MO 18: The Modelling of Molecular Dynamics

Time: Thursday 14:30–16:15 Location: f142

MO 18.1 Thu 14:30 f142

Caldeira-Leggett Model Description of Condensed Phase Vibrational Spectroscopy — •Fabian Gottwald, Sergei D. Ivanov, and Oliver Kühn — Institut für Physik, Universität Rostock, Rostock

Formulating a rigorous system-bath partitioning approach remains an open issue. In this context the popular Caldeira-Leggett (CL) model enables simple modeling of system-bath interactions via spectral density functions. For parametrizing spectral densities we propose a Fourier-based method that outperforms existing time-domain methods [1]. Moreover, the widely used rigid bond method turns out to be inappropriate and leads to a systematic overestimation of relaxation times, unless the system under study is indeed of CL form. The validity of the CL model for describing anharmonic dynamics of real systems is often taken for granted. It is shown that such a use does not pass the self-consistency check for a broad class of solute-solvent systems, unless the system part of the potential is effectively harmonic [2]. The check is performed by comparing the spectra resulting from the corresponding generalized Langevin dynamics with their counterparts from explicit classical molecular dynamics. Although there exist systems that can be mapped onto the CL model, no a priori criteria are found and the ultimate verdict is provided by the self-consistency check only.
[1] F. Gottwald, S. Karsten, S. D. Ivanov, O. Kühn. *J. Chem. Phys.* **142**, 244110 (2015).
[2] F. Gottwald, S. D. Ivanov, O. Kühn. *J. Phys. Chem. Lett.* **6**, 2722 (2015).

MO 18.2 Thu 14:45 f142

Unraveling the Quantum State Mixing of Excitonic and Vibronic Excitations in the Dynamics of Molecular Aggregates — •Marco Schröter[1], Tõnu Pullerits[2], and Oliver Kühn[1] — [1]Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany — [2]Chemical Physics, Lund University, Box 124, 22100 Lund, Sweden

One possible source of coherent oscillations observed in two-dimensional electronic spectroscopy experiments is the quantum state mixing (QSM) of electronic and vibronic excitations in molecular aggregates. In the present contribution the signatures of Coulomb coupling induced QSM between excitonic and vibronic excitations in the dynamics of a model aggregate are discussed. To this end numerically exact dissipative exciton dynamics calculations applying the hierarchy equations of motion (HEOM) method are performed. A Fourier analysis of the coherent oscillations in the population dynamics after an initial excitation of the highest exciton state is supplemented by exciton-vibronic structure calculations employing direct diagonalization [1]. This allows us to unravel the origin of the oscillations and to obtain insights on the general influence of QMS on the dynamics as a function of Coulomb and vibronic coupling strengths [2].
[1] M. Schröter et al., Physics Reports 567, 1 (2015)
[2] M. Schröter et al., Annalen der Physik 527, 536 (2015)

MO 18.3 Thu 15:00 f142

Using vibrational dynamics in complex time to investigate the isotope dependence of High-Harmonic Generation in H_2 — Manfred Lein and •Marc Ruhmann — Institut für Theoretische Physik and Centre for Quantum Engineering and Space-Time Research (QUEST), Leibniz Universität Hannover, Appelstraße 2, 30167 Hannover, Germany

High-Harmonic generation takes place when an atom or molecule is subject to a strong laser field. It is commonly understood as a sequence of ionization, electron excursion and recombination. In the quantum mechanical strong-field approximation (SFA), the times of ionization and recombination, which are real in a classical model, are complex numbers.

In (small) molecules such as H_2, the harmonic intensity is approximately proportional to the modulus squared of the vibrational autocorrelation acquired over the electron excursion time. This provides a link between harmonic spectra and vibrational dynamics and explains why heavier isotopes produce more intense radiation.

Here we investigate the ratio of harmonics from D_2/H_2 by evolving the nuclear wave packets in complex time as given by the SFA. We consider, on the one hand, a reduced-dimensional model where we compare with exact solutions of the TDSE, on the other hand, a three-dimensional model including orientation averaging. We find, for both short and long trajectories, the ratio to be generally lower compared to the classical times and with a different qualitative shape.

MO 18.4 Thu 15:15 f142

Wie hängen Elektronenimpulsverteilungen aus Ionisation von Molekülen in linear und zirkular polarisierten Laserpulsen zusammen? — •Simon Brennecke und Manfred Lein — Institut für Theoretische Physik, Appelstraße 2, 30167 Hannover

