

O 108: Electronic Structure Theory II

Time: Friday 10:30–12:30

Location: MA 043

O 108.1 Fri 10:30 MA 043

Downfolding approaches to electron-phonon coupling — ●JAN BERGES¹, NINA GIROTTO², ARNE SCHOBERT³, ERIK VAN LOON⁴, MICHAEL SENTEF¹, SERGEY BRENER³, MARIANA ROSSI⁵, TIM WEHLING³, SAMUEL PONCÉ^{6,7}, and NICOLA MARZARI^{8,1} — ¹University of Bremen, Germany — ²Institute of Physics, Zagreb, Croatia — ³University of Hamburg, Germany — ⁴Lund University, Sweden — ⁵MPI for the Structure and Dynamics of Matter, Hamburg, Germany — ⁶ETSF, UCLouvain, Belgium — ⁷WEL Research Institute, Wavre, Belgium — ⁸EPFL, Lausanne, Switzerland

Despite the success of density-functional perturbation theory (DFPT), the simulation of electron-phonon interactions in materials remains challenging, especially for large systems or in presence of strong correlations. We address this problem by downfolding it to effective low-energy models, using localized representations in the basis of Wannier functions. Based on data from DFPT, this allows us to obtain phonon frequencies at high precision and low computational cost via corrections to the static phonon self-energy [Phys. Rev. X **13**, 041009 (2023)]. A generalization beyond the harmonic approximation is possible, providing free energies, forces, and force constants for structurally distorted systems on supercells, based on DFPT data for the primitive cell of the undistorted system alone. This is an ideal platform for the study of charge-density waves (CDWs) and polarons. We apply it to perform molecular-dynamics simulations [arXiv:2303.07261] and to calculate phonon dispersions [Nano Lett., in press (2023), arXiv:2307.13791] for two-dimensional transition-metal dichalcogenides in the CDW phase.

O 108.2 Fri 10:45 MA 043

All-electron Periodic GW Method with Numeric Atom-centered Orbitals: Systematic Benchmark and Application to Temperature-dependent Band Structure — ●MIN-YE ZHANG^{1,2}, UTHPALA HERATH³, VOLKER BLUM³, XINGUO REN², HONG JIANG⁴, and MATTHIAS SCHEFFLER¹ — ¹The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin — ²Institute of Physics, Chinese Academy of Sciences, China — ³Department of Mechanical Engineering and Materials Science, Duke University, U.S. — ⁴College of Chemistry and Molecular Engineering, Peking University, China

The many-body G_0W_0 method is the state-of-the-art for theoretically analyzing the electronic structure of materials. The all-electron approach was recently implemented in FHI-aims for periodic systems. This method employs numeric atom-centered orbitals (NAOs) and localized resolution-of-identity approximation.^[1] A thorough benchmark is still needed. Here we benchmark the precision in terms of standard NAOs and auxiliary basis functions for 50 gapped systems. We also measure the strong scaling with different system sizes for efficiency benchmark. By combining G_0W_0 with molecular dynamics, we showcase the possibility to study the temperature dependence of the band structure with electron-electron and electron-vibration self-energy considered jointly. This approach enables the study of strongly anharmonic materials where the phonon picture and electron-phonon coupling concepts break down.

[1] X. Ren *et al.*, *Phys. Rev. Materials* **5**, 013807 (2021).

O 108.3 Fri 11:00 MA 043

A Multimer Embedding Approach for Molecular Crystals up to Anharmonic Vibrational Properties — ●JOHANNES HOJA, ALEXANDER LIST, and ADRIAN DANIEL BOESE — University of Graz, Graz, Austria

Accurate modeling of molecular crystals is crucial for drug design and crystal engineering. However, periodic density functional calculations using hybrid functionals are often prohibitively expensive for practically relevant molecular crystals. One way of circumventing expensive periodic calculations is the usage of a subtractive embedding scheme, where the periodic calculation is only performed with a lower-cost method and then monomer energies and multimer interaction energies are replaced by those of the high-level method. Herein, we present such a multimer embedding approach for energies, structures, and vibrational properties of molecular crystals containing up to trimer interactions [1]. We evaluate this approach for the X23 benchmark set by approximating periodic PBE0+MBD by embedding multimers into less expensive PBE+MBD calculations. We show that trimer inter-

actions are crucial for approximating lattice energies within 1 kJ/mol and cell volumes within 1 %. Harmonic vibrational free energies can already be approximated within 1 kJ/mol at the monomer or dimer level. Finally, we also utilize this embedding approach to incorporate anharmonic effects via second-order vibrational perturbation theory (VPT2) calculations of monomers and dimers.

[1] J. Hoja, A. List, A.D. Boese, *J. Chem. Theory Comput.*, in press, DOI: 10.1021/acs.jctc.3c01082.

O 108.4 Fri 11:15 MA 043

Interpreting ultrafast electron transfer on surfaces with first-principles electronic couplings — ●SIMIAM GHAN¹, ELIAS DIESEN¹, CHRISTIAN KUNKEL¹, KARSTEN REUTER¹, and HARALD OBERHOFER² — ¹Fritz-Haber Institute of the Max-Planck Society, Berlin — ²Department of Physics, University of Bayreuth

The electronic coupling between adsorbates and surfaces is invoked in models of e.g. charge transfer, chemisorption, and quantum impurities (Kondo physics). While the coupling matrix element H_{ad} is usually approximated, we demonstrate here that it can be calculated directly from first principles Density Functional Theory. This is achieved through a projection of the Kohn-Sham Hamiltonian upon a basis of diabatic states localized on either the adsorbate or surface systems. An appropriate integration of couplings over the Brillouin zone allows for calculation of the Newns-Anderson chemisorption function, a coupling-weighted density of states which gives the line broadening of an adsorbate frontier state upon adsorption. This broadening corresponds to the experimentally-observed lifetime of an electron in the state, which we confirm for core-excited $\text{Ar}^*(2p_{3/2}^{-1}4s)$ atoms on a number of transition metal surfaces. The use of explicit coupling matrix elements is found to be highly advantageous, elucidating the ultrafast electron transfer process in terms of coupling to the various bands of the surface[1]. The suitability of the scheme for treating fully chemisorbed systems is discussed.

[1] S. Ghan *et al.* *J. Chem. Phys.* **158**, 234103 (2023).

O 108.5 Fri 11:30 MA 043

Efficient Force Implementation for Implicit Solvation in All-Electron Full-Potential DFT — DANIEL WALDSCHMIDT¹, ●JAKOB FILSER², and HARALD OBERHOFER^{1,3} — ¹Technical University of Munich — ²Fritz-Haber-Institut der MPG, Berlin — ³University of Bayreuth

Implicit solvation remains a popular method to incorporate solvation effects into density functional theory (DFT). Rather than explicitly including solvent molecules in the *ab initio* calculation, this family of methods treats the solvent as a structureless dielectric medium, in which the solute resides in a cavity. This drastically reduces the size of the computationally expensive *ab initio* system while also removing the need to sample over different solvent configurations.

We have previously developed a multipole expansion implicit solvation model with multiple subcavities (MPE-*nc*) and implemented it in the DFT package FHI-aims. It solves the electrostatic problem to good accuracy at high computational efficiency. In a DFT context, we found it to not be the bottleneck of the calculation. Here, we discuss the derivation and implementation of analytical forces for MPE-*nc*, as well as their computational efficiency. This recent development lifts a rather severe limitation for the practical applicability, now making common modeling tasks such as geometry optimization and molecular dynamics accessible. We further address some minor adaptations to the model which are necessary to ensure the continuity of the potential energy surface and its agreement with the analytic forces, both prerequisites for most applications involving forces.

