TT 38: Frontiers of Electronic Structure Theory: Nuclear Dynamics, Methods (jointly with O, HL)

Time: Tuesday 10:30–13:30   Location: MA 004

Invited Talk   TT 38.1   Tue 10:30   MA 004
Electronic structure in the vicinity of strong non-adiabatic couplings — •Eberhard K.U. Gross — Max Planck Institute of Microstructure Physics, Halle (Saale), Germany

The Born-Oppenheimer (BO) approximation is among the most fundamental ingredients of modern Condensed-Matter Theroy. Yet, some of the most fascinating phenomena such as the process of vision or phonon-driven superconductivity occur in the regime where the BO approximation breaks down. To tackle such situations one has to face the Hamiltonian of the complete system of interacting electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wavefunction into a purely nuclear part and a many-electron wavefunction which parametrically depends on the nuclear configuration. The resulting equations of motion for the nuclear and electronic wavefunctions lead to a unique definition of exact potential energy surfaces as well as exact geometric phases. We show an example [2] where the geometric phase associated with the conical intersection of BO surfaces has no counterpart in the true electron-nuclear wavefunction. In the time-domain, whenever there is a splitting of the nuclear wavepacket in the vicinity of an avoided crossing, the exact time-dependent surface shows a nearly discontinuous step [3], reminiscent of Tully surface hopping algorithms. Based on this observation we propose novel mixed-quantum-classical algorithms.

[1] Abedi, Maitra, Gross, PRL 105, 123002 (2010).
[2] Min, Abedi, Kim, Gross, PRL 113, 263004 (2014).
[3] Abedi, Agostini, Suzuki, Gross, PRL 110, 263001 (2013).

TT 38.2   Tue 11:00   MA 004
Towards First-Principles Modeling of Electrolytic Solvent Effects in Photo-Catalytic Water Splitting — •Stefan Ringe[1], Sebastian Matera[2], Harald Oberhofer[1], and Karsten Reuter[1] — [1]Technische Universität München — [2]Freie Universität Berlin

Due to the complexity of the physical processes underlying photo-catalytic surface reactions, ab-initio computational approaches have to overcome major challenges concerning accuracy and computational costs. In particular, an efficient description of electrolytic solvent effects—which are crucial for charge driven reactions—is highly necessary.

We present an implementation of the modified Poisson-Boltzmann (MPB) model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. In contrast to most implicit solvent models, this technique combines nonlinear dielectric solvent response with a statistical description of solvated finite-sized ions. This has been shown to capture a majority of electrochemical solvent effects appearing in heterogeneous photo-catalysis.[1]

We developed a self-consistent function-space oriented solution scheme for Poisson-Boltzmann-like equations which in contrast to common multi-grid solvers is able to exploit the specialized grids and optimized integration schemes of FHI-aims. We demonstrate the approach and its efficiency for the linearized Poisson-Boltzmann equation and a range of molecular systems. Finally, we discuss how the methodology can be employed for the solution of non-linear problems. [1] Kilic,M.S., Bazant, M.Z., *Phys. Rev. E, 75*, **2007**, 021502.

TT 38.3   Tue 11:15   MA 004
Phonons in Molecular Crystals: The Role of Collective van der Waals Interactions — •Johannes Hoja and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

By now, it is well established that dispersive van der Waals (vdW) interactions are crucial for the structure and stability of molecular crystals [1]. However, complete understanding of functionality of molecular crystals also requires a predictive description of response to external perturbations. Here we study the role of vdW interactions on phonons in molecular crystals. This subject is important since such low-frequency vibrations can be used to identify for instance drugs, explosives, and different polymorphic forms of molecular crystals. We studied the vibrational spectra of several molecular crystals with density-functional theory, including many-body dispersion interactions (DFT+MBD method). We find that long-range MBD effects

can give rise to novel peaks in the phonon density of states [2], which can not be observed with a simple pairwise treatment of vdW interactions. We further discuss the nature of these vibrations and demonstrate a non-trivial connection between collective vdW interactions and entropy of molecular crystals.

[1] L. Kronik, A. Tkatchenko, Acc. Chem. Res. 47, 3208 (2014).
[2] A. M. Reilly, A. Tkatchenko, Phys. Rev. Lett. 113, 055701 (2014).

TT 38.4   Tue 11:30   MA 004
Converged Nuclear Quantum Statistics from Semi-Classical Path Integrals — •Igor Poltavskyi and Alexandre Tkatchenko — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The quantum nature of nuclear motions plays a vital role in the structure, stability, and thermodynamics of molecular systems. The standard approach to take nuclear quantum effects (NQE) into account is the Feynman-Kac imaginary-time path-integral molecular dynamics (PIMD). Conventional PIMD simulations require exceedingly large number of classical subsystems (beads) to accurately capture NQE, resulting in considerable computational cost even at room temperature due to the rather high internal vibrational frequencies of many molecules of interest.

We propose a novel parameter-free form for the PI partition function and estimators to calculate converged thermodynamic averages. Our approach requires the same ingredients as the conventional PIMD simulations, but decreases the number of required beads by roughly an order of magnitude. This greatly extends the applicability of *ab initio* PIMD for realistic molecular systems. The developed method has been applied to study the thermodynamics of N_2, H_2O, CO_2, and C_6H_6 molecules. For all of the considered systems at room temperature, 4 to 8 beads are enough to recover the NQE contribution to the total energy within 2% of the fully converged quantum result.

TT 38.5   Tue 11:45   MA 004
Can we get reliable quantum dynamics simulations for vibrational spectra in the condensed phase? — •Mariana Rossi[1], David Manolopoulos[1], and Michele Ceriotti[2] — [1]University of Oxford, Oxford, UK — [2]EPFL, Lausanne, Switzerland

At the level of accuracy we can now achieve in first-principles calculations, the inclusion of more subtle nuclear quantum effects (NQE) in simulations become more relevant. However, their inclusion is challenging for anharmonic and dynamical processes, in particular in the condensed phase. We show a new method to approximate quantum corrections in time-dependent properties based on a path integral framework, called thermostatted ring polymer molecular dynamics (TRPMD) [1], which is immune to pathological problems of previously proposed methods. We perform a systematic comparison of TRPMD with other approaches that rely on different approximations to quantum dynamics, to assess their performance for the IR spectrum of HOD in D_2O and water at different phases/temperatures [2]. Using an empirical potential energy surface (q-TIP4P/f), we find that the different techniques are largely consistent with one another, within a few tens of cm^{-1}. Comparison with classical molecular dynamics demonstrates the importance of NQE even up to 600K. The cross validation between these different approaches provides clues to limitations of their underlying approximations and paves the way for more reliable approaches to nuclear quantum dynamics that are feasible together with electronic structure methods. [1] M. Rossi, M. Ceriotti, D. Manolopoulos, JCP 140, 234116 (2014); [2] M. Rossi, et al., JCP 141, 181101 (2014)

TT 38.6   Tue 12:00   MA 004
Ultra-high temperature properties of ZrC: a fully-anharmonic ab-initio approach — •Andrew Duff[1], Dominique Korbmacher[2], Albert Glensk[2], Blazej Grabowski[2], Joerg Neugebauer[2], and Mike Finnis[1] — [1]Department of Physics and Department of Materials, Thomas Young Centre, Imperial College London, Exhibition Road, London SW7 2AZ, UK — [2]Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, Düsseldorf 40237, Germany

As a binary end-member of many of the technologically highly interesting MAX phases, as well a useful refractory material in its own

right, there is much to be gained from achieving a more accurate first-principles assessment of the behaviour of ZrC at ultra-high temperatures. Exploiting recent developments in finite-temperature density functional theory (DFT) calculations, we provide valuable data at temperatures where the available experimental data is of low accuracy. Within the framework of the UP-TILD approach [Grabowski 2007], the thermal expansion and heat-capacity of ZrC are calculated up to the melting-point. These fully anharmonic results are compared to calculations performed within the widely used quasi-harmonic approximation (QHA), which treats anharmonic effects in only an approximate manner. Sizeable deviations are found close to the melting point, consistent with the strongly anharmonic lattice vibrations present at such temperatures.

TT 38.7   Tue 12:15   MA 004

Quo vadis electronic friction? Assessing vibrational lifetimes beyond the independent atom approximation — •Simon P. Rittmeyer[1], J. Iñaki Juaristi[2], Jörg Meyer[3], and Karsten Reuter[1] — [1]Technische Universität München, Germany — [2]Depto. & Centro de Física de Materiales (CSIC-UPV/EHU), San Sebastián, Spain — [3]Leiden University, Leiden, The Netherlands

The quest for a both accurate and numerically efficient first-principles-based treatment of electronically non-adiabatic adsorbate dynamics on metal surfaces is still ongoing. A promising candidate in this regard is the concept of electronic friction within the local density friction approximation (LDFA). The numerical efficiency of this approach stems from an intrinsic decomposition and mapping of the interacting system to independent atoms individually embedded in a free electron gas. This inherent simplicity has raised serious conceptual concerns about the accuracy of this theory. On the other hand, it is not clear how much these approximations actually affect the description of "real" observables. In this regard, vibrational lifetimes of high-frequency adsorbate modes on metal surfaces provide a sensitive measure to gauge a non-adiabatic theory. We thus target this observable applying the LDFA for several well-studied systems and discuss it by comparing the results to other theoretical approaches as well as experimental data. Moreover, we present a simple and computationally efficient strategy to extend the LDFA beyond the yet indispensable frozen-surface and independent-atom approximation.

TT 38.8   Tue 12:30   MA 004

Polynomial-oriented linear least squares fits of potential energy surfaces for quantum dynamics — •Florian Habecker and Thorsten Klüner — Universität Oldenburg, Germany

The field TD-QM Molecular Dynamics is facing two major problems within the BO-approximation: I. Solution of the TISE for the electrons and II. Solution of the TDSE for the nuclei. Electronic structure calculations result in a K-dimensional PES (K: number of d.f. for the nuclei) on which the motion of the nuclei is simulated, subsequently.

