron-electron and electron-nuclear interactions. The investigation of such processes is challenging since it requires preparing and monitoring a coherent superposition of quantum states in the ionized molecule. We create a coherent hole wavepacket near a conical intersection in photoionized CO₂ and study the coupled nuclear-hole dynamics in real-time by employing a femtosecond extreme-ultraviolet (XUV) pump and near infrared (NIR) probe. We directly observe the oscillation of the electron hole density between σ and π character, driven by the coupled bending and asymmetric stretch vibrations of the molecule, and provide a detailed theoretical investigation of the observed phenom-

ena. We find that the degree of electronic coherence for the electron hole motion decreases with time due to Coulombic interaction of the excited photoelectron with the ion and we measure the rate of this decohering process.

MO 4.4 Mon 15:00 BEBEL SR144

Angle-resolved coarse-grained approach for molecules with high rotational mobility — ●THOMAS HEINEMANN¹, KAROL PALCZYNSKI², JOACHIM DZUBIELLA², and SABINE H. L. KLAPP¹ — ¹Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin — ²Institut für Physik - Komplexe Systeme, Humboldt Universität Berlin, Newtonstr. 15, 12489 Berlin

Defining an effective potential from a statistical mechanics point of view states back to Kirkwood [1], who introduced the potential of view force. For a two-molecule system it can be used as an effective pair potential, if the configuration entropy is removed. This entropy represents the number of atomic states for each macroscopic state. The resulting pair potential is temperature dependent.

A method is introduced, which is capable to calculate the angle-resolved effective pair potential using steered dynamics only. Results are compared to those from umbrella sampling. Constraints or restraints are only attached to the center of mass distance. In our investigations, we focused on coronene molecules, bearing no charges, as a benchmark system. The coarse-grained potential is then mapped onto a modified version of the Gay-Berne potential with minor improvements, such as contact distance [2]. A qualitative comparison between the all-atom and coarse-grained-fitted model is presented using many-particle simulations in the isotropic and hexagonal columnar regime.

- [1] J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).
- [2] F. de J. Guevara-Rodríguez and G. Odriozola, *J. Chem. Phys.* **135**, 084508 (2011).

MO 4.5 Mon 15:15 BEBEL SR144

A New Efficient Method for Calculation of Frenkel Exciton Parameters in Molecular Aggregates — ●PER-ARNO PLÖTZ¹, THOMAS NIEHAUS², and OLIVER KÜHN¹ — ¹Institut für Physik, Universität Rostock, D-18051 Rostock, Germany — ²Institut I - Theoretische Physik, Universität Regensburg, D-93040 Regensburg, Germany

The Frenkel exciton Hamiltonian models an aggregate as Coulomb-coupled monomers. In addition to the monomeric excitation energies the Coulomb coupling is an essential parameter for its description. It is shown that this coupling can be very efficiently calculated using time-dependent tight-binding based density functional theory (TD-DFTB), which offers a consistent way to describe the electronic structures of the monomers and the exciton coupling in the aggregate. Coulomb couplings are expressed in terms of self-consistently determined Mulliken transition charges, obtained in a sub-system-like formulation. This opens the possibility for a consistent on-the-fly determination of Frenkel exciton parameters in molecular dynamics simulations.

The performance of the method is studied by comparing to DFT-based calculations for a small test system of a formaldehyde oxime dimer. Applied to a perylene bisimide dimer it offers the possibility to explore the dependence of the Coulomb coupling on the intermolecular coordinates. This yields an interpretation of the observed biphasic aggregation (F. Fennel *et al.*, *JACS* 2013, doi:10.1021/ja409597x).

MO 4.6 Mon 15:30 BEBEL SR144

Linear dimensionality reduction in reactive quantum dynamics using reduced intrinsic reaction coordinates — ●JULIUS ZAULECK, SEBASTIAN THALLMAIR, MATTHIAS LOIPERSBERGER, and REGINA DE VIVIE-RIEDLE — Department Chemie, Ludwig-Maximilians-Universität München

The curse of dimensionality might be the most important obstacle for quantum dynamical calculations of molecules with more than only a few atoms. In the field of reaction dynamics this usually is approached by reducing the dimensionality of the problem. This reduction presents itself with some intrinsic problems, since one has to find dimensions which can be neglected without knowing the quantum dynamical propagation in full dimensions. A common method is to choose a number of internal coordinates which appear to describe most of the chemical reaction. Valuable information for this choice is often given by critical points along the reaction as well as the intrinsic reaction coordinate.

We present an alternative way by also using the intrinsic reaction coordinate and additional criteria to find a suited subspace of the full problem. Here it is demanded of the subspace to be a constant linear combination of the underlying Cartesian coordinates of the atoms. This pleasantly results in a diagonal kinetic energy operator. The subspace also has to be the best choice of all the analyzed subspaces. Possible criteria defining the quality of this choice will be presented along with examples.

MO 4.7 Mon 15:45 BEBEL SR144

Ultrafast Energy Transfer by Short and Intense THz Pulse

— •PANKAJ KUMAR MISHRA^{1,2,3}, ORIOL VENDRELL^{1,3}, and ROBIN SANTRA^{1,2,3} — ¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany — ²Department of Physics, University of Hamburg, Hamburg, Germany — ³Center for Ultrafast Imaging, University of Hamburg, Hamburg, Germany

Liquid water is the single most important medium in which chemical

and biological processes take place. The possibility to generate sub-ps and very intense THz pulses at free-electron lasers in full synchronization with the X-rays (XFEL) opens the possibility to time-resolved investigations of transient state of water and of molecular species dissolved in it.

Here, we investigated the response of liquid water to one-cycle, 200fs long THz pulses spectrally centered at about $100/\text{cm}^{-1}$ (~ 3 THz). At an intensity of about $10\text{E}10$ W/cm², the pulse transfers energy mostly to translational mode of the water monomers along the polarization axis of the electric field. In a time-scale of 500fs to 1ps the energy redistributes to hindered rotational modes first, and to intramolecular vibrations last. We also investigated the response of Phenol molecule to such THz pulse in vapor phase and in liquid water environment. This study implies that the energy supplied by the THz can potentially activate chemical processes long before the large amount of energy supplied leads to volume increase and vaporization of the medium. In this study, we have used CP2K package for Ab-Initio Molecular Dynamics.