

O 10: Focus Session: Frontiers of Electronic-Structure Theory – Advances in Time-Dependent and Nonequilibrium Ab Initio Methods II

Time: Monday 15:00–17:15

Location: HE 101

O 10.1 Mon 15:00 HE 101

Thermoelectric efficiency in multiterminal quantum thermal machines from steady-state density functional theory — NAHUAL SOBRINO¹, ROBERTO D'AGOSTA^{1,2}, and STEFAN KURTH^{1,2,3} — ¹Nano-Bio Spectroscopy Group and European Theoretical Spectroscopy Facility (ETSF), Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología, Basque Country University UPV/EHU, San Sebastián, Spain — ²IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — ³Donostia International Physics Center, San Sebastián, Spain

Steady-state density Functional Theory for electronic and thermal transport (iq-DFT) is a formalism to describe open quantum systems in nonequilibrium steady states. iq-DFT relies on the one-to-one map between the set of "density" variables (particle density, electrical, and heat current) and the set of "potentials" (local potential, applied voltage, and thermal gradient). The resulting Kohn-Sham system features three exchange-correlation (xc) potentials: a local xc potential, an xc contribution to the voltage, and an xc contribution to the thermal gradient. In the linear-response regime, we arrive at exact expressions for the many-body transport coefficients and thermoelectric efficiency purely in terms of quantities accessible to iq-DFT. We generalize iq-DFT to the multiterminal situation and apply the formalism to a multiterminal interacting quantum dot in the Coulomb blockade regime for which accurate parametrizations of the xc kernel matrix are given, allowing us to study the thermoelectric efficiency and output power of the multiterminal system.

O 10.2 Mon 15:15 HE 101

Anisotropic Charge, Thermal, and Thermoelectric Transport in β -Ga₂O₃ from First Principles — SEBASTIAN TILLACK, NAKIB PROTIK, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin and IRIS Adlershof, 12489 Berlin, Germany

Gallium oxide gained interest for high-power applications due to its large band gap of ~ 5 eV and a high breakdown voltage. On the other hand it shows only modest electron mobility and relatively low thermal conductivity. While the latter is a clear limitation for power electronics it might render the material useful for thermoelectric applications.

We present an *ab initio* study of transport in β -Ga₂O₃ including electron-phonon and phonon-phonon interactions. Electrons and phonons are described within a full-potential all-electron framework [1] using many-body perturbation theory and density-functional perturbation theory. Maximally localized Wannier functions and Wannier-Fourier interpolation facilitate ultra fine samplings of the Brillouin zone. We solve the coupled electron-phonon Boltzmann transport equations [2] to compute the anisotropic electron mobility, Seebeck coefficient and thermal conductivity for different temperatures and electron doping levels, and the effect of the mutual electron-phonon drag on these transport coefficients. Our work provides insight into the fundamental scattering processes limiting transport in this material and explores its usefulness for various applications.

[1] A. Gulans, *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014).[2] N.H. Protik, *et al.*, npj Comput. Mater. **8**, 28 (2022).

O 10.3 Mon 15:30 HE 101

Defect assisted charge transfer across silicon-related heterojunctions — MARVIN KRENZ, WOLF GERO SCHMIDT, and UWE GERSTMANN — Paderborn University, Warburger Str. 100, 33098 Paderborn

Charge transfer is highly relevant for many physical, chemical, and biological processes. The transfer of triplet excitons across the tetracene (Tc)-silicon interface in sensitized solar cells is a recent example. Another one is the active a-Si:H/c-Si interface of silicon-based solar cells. In both cases, the presence of dangling bond (db) defects are often considered detrimental to material performance. While the atomistic details of the interfaces are decisive for maximizing the charge transfer, the transfer mechanism and related dynamics are essentially unknown.

Here, we present *ab initio* molecular dynamics calculations that provide a microscopic understanding of the charge and exciton transfers across the above mentioned interfaces. The related electron hopping at level crossings in the band structure of the 2D periodic structures is

described by c-DFT based surface hopping algorithms [1]. The transfer characteristics are found to depend in fact strongly on the presence of Si dangling bonds at the interfaces. At the Tc-Si(111):H interface they are even required to enable the excitation transfer. Defect induced states close to the valence band directly assist the hole transfer into Si bulk, and the exciton's electron is found to follow the hole within a few femtoseconds.

[1] M. Krenz, U. Gerstmann, W.G. Schmidt, ACS Omega **5**, 24057 (2020).

O 10.4 Mon 15:45 HE 101

Deciphering the Mechanisms of Oxygen Reduction Reaction and Reactive Sites in Polymeric Carbon Nitride Structures for Photocatalysis — CHANGBIN IM and TIMO JACOB — Ulm University, Institute of Electrochemistry, Ulm, Germany

Solar-to-Fuel technology holds immense promise for sustainable energy solutions, with polymeric carbon nitrides (PCN) emerging as pivotal catalysts in harnessing solar energy for hydrogen peroxide production through water reduction. Our *ab initio* calculations meticulously examine the oxygen reduction reaction (ORR) on diverse monolayers of PCNs, unraveling the energetics and mechanisms underlying ORR. Notably, structural factors, including condensation and corrugation degrees, exert profound influences on these processes. Departing from conventional 4-electron transfer mechanisms, our research introduces an innovative perspective by highlighting the significant contribution of electron shooting to the outer Helmholtz plane. Furthermore, we underscore the imperative nature of a pre-protonation process preceding ORR initiation. Employing calculated absorption patterns from TDHF@Casida, we uncover potential reactive sites within the structural features of polymeric carbon nitrides during photo-induced ORR. This investigation enhances our comprehension of the ORR mechanism on PCN structures, shedding light on photo-induced ORR mechanisms and identifying promising reactive sites. Our comprehensive exploration not only deepens understanding but also provides insights crucial for optimizing reactive sites in PCN structures, thereby amplifying their efficacy in sustainable energy applications.