For economical reasons, the number of sampling points calculated by QC methods is generally smaller than those needed in the QD calculation. Hence, an interface is required to link the two major tasks. Taking the scalar energies E with the corresponding geometry parameters as input, the output of such an interface is a function to calculate any points of the PES, i.e. interpolated and extrapolated values.

Following classical papers on H_3^+ [1 and refs. therein], the linear model function was chosen as a K-dimensional polynomial in this study. The lack of flexibility in this uniform ansatz was restored using appropriate non-linear variable transformations. Applying the method of LLS, precise fits can be calculated in a single non-iterative step. The capability of this approach was validated with a set of 7942 ab initio data points from a 3-D PES of a CO/$Ti_9O_{18}Mg_7^{14+}$-system [2]. Precise fits with chemical accuracy and better have been obtained for moderate expansions of the model function.

[1] W. Meyer, P. Botschwina, P. Burton, *J. Chem. Phys.* **84**, 891 (1986).
[2] H. Spieker, T. Klüner, *Phys. Chem. Chem. Phys.* **16**, 18743 (2014).

TT 38.9   Tue 12:45   MA 004

Representing Complex Potential Energy Surfaces by Artificial Neural Networks — •Christopher Handley and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universit*at Bochum, D-44780 Bochum, Germany

Computer simulations of large systems are computationally costly, and in many cases intractable, when using ab initio methods. More efficient potentials are typically based on approximations specific for particular atomic interactions, and the fitting of these potentials is not straightforward. Neural Networks (NNs) can provide interatomic potentials that are comparable to the accuracy of quantum mechanical calculations [1,2]. They are flexible enough to fit complex functions to quantum mechanical training data and yield accurate energies and forces. Here, we present our recent work towards more transferable NN potentials. [1] C. M. Handley and P. L. A. Poplier, J. Phys. Chem. A, 114, 3371- 3383, (2010). [2] J. Behler, PCCP, 13, 17901-18232 (2011).

TT 38.10   Tue 13:00   MA 004

Kinetic Monte Carlo simulations of thin film growth with anisotropic particles — •Miriam Klopotek, Martin Oettel, and Frank Schreiber — Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Thin film growth is a topic of fundamental experimental research, in particular for organic molecules with semiconducting properties. Thin films of organic molecules are composed of multiple 'imperfect' layers of the molecules, and the structures formed are of fundamental interest for various applications. Organic molecules are mostly highly anisotropic, rendering complex ordering at various length- and time-scales within the growing film that is not seen in the case of isotropic molecular/atomistic films [1]. We explore how this particle anisotropy affects the growth dynamics by means of computer simulations. We have developed a novel algorithm to simulate large-scale thin film growth with rod-like particles using an accelerated Monte Carlo technique called *kinetic Monte Carlo* [2]. We disuss the simulations and the most relevant findings arising from statistical observables related to the orientational order of the rods. To relate the non-equilibrium growth structures to equilibrium we performed equilibrium calculations of a single layer of rods, as well. [1] S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti, and O. Konovalov. Real-time observation of structural and orientational transitions during growth of organic thin films. *Phys. Rev. Lett.*, 96:125504, March 2006. [2] Andrea C. Levi and Miroslav Kotrla. Theory and simulation of crystal growth. *Journal of Physics: Condensed Matter*, 9(2):299, 1997.

TT 38.11   Tue 13:15   MA 004

Ti and N adatom diffusion on, and N_2 desorption from TiN(001) surfaces via *ab initio* and classical molecular dynamics — •Davide G. Sangiovanni[1], Daniel Edström[1], Lars Hultman[1], Ivan Petrov[1,2], Valeriu Chirita[1], and Joe E. Greene[1,2] — [1]Thin Film Physics, IFM, Linköping University, Sweden — [2]University of Illinois, Urbana-Champaign, Illinois, USA

We use classical and *ab initio* molecular dynamics to investigate fundamental atomistic processes and surface properties responsible for TiN surface evolution during thin film growth. The rate of adatom migration and N_2 desorption events are determined as a function of temperature to extract activation energies, attempt frequencies, and diffusion coefficients. Ti adatoms (Ti_{ad}), highly mobile on TiN(001) terraces, diffuse among fourfold hollow sites, primarily along <100> channels via single and long jumps. Ti_{ad} jumps on TiN(001) are highly correlated; an effect which leads to smaller diffusion coefficients than those determined via adatom random walks. Due to strong bonds formed with underlying N surface (N_{surf}) atoms, N adatoms (N_{ad}) are considerably less mobile on TiN(001) than Ti adatoms. After several N_{ad}/N_{surf}-pair exchange reactions, with very few N_{ad} jumps among neighboring stable surface sites, the N_{ad}/N_{surf} pair desorbs, leaving an anion surface vacancy which acts, in turn, as a catalyst for N_2 dissociative chemisorption. This pathway for N_2 desorption from TiN(001) is considerably more probable than N adatom recombination, which is kinetically hindered due to short-range N_{ad}/N_{ad} repulsive interactions.