MO 9: Theory 2: Molecular Dynamics & Quantum Chemistry

Time: Tuesday 14:00–16:00   Location: BEBEL SR144

MO 9.1   Tue 14:00   BEBEL SR144
Simulation of time-resolved pump-probe IR spectra —
•Matthias Wohlgemuth and Roland Mitric — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Würzburg, Deutschland

We present a new approach for the simulation of time-resolved pump-probe infrared (TRIR) spectra based on the molecular dynamics (MD) "on-the-fly". The simulations are carried out in the frame of density functional theory and have been combined with the Wigner phase space approach for the simulation of pump-probe spectra.

Our method was applied to the C=O to N-H water migration motion around a peptide linkage, which is observed by experimental TRIR spectroscopy. Our simulations reproduce all details of the measured time-resolved infrared spectra. The simulations show two concurrent mechanisms involved in the migration process, which were previously not derived from conventional stand-alone MD simulation and the simple experimental interpretation based on classical rate-equation analysis.

Altogether, our methods are uniquely suitable for the simulation of TRIR spectra in complex systems and provide a valuable help in the interpretation of the state-of-the-art experiments and it emphasizes the importance of the theoretical validation of TRIR experiments.

MO 9.2   Tue 14:15   BEBEL SR144
Nonlinear Absorption Dynamics Using Field-Induced Surface Hopping: Zinc Porphyrin in Water — •Merle I. S. Röhr[1], Jens Petersen[2], and Roland Mitric[2] — [1]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — [2]Institut für Physikalische und Theoretische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg

The field-induced surface hopping (FISH) method [1] for the simulation and control of light-induced nonadiabatic dynamics in complex systems will be introduced and applied to the investigation of nonlinear absorption processes [2]. For this purpose, a systematic comparison of the FISH approach with exact quantum dynamics simulations on a multistate model system is provided, and it is demonstrated that FISH allows for accurate simulations of nonlinear excitation processes including multiphoton electronic transitions. The applicability of our method to complex molecular systems is illustrated by simulating the linear and nonlinear laser-driven dynamics in zinc (Zn) porphyrin in the gas phase and in water. To this end, the FISH approach is connected with the quantum mechanical-molecular mechanical approach (QM/MM) [2] which is generally applicable to large classes of complex systems. Our findings that multiphotonic processes increase the population of higher excited states of Zn porphyrin in the nonlinear regime provides a means for manipulating excited-state properties, such as transient absorption dynamics and electronic relaxation.

1. R. Mitric et al., Phys. Rev. A 79, 053416 (2009).
2. M. I. S. Röhr et al., ChemPhysChem 14, 1377 (2013).

MO 9.3   Tue 14:30   BEBEL SR144
Protein long timescale simulations using kinetic Monte Carlo — •Mateusz Marianski, Carsten Baldauf, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, Germany

The time scales that govern the structure formation and dynamics of biopolymers are hardly accessible with established molecular dynamics (MD) simulations. Too short simulation times may even lead to misinterpretation of the data, as previously shown for the dynamics of the amyloid beta peptide (Lin *et al. Biophys. J.* **2012**, 102, 315).

This project aims at the development of an universal kinetic Monte Carlo (kMC) protocol based on a separation of short- (bonded) and long-range (non-bonded) contributions as an alternative sampling technique applicable to peptides. Such kMC model of the structural dynamics of a molecule requires two components: (1) a library of accessible conformations, and (2) the transition states between these conformers. For the development, we turn to classical force fields, especially since we can compare to results from brute-force parallel-tempering MD sampling.

In this contribution, we will present results for polyalanine peptides of different lengths. The conformational library is constructed using structure-search algorithms and refined with clustering techniques. The resulting conformational basins are connected by transition states

which later are used, by applying harmonic transition state theory, to estimate rates that are the input to the kMC simulation. Here we compare these results to brute-force sampling based on MD simulations to test the potential of such a protocol.

MO 9.4   Tue 14:45   BEBEL SR144
Non-Adiabatic Molecular Dynamics with Conditional Wave Functions — •Guillermo Albareda[1], Heiko Appel[1], Ignacio Franco[2], Ali Abedi[3], and Angel Rubio[1,4] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany — [2]Chemistry Department, University of Rochester, USA — [3]Max-Planck Institut für Mikrostrukturphysik, Germany — [4]Nano-Bio Spectroscopy group and ETSF Scientific Development Center, Spain

A rigorous trajectory-based approach to treat the coupled electron-nuclear motion in terms of conditional wave functions is presented. By projecting the Schrödinger equation on the actual configuration of an infinite set of nuclear trajectories, an ensemble of conditional electronic equations of motion is obtained. These equations do not rely on any tracing-out of degrees of freedom and their propagation does not require a prior knowledge of the involved potential-energy surfaces. Using an exact factorization of the full molecular wave function, we establish a formal connection with the recently proposed exact potential energy surfaces [1]. This connection is used to gain insight from a simplified propagation scheme, which is demonstrated to capture non-adiabatic dynamics accurately in the limit of weak nuclear splitting. For pronounced branchings, we show how this simple algorithm partially captures dynamical steps between adiabatic surfaces [2] and discuss a route to improve the method. [1] A. Abedi, N. T. Maitra, and E. K. U. Gross, Phys. Rev. Lett. **105**, 123002 (2010). [2] A. Abedi, F. Agostini, Y. Suzuki, and E. K. U. Gross, Phys. Rev. Lett. **110**, 263001 (2013).

