MO 23: Molecular Theory

Time: Friday 10:30–12:30   Location: S HS 001 Biologie

Invited Talk   MO 23.1   Fri 10:30   S HS 001 Biologie
Efficient charge transfer by electron transfer mediated decay mechanism — •Kirill Gokhberg — Theoretical Chemistry, Heidelberg University, Heidelberg, Germany

Charge transfer between atoms and molecules is enabled by several mechanisms. It can proceed due to the coupling to the vibrational degrees of freedom, or via photon emission, in which case it is typically slow. In this talk I will present electron transfer mediated decay (ETMD), a charge transfer process enabled by interatomic electron correlation, which is usually fast. In ETMD charge transfer takes place between singly or multiply ionised atoms embedded in chemical environment and their neighbours, such that the transfer of the electron to the ion is accompanied by the emission of a second electron from the environment to the continuum. Whenever energetically allowed the process is highly efficient. Calculated ETMD lifetimes in rare gas clusters are less than a few picoseconds, while for solvated positive ions they can be as short as few tens of femtoseconds. The theoretical findings were confirmed by recent experiments, which showed the existence of ETMD in salt solutions and mixed rare gas clusters. Importantly, it was demonstrated that this process plays a crucial role in redistributing throughout a larger chemical system a localised positive charge produced by the action of ionising radiation. ETMD was also shown in theory and experimentally to furnish an efficient indirect pathway for producing cold doubly ionised species embedded in He nanodroplets by ionising the host He matrix.

MO 23.2   Fri 11:00   S HS 001 Biologie
Time-dependent Matrix Product States for the Study of Ultrafast Electron Dynamics in Molecules — •Lars-Hendrik Frahm and Daniela Pfannkuche — I. Institut Für Theoretische Physik, Universität Hamburg, Deutschland

Ultrafast dynamics allow to access the complex mechanisms in molecular systems in a very controlled manner. A complete quantum mechanical description, however, is very challenging due to the usually strong correlation of the electrons and the large number of degrees of freedom. The concept of matrix product states (MPS) is able to reduce the effective number of degrees of freedom and to describe strongly correlated systems efficiently. In this work, we present a newly developed ab-initio method using MPS to study such ultrafast electron dynamics in molecules. We show that the method is able to capture the electron dynamics on a full configurational interaction (CI) level up to a few femtoseconds after ionization. We compare results from our MPS method and the full CI method for two distinct molecules, namely the chain of hydrogen atoms and the water molecule. Further, we apply the method to describe ultrafast charge migration in iodoacetylene, for which CI methods are out of range. We find direct agreement between our results, existing experiments, and the literature.

MO 23.3   Fri 11:15   S HS 001 Biologie
An angulon quasiparticle perspective on impulsive molecular alignment in He nanodroplets. — •Igor Cherepanov, Giacomo Bighin, and Mikhail Lemeshko — IST Austria (Institute of Science and Technology Austria), Am Campus 1, Klosterneuburg, Austria

A quasiparticle picture provides a more straightforward and intuitive understanding of collective many-body phenomena arising in a variety of physical and chemical systems. Moreover, the problems which seem unsolvable within the classical approaches quite often become tractable from the quasiparticle perspective. This is the case for the microscopic dynamics of a single impurity immersed into a superfluid He droplet. Recently, the first experiments [1] showed that a short laser pulse can induce alignment of molecules dissolved in a He droplet. The rotational wavepacket dynamics herewith cannot be understood in terms of interference of the rigid rotor states due to the strong interactions with surrounding helium. Here we develop a dynamical theory of angulons [2] – quasiparticles consisting of a rotating impurity dressed by a field of surrounding bath excitations (phonons). We demonstrate that the superfluid helium environment strictly limits the number of molecular states which can survive for a long time. Our theoretical framework allows to compute the change of the angular momentum belonging to the molecule and the helium bath in time. It opens up a possibility to have a look at the molecular alignment experiments from the point of view of redistribution of angular momentum. [1] D. Pantlehner et al.,

Phys. Rev. Lett. 110, 093002 (2013) [2] R. Schmidt, M. Lemeshko, Phys. Rev. Lett. 114, 203001 (2015)

MO 23.4   Fri 11:30   S HS 001 Biologie
The multiconfigurational Ehrenfest method for the relaxation of excited molecules in the condensed phase — •Martin Peschel[1], Matteo Bonfanti[2], David Picconi[2], Irene Burghardt[2], and Regina de Vivie-Riedle[1] — [1]Ludwig-Maximilians-University Munich — [2]Goethe-University Frankfurt

Coherences and correlation with the environment can affect the relaxation behaviour of excited molecules in the condensed phase. Multiconfigurational methods enable us to systematically study these effects. In the multiconfigurational Ehrenfest (MCE) method the amount of correlation described is tuned by successively including more and more configurations, thus smoothly transitioning from uncorrelated to fully correlated dynamics [1]. MCE so far has mainly been used to study quantum subsystems with only a small number of states, but it can readily be extended to allow a grid-based description of a quantum subsystem in the condensed phase.

