

O 50: Frontiers of Electronic Structure Theory: Focus on Artificial Intelligence Applied to Real Materials 2

Time: Wednesday 15:00–18:00

Location: S054

O 50.1 Wed 15:00 S054

Automating the Generation of Linearized Augmented Planewave Basis Functions — ●HANNAH KLEINE¹, SVEN LUBECK¹, ANDRIS GULANS², and CLAUDIA DRAXL¹ — ¹Humboldt-Universität zu Berlin — ²University of Latvia

The linearized augmented planewave (LAPW) and local orbitals (LO) method is known to be a highly precise scheme for solving the Kohn-Sham equations of density-functional theory (DFT) for solids. One drawback, however, is that the LAPW and LO basis functions depend on linearization energies which are material dependent. We propose an approach that allows us to compute the linearization energies from the number of nodes of the respective atomic function. It is implemented in the all-electron full-potential computer package exciting [1]. Following this prescription, we are able to automatize the generation of linearly independent basis functions for any material. This approach not only improves the usability of the method, it also leads to better reproducibility of results, and prepares the code for high-throughput calculations.

[1] A. Gulans et al., *J. Phys. Condens. Matter* **26**, 363202 (2014).

O 50.2 Wed 15:15 S054

Hybrid Density-Functional Theory at the Limit: All-electron Exact Exchange beyond 10,000 Atoms — FLORIAN MERZ¹, ●SEBASTIAN KOKOTT², CHRISTIAN CARBOGNO², YI YAO³, MARKUS RAMPP⁴, MATTHIAS SCHEFFLER², and VOLKER BLUM³ — ¹Lenovo HPC Innovation Center, Stuttgart — ²The NOMAD Laboratory at the FHI-MPG and HU, Berlin — ³Duke University, North Carolina, USA — ⁴Max Planck Computing and Data Facility, Garching

The computational bottleneck of hybrid density functionals, such as HSE [1], is the evaluation of the exact exchange (EXX) contribution. In this work, we present algorithmic advances in the resolution-of-identity [2] based, real-space implementation of EXX in *FHI-aims* [3,4]. By exploiting MPI-3 intra-node shared memory and enhancing the parallelization scheme, scalability and workload distribution has been drastically improved, which results in memory efficiency and performance increases of up to two orders of magnitude compared to the original implementation, for both total energies and forces/stresses. [3,4] We discuss the details of our implementations and demonstrate the performance as well as scalability for a balanced test set covering inorganic solids, large molecules, and organic crystals with up to 10,000 atoms. Eventually, we show how these advancements enable insights for the design and optimization of hybrid organic/inorganic perovskites.

[1] Heyd, Scuseria, and Ernzerhof, *J. Chem. Phys.* **118.18**, (2003).[2] Ihrig et al., *New J. Phys.* **17.9**, (2015).[3] Levchenko et al., *Comp. Phys. Commun.* **192**, (2015).[4] Knuth et al., *Comp. Phys. Commun.* **190**, (2015).

O 50.3 Wed 15:30 S054

Studying nuclear quantum effects on water splitting at a charged interface — ●KAREN FIDANYAN and MARIANA ROSSI — Max Planck Institut for the Structure and Dynamics of Matter

Interfaces of water with charged metallic surfaces are relevant for multiple technological processes.¹ In particular, in electrolyzers, the water splitting reaction happens at charged metallic electrodes. The atomistic mechanisms of this fundamental reaction is determined not only by the surface charge induced by the potential bias, but also by nuclear quantum effects (NQE), which are known to impact such reactions strongly.² In this work, we present steps towards a framework for an *ab initio* evaluation of the interplay between these two effects. By making use of a new implementation of the nudged-elastic-band method in the i-PI software,³ we are able to calculate forces for this reaction from a variety of electronic-structure codes. At first, we approximate the electrode by a slab using density-functional theory with an applied homogeneous electric field and study how NQEs are changed through the water dissociation paths under different field strengths. Taking advantage of the capabilities of i-PI to connect to other codes, our framework can be extended to more accurate models of the potential bias, as for example grand-canonical electronic structure methods.