O 108.6 Fri 11:45 MA 043

A comprehensive exploration of structural and electronic properties of Molybdenum clusters — ●YAO WEI, ALEJANDRO SANTANA BONILLA, and LEV KANTOROVICH — Department of Physics, King's College London, London, WC2R 2LS, United Kingdom

Molybdenum clusters, characterised by their unique structure and intriguing catalytic properties, have gained significant attention in recent years. In several existing studies density functional theory (DFT) methods have been used to find the lowest energy Mo clusters and explore their electronic and magnetic structure. In all cases, with the

exception of a single recent study, where a genetic algorithm was employed, initial geometries of the clusters, prior to geometry optimisation, were chosen using heuristic approaches based on symmetry considerations and known structures. DFT calculations were performed using different types of pseudopotentials, from hard to soft, and different types of basis sets. However, no comprehensive study has yet been done in which a DFT method with the best control on its precision would be complemented by a reliable global minimum search method to find the lowest energy Mo clusters. In this work, we employ a combination of a plane wave-based DFT method and ab initio random structure searching (AIRSS) technique to find the lowest energy clusters of up to 10 Mo atoms. In each case, the search has been performed for clusters with different spin multiplicities, which enabled us to explore their magnetic structure. Free energies of the Mo clusters, within the quasi-harmonic approximation, are also calculated and discussed. Similar methodology based on a stochastic exploration of the coordinate phase space is then presented for studying adsorption of Mo clusters on graphene and investigating their catalytic properties towards the CO dissociation reaction.

O 108.7 Fri 12:00 MA 043

Benchmark Auxiliary-Field Quantum Monte Carlo Method — •ZORAN SUKURMA¹, MARTIN SCHLIPF², MORITZ HUMER¹, AMIR TAHERIDEHKORDI¹, and GEORG KRESSE^{1,2} — ¹Kolingasse 14-16, University of Vienna — ²Berggasse 21, VASP GmbH

Phaseless Auxiliary-Field Quantum Monte Carlo (ph-AFQMC) is a promising method to approximate the ground state properties of various quantum systems, including molecules, solids, and lattice models.

We present a scalable Fortran implementation of ph-AFQMC and demonstrate its excellent performance and favorable computational scaling. We apply the method to the HEAT set, the benzene molecule, water clusters, and a 2x2x2 diamond supercell. We observe a mean absolute deviation of the total energy of 1.15kcal/mol for the HEAT set. For water clusters, we find that ph-AFQMC yields binding energies that differ from CCSD(T) by typically less than 0.5kcal/mol. Excellent agreement with CCSD(T) is observed for diamond. In addition,

we investigate modifications of the phaseless approximation that can help to reduce overcorrelation problems common to ph-AFQMC. Using the benzene molecule as an example, we demonstrate that the modified algorithm reproduces the same energy as the original algorithm with 400 Slater determinants.

Our results underscore the potential of ph-AFQMC to accurately predict ground-state properties in various systems.

Z. Sukurma, M. Schlipf, M. Humer, A. Taheridehkordi, and G. Kresse, *J. Chem. Theory Comput.* 19, 4921 (2023)

O 108.8 Fri 12:15 MA 043

Phaseless auxiliary field quantum Monte Carlo with projector-augmented wave method for solids — AMIR TAHERIDEHKORDI¹, MARTIN SCHLIPF², ZORAN SUKURMA¹, •MORITZ HUMER¹, and GEORG KRESSE^{1,2} — ¹University of Vienna, Faculty of Physics and Center for Computational Materials Physics, Austria — ²VASP Software GmbH, Vienna, Austria

In this talk, we present our phaseless auxiliary field quantum Monte Carlo (ph-AFQMC) implementation using the plane-wave based projector augmented wave method. We showcase the accuracy and the feasibility of its application to solids. The AFQMC groundstate wavefunction is represented as an ensemble of Slater determinants placed in fluctuating auxiliary fields. This is achieved by transforming the two-body component of the many-body Hamiltonian into an effective one-body potential through the Hubbard Stratonovich transformation. Our implementation is numerically verified by consistent correlation energies from the primitive-cell sampling and the corresponding supercell calculations. We compare the equation of state of diamond and the correlation energies for a range of prototypical solid materials to conventional deterministic quantum-chemistry methods. A down-sampling technique along with natural orbitals accelerates the convergence with respect to the number of orbitals and crystal momentum points. Additionally, we demonstrate that our implementation is competitive in terms of accuracy and computational cost for dense crystal momentum point meshes compared to a well-established coupled-cluster singles-doubles with perturbative triples approach.