Für ausgerichtete symmetrische Moleküle wie z.B. homonukleare zweiatomige Moleküle vergleichen wir die Ionisation in linear und zirkular polarisierten starken Laserfeldern. Innerhalb der Strong-Field Approximation zeigen wir, dass die Winkelverteilung der Elektronen bei zirkularem Laserfeld im Grenzfall kleiner Frequenzen und kleiner Feldstärke bis auf eine Drehung um 90° gleich der Orientierungsabhängigkeit des Signals in Feldrichtung bei linearem Feld wird. Dies gilt, wenn die Laserpulse genügend lang sind. Für den Fall von H_2^+ demonstrieren wir dies durch explizites Auswerten der Theorie. Die numerische Lösung der zeitabhängigen Schrödingergleichung zeigt den Effekt ebenfalls. Für realistische Laserparameter ist die Modulationstiefe der Winkelabhängigkeit beim zirkularen Feld größer als beim linearen Feld, sofern das σ_g-Grundzustandsorbital betrachtet wird. Bei vorhandenen Knotenebenen kann hingegen die zirkulare Modulationstiefe geringer als beim linearen Feld ausfallen.

MO 18.5 Thu 15:30 f142

Tuning the nonradiative lifetime via excitonic interaction — •Alan Celestino and Alexander Eisfeld — MPIPKS, Dresden, Germany

Nonradiative electronic transitions are typical in many molecules. These transitions can occur in the pico- or even femtosecond scale. For being able to occur so rapidly, nonradiative transitions can also sup- press the slower spontaneous emission in certain molecules. For these molecules, controlling the nonradiative lifetime equals controlling the lifetime of an electronic excitation. Depending on the application in mind one would like to make this lifetime longer or shorter. Aggregated molecules interact and both their radiative and nonradiative lifetimes are in general changed by this interaction. In the present work we study the influence of transition dipole-dipole interaction (excitonic interaction) between molecules on their nonradiative lifetime. As an example, we consider the dynamics of Frenkel excitons in a homodimer. The monomer is a two electronic level system coupled to nuclear vibrations. We consider the nonradiative channel to be well localized in the nuclear space. We calculate numerically the nonradiative lifetime of the dimer for different excitonic interaction strengths, positions of the nonradiative coupling and nuclear relaxation times. Using a Born-Oppenheimer approximation in the dimer level, we obtain the relevant dimeric potential surfaces. By using them, we can explain the direction of the changes in lifetime induced by excitonic interaction depending on the nonradiative channel position. For strong excitonic interaction, we can quantitatively predict the nonradiative lifetime.

MO 18.6 Thu 15:45 f142

Molecular quantum dynamics coupled with classical molecular dynamics of the solvent environment — •Florian Rott[1], Sebastian Thallmair[1,2], Julius Zauleck[1], and Regina de Vivie-Riedle[1] — [1]Department Chemie, LMU München — [2]LS für BioMolekulare Optik, LMU München

Recently, we introduced a new method combining quantum dynamics (QD) and classical molecular dynamics (MD) to model the influence of an explicit solvent environment on the QD of molecular reactions [1]. In this QD/MD approach we extract solvent potentials from MD trajectories by evaluating a set of different snapshots. The solvent potentials are included in the Hamiltonian used for the QD calculations. Using this method we were able to describe the photochemical bond cleavage of diphenylmethylphosphonium ions in solution.

So far, the solvent molecules have been frozen and no feedback from the QD system to the MD system has been included. We will present an extension of the method where both systems are propagated at the same time. Using the Ehrenfest method, we will show how the interactions between the quantum system and the calssical MD system are calculated. We demonstrate our method for the photoinduced dynamics of ICN in liquid argon and present first results.

[1] S. Thallmair, J. P. P. Zauleck, R. de Vivie-Riedle, *J. Chem. Theory Comput.* **11**, 1987 (2015).

MO 18.7 Thu 16:00 f142

Resonant inelastic X-ray Scattering (RIXS) Studies of Hydrogen-Bonded Cyano-Groups at the Nitrogen K-edge — •Abid Hussain[1], S. Schreck[4], P. Wernet[4], A. Fhlisch[4], O. Vendrell[2], and Nils Huse[1,3] — [1]MPSD,CFEL, Luruper Chaussee 149, 22761 Hamburg, Germany — [2]CFEL, DESY Notkestraße 85, 22607 Hamburg, Germany. — [3]INF, University of Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany. — [4]Institute for Methods and Instrumentation in Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

To probe the influence of hydrogen bonding on the electronic structure of the nitrogen atoms in cyano-groups, acetonitrile and acetonitrile-water mixtures have been investigated using X-ray absorption spectroscopy and Resonant Inelastic X-ray Scattering (RIXS). We employed first principles restricted active space self-consistent field (RASSCF) calculations in order to interpret experimental electronic structure probes via nitrogen core-level transitions. In the current study, we elucidate with highest chemical specificity the relative involvement of different molecular orbitals (MO). These calculations give explicit access to each electronic state with the extracted information allowing to assign the dominant transitions in the X-ray absorption spectrum, and unearthing the electronic character of every final valence excitation resulting from RIXS at a specific incident photon energy. Our theoretical results are in very good agreement with experimental spectra, highlighting the sensitivity of RIXS even for weak interactions.