

MO 14: Theory of Coupled Systems

Time: Thursday 11:00–13:00

Location: N 25

MO 14.1 Thu 11:00 N 25

Quantum dynamics of large molecular complexes using stochastic pure states — ●PANPAN ZHANG and ALEXANDER EISFELD — MIPK Dresden

The Hierarchy of Pure States (HOPS)[1] is a stochastic method to efficiently solve non-Markovian open quantum system dynamics. It can also be used to calculate the linear [2] and nonlinear [3] spectra of molecular aggregates. Here we discuss the application of HOPS to these aggregates and present a new scheme how to truncate the hierarchy, which allows to treat large systems with complex environments.

[1] D. Suess et al; Phys. Rev. Lett. 113, 150403 (2014) [2] G. Ritschel et al; J. Chem. Phys. 142, 034115 (2015) [3] P. Zhang and A. Eisfeld; J. Phys. Chem. Lett. 7, 4488 (2016)

MO 14.2 Thu 11:15 N 25

Electron-phonon coupling with DFT — ●OLIVER STAUFFERT — Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg

We describe electronic structures for organic molecules, which are interesting for current research on organic solar cells, with time dependent density functional theory (DFT). Hereby we are especially interested in coupling of nuclear and electronic degrees of freedom. The most widely known occurrence of this coupling can be seen in the vibrational substructure of electronic spectra. These vibrational lines are described by the Franck-Condon factors and can be calculated in a DFT framework. Results of simulations for polycyclic aromatic hydrocarbon show excellent agreements with the experimental data. We further investigate the influences of the environment, like a rare gas matrix and additional molecules on the vibrational degrees of freedom. Another consequence of electron-phonon coupling can be seen in phonon assisted electron hopping. Conduction in organic systems is often described by electronic hopping in terms of a Hubbard Hamiltonian. The hopping parameter hereby depends on the distance of next neighbor atoms. Vibrations along the atomic axis can change the distance accordingly and enhance electronic hopping. This can lead to interesting new effects that we are investigating with DFT and an Su-Schrieffer-Heeger [1] model.

[1] W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. 42, 1698 (1979)

MO 14.3 Thu 11:30 N 25

Towards a mobile solvent environment in quantum control optimizations — ●DANIEL KEEFER and REGINA DE VIVIE-RIEDLE — Department Chemie, LMU München

Recently, we introduced an approach to explicitly include solvent molecules in quantum control optimizations [1]. The explicit environment was identified to have a significant influence on the relevant molecular properties. In a first approximation, movement of the solvent molecules was not considered during the quantum dynamical treatment of the reactant and the optimization of controlling laser pulses.

In our present study, we address this issue and extend our approach towards a fluctuating environment. The methodical techniques to achieve this will be presented, and the impact of mobile solvent molecules will be discussed on a molecular, synthetically relevant example.

[1] D. Keefer et al., *J. Phys. B* 48 (2015), 234003.

MO 14.4 Thu 11:45 N 25

Sub-picosecond Energy Transfer Mechanism with Highly Intense and Ultrashort THz Pulses — ●PANKAJ KUMAR MISHRA^{1,2} and ROBIN SANTRA^{1,2,3} — ¹Centre for Free Electron Laser Science, DESY, Hamburg, Germany — ²The Hamburg Centre for Ultrafast Imaging, University of Hamburg, Germany — ³Department of Physics, University of Hamburg, Germany

With the advent of femtosecond lasers a couple of decades ago, ultrafast Temperature-jump experiments became possible and have since been used to study the very fast kinetics of fundamental steps in chemical reactions, folding processes in proteins and other biomolecules. Interestingly, T-jump experiments are also being used to study the fundamental aspects of the hydrogen bond dynamics and energy transfer

in liquid water and other liquids in ultrashort timescales. We computationally investigated that one and half cycle, 141 fs long (fwhm) THz pulses spectrally centered at about 100 cm⁻¹ (3 THz) can transfer the large amount of energy to the liquid water, generating a t-jump of 700 K within less than a ps time-scale. Here, I will talk about the dynamics of ultrafast energy transfer from water clusters to bulk water by such THz pulses. I will present the mechanisms by which rotational and translational degrees of freedom of the water monomers gain energy from these sub-cycle pulses and discuss the ultrafast H-bond modification. Through their permanent dipole moment, water molecules are acted upon by the electric field and forced off their preferred H-bond network conformation.

MO 14.5 Thu 12:00 N 25

Kraftberechnungen in Spiropyran — ●OLIVER BRÜGNER und MICHAEL WALTER — FIT Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien, Universität Freiburg

Spiropyrane sind photo- und mechanochrome Moleküle. Die ursprünglich farbneutralen Moleküle können sich durch Bestrahlung mit ultraviolettem Licht beziehungsweise durch mechanische Kräfte durch Brechung einer kovalenten Bindung in farbige Isomere mit dem Namen Merocyanin umwandeln. Die induzierte Verfärbung ist reversibel und die Entfärbung lässt sich z.B. durch ultraviolettes Licht induzieren. Diese erstaunliche Eigenschaft macht Spiropyran zu einem Stoff, welcher für die Zukunft viele Anwendungen verspricht.