[1] G. Gonella et al., *Nat Rev Chem* **5**, 466–485 (2021).[2] Y. Litman, D. Donadio, M. Ceriotti and M. Rossi, *J. Chem. Phys.*

148 102320 (2018).

[3] V. Kapil et al., *Comp. Phys. Comm.* **236** 214–223 (2019).

O 50.4 Wed 15:45 S054

All-Electron BSE@GW Method for K-Edge Core Electron Excitation Energies — ●YI YAO^{1,2}, DOROTHEA GOLZE^{3,4}, PATRICK RINKE⁴, VOLKER BLUM^{2,5}, and YOSUKE KANAI¹ — ¹Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States — ²Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, United States — ³Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany — ⁴Department of Applied Physics, Aalto University, P.O. Box 11100, FI-00076 Aalto, Finland — ⁵Department of Chemistry, Duke University, Durham, North Carolina 27708, United States

We present an accurate computational approach to calculate K-edge core electron excitation energies, achieved by combining all-electron GW and Bethe-Salpeter equation (BSE) methods. We assess the BSE@GW approach for calculating K-edge X-ray absorption spectra using a set of small organic molecules and also a medium-sized sulfur-containing molecule, which was used in a past benchmark of an equation-of-motion coupled-cluster (EOM-CC) method by Peng and coworkers [Peng et al., *J. Chem. Theory Comput.*, **11**, 4146 (2015)]. We present the influence of different numerical approximations. We assess the basis set dependence and convergence. We identify the importance of core-correlation basis functions as well as the augmenting basis functions. Compared to the experimental values, the predicted mean absolute error by BSE@GW is as low as 0.6-0.7 eV.

O 50.5 Wed 16:00 S054

Hybrid excitations at the interface between MoS₂ monolayer and organic molecules from first-principle calculation — ●IGNACIO GONZALEZ OLIVA¹, FABIO CARUSO^{1,2}, PASQUALE PAVONE¹, and CLAUDIA DRAXL¹ — ¹Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ²Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24118 Kiel, Germany

Hybrid materials composed of organic and two dimensional (2D) inorganic semiconductors are receiving increasing attention due to the interesting physical processes happening at the interface. We present a first-principles investigation of the electronic and optical properties of hybrid organic-inorganic interfaces consisting of a MoS₂ monolayer and the π -conjugate molecules pyrene and pyridine. Employing the G_0W_0 approximation to obtain the quasi-particle band structures, and solving the Bethe-Salpeter equation, we compute the absorption spectra. The latter reveal intralayer excitons on the MoS₂ side, and also hybrid as well as charge-transfer excitons at the interface. Our findings indicate that hybrid systems consisting of semiconducting transition-metal dichalcogenides and organic π -conjugate molecules can host a rich variety of optical excitations and thus provide a promising venue to explore exciton physics in low dimensionality.

O 50.6 Wed 16:15 S054

Mott Metal-Insulator Transition from Steady-State Density Functional Theory — ●DAVID JACOB^{1,2}, GIANLUCA STEFANUCCI³, and STEFAN KURTH^{1,2,4} — ¹Universidad del País Vasco UPV/EHU, San Sebastian, Spain — ²Ikerbasque Foundation, Bilbao, Spain — ³Università di Roma Tor Vergata, Rome, Italy — ⁴Donostia International Physics Center, San Sebastian, Spain

We present a computationally efficient method to obtain *many-body* spectral functions of bulk systems in a *density functional theory* framework [1]. To this end we generalize a recently developed method for computing many-body spectral functions of nanoscale systems [2], based on steady-state density functional theory (i-DFT) and using an idealized scanning tunneling microscope (STM) setup, to the case of bulk systems. In this setup the spectral function can be obtained from the finite-bias differential conductance of the current through the STM tip. The fictitious noninteracting system of i-DFT features an exchange-correlation (XC) contribution to the bias which guarantees the same current as in the true interacting system. Exact properties of

the XC bias are established using Fermi-liquid theory and subsequently implemented to construct approximations for the Hubbard model. We show for two different lattice structures that our method captures the Mott metal-insulator transition.

