

O 4: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge I (joint session O/CPP/DS/TT)

First-principles electronic structure calculations have become an indispensable tool in many research areas where materials surfaces or interfaces play a central role. Corresponding calculations provide insight into catalytic mechanisms, interfacial ionic and charge transport in batteries or solar cells, materials degradation through corrosion or wear, and many other highly relevant application areas. Despite this prolific use, corresponding calculations face multiple issues. While the invited lectures will have a focus on this interface challenge, the symposium will also cover the general field of computational materials science and electronic-structure theory.

Organizers: Jens Nørskov (Technical University of Denmark), Karsten Reuter (Technical University Munich), and Matthias Scheffler (Fritz Haber Institute of the Max Planck Society, Berlin)

Monday 10:30–13:00

H9

Topical Talk O 4.1 Mon 10:30 H9
Scaling relations and beyond for kinetic Monte Carlo models in heterogeneous catalysis — ●MIE ANDERSEN — Theoretical Chemistry, Technische Universität München, Germany

Heterogeneous catalysis typically operates at the interface between a gas or liquid and a solid catalytic material. In my talk, I will discuss mean-field and kinetic Monte Carlo models for the operating catalyst. These often rely on input data calculated using either first principles or more approximate methods, e.g. scaling relations, which use only selected adsorption energies as descriptors for the catalyst function [1,2]. I will also discuss recent work [3] where we used compressed sensing methods to identify new low-cost and accurate descriptors that allow to predict adsorption energies for a wide range of adsorbates, multi-metallic transition metal surfaces and facets. The descriptors are expressed as non-linear functions of intrinsic properties of the clean catalyst surface, e.g. coordination numbers and *d*-band moments. From a single DFT calculation of these properties, we predict adsorption energies at all potential surface sites, and thereby also the most stable geometry. Compared to previous approaches such as scaling relations, we find our approach to be both more general and more accurate for the prediction of adsorption energies on alloys with mixed-metal surfaces, already when based on training data including only pure metals.

[1] M. Andersen *et al.*, *Ang. Chem. Int. Ed.* **55**, 5210 (2016)

[2] M. Andersen *et al.*, *J. Chem. Phys.* **147**, 152705 (2017)

[3] M. Andersen *et al.*, submitted

Talk O 4.2 Mon 11:00 H9
The Teacher and the Student: Exchange-Correlation Energy Densities from Quantum Chemistry and Machine-Learning — ●JOHANNES T. MARGRAF, CHRISTIAN KUNKEL, and KARSTEN REUTER — Chair for Theoretical Chemistry, Technische Universität München, Germany

(Semi-)local density functional approximations (DFAs) are the workhorse electronic structure methods in condensed matter theory and surface science. Central to defining such DFAs is the exchange-correlation energy density ϵ_{xc} , a spatial function that yields the exchange-correlation energy E_{xc} upon integration.

Unlike E_{xc} , ϵ_{xc} is not uniquely defined. Indeed, there are infinitely many functions that integrate to the correct E_{xc} for a given electron density ρ . The challenge for constructing a useful DFA is to find a systematic connection between ρ and ϵ_{xc} . While several empirical and rigorous approaches to this problem are known, there has been little innovation with respect to the fundamental functional forms of DFAs in recent years.

Herein, we discuss two less explored routes to constructing DFAs. Specifically, a recipe for deriving ϵ_{xc} directly from many-body wavefunctions is compared to a machine learning (ML) approach that infers the optimal ϵ_{xc} for a given functional form. We find that local DFAs based on the many-body ϵ_{xc} are not transferrable between systems because the underlying energy densities are inherently non-local. In contrast, the ML ϵ_{xc} is by construction as local as possible. The extension of both approaches to non-local DFAs will be discussed.

Talk O 4.3 Mon 11:15 H9
Self-Interaction Corrected SCAN for Molecules and Solids: All-Electron Implementation with Numerical Atom-Centered Basis Functions — ●SHENG BI, IGOR YING ZHANG, CHRISTIAN CARBOGNO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Electronic self-interaction is the most severe cause of inaccuracies

in all semilocal density-functional approximations (DFAs), including the promising meta-GGA “strongly constrained and appropriately normed” (SCAN) functional [1]. This error can be alleviated via localized orbital scaling corrections [2] or via self-interaction corrections (SIC) based on Fermi-orbitals [3]. In this contribution, we follow the latter concept which involves solving a set of SIC constraints. Here, we present an all-electron implementation of the self-consistent SIC for semilocal DFAs, including SCAN. We first validate our implementation by inspecting certain properties (HOMO and dissociation energies) for a molecular test set, showing that SIC improves SCAN calculations. Furthermore, we compare the performance of SCAN-SIC and SCAN α , i.e., SCAN with a fraction of exact exchange, in predicting the broken symmetry in pentacene – note that standard semilocal DFAs always favor symmetric solutions. Eventually, we discuss the extension of our SIC approach to periodic solids.

[1] J. Sun *et al.*, *Phys. Rev. Lett.* **115**, 036402 (2015).

[2] N. Q. Su *et al.*, *Proc. Natl. Acad. Sci.* **115**, 9678 (2018).