We apply this method to a description of excited iodine in a krypton matrix with a look at dissipation, decoherence and the autocorrelation function [2]. We then advance to the more involved example of uracil in water at room temperature. Here we combine MCE with our previously developed coupled quantum dynamics/molecular dynamics approach to fully capture the solute-environment interaction during the relaxation process.

[1] T. Ma *et al.*, *J. Chem. Phys.*, **149** (2018), accepted manuscript.
[2] D. Picconi *et al.*, submitted.

MO 23.5   Fri 11:45   S HS 001 Biologie
Non-Markovian quantum dynamics of vibronic systems with controlled factorization of the environment — •Alejandro D. Somoza, Oliver Marty, Jaemin Lim, Susana F. Huelga, and Martin B. Plenio — Institut für Theoretische Physik and IQST, Universität Ulm, Ulm, Germany

Charge and energy transfer in biological and organic materials are often characterized by the coupling of excitations to high-frequency underdamped vibrations and a slow background accounting for solvent reorganization effects. The simulation of many interacting chromophores, strongly coupled to intramolecular modes of vibration and embedded in a dissipative environment requires a substantial computational effort. Numerically exact methods are typically limited to just a few sites and, often, severe approximations with poor error control are required in order to address large systems. In this work, we devise an algorithm that partially eliminates weak correlations among oscillators, while preserving as much as possible the entanglement between the electronic system and the vibrational environment. We exploit the memory-efficient representation of matrix product operators (MPOs) to rewrite the bosonic states in a form that parametrically interpolates between fully factorized oscillators and an exact description of the vibrational environment where no correlations are discarded. A straight forward measure of the error is obtained and the factorization can be adaptively controlled to keep the error below a well-defined bound.

MO 23.6   Fri 12:00   S HS 001 Biologie
Ab Initio Simulations of P-Compounds at Mineral Surfaces — •Prasanth Babu Ganta, Ashour Ahmed, and Oliver Kühn — Institute of Physics, University of Rostock, D-18059 Rostock, Germany

Phosphorus (P) plays an important role in the environmental nutrient cycle. Facing the projected peak P scenario, substantial research work have been triggered for efficient use of P resources. One major factor playing a role in the P immobilization is the strong interaction of phosphates to soil mineral surfaces (Fe-, Al- oxyhydroxides). We have studied binding of two abundant phosphates (inositol-hexa phosphate (IHP), glycerolphosphate (GP)) at two different mineral surfaces (goethite (FeOOH) and diaspore (AlOOH)). Here, water as an aqueous solution in soil was involved around each phosphate mineral model. Here, all models are treated by DFT using PBC. Due to size of our models, QM/MM calculations have been performed to have good accuracy with less computational time. Here, the top two layers of mineral surface, phosphate, and the surrounding water molecules are described

at QM level. During MD simulations, different binding motifs including monodentate and bidentate are observed between the phosphates and mineral surfaces. Moreover, protons transfer from phosphates to the mineral surfaces as well as to the surrounding water molecules. More details will be given in the presentation.

MO 23.7   Fri 12:15   S HS 001 Biologie

Low temperature HD + *ortho-*/*para-*H_2 and HD+H inelastic scattering of astrophysical interest — •Renat Sultanov — 201 W. University Blvd., Department of Mathematics and Engineering, Odessa College, Wood Building of Math and Science (WOOD) Room 213, Odessa, TX 79764

State-selected total cross sections and thermal rate coefficients are computed for the 4-atomic HD + H_2 and 3-atomic HD+H rotational energy transfer collisions at low temperatures (T) of astrophysical interest: $5K < T < 500K$. Together with the $H_2 + H_2$ and $H_2 + H$ collisions, the scattering processes with the participation of the HD molecule (D is deuterium) are of significant importance in the astrophysics of the early Universe, in terms of the modeling of pre-galactic clouds and planetary atmospheres [1]. In the 4-atomic case a precise H_2-H_2 potential energy surface (PES) from paper [2] has been modified and used. The modification procedure was developed in a recent paper [3]. A quantum-mechanical dynamical approach is applied in the current calculation. A comparison between our new results for HD + H_2 and previous calculations [3,4,5] will be presented. The HD+H non-reactive scattering cross sections will also be presented and discussed.

1. A. Dalgarno, R. McCray, Ann. Rev. Astron. Astroph. 10, 375 (1972).
2. K. Patkowski at el., J. Chem. Phys. 129, 094304 (2008).
3. R.A. Sultanov at el., J. Phys. B49 015203 (2016).
4. D. R. Flower, J. Phys. B32, 1755 (1999).
5. J. Schaefer, Astron. Astrophys. Suppl. Ser. 85, 1101 (1990).