References: [1] D. Jacob, S. Kurth, G. Stefanucci, Phys. Rev. Lett. **125**, 216401 (2020); [2] D. Jacob and S. Kurth, Nano Lett. **18**, 2086 (2018).

O 50.7 Wed 16:30 S054

Network of 1d edge channels and localized states emerging in moiré system — ●JEYONG PARK, JINHONG PARK, and ACHIM ROSCH — Institute of theoretical physics, University of Cologne, Germany

For the general moiré system, we theoretically study the effective Hamiltonian for single layer considering the smooth periodic moiré potential induced by other layer, which appears because of distance difference between each pair of atoms located on different layer. For moiré potential larger than tunable moiré energy scale, we find the coexistence of 1D channels and localized state in real space. The 1D channels emerge along the three 1D lines where the mass gap of single layer coming from moiré potential becomes zero, which is showing that these channels are the edge states. Localized states emerge at the crossing point of three 1d lines. We construct the toy model which describes the coexistence of these states by symmetry analysis and consider the RKKY interaction between localized states which is mediated by 1D channels by including whole spin and valley degrees of freedom. Expanding the effective action for the toy model and controlling chemical potential to suppress oscillation coming from fermi momentum gives three spin interaction $S \cdot (S \times S)$, which can give chiral spin liquid phase. We show how the analytical result can be seen in our model numerically and propose the graphene on top of AB stacking bilayer with twist as the candidate material for realization.

O 50.8 Wed 16:45 S054

Incorporating First-Principles Electronic Friction in Instanton Rate Theory — ●YAIR LITMAN¹, ESZTER S. POS¹, CONNOR L. BOX², ROCCO MARTINAZZO³, REINHARD J. MAURER², and MARIANA ROSSI¹ — ¹MPI for the Structure and Dynamics of Matter, Hamburg, Germany. — ²Department of Chemistry, University of Warwick, Coventry, United Kingdom — ³Department of Chemistry, Università degli Studi di Milano, Milano, Italy

Reactions involving impurities in bulk metals are ubiquitous in a wide range of technological applications. The theoretical modelling of such reactions present a challenge for theory because nuclear quantum effects (NQEs) can play a prominent role and the coupling of the atomic motion with the electrons in the metal gives rise to important non-adiabatic effects (NAEs). In this work, we present a theoretical framework for the calculation of reaction rates capable of capturing both NQEs and NAEs for high-dimension realistic systems [1,2]. This is achieved by combining the ring polymer instanton (RPI) formalism with *ab initio* electronic friction from Ref. [3]. We derive equations that incorporate the spatial and frequency dependence of electronic friction, and name the new method RPI with explicit friction (RPI-EF). We validate RPI-EF against numerically exact results and find, quantitatively, how the friction modifies reaction rates and tunnelling pathways. Finally, we present *ab initio* results for H-hopping in selected bulk metals. [1] Y. Litman, E. S. Pócs, C. L. Box, R. Martinazzo, R. J. Maurer, and M. Rossi, *JCP* **156**, 194106 (2022) [2] *id.* *JCP* **156**, 194107 (2022) [3] M. Head-Gordon, J. C. Tully, *JCP* **96**, 3939 (1992).

O 50.9 Wed 17:00 S054

Real-Time Time-Dependent Density Functional Theory within the FHI-aims code — JOSCHA HEKELE¹, YI YAO², VOLKER BLUM², YOSUKE KANAI³, and ●PETER KRATZER¹ — ¹Faculty of Physics, University Duisburg-Essen, 47057 Duisburg, Germany — ²Thomas Lord Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, USA — ³Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, USA

We present a high-precision all-electron RT-TDDFT implementation using numerical atom-centered orbital (NAO) basis functions into FHI-aims. First, RT-TDDFT results are validated against linear-response TDDFT results for the molecules of Thiel's test set and the importance of basis augmentation for adequate convergence is confirmed. Adopting a velocity-gauge formalism, dielectric properties of crystalline materials are calculated. Taking advantage of the all-electron full-potential implementation, we present applications to soft X-ray spectra of H₂O using hybrid functionals. Moreover, numerical performance tests are presented showing almost linear scaling on parallel computers.

