O 85: New Methods: Theory

Time: Thursday 10:30–12:45 Location: H25

O 85.1 Thu 10:30 H25

Quantifying the conductance of molecular structural variables using machine learning — •Hector Vazquez — Inst. of Physics, Czech Academy of Sciences

In single molecule electronics, where individual molecules are placed between two nanoscale electrodes, conductance depends critically on the geometry at the junction. Atomistic simulations using DFT-NEGF are ideally suited to address this, but their computational cost restricts their use to only few junction geometries. In experiments, however, molecular geometry is thought to change significantly since measurements are often carried out at room temperature.

Here we use an approximate method to calculate molecular conductance within DFT for thousands of geometries [1]. The method uses small Au-molecule-Au clusters and is thus computationally very efficient, yet reproduces DFT-NEGF conductance well. Combined with MD simulations of the junction, we compute for thousands of geometries the variation in conductance arising from thermally-induced conformational changes in the molecule.

We use machine-learning methods to identify which of the molecular structural parameters, all of which are changing continuously and simultaneously during the MD simulations, have a greater impact in conductance. This elucidates how molecular conformational changes contribute to the width of the conductance signal in single molecule junctions.

[1] H. Vazquez, J. Phys. Chem. Lett. 13 9326 (2022)

O 85.2 Thu 10:45 H25

Efficient implementation of charge-equilibration schemes for fourth-generation machine learning potentials — •Moritz R. Schäfer^{1,2}, Moritz Gubler^{3}, Stefan Goedecker^{3}, and Jörg Behler^{1,2} — ^{1}Theoretische Chemie II, Ruhr-Universität Bochum, Germany — ^{2}Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany — ^{3}Department of Physics, University of Basel, Switzerland

Fourth-generation high-dimensional neural network potentials (4G-HDNNPs) are a modern technique to compute energies and forces with close to ab initio accuracy for conducting extensive molecular dynamics simulations of complex systems. They are based on global information and include long-range charge transfer, electrostatics and atomic energies to describe the interactions in a system. A central component of 4G-HDNNPs is a charge equilibration (Q_{eq}) step, which due to its non-local nature dominates the computational costs. Here, we discuss efficient implementation strategies, and show their performance on selected benchmark systems.

O 85.3 Thu 11:00 H25

Real-time Bethe-Salpeter Equation for optical properties of molecules – Implementation and benchmark calculations — •Štěpán Marek, Maximilian Graml, and Jan Wilhelm — Institute of Theoretical Physics and Regensburg Center for Ultrafast Nanoscopy, University of Regensburg, Regensburg, Germany

We present an implementation of a real-time version of the Bethe-Salpeter equation (RT-BSE) in CP2K, offering new capabilities for investigating electron dynamics in molecules under laser excitation. The RT-BSE implementation is tested on Thiel's molecular benchmark set - a set of organic molecules of various types. We evaluate the accuracy and performance of the RT-BSE approach for the determination of absorption spectra of molecules, with respect to the Casida-BSE approach. We discuss the scaling of the method to show its potential for studying optical properties of large molecules and complex materials.

O 85.4 Thu 11:15 H25

Extension of FLAPW method `FLEUR` to phonon calculations of polar solids using DFPT — •Friedrich Hanrath^{1,2}, Thomas Bornhake^{1,2}, Gregor Michalicek^{1}, Daniel Wortmann^{1}, Gustav Bihlmayer^{1}, and Stefan Blügel^{1,2} — ^{1}Peter Grünberg Institut, Forschungszentrum Jülich and JARA, Jülich, Germany — ^{2}Physics Department, RWTH Aachen University, Aachen, Germany

Phonons play a pivotal role in determining important properties of solids. In polar materials, phononic vibrations are altered by the interaction of macroscopic electric fields in the limit of long wavelengths. This gives rise to the characteristic splitting of longitudinal and transversal optical phonon frequencies. Density function perturbation theory (DFPT) is a state-of-the-art approach to calculate many essential physical properties of solids from first principles. By using an ionic displacement perturbation, it has previously been employed in order to calculate phonons in the framework of the full-potential linearized augmented plane-wave method `FLEUR` [1, 2]. — In this talk, this method is extended to a macroscopic homogeneous electric field perturbation allowing the calculation of static dielectric properties, Born effective charges and hence LO-TO-splitting. We present the current results for the static dielectric tensor for various semiconductors and insulators by comparing them with experimental results.
This work was supported by the CoE-MaX (EuroHPC JU, Grant No. 101093374) and DFG through CRC 1238 (Project C01).

[1] D. Wortmann *et al.*, 10.5281/zenodo.7576163; www.flapw.de

[2] C.-R. Gerhorst *et al.*, Electron. Struct. **6**, 017001 (2024).

O 85.5 Thu 11:30 H25

Efficient treatment of long-range electrostatics in charge equilibration approaches — •Kamila Savvidi, Ludwig Ahrens-Iwers, and Robert Meissner — Hamburg University of Technology, Hamburg, Germany

We present a charge equilibration (QEq) method in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) based on real-space Gaussians of width η_i as charge densities. This implementation builds on the `ELECTRODE` package, which already supports Gaussian charge densities [1]. In addition, an efficient particle-particle particle-mesh k-space solver [2] is used, which significantly improves the computational performance compared to existing QEq implementations in LAMMPS. We validate our approach with the test cases of Ti/TiO_x and SiO_2 polymorphs. In the limit of very narrow Gaussians, we were able to show that our algorithm converges to EEM results for the case of Ti/TiO_x. By fitting the Coulomb energy of two isolated Gaussian charge distributions to the repulsion between two Slater-type orbitals, optimized widths for Si and O were obtained that led to results in good agreement to previous studies using STOs instead of Gaussians.

