

MO 13: Quantum Chemistry and Molecular Dynamics II

Time: Tuesday 14:00–16:15

Location: F 107

MO 13.1 Tue 14:00 F 107

Nonadiabatic Dynamics and Energy Transfer in Molecular Aggregates — MARCO SCHRÖTER and •OLIVER KÜHN — Institute of Physics, University of Rostock

The quantum dynamics of linear molecular aggregates in the presence of S_0 - S_1 and S_0 - S_2 transitions is investigated putting emphasis on the interplay between local nonadiabatic S_2 to S_1 deactivation via conical intersections and Frenkel exciton transfer. The theoretical approach combines aspects of the linear vibronic coupling and Frenkel exciton models. Dynamics simulations are performed for the linear absorption spectrum and the electronic state populations using the multiconfiguration time-dependent Hartree (MCTDH) approach. Exemplary calculations have been focussed on perylene bisimide J-type dimer and trimer aggregates taking into account four tuning and one coupling mode per monomer. This leads to a dynamical model comprising up to 7 electronic states and 15 vibrational modes. The unknown nonadiabatic coupling strength is treated as a parameter that is chosen in accordance with available absorption spectra. This leaves some flexibility, but leads to clearly distinguishable population dynamics.

MO 13.2 Tue 14:15 F 107

Implementation and first Applications of a Continuum Solvent Model for the DFT Package GPAW — •ALEXANDER HELD, MOHAMED HASSAN, and MICHAEL WALTER — FMF Uni Freiburg, Germany

Continuum solvent models provide a tool to transfer quantum mechanical (QM) calculations from the gas phase into the liquid phase with little extra computational costs. The solute is treated at the QM level, whereas the interaction with the solvent is described by a continuum model [1].

We present the implementation of a continuum solvent model with a smooth dielectric function [2, 3] for the density functional theory package GPAW [4]. The calculated solvation free energies for a test set consisting of ions and neutral organic molecules agree well with previous implementations.

As a first application, we compare spiropyran/merocyanine isomerization energies in the gas phase and in water with and without interaction with graphene.

[1] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.* 2005, 105, 2999-3093

[2] V. M. Sánchez, M. Sued and D. A. Scherlis, *J. Chem. Phys.* 131, 174108 (2009)

[3] O. Andreussi, I. Dabo and N. Marzari, *J. Chem. Phys.* 136, 064102 (2012)

[4] <https://wiki.fysik.dtu.dk/gpaw/>

MO 13.3 Tue 14:30 F 107

From the dimer to bulk – Chromium bonding revisited — •ROLF WÜRDEMANN and MICHAEL WALTER — Freiburger Materialforschungszentrum, Freiburg, Germany

The ground-state of the chromium dimer cation has a ferromagnetically aligned spin state, in strong contrast to the ground-state of the anti-ferromagnetically aligned neutral dimer.

We use density functional theory in various different approximations for the exchange-correlation functional on this numerically involved problem. We find that the revPBE and revTPSS approximations are able to predict the spin states of both systems correctly. Based on these results, we rule out the so called dimerization effect in Cr clusters as consequence of the LDA and PBE functionals and rationalize the structure of small chromium clusters from a new viewpoint.

MO 13.4 Tue 14:45 F 107

Relativistic time-dependent density functional calculations for the excited states of the cadmium dimer — •OSSAMA KULLIE — Institute de Chimie de Strasbourg, CNRS et Université de Strasbourg, Laboratoire de Chimie Quantique, Strasbourg, France. — Theoretical Physics, Department of Mathematics and Natural Science, University of Kassel, Germany. kullie@uni-kassel.de

Similar to our previous work on Zn2 dimer [1] we present in this work [2] a time-dependent density functional study for the ground-state as well the 20-lowest lying excited states of the cadmium dimer Cd2, we analyze its spectrum obtained from all electrons calculations

performed with time-dependent density functional for the relativistic Dirac-Coulomb- and relativistic spin-free-Hamiltonian as implemented in DIRAC-PACKAGE. Our result is very encouraging, especially for the lowest excited states of this dimer, and is expected to be enlightened for similar systems. The result shows that only long-range corrected functionals such as CAMB3LYP, gives the correct asymptotic behavior for the higher states. A comparable but less satisfactory results were obtained with B3LYP and PBE0 functionals. Spin-free-Hamiltonian is shown to be very efficient for systems containing heavy elements such as Cd2 in frameworks of (time-dependent) density functional without introducing large errors. A preliminary result for Hg2 dimer will be presented too. [1](open access) *J. of At. Mol. Opt. Phys.* (2012). [2] Accepted for publication in *Chem. Phys.* 2012.

MO 13.5 Tue 15:00 F 107

Core hole screening and decay rates of double core ionized first row hydrides — •LUDGER INHESTER¹, GERRIT GROENHOF², and HELMUT GRUBMÜLLER¹ — ¹Max Planck Institut für biophysikalische Chemie, Göttingen — ²Nanoscience Center, University of Jyväskylä, Finland

Because of their high intensity, X-ray free electron lasers provide the opportunity to create and probe double core ionized states in molecules. The decay of these multiple core ionized states crucially contributes to radiation damage in single molecule diffractive imaging experiments. Here we have studied the Auger decay after single and double core ionization in hydrides of first row elements by quantum mechanical ab initio methods[1]. In our approach the continuum wave function of the emitted Auger electron is expanded into spherical harmonics on a radial grid, centered on the core hole site. A systematic increase in the total double core ionized state decay rate is seen – markedly beyond the expected two-fold rate increase. We explain this enhancement in terms of the stronger valence shell contraction that screens the core hole.