Mit dem langfristigen Ziel die mechanochromen Eigenschaften zu nutzen, um die Grundlage für die Herstellung von polymeren Kraftsensoren zu entwickeln, haben wir theoretische Untersuchungen basierend auf der Dichtefunktionaltheorie durchgeführt. Bestehende Methoden, um die Kraft zu berechnen, welche zur Verfärbung eines Spiropyranmoleküls benötigt wird, wurden von uns weiterentwickelt. Dabei ergibt sich, dass das Molekül für den Übergang nach Merocyanin zwei verschiedene Energiebarrieren überwinden muss. Die korrekte Bestimmung der benötigten Kraft verlangt die Betrachtung von zwei Reaktionskoordinaten und den zugehörigen Energiebarrieren. Berücksichtigung finiter Temperaturen bringt die berechneten Kräfte in Einklang mit dem Experiment [Gos].

[Gos] Gregory R. Gossweiler, Tatiana B. Kouznetsova, Stephen L. Craig, *J. Am. Chem. Soc.* 137 (2015) 6148-6151

MO 14.6 Thu 12:15 N 25

Energetics of charge transfer excitations from DFT ground-state calculations — ●ROLF WÜRDEMANN¹ and MICHAEL WALTER^{1,2,3} — ¹FMF, Universität Freiburg, Freiburg, Germany — ²FIT, Universität Freiburg, Freiburg, Germany — ³IWM, Freiburg, Germany

Charge transfer excitations (CTE) are of interest in photovoltaics, organic electronics and molecular and organic magnetism. The energetics of CTE can be calculated by linear response time dependent density functional theory (lrTDDFT) using range separated functionals (RSF).

Compared to ground-state calculations, the use of lrTDDFT is computational very demanding.

Applying Huzinaga's improved virtual orbitals from Hartree-Fock Theory, we present a way to calculate the energetics of CTE using RSF by means of DFT ground-state calculations.

MO 14.7 Thu 12:30 N 25

Impact of dipole dispersion forces on the spectroscopic properties of a molecule — ●JOHANNES FIEDLER¹, SAUNAK DAS^{2,3}, MARTIN PRESSELT^{2,3}, MICHAEL WALTER^{1,4}, and STEFAN YOSHI BUHMANN¹ — ¹Institute of Physics, University of Freiburg, Germany — ²Institute of Physical Chemistry, University of Jena, Germany — ³Leibniz Institute of Photonic Technology, Germany — ⁴Fraunhofer Institute for Mechanics of Materials, Germany

In molecular systems, dipole forces play an important role in determining their physical properties, such as bond length, binding energy and the electromagnetic response of the whole aggregate. Their impact is investigated in recent experiments and theories [1,2]. One typically distinguishes forces may arising from permanent from those being due to induced dipole moments.

We investigate the influence of dielectric response of a particle in the presence of a second one, where the two interact via the London dis-

persion force. We present the results of a quantum optical description based on macroscopic quantum electrodynamics and compare them with results obtained from density functional theory [3]. In particular, we study how the impact of the second particle on the first depends on the interparticle separation and their mutual orientation.

[1] V.V. Gobre, A. Tkatchenko, *nature communications* **4**, 2341 (2013).

[2] S.Y. Buhmann, *Dispersion forces I*, Springer (Heidelberg, Berlin) 2012.

[3] T.E. Shubina *et al.*, *J. Am. Chem. Soc.* **136**, 10890 (2014).

MO 14.8 Thu 12:45 N 25

Scalable composition of many-body interactions with linear size, linear/logarithmic-depth quantum circuits —

•MICHAEL KAICHER¹, FELIX MOTZOI², and FRANK K. WILHELM¹

— ¹Universität des Saarlandes, Saarbrücken, Deutschland —

²Department of Physics and Astronomy, Aarhus, Dänemark

We develop a generalized framework for constructing many-qubit operator strings in linear time, with exact decompositions given for Pauli strings, number-conserving strings, parity-conserving strings, many-control Toffoli gates, Unitary Coupled Cluster operations, and sparse matrix generators. To this end, we use nearest-neighbour chaining operations to iteratively increase string length, in combination with a dynamical decoupling gate sequence to undo any changes outside the support of the many-body string. Moreover, we show that such constructions can be exponentially sped up via parallelization, with linear number of ancillary scratch registers required when the operators are not full rank. The formalism is readily applicable to different kinds of interactions including, CNOT, XX , and $XX + YY$.