[1] Ludwig J. V. Ahrens-Iwers, Mathijs Janssen, Shern R. Tee, Robert H. Meißner; ELECTRODE: An electrochemistry package for atomistic simulations. J. Chem. Phys. 28 August 2022; 157 (8) [2] Ahrens-Iwers LJV, Meißner RH. Constant potential simulations on a mesh. J Chem Phys. 2021 Sep 14;155(10)

O 85.6 Thu 11:45 H25

Machine Learning for Polaronic Materials: TiO_2(110) at the nanoscale — •Firat Yalcin^{1}, Simon Trivisonne^{1}, Viktor Birschitzky^{1}, Carla Verdi^{2}, and Michele Reticcioli^{1,3} — ^{1}University of Vienna, Austria — ^{2}University of Queensland, Australia — ^{3}CNR-SPIN L'Aquila, Italy

The combination of machine learning (ML) with density functional theory accelerates material simulations, expanding both spatial and temporal scales. However, current ML methods struggle to address polaron trapping. We present a novel machine learning force field (MLFF) approach that incorporates polaron trapping descriptors, enabling large-scale studies of polaronic materials. Using TiO_2(110) as a case study, we reveal how Nb dopants and oxygen vacancies affect polaron configurations and drive catalytic CO adsorption. Additionally, our method captures the dynamic evolution of polarons with unprecedented statistical robustness. This work advances fundamental understanding of defect-polaron interactions while offering a fully-automated and efficient computational suite for the study of polaronic materials.

O 85.7 Thu 12:00 H25

Uncertainty quantification for DFT calculations — •Teitur Hansen^{1}, Thomas Bligaard^{2}, and Karsten W. Jacobsen^{1} — ^{1}DTU Physics, Kongens Lyngby, Denmark — ^{2}DTU Energy, Kongens Lyngby, Denmark

Density functional theory (DFT) is widely used for understanding material properties and chemical reactions. DFT simulations use approximations which result in errors when comparing to experiments. There are errors in different types of energies, lattice constants and other properties. Quantitative uncertainty estimates would be helpful for DFT simulations to highlight which results are trustworthy. Quantifying uncertainties not only improves trust in calculations but also identifies high-uncertainty predictions that can subsequently be revisited and reanalyzed.

We propose a method to model uncertainties using a probability distribution over exchange-correlation functionals. The probability distribution is trained on experimental values of molecular atomization energies, cohesive energies of solids, reactions energies, heat of formations, and lattice constants. The optimized probability distribution is then used to define an ensemble method which can be used to estimate the bias and variance on simulated materials properties. I will demonstrate that the method gives systematic improvements in error estimates over the Bayesian error estimation class of functionals (BEEF).

The proposed method is general enough to be applied to any simulation methodology where accurate reference benchmarks exist.

O 85.8 Thu 12:15 H25

Assessment of the Accuracy of Equation-of-motion Coupled-cluster band gaps in the Bulk Limit — •Evgeny Moerman[1], Alejandro Gallo[2], Andreas Irmler[2], Andreas Grüneis[2], and Matthias Scheffler[1] — [1]The NOMAD Laboratory at the FHI-MPG, Berlin — [2]Institute for Theoretical Physics, TU Wien, Vienna

As a highly regarded theoretical framework in molecular quantum chemistry, coupled-cluster (CC) theory is expected to yield reliable and systematically improvable results for both ground-state and ex cited state properties of materials. One major obstacle to obtaining converged CC results for periodic solids is the often slow convergence with respect to system size. We have investigated the finite-size convergence behaviour of band gaps in equation-of-motion CC (EOM-CC) theory and revealed a direct relation to the GW approximation [1]. Based on these findings, a GW-aided scheme to reliably estimate the size-converged EOM-CC band gap has been developed and tested [2], allowing to assess the true accuracy of the widely used EOM-CCSD method in the periodic case. We find that the accuracy of EOM-CCSD band gaps sensitively depends on the magnitude of orbital relaxation effects, suggesting that such low-order truncation methods as EOM-CCSD may not be sufficiently accurate even for simple materials and that higher orders of correlations seem to be necessary. - This work received support from the European Union's Horizon 2020 research and innovation program under Grant Agreement No.740233.

[1] Moerman et al., arXiv:2409.03721 (2024)

[2] Moerman et al., to be published

O 85.9 Thu 12:30 H25

Full periodic real-time TD-DFTB implementation for solids and low-dimensional materials — •Carlos R. Lien-Medrano[1], Franco P. Bonafé[2], Matías Berdakín[3], Cristián G. Sánchez[4], and Michael Sentef[1,2] — [1]University of Bremen, Bremen, Germany — [2]MPSD, Hamburg, Germany — [3]Universidad Nacional de Córdoba, Córdoba, Argentina — [4]Universidad Nacioanl de Cuyo, Mendoza, Argentina

The current real-time time-dependent density functional tight-binding (TD-DFTB) dynamics implementation in the DFTB+ package [1] employs the length gauge of the electric field. In this work, we introduce an implementation of the vector potential within the velocity gauge framework. This approach enables the extension of real-time dynamics simulations to periodic systems along arbitrary spatial directions, making it applicable to photo-induced dynamical processes in bulk, low-dimensional materials, and surfaces. To demonstrate its potential, we present proof-of-concept applications, including the inhomogeneous optical absorption around the K point in graphene, light absorption in bulk materials, and prospective applications in the field of valleytronics.

[1] Hourahine, B., et al. (2020). DFTB+, a software package for efficient approximate density functional theory based atomistic simulations. The Journal of Chemical Physics, 152(12), 124101.