[1] L. Inhester et al., *JCP* 136, 144304 (2012).

MO 13.6 Tue 15:15 F 107

Beyond the Born-Oppenheimer approximation in the spectroscopy of three-body systems — •RENÉ JESTÄDT¹, HEIKO APPEL¹, ALISON CRAWFORD URANGA², LORENZO STELLA², and ANGEL RUBIO^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Nano-Bio Spectroscopy group, Departamento Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, San Sebastián, Spain

In this work we utilize a Lagrange-Laguerre variational method [1] to construct highly accurate numerical solutions for non-relativistic three-body systems (Helium atom, H_2^+ , HD^+ and $dt\mu$ in 3D). Our approach does not rely on the Born-Oppenheimer approximation. This allows us to investigate the mass-dependence of optical dipole absorption spectra. For the molecular systems H_2^+ , HD^+ and $dt\mu$, we find pronounced mass dependence of the dipole transition matrix elements and the appearance of a new excitation close to the second ionization threshold that is not in a Born-Oppenheimer description of the molecular system. We compare our 3D results to one-dimensional model calculations and provide a mechanism in terms of non-adiabatic coupling elements.

MO 13.7 Tue 15:30 F 107

Exact electronic and nuclear time-dependent potential energy surfaces for attosecond electron localization in the dissociation of H2+ — •YASUMITSU SUZUKI¹, ALI ABEDI¹, NEPTA T. MAITRA², KOICHI YAMASHITA³, and EBERHARD K. U. GROSS¹ — ¹Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the City University of New York, 695 Park Avenue, New York, New York 10065, USA — ³Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

We study the electron localization dynamics in the dissociation of H2+ using a 1D model Hamiltonian. To this end we calculate the exact time-dependent potential energy surfaces (TDPEs) both for the electron and for the nuclei. The exact electronic TDPEs shows that the final electron localization is determined when the interatomic barrier becomes large and prohibits electron tunneling. The exact nuclear TD-

PES shows the mechanism of slowdown of the dissociation. It is found that the nuclear potential cannot be approximated by the weighted average of the quasi-static state potential energy surfaces, but can be approximated well by the transition between them. We show these two time-dependent potentials are the exact potential functionals of the time-dependent multicomponent density functional theory and can reproduce the whole phenomena of electron localization dynamics.

MO 13.8 Tue 15:45 F 107

Fluctuations in Laser-Aligned Molecules — ●YI-JEN CHEN^{1,2}, STEFAN PABST^{1,2}, ZHENG LI^{1,2}, ORIOL VENDRELL¹, and ROBIN SANTRA^{1,2} — ¹Center for Free-Electron Laser Science (CFEL), DESY, Hamburg, Germany — ²Department of Physics, University of Hamburg, Hamburg, Germany

Aligning molecules is essential for probing and controlling various kinds of physical processes and chemical reactions. Therefore, the field of laser-aligned molecules has been of much and growing research interest in the past decade. In the present study, we address the following fundamental question: To what degree is it possible to describe laser-induced molecular alignment using classical mechanics? It is known that the appearance of periodic revivals in impulsive alignment is a purely quantum-mechanical phenomenon. However, the alignment dynamics during and right after the laser pulse has been shown to have strongly classical features. The observable generally used for describing molecular alignment is $O = \cos^2 \theta$, where θ is the angle between the figure axis of the molecule and the direction of the laser polarization. Conventionally, the degree of alignment is characterized by the expectation value $\langle O \rangle$. Here, we investigate fluctuations in molecular alignment by calculating the uncertainty ΔO . Specifically, we computationally investigate an ensemble of laser-aligned bromine molecules. The time evolution of the ensemble is numerically determined by quan-

tum as well as classical simulations under various temperatures and laser-pulse parameters. By comparing the quantum to the classical results, we assess the role of quantum fluctuations in molecular alignment.

MO 13.9 Tue 16:00 F 107

Ultrafast Energy Transfer to Liquid Water by Short and Intense THz Pulses — ●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 — ³Centre for Ultrafast Imaging, University of Hamburg, Hamburg, Germany

Water is the most common solvent in which chemical reactions take place. In recent years it is becoming clear that low frequency modes in the THz domain play an important role in the structure and dynamics of water. Recently, the possibility to generate sub-ps and very intense THz pulses at free-electron lasers in full synchronization with the x-rays opens the possibility to time-resolved investigations of transient states of water and of molecular species dissolved in it. Here, we investigate the response of liquid water to one-cycle, 200fs long THz pulses spectrally centered at about 3THz. The THz pulse does not target any particular modes of the liquid. At an intensity of about 10^{10} W/cm⁻², we find that the pulse transfers energy mostly to translational modes 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. This 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.