[3] Z. Yan *et al.*, *Phys. Rev. A* **95**, 052505 (2017).

Talk O 4.4 Mon 11:30 H9
Progress in Fermi-Löwdin orbital self-interaction correction to DFT — ●TORSTEN HAHN, SEBASTIAN SCHWALBE, and JENS KORTUS — Institute for Theoretical Physics, Freiberg, Germany

The accuracy of density functional theory (DFT) calculations is limited by the so called self-interaction error [1]. The recently proposed Fermi-Löwdin orbital based method [2,3,4] for self-interaction correction (FLO-SIC) is a unitary invariant and size extensive approach to overcome this error. We present the current state of the method and discuss selected applications. In addition we discuss strategies to improve the thermochemical and numerical performance of the FLO-SIC approach in combination with state-of-the-art exchange-correlation functionals.

[1] J. P. Perdew, A. Zunger, *Phys. Rev. B* **23**, 5048 (1981)

[2] M. R. Pederson *et al.*, *J. Chem. Phys.*, vol. 140, 121103 (2014)

[3] M. R. Pederson, *J. Chem. Phys.*, vol. 142, 064112 (2015)

[4] S. Schwalbe *et al.*, *J. Comp. Chem.*, vol. 39, 2463 (2018).

Talk O 4.5 Mon 11:45 H9
Time evolution of the natural occupation numbers — ●CARLOS BENAVIDES-RIVEROS and MIGUEL A. L. MARQUES — Martin-Luther Universität Halle Wittenberg

Reduced density matrix functional theory (RDMFT) is based on the Gilbert theorem, which asserts that the ground-state wave function can be written as a functional of the one-body reduced density matrix. Since RDMFT accounts for fractional natural occupation numbers, it captures quite well static (strong) electron correlation (unlike DFT, RDMFT correctly predicts the insulating behavior of Mott-type insulators). Yet the time-dependent extension of RDMFT suffers from various shortcomings. Chief among them, the current status of the theory does not allow the fermionic occupation numbers to evolve in time. It is known that this deficiency is connected to the failure of RDMFT to account for relative phases at the level of the two-body reduced density matrix. Based on recent results on fermionic exchange symmetry, we propose a new equation for the time evolution of the fermionic occupation numbers.

Talk O 4.6 Mon 12:00 H9
Nonempirical hybrid functionals constructed through adjustable potential probes for band gap predictions of extended systems — ●THOMAS BISCHOFF, IGOR RESHETNYAK, and

ALFREDO PASQUARELLO — Chaire de Simulation a l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

We describe a nonempirical procedure for achieving accurate band gaps of extended systems through the insertion of suitably defined potential probes. By enforcing Koopmans' condition on the resulting localized electronic states, we determine the optimal fraction of Fock exchange to be used in the adopted hybrid functional. As potential probes, we consider native defects, the extrinsic hydrogen impurity, and various adjustable potentials that allow us to vary the energy level of the localized state in the band gap and its degree of localization. By monitoring the delocalized screening charge, we achieve a measure of the hybridization with the band states, which can be used to improve the band gap estimate. Application of this methodology to AlP, C and MgO yields band gaps differing by less than 0.2 eV from experiment.

Talk O 4.7 Mon 12:15 H9
Quantum-mechanical relation between atomic dipole polarizability and van der Waals radius — ●DMITRY FEDOROV, MAINAK SADHUKHAN, MARTIN STÖHR, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

The atomic dipole polarizability α and the van der Waals (vdW) radius R_{vdW} are two key quantities to describe the ubiquitous vdW forces important for the structure and dynamics of molecules and materials [1]. The commonly assumed relation between them, $R_{\text{vdW}} \propto \alpha^{1/3}$, is based on a classical picture of hard-sphere atoms. Employing the quantum Drude oscillator model [2], we reveal [3] the quantum-mechanical relation $R_{\text{vdW}} = \text{const.} \times \alpha^{1/7}$ which is markedly different from its classical counterpart. Based on the accessible accurate reference data for α and R_{vdW} , we demonstrate that the obtained formula can be used as a unified definition of the vdW radius solely in terms of the atomic polarizability for all chemical elements. Moreover, for vdW-bonded heteronuclear dimers consisting of atoms A and B, the simple combination rule $\alpha = (\alpha_A + \alpha_B)/2$ provides a remarkably accurate way to calculate their equilibrium interatomic distance. These findings unveil a fundamental relationship between the geometric and electronic properties of atoms. From a practical point of view, they allow us to reduce the empiricism and improve the efficiency of computational models for vdW interactions.

