O 92: Electronic Structure Theory

Time: Thursday 15:00–18:15 Location: H25

O 92.1 Thu 15:00 H25

Electronic and Optical properties of K-Sb and Na-Sb binary crystals from ab initio many-body theory — •Richard Schier and Caterina Cocchi — Carl von Ossietzky Universität Oldenburg, Institut für Physik

Alkali-based photocathode materials have come into the limelight as novel semiconducting materials for electron sources. However, challenges in sample purity and polycrystallinity hinder the direct experimental determination of their intrinsic properties. First-principles methods can effectively complement experiments in predicting favorable structures and gaining insight into their electronic and optical properties. In this work, we investigate K-Sb and Na-Sb binary crystals emerged as stable phases from high-throughput screening [1]. Using many-body perturbation theory on top of density functional theory, we find that all considered materials have optical gaps in the near-infrared region between 0.7 - 1.2 eV. The character of the excitations and electron-hole correlations therein are highly dependent on the composition and crystal structure of the compound. Excitonic effects appear more pronounced in the K-Sb crystals, where binding energies are of the order of 100 - 200 meV and the oscillator strength is sizably redistributed to lower-energy peaks. These characteristics indicate that K-Sb crystals are favorable candidates for efficient electron sources. [1] R. Schier, D. Guo, H.-D. Saßnick, and C. Cocchi, Adv. Theory Simulations (2024), https://doi.org/10.1002/adts.202400680.

O 92.2 Thu 15:15 H25

Automated Wannier functions inspired by topological quantum chemistry — •Stepan S. Tsirkin — Centro de Física de Materiales, San Sebastián, Spain

Despite Wannier functions (WFs) becoming a popular and powerful technique for studying diverse electronic properties of materials, the construction of high-quality WFs remains a non-trivial task, often requiring manual intervention and expertise, which obstructs high-throughput calculations using WF-based methods.

I present an approach for selecting initial projections for Wannier functions based on the symmetry indicators of DFT bandsstructure. The initial projections are searched among the possible orbitals at the Wyckoff positions of the crystal, referred to as Elementary Band Representations in the terminology of Topological Quantum Chemistry [Nature 547, 298 (2017)]. Thus, the projections are by construction compatible with the symmetry of the bands, making them suitable for the construction of symmetry-adapted WFs (SAWFs) [Sakuma, PRB 87, 235109 (2013)]. This approach has been implemented in the codes WannierBerri (WB) [NPJ Comput. Mater. 7, 33 (2021)] and IrRep [CPC 272, 108226 (2022)]. Additionally, WannierBerri now implements the construction of SAWFs without several limitations found in the corresponding implementation in Wannier90. In particular, WB can handle spin-orbit coupling, a frozen window, and is compatible with multiple DFT codes (VASP, Quantum Espresso, Abinit, etc.).

This method does not require manual inspection on bands, which makes it suitable for high-throughput calculations.

O 92.3 Thu 15:30 H25

Learning conductance of aromatic and antiaromatic molecular junctions — •Mohammad Ali Mohammadi Keshtan and Hector Vazquez — Inst. of Physics, Czech Academy of Sciences

Single-molecule junction conductance depends on molecular conformation. The standard computational method to study the conductance of a molecular junction is DFT-NEGF. However, DFT-NEGF is computationally expensive, so finding a fast and accurate method to compute the conductance of a large numbers of structures is vital.

Here, we use machine learning (ML) methods, including kernel ridge regression and Gaussian process regression, to overcome these limitations. To train the regression models, we first generate thousands of junction geometries using classical molecular dynamics at room temperature. For each geometry we then compute conductance using a computationally efficient approximation which considers a Au-molecule-Au complex [1], and build SOAP and Coulomb matrix descriptors.

We study a pair of aromatic/antiaromatic porphyrin-like molecules [2], whose large size further hampers the use of DFT-NEGF. We explore the performance of the different ML models, compare the results with DFT-NEGF, and discuss the relative importance of the different descriptors. Our work demonstrates how ML models can be efficiently trained and used to compute single molecule junction conductance.

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

[2] S. Fujii et al., Nat. Commun. 2017, 8, 15984

O 92.4 Thu 15:45 H25

Electronic excitations in nanostructures from the Bethe-Salpeter equation — •Maximilian Graml, Štěpán Marek, and Jan Wilhelm — Institute of Theoretical Physics and Regensburg Center for Ultrafast Nanoscopy (RUN), University of Regensburg, Regensburg, Germany

Electronic structure calculations are a well-established tool for the identification of candidate materials for technological applications, e.g., in photocatalysis, photovoltaics and energy storage. For the quantitative description of optical properties, many-body perturbation theory within the GW approximation and the Bethe-Salpeter equation (BSE) on top of GW is regarded as the state-of-the-art method.

In this contribution, we present the implementation of the BSE within the open-source package CP2K, enabling the accurate calculation of electronic excitations in molecules and nanostructures. To validate our approach, we benchmark the excitation energies against those obtained with the FHI-aims package.

We further apply our BSE implementation to study electronic excitations in graphene nanostructures, where we investigate the optical absorption spectra and the spatial extent of excited states as a function of nanostructure size. We observe that both properties converge on the scale of 5 nm nanostructure size, guiding experiments towards the rational design of nanostructures in graphene-based optical devices.

O 92.5 Thu 16:00 H25

Electronic Coupling on Surfaces from First-Principles: Chemisorped Systems — •Simiam Ghan and Jens Nørskov — Technical University of Denmark DTU

We use density-functional theory to calculate the electronic coupling matrix elements between adsorbates and surfaces, applying a recently developed diabatization method[1] to fully chemisorped systems. The scheme is demonstrated by calculating ultrafast electron transfer lifetimes within a Fermi golden rule framework, which compares favorably to core-hole-clock measurements for systems including Black Phosphorous, S/Ru(0001) and CO/Ru(0001). We thereby demonstrate the suitability of diabatization schemes for the description of coupling in chemisorped systems, enabling an advantageous interpretation of the electron transfer process. We discuss prospects for the use of first-principles coupling matrix elements to describe other surface phenomena, such as chemisorption and heterogenous catalysis, e.g. within Newns-Anderson models.

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

O 92.6 Thu 16:15 H25

Enhancing structure relaxation with machine-learned interatomic potentials — Sudarshan Vijay[1,2], Martijn Marsman[1], Georg Kresse[1,3], and •Martin Schlipf[1] — [1]VASP Software GmbH, Berggasse 21, 1090 Vienna, Austria — [2]Department of Chemical Engineering, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra 400076 India — [3]Faculty of Physics and Center for Computational Materials Science, University of Vienna, Kolingasse 14-16, A-1090 Vienna, Austria

Machine learning interatomic potentials (MLIPs) offer a cost-effective way to predict ground-state properties of materials compared to density functional theory (DFT) calculations. MLIPs are often used to replace DFT due to their ability to access large length and longer time scales. In this study, we explore whether MLIPs can also enhance DFT by preconditioning commonly used optimization algorithms for structure relaxation. We demonstrate that applying this preconditioner to methods such as conjugate gradient (CG) and Broyden-Fletcher-Goldfarb-Shanno (BFGS) results in faster convergence but at the expense of stability. For this particular tasks, state-of-the-art MLIPs are not accurate enough to replace DFT; prerelaxing the structures with MLIPs tends to perform worse compared to starting the relaxation directly within DFT. Our analysis of the convergence behavior for both standard and preconditioned methods suggests that advancements in line-search techniques could enhance the effectiveness of this preconditioning approach for structure relaxation.

O 92.7 Thu 16:30 H25

Constrained Density Functional Theory with Numeric Atomic Orbitals — •Tavinder Singh[1,2] and Harald Oberhofer[1,2] — [1]University of Bayreuth — [2]Bavarian Center for Battery Technology

Even in perfectly crystalline materials, simulation of some phenomena, such as the occurence and transport of polarons, rests on the simulation method's ability to describe localized charge carriers. This is generally hampered by both, the need to break a system's symmetry to accommodate such a localized state, and the infamous electron delocalization error of most semi-local density functionals. In this respect, constrained density functional theory (CDFT) has proven to be a viable tool addressing both. Constraining charges to pre-selected localized states naturally breaks the symmetry and mitigates DFT errors. In our contribution, we describe our implementation of CDFT in the FHI-aims package based on Numeric Atomic Orbital (NAOs) projectors. As a prototype, we consider polaron localization in the zero-strain anode material, $Li_4Ti_5O_{12}$ (LTO), and compared the computed relative energies and barriers with the literature as benchmark. Our results provide valuable insights into the applicability and accuracy of CDFT for studying localized electronic states in complex materials.

O 92.8 Thu 16:45 H25

Efficient Phonon Dispersions of 2D Films by Extension of DFPT in FLAPW Method *FLEUR* to Film Geometry. — •Thomas Bornhake[1,2], Alexander Neukirchen[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 are crucial in 2D materials, governing a range of physical properties and phenomena, *e.g.* from dynamical stability to spin-flip scattering. Thus, an efficient method for calculating phonons under arbitrary excitations is inevitable. Typically, phonons of film systems are calculated from *ab initio* using supercells that separate the film from periodic images by computationally costly empty space. Recently, we have succeeded in calculating the phonon dispersion using the state of the art density functional perturbation theory (DFPT) in the all-electron full-potential linearized augmented planewave (FLAPW) method *FLEUR* [1,2]. In this talk we present our extension to a truly 2D treatment of films embedded in semi-infinite vacuum [3]. We discuss some details of the implementation and compare results with respect to accuracy and efficiency to the repeated slab approaches.

This work was supported by 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).

[3] H. Krakauer *et al.*, Phys. Rev. B **19**, 1706 (1979).

O 92.9 Thu 17:00 H25

Excitations in oxides: from bits to qubits — •Vijaya Begum-Hudde[1], Yi-Ting Lee[1], Barbara Jones[2], and Andre Schleife[1] — [1]University of Illinois, Urbana-Champaign, USA. — [2]IBM

Defects in materials are ubiquitous and may adversely affect their functional properties. Often the defects are confined to a small space, and defect embedding allows us to define an active space comprising of these defect states and to incorporate screening effects of the host material, enabling access to electronic properties with a high-level theory. In this talk I will focus on the structural and electronic properties of near-surface vacancies in α-Al_2O_3 (0001) to investigate the influence of defects and hydration on the initiation and propagation of corrosion in this material. Utilizing first-principles calculations and quantum-defect embedding theory calculations, this study will analyse defect states and their ground- and excited-state properties. An active space is defined consisting of strongly localized states of the surface O vacany, and the remainder is treated as the environment. Next, an effective Hamiltonian is used for the active space that also includes the environment's effective screening and is solved via full configuration interaction (FCI). Simulations are performed on a quantum computer with a Unitary coupled-cluster ansatz for the determination of ground- and excited-state properties. Error mitigation techniques will be demonstrated, reducing error due to the hardware noise and showing very good concordance with the FCI results within chemical accuracy.

We acknowledge funding by the IBM-Illinois Discovery Accelerator Institute.

O 92.10 Thu 17:15 H25

Electronic band structure at finite temperature: A unifying approach that incorporates electron-electron and electron-vibration interactions — •Min-Ye Zhang[1,2], Xinguo Ren[2], and Matthias Scheffler[1] — [1]The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft — [2]Institute of Physics, Chinese Academy of Sciences, China

An accurate first-principles description of electronic band structure at finite temperature requires accounting for self-energy contributions from both electron-electron (e-e) and electron-vibration (e-vib) interactions. In the widely used electron-phonon coupling (EPC) model[1], the two types of interactions are considered separately, and the model fails for strongly anharmonic materials. In this work, we integrate the two types of interactions beyond the EPC model by extending the statistically anharmonic, higher-order vibronic coupling approach[2] with the many-body GW method. This is achieved by combining *ab initio* molecular dynamics and periodic G^0W^0 method in an all-electron framework employing numeric atom-centered orbitals[3]. We demonstrate the robustness and efficiency of our G^0W^0 implementation, particularly through a proper treatment of long-range dielectric responses. As a proof of concept, we present the temperature-dependent electronic band structure of Si, incorporating both e-e and e-vib interactions.