O 10.5 Mon 16:00 HE 101

Multi-channel Dyson equation: coupling many-body Green's functions — ARJAN BERGER — Paul Sabatier University, Toulouse, France

We present the multichannel Dyson equation that combines two or more many-body Green's functions to describe the electronic structure of materials. In this work we use it to model photoemission spectra by coupling the one-body Green's function with the three-body Green's function. We demonstrate that, unlike methods using only the one-body Green's function, our approach puts the description of quasi-particles and satellites on an equal footing. We propose a multichannel self-energy that is static and only contains the bare Coulomb interaction, making frequency convolutions and self-consistency unnecessary. Despite its simplicity, we demonstrate with a diagrammatic analysis that the physics it describes is extremely rich. Finally, we present a framework based on an effective Hamiltonian that can be solved for any many-body system using standard numerical tools.

References:

G. Riva, P. Romaniello, and J. A. Berger, Phys. Rev. Lett. **131**, 216401 (2023)G. Riva, T. Audinet, M. Vladač, P. Romaniello, and J. A. Berger, SciPost Phys. **12**, 093 (2022)

O 10.6 Mon 16:15 HE 101

Third-order susceptibility of crystalline materials from time-dependent density functional theory — XIAO CHEN — ZGH,RUB,Bochum,Germany

We use real-space real-time time-dependent density functional theory to investigate the non-linear properties of centrosymmetric crystals. We perform calculations varying laser intensities and extract non-linear coefficients, such as the Kerr coefficient, the two-photon absorption and the third-order susceptibility. In semiconductors such as diamond, we investigate nonlinear properties at different laser frequencies. In metals

such as gold, we investigate the effect of different laser pulse durations. The results compare well with experimental reference data.

O 10.7 Mon 16:30 HE 101

Linear scaling approach for optical excitations using maximally localized Wannier functions — ●KONRAD MERKEL and FRANK ORTMANN — TUM School of Natural Sciences, Technische Universität München

We present a theoretical method for calculating optical absorption spectra based on maximally localized Wannier functions, which is suitable for large periodic systems. For this purpose, we calculate the exciton Hamiltonian, which determines the Bethe-Salpeter equation for the macroscopic polarization function and optical absorption characteristics. The Wannier functions are specific to each material and provide a minimal and therefore computationally convenient basis. Furthermore, their strong localization greatly improves the computational performance in two ways: first, the resulting Hamiltonian becomes very sparse and, second, the electron-hole interaction terms can be evaluated efficiently in real space, where large electron-hole distances are handled by a multipole expansion. For the calculation of optical spectra we employ the sparse exciton Hamiltonian in a time-domain approach, which scales linearly with system size. Further information can be found in *J. Phys. Mater.* 7 015001 (2024)

O 10.8 Mon 16:45 HE 101

Exploiting Crystal Symmetry in the LAPW Method — ●MARA VOICULESCU, SVEN LUBECK, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Berlin, Germany

In the framework of density functional theory (DFT) calculations, the linearized augmented planewave (LAPW) method uses a dual representation for physical quantities such as the charge density and potential. This approach consists of a spherical harmonic expansion inside the so-called muffin-tin spheres around the nuclear positions and a planewave expansion in between them. The direct implementation results in a large number of expansion coefficients which need to be computed. Exploiting symmetry by employing group-theoretical methods simplifies the mathematical description and therefore re-

duces computational expenses. Consequently, symmetry can be used to speed up the setup of the Hamiltonian matrix, while at the same time resulting in better numerical precision. We implement this approach in the all-electron full-potential computer package exciting [1], by using symmetrized spherical harmonics (lattice harmonics) and planewaves (stars), yielding a considerable computational speedup for a variety of different materials.

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

O 10.9 Mon 17:00 HE 101

Brillouin zone sampling in ONETEP — ●CHENGCHENG XIAO, PETER HAYNES, and ARASH MOSTOFI — Departments of Materials and Physics, and the Thomas Young Centre for Theory and Simulation of Materials, Imperial College London, London SW7 2AZ, United Kingdom

ONETEP is a linear-scaling density functional theory (DFT) program with large basis set (plane-wave) accuracy on parallel computers. ONETEP was originally designed to study large-scale systems, including macromolecules and nanocrystals. Because of this, ONETEP is restricted to Gamma-point only for self-consistent calculations. However, many systems of interest are periodic at short-scales in one or two dimensions, e.g., nanowires and surfaces. In such cases, significant computational efficiency can be achieved via dense sampling of the Brillouin zone (rather than creating large supercells).

Here, we introduce two types of Brillouin zone sampling methods in ONETEP. The first is targeted at small periodic systems and exploits the fact that the localization constraints of the non-orthogonal Wannier functions (NGWFs) can be lifted. The second keeps the NGWFs localized and the k-dependence is introduced as phase factors to the Hamiltonian matrix elements (similar to the tight-binding method). This method keeps the code linear scaling with k-points and is aimed at intermediate-sized systems.

These developments extend the operability of ONETEP to short- and intermediate-scale periodic systems, including 2D materials, nanowires, nanotubes, surfaces, and interfaces.