- [1] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
- [2] Jones *et al.*, Phys. Rev. B **87**, 144103 (2013)
- [3] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)

Talk O 4.8 Mon 12:30 H9
impact of continuum electronic states on van der Waals dispersion interactions — ●MOHAMMAD REZA KARIMPOUR, DMITRY FEDOROV, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

The ubiquitous van der Waals (vdW) forces play an important role for structure, stability, and dynamics of molecules and materials. Their description on atomistic level is important for molecular physics, crystal chemistry, surface science, structural biology, and pharmacy. To this end, the development of simple yet efficient models is of high importance. Normally, such models focus only on fluctuations to bound electron states, described via quantum harmonic oscillator potentials. However, the polarizability of real atomic and molecular systems has important contributions also from fluctuations to continuum states. To study their influence on the vdW dispersion interactions from a general point of view, here we consider models based on the Dirac delta-function potentials. In one-dimensional case, such a potential provides just one bound state whereas all excited states belong to the continuum electron spectrum. We apply both the atomistic method and the scattering picture representing the van der Waals and Casimir approaches for dispersion interactions, respectively. In the atomistic framework we compare our results to the ones of the quantum oscillator models. Within the other picture, we discuss an obtained new scaling law in comparison to the results known for excited atomic systems.

- [1] Woods *et al.*, Rev. Mod. Phys. **88**, 045003 (2016)
- [2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)

Talk O 4.9 Mon 12:45 H9
Relation between the van der Waals radius and higher-order atomic polarizabilities — ●ORNELLA VACCARELLI, DMITRY FEDOROV, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

The atomic polarizabilities and van der Waals (vdW) radii describe the electronic and geometric aspects of the ubiquitous vdW interactions [1, 2], respectively. Normally, these quantities are assumed to be independent. Therefore, they are determined separately from each other. Based on the quantum Drude oscillator model [3], recently we revealed [4] a remarkable direct relationship between the vdW radius and the dipole polarizability. This provides a unified determination of the vdW radius for all chemical elements solely in terms of their dipole polarizabilities. In addition, further relations between the vdW radius R_{vdW} and higher-order atomic polarizabilities α_n ($n = 1, 2, \dots$) were found empirically. Here, we present a physical background for these results. The derivation of the corresponding scaling laws is performed by going beyond the dipole approximation for the Coulomb interaction to obtain higher-order contributions to attractive and repulsive forces acting on atoms in a vdW-bonded homonuclear dimer. We focus on the derivation of the proportionality constants C_n in the general relation $R_{\text{vdW}}(\alpha_n) = C_n \alpha_n^{2/7(n+1)}$ unveiling their quantum nature.

- [1] Woods *et al.*, Rev. Mod. Phys. **88**, 045003 (2016)
- [2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
- [3] Jones *et al.*, Phys. Rev. B **87**, 144103 (2013)
- [4] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)

O 11: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge II (joint session O/CPP/DS/TT)

Monday 15:00–17:30

H9

Talk O 11.1 Mon 15:00 H9
Influence of structural deformations on the applicability of the Tamm-Dancoff approximation for organic molecules — ●TOBIAS LETTMANN and MICHAEL ROHLFING — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

When calculating excited state properties of electronic systems within the many-body perturbation theory (MBPT), the Bethe-Salpeter equation (BSE) needs to be solved. This is often done within the Tamm-Dancoff approximation (TDA), neglecting the coupling of resonant and anti-resonant excitations.

It is generally accepted that the TDA is justified for large, extended systems e.g. bulk crystals. However it has been shown that the TDA may no longer hold for small organic molecules [1]. In this talk we discuss the applicability of the TDA for molecules of different sizes and show the transition between the two regimes. We then discuss how the applicability is influenced by deformations of the molecules, in particular by the related conjugation length of the π -system.

- [1] B. Baumeier *et al.*, J. Chem. Theory Comput. **8**, 997 (2012)

Talk O 11.2 Mon 15:15 H9

Momentum-Resolved Electron Energy-Loss Spectroscopy in Oxides from Many-Body Perturbation Theory — ●CHRISTIAN VORWERK^{1,2}, CATERINA COCCHI^{1,2}, and CLAUDIA DRAXL^{1,2} — ¹Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ²European Theoretical Spectroscopy Facility

Electron energy-loss spectroscopy (EELS) is a powerful tool to investigate the local electronic and structural properties of crystalline materials. The accurate determination of these spectra from first principles requires a reliable description of the electron-hole interaction, screened by the surrounding many-electron system. We perform *ab initio* many-body perturbation theory calculations of EELS through the solution of the Bethe-Salpeter equation (BSE), including the screened non-local interaction between electron and hole. Employing an implementation in the all-electron full-potential package **exciting**, we show results for a wide range of energy loss, from the optical to the hard x-ray region. We study EELS at finite momentum loss \mathbf{q} , from small \mathbf{q} close to the dipole limit to large \mathbf{q} well beyond the first Brillouin zone. This momentum resolution of EELS reveals dipole-forbidden excitations that are invisible in absorption spectroscopy. Our calculations also yield insight into the excitonic dispersion, *i.e.* the excitonic bandstructure. We discuss the effects of momentum loss in the EELS spectra of oxide

materials, including CaO, CeO₂, and the wide-gap transparent oxide Ga₂O₃, considering both the optical and x-ray energy-loss range.

Talk O 11.3 Mon 15:30 H9
Electron-magnon scattering in elementary ferromagnets from first principles: implementation and results — ●CHRISTOPH FRIEDRICH, MATHIAS C.T.D. MÜLLER, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute of Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Propagating electrons and holes can scