

MO 17: Theory

Time: Thursday 14:00–16:00

Location: f142

MO 17.1 Thu 14:00 f142

Towards Machine-Learned Coordinate Grids for Wave Packet Dynamics — ●SEBASTIAN REITER, THOMAS SCHNAPPINGER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich

The dynamics of ultrafast (photo)chemical processes are frequently studied quantum mechanically by propagating wave packets on a spatial grid of nuclear coordinates, thus solving the time-dependent Schrödinger equation. Here, dimensionality reduction is imperative for all but the smallest systems, as the number of grid points scales exponentially with the number of dimensions. This issue is commonly addressed by manually constructing a reduced-dimensional subspace that describes the process in question, for example by employing a few selected normal modes or a linear combination thereof as basis vectors. However, finding such a subspace can prove challenging as it requires a large amount of prior knowledge about the system.

We therefore present a semi-automatic technique to generate non-linear coordinate grids for use in quantum dynamics. It relies on a special type of artificial neural network, called autoencoder, which is capable of learning a low-dimensional representation of trajectory data. Starting from standard quantum chemical reaction path calculations, our software package is designed to assist the user in generating a suitable data set of molecular geometries, setting up and training the neural network and finally constructing the grid. We discuss the advantages of using non-linear over linear coordinate subspaces and present applications for our technique to quantum dynamics in both the ground state and excited states.

MO 17.2 Thu 14:15 f142

The [H,C,N] dynamics project — ●GEORG CH. MELLAU¹, VLADIMIR YU. MAKHNEV², NIKOLAY F. ZOBOV², ALEKSANDRA A. KYUBERIS², and OLEG L. POLYANSKY^{2,3} — ¹University of Giessen, Institute of Physical Chemistry, Giessen, Germany — ²Institute of Applied Physics, Russian Academy of Science, Nizhny Novgorod, Russia — ³Department of Physics and Astronomy, University College London, London, UK

A chemical reaction is a reorganization of particles in a complex many-body quantum system. Within the frequency domain description, the eigenstates relevant for chemical dynamics are the highly excited eigenstates. I started 20 years ago the [H,C,N] Chemical Dynamics project to get a model-free description of a chemical reaction in the frequency domain. The [H,C,N] molecular system has two HCN and HNC minima and the transition between the localized states corresponds to a prototypical chemical reaction. With numerical methods is not possible to calculate the exact eigenstates of a molecular system, but we can use spectroscopic experiments to measure the complete set of model-free exact eigenstates and thus solve the many-body Schrödinger equation exactly. I will give an overview of this project and the current results of the MAP Data Science project, where the experimental and a vibrational assigned ab initio eigenenergy list are correlated with new ab initio lists. Since the quality of a global PES is determined by its ability to reproduce experimental rovibrational energies this project gives an immediate automatic quality map of a PES or any theoretical model of the molecule.

MO 17.3 Thu 14:30 f142

Charge Transfer Through Redox Molecular Junctions in Non-Equilibrated Solvents — ●HENNING KIRCHBERG¹, MICHAEL THORWART¹, and ABRAHAM NITZAN² — ¹I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstraße 9, 20355 Hamburg, Deutschland — ²Department of Chemistry, University of Pennsylvania, 231 s 34th St. Philadelphia, PA 19104, USA

Charge transport in solvated molecular junctions is commonly described by sequential electron hopping between molecular sites as well as between the molecule and the metal leads. Each such hopping event is accompanied by complete solvent relaxation and the process is thus described by Marcus electron transfer theory, which accounts for thermally activated processes under equilibrium conditions. When the time scale of the solvent relaxation is finite, the thermal distribution determining the charge transfer rates needs to be replaced by a time-dependent probability distribution. We determine this distribution by suitable diffusion equations in the high- and low-friction limits and calculate the nonequilibrium charge current and the Fano factor

as a function of the solvent damping strength. The charge hopping becomes correlated by a finite solvent relaxation. Moreover, we find a Kramers-like turnover of the nonequilibrium current as a function of the solvent induced damping.

MO 17.4 Thu 14:45 f142

Synthetic spin-orbit coupling mediated by a bosonic environment — ●MIKHAIL MASLOV, MIKHAIL LEMESHKO, and ENDER-ALP YAKABOYLU — Institute of Science and Technology Austria, 3400 Klosterneuburg, Austria

We study a mobile quantum impurity, possessing internal rotational degrees of freedom, confined on a circular ring in the presence of a many-particle bath. By considering the recently introduced rotating polaron problem [1], we define the Hamiltonian and examine the energy spectrum. The weak-coupling regime is studied by means of a variational ansatz in the truncated Fock space. The corresponding spectrum, presented for selected angular quantum numbers of the impurity, indicates the emergence of a coupling between the angular momenta of circular motion and internal impurity rotation due to the phonon exchange mediated by the bosonic environment. We interpret the arising coupling as a phonon-induced spin-orbit coupling, which is quantified by the correlation function between the external and internal angular momentum operators. The same observation in the regime of strong impurity-bath coupling is elaborated within the Pekar approach. The correlation function shows a kink at a critical coupling, which is explained by a sharp transition between the ground state of the system and the states maximizing the interaction with surroundings. This result is of particular interest for the related fields involving the phenomena induced by spin-orbit interaction, such as spintronics and topological insulators.

[1] E. Yakaboylu, et al., Physical Review B 98, 224506 (2018)

MO 17.5 Thu 15:00 f142

Efficient Charge Generation Via Hole Transfer in Dilute Organic Donor-Fullerene Blends: A High-Dimensional Multi-Step Kinetics Approach Based On Fermi's Golden Rule Rate Theory — ●ALEXANDER SCHUBERT^{1,2,3}, YIN SONG², SRIJANA BHANDARI³, JENNIFER P. OGILVIE², BARRY D. DUNIETZ³, and EITAN GEVA^{2,3} — ¹Friedrich-Schiller Universität Jena, Germany — ²University of Michigan, Ann Arbor, USA — ³Kent State University, USA

For efficient organic photovoltaics a broadband photoabsorption that exploits all charge generating pathways would be highly desirable. Electron transfer from organic donors to acceptors has been well-studied and is considered the primary path to charge photogeneration in OPVs, whereas much less is known about the hole transfer pathway. Here we study charge photogeneration in an archetypical system comprising tetraphenylbenzoperiflanthene(DBP):C70 blends via time-dependent density functional theory (TDDFT) employing a recently developed framework based on a screened range-separated hybrid functional within a polarizable continuum model (SRSH-PCM). Based on such first principles calculations Fermi's golden rule (FGR) rate theory is applied to reveal the multi-state transition kinetics at the donor-acceptor interface. Our simulations support the interpretation of recent multispectral two-dimensional electronic spectroscopy (M-2DES) measurements revealing charge transfer pathways originating in donor and acceptor excitons. We find that both electron and hole transfer occur with comparable rates and efficiencies.

MO 17.6 Thu 15:15 f142

From spectral lines to Energy Terms without a Model — ●STEFAN BRACKERTZ, SVEN KRISTKEITZ, OSKAR ASVANY, and STEPHAN SCHLEMMER — I. Physikalisches Institut, University of Cologne, Cologne, Germany

The fundamental Ritz combination principle originally found in 1908 for atoms has also been applied to molecules as a method to reconstruct the energy states from measured transitions without relying on any model Hamiltonian. In 2006 Nesbitt and coworkers proposed to apply it to protonated methane, CH₅⁺, which was first done in 2015 and extended in 2017 by our group. Currently, we are elaborating this method to a universal, easy to use tool which can be used for arbitrary spectra as there is a broad field of potential applications:

- Preprocessing for the assignment of rich experimental spectra to analytical models or numerical data
- First step of understanding of molecular spectra for which not even a zeroth order Hamiltonian exists, as for CH_5^+ in 2015
- Separation of mixed spectra consisting either of spectra of different molecules, e.g., from an experiment in a discharge tube or spectra consisting of subspectra originating from different nuclear spin species, e.g., para- and ortho- He-H_3^+

The challenges in generalizing the method and first results will be discussed.

MO 17.7 Thu 15:30 f142

Is nuclear motion classical? The success of the Maxwell-Boltzmann distribution — ●IRMGARD FRANK — Theoretical Chemistry, Leibniz University of Hannover, Callinstr. 3A, 30167 Hannover

The Born-Oppenheimer approximation can be replaced by a better approximation in a very simple way. The consideration starts from the notion that it is problematic to describe the nuclear motion and the electronic cloud in a similar way, hoping that the Schrödinger equation will generate meaningful results for both of these two completely different types of objects. As the result of the simulation of a chemical reaction one wants to obtain well localized nuclei which clearly define the product state, not a nuclear cloud. The only consistent way to achieve this is by treating the motion of the nuclei classically right from the beginning. The immediate result is ab-initio molecular dynamics (AIMD). Movies of chemical reactions generated with AIMD show clearly that this approach is working well at normal energies. Tunneling is electronic tunneling in every case. Chemical reactions are explained by outliers of the classical Maxwell-Boltzmann velocity distribution. The development of this distribution is guaranteed

in a molecular dynamics run as it is the most likely distribution and defines the temperature of the system. In the present study we investigate some critical cases, namely the ammonia inversion and the heat capacities of hydrogen and water.

MO 17.8 Thu 15:45 f142

On the Molecular Symmetry of Protonated Methane — ●STEFAN BRACKERTZ¹, BENJAMIN NUKIC¹, THOMAS SALOMON¹, PER JENSEN², and STEPHAN SCHLEMMER¹ — ¹I. Physikalisches Institut, University of Cologne — ²Physikalische und theoretische Chemie, Universität Wuppertal

The energy term diagram of the lowest energy ro-vibrational states of CH_5^+ has eluded any analytical description until Schmiedt et al. proposed a 5d superrotor model in 2015. In 2018 Fábri and Császár used quantum graphs to describe the internal motions. Numerical results have been published in 2016 by Wang et al. All of these approaches describe the experimental energies reasonably well but seem to be incompatible regarding molecular symmetry.

We present results on the relations between these approaches:

- Schmiedt et al. showed the non-existence of equivalent rotations for the permutations of CH_5^+ because S_5 is not isomorphic to any subgroup of $\text{SO}(n) \times \{E, E^*\}$ for $n < 5$. This can also be understood geometrically using the results of Fábri and Császár.
- Fábri and Császár do a splitting of $S_5 = S_4 \times S_2$ associated with an internal equivalent rotation for the S_4 part. This approach gives some clues to the interpretation of the 5d superrotor model.

These considerations are also used for the modeling of a simpler case of a fluxional molecule, He-H_3^+ , which is subject to internal as well as end-over-end rotation.