[1] F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).

[2] M. Zacharias, M. Scheffler, and C. Carbogno, *Phys. Rev. B* **102**, 045126 (2020).

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

O 92.11 Thu 17:30 H25

Electronic and optical properties of computationally predicted Na-K-Sb crystals — •Chung Xu, Richard Schier, and Caterina Cocchi — University of Oldenburg

Due to their favorable electronic and optical properties, sodium-potassium-antimonides are an emerging class of crystals used as photocathodes in particle accelerators. Using first-principles methods based on density-functional theory and many-body perturbation theory, we investigate the electronic and optical properties of cubic NaK_2Sb and hexagonal Na_2KSb, two computationally predicted polymorphs of established photocathode materials that can emerge as metastable phases in polycrystalline samples. Our results indicate that both systems are indirect band-gap semiconductors with fundamental gaps on the order of 0.7 and 0.8 eV, respectively. Their direct gaps are very close to these values and Their optical spectra are characterized by weakly bound excitons in the near-infrared region which represent favorable characteristics for efficient photoemission. Our study suggests that the presence of cubic NaK_2Sb and hexagonal Na_2KSb in photocathode samples is not detrimental for their application as photocathodes [1].

[1] arXiv:2411.13330

O 92.12 Thu 17:45 H25

Thermal dependence of conductance in short pi-conjugated single-molecule junctions — •Václav Kubíček and Hector Vazquez — Inst. of Physics, Czech Academy of Sciences

Conductance measurements at room temperature in single-molecule junctions are affected by the internal dynamics of the molecule, since many different internal conformations are averaged. Further temperature changes lead to different conformational sampling and may alter conductance values, opening the possibility of thermally active molecular devices.

For example, it was measured that raising the temperature from 300 K to 330 K results in a change in conductance for oligophenylenes [1]. In our work, we calculate the temperature dependence of conductance for several short pi-conjugated molecular wires. By combining classical statistical model with DFT simulations, we explore their accessible geometries and compute the resulting changes in conductance.

Our results show that by engineering chain composition, conductance increases or decreases are achievable with increasing temperature. Our results demonstrate the importance and potential applicability of thermally induced conformational changes in conductance.

[1] Lee, W.; et al., Nano Lett. 2022, 22, 4919

O 92.13 Thu 18:00 H25

Comparison of non-equilibrium Green function and wave packet methods for studying the CISS effect — •Thibaut Lacroix, Clemens Vittmann, Jaemin Lim, Susana F. Huelga,

and Martin B. Plenio — Intitut für Theoretische Physik, Universität Ulm, Ulm, Deutschland

Non-equilibrium Green function (NEGF) technique has been widely employed to simulate quantum transport at the molecular scale. It is one of the main methods used to study transport properties of chiral molecules which are central to the investigation of chirality induced spin selectivity (CISS). Equivalent to the solution of a scattering problem, this approach leads to an energy resolved description of transport properties that can be used to obtained spin-dependent currents.

Alternatively, the description of electronic transport can be performed at the level of the Schrödinger equation. In that case, one considers an initial wave packet in the position basis – which therefore corresponds to a superposition of energy eigenstates – and computes its dynamics under the total Hamiltonian of the molecule and the leads. One benefit of this approach is to readily give access to the transient dynamics of the electron inside of the molecule, thus opening the possibility to study the internal mechanisms underlying CISS. We demonstrate that NEGF results can be recovered from wave packet evolution and that tailored wave packets enable to access directly specific transport properties of interest. These results show that while they rely on different formalisms wave packet evolution and NEGF do give the same information about the response of the system.