O 50.10 Wed 17:15 S054

Ab initio study of many-body interacting nonlinear optical photoconductivity tensors — ●PEIO GARCIA-GOIRICELAYA¹, JYOTI KRISHNA¹, and JULEN IBAÑEZ-AZPIROZ^{1,2} — ¹Centro de Física de Materiales, University of the Basque Country UPV/EHU, Spain — ²IKERBASQUE Basque Foundation for Science, Spain

We present a general scheme for calculating the many-body interacting second-order optical photoconductivity tensor from first-principles. Our practical implementation starts from the length-gauge formulation of the single-particle non-interacting second-order response tensor [1] that is efficiently calculated using Wannier interpolation [2]. In a second step, we make use of the TD-CDFT in order to extract the many-body interacting response tensor, taking into account collective excitations, i.e. excitonic effects for semiconductors and plasmonic effects for metals. We employ this scheme to assess the impact of many-body excitations on second harmonic generation and benchmark our results with experiments on the semiconducting GaAs [3] and the semimetal TaAs [4], as well as with early calculations [5].

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- [2] G. Pizzi *et al.*, J. Phys. Cond.Matt. **32**, 165902 (2020)
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- [4] Shreyas Patankar *et al.*, Phys. Rev. B **98**, 165113 (2018).
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O 50.11 Wed 17:30 S054

Electron-phonon drag in MgB₂ — ●NAKIB PROTIK and CLAUDIA DRAXL — Institut für Physik and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

MgB₂ is a well known phonon-mediated superconductor with a transition temperature around 40 K. The strong electron-phonon interactions present in the material also give rise to strong drag phenomena, as has been demonstrated experimentally in Refs. [1, 2]. While the measured thermopower in the normal phase shows hole-like transport, there is, however, no consensus regarding the sign and temperature dependence of the drag contribution. In this work, we carry out anisotropic and band-resolved *ab initio* transport calculations to investigate this puzzle. Our findings will shed light on the roles of the microscopic interactions on the strong drag behavior in metals.

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- [2] Putti, M., E. Galleani d'Agliano, D. Marre, F. Napoli, M. Tassisto, P. Manfrinetti, A. Palenzona, C. Rizzuto, and S. Massidda. "Electron transport properties of MgB₂ in the normal state." The European Physical Journal B-Condensed Matter and Complex Systems 25, no. 4 (2002): 439-443.

O 50.12 Wed 17:45 S054

Ab initio simulations of vibrational sum frequency generation without molecular decomposition — ●PAOLO LAZZARONI, ALAN LEWIS, and MARIANA ROSSI — Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany

Hydrogen evolution through heterogeneous catalysis is an increasingly popular solution for storage of energy generated from renewable sources, and as such is becoming a central part of green energy grids. Understanding the structure of water at solid interfaces is vital to find more efficient and cost-effective catalysts of this reaction, and sum-frequency generation spectroscopy provides a surface-specific method of investigating these structures [1]. In this work we present a new framework for *ab initio* calculations of the sum-frequency response which avoids the need for an arbitrary molecular decomposition of the polarizability and dipole moment. Within this approach, based on Density Functional Theory, the observables are evaluated using real space integrals directly on the whole system [2]. This allows us, for example, to unravel the effect of this decomposition on the sum-frequency response of the much-studied water/vacuum interface. This scheme also enables us, in the context of water-solid interfaces, to account explicitly for the contribution of the solid to the polarizability and dipole moment of the interface, which are commonly neglected.

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