MO 9.5   Tue 15:00   BEBEL SR144
Temperature-Dependent Absorption Spectra of Molecular Aggregates: Influence of non-Markovian Environment — •Gerhard Ritschel[1], Walter T. Strunz[2], and Alexander Eisfeld[1] — [1]Max-Planck Institute for the Physics of Complex Systems, Dresden — [2]Technical University Dresden

We investigate theoretically absorption spectra of complexes of chromophores interacting electronically via resonant transition dipole-dipole interactions. Often the electronic excitation couples to vibrational degrees of freedom in a strongly frequency-dependent way, leading to non-Markovian effects. We developed a new approach based on non-Markovian quantum state diffusion, with which it is possible to non-perturbatively calculate optical spectra. The approach explicitly takes the coupling to peaked spectral densities into account. The method is highly effective, allowing systematic investigations of large parameter spaces. We study absorption spectra of linear chains of identical monomers in the J-aggregate limit, and identify several distinct regimes for the temperature-dependent widths of these absorption specta.

MO 9.6   Tue 15:15   BEBEL SR144
A route via X-ray emission spectroscopy for monitoring electron configuration during nuclear dynamics in excited molecules — •Hossein Ebadi[1] and Simone Techert[1,2,3] — [1]Structural dynamics of (bio)chemical Systems, MPI-BPC, Am Fassberg 11, 37077 Goettingen, Germany — [2]Structural dynamics of (bio)chemical Systems, DESY, Notkestrasse 85, 22607 Hamburg, Germany — [3]Institute for X-ray physics, Goerg-August University,37077 Goettingen, Germany

Core-hole spectroscopy, sensitive to the electron configuration of molecules and solids [1,2], has been traditionally used to get insight in the structure of matter from molecular to macroscopic scales. In this study, the main characteristics of azobenzene isomers, as a benchmark system for fundamental and applied studies in molecular electronics [3,4], are identified in the X-ray emission spectrum. The electron configuration has been examined using the shape of orbitals and via their contribution in the excited-state of UV-Vis regime. By applying an appropriate coordinate-to-time mapping [5,6], the change of electron configuration during the isomerization can be probed using time-resolved X-ray emission spectroscopy. [1] F. de Groot and A. Kotani, "Core

level spectroscopy of solids", CRC Press, London, New York (2008). [2] I. Josefsson et al., J. Phys. Chem. Lett., 3, 3565 (2012). [3] J. M. Mativetsky et al., J. Am. Chem. Soc., 130, 9192 (2008). [4] A. Toniolo et al., J. Chem. Phys., 123, 234308 (2005). [5] H. Ebadi, C. H. Keitel, and K. Z. Hatsagortsyan, Phys. Rev. A, 83, 063418 (2011). [6] H. Ebadi, J. Opt. Soc. Am. B, 29, 2503 (2012).

MO 9.7　Tue 15:30　BEBEL SR144

A Relativistic Time-Dependent Density Functional study of the excited states of the mercury dimer — ●Ossama Kullie — Institute for Physics, Department of Mathematics and Natural Science, Uni of Kassel. And Institute de Quantique Chimie, Uni Strasbourg, 4, rue de Blais Pascal, 67000 Strasbourg, France.

In this talk I present a time-dependent density functional (TDDFT) study for the ground-state as well as the excited states corresponding to the $(6s^2 + 6s6p)$, $(6s^2 + 6s7s)$ and $(6s^2 + 6s7p)$ atomic asymptotes for the mercury dimer Hg2 [1]. I give analyze for its spectrum obtained from all-electron calculations performed with the relativistic Dirac-Coulomb and relativistic spinfree Hamiltonian. A comparison with the literature is given as far as available. Our result is excellent for the most of the lower excited states and very encouraging for the higher excited states, it shows generally good agreements with experimental results and outperforms other theoretical results. This enables us to give a detailed analysis of the spectrum of the Hg2 including a comparative analysis with the lighter dimers of the group 12, Cd2 and Zn2, especially for the relativistic effects, the spin-orbit interaction, and the performance of CAMB3LYP functional approximation and is enlightened for similar systems. [1] submitted to J. Chem. Phys.

(2013).

MO 9.8　Tue 15:45　BEBEL SR144

Exact factorization of the electron-nuclear wave function: Is the molecular Berry phase an artefact of the Born-Oppenheimer approximation? — ●Seung Kyu Min[1,2], Ali Abedi[1], Kwang S. Kim[2], and E.K.U. Gross[1] — [1]Max-Planck-Institut für Mikrostrukturphysik Weinberg 2, D-06120 Halle, Germany — [2]Pohang University of Science and Technology, Korea

The Born-Oppenheimer (BO) potential energy surfaces (PESs) provide an intuitive picture to analyze and interpret molecular processes. In this context, conical intersections (CIs) of the BO PESs are particularly important. They provide pathways for radiationless relaxation processes within the BO framework. Berry phases may arise when the Hamiltonian of a system depends on a set of parameters. In the BO approximation, the electronic Hamiltonian depends parametrically on the nuclear positions. If the full wave function (WF) is approximated by a single product of an electronic BO WF and a single nuclear WF, the varational equation determining the latter contains a Berry-type vector potential. However, in experiment, CIs and the associated Berry phases do not appear directly. One wonders whether the specific topological feature of Berry phase is an artifact of the BO approximation or whether it can be found for the exact full WF as well. To adress this question we employ the exact factorization of the full WF which leads to a rigorous definition of the Berry connection [1,2]. Using a numerical study of a simple model, we answer the question whether the appearance of CIs and Berry phases survives in the exact treatment.[1]arXiv cond-mat/0502433 [2]PRL 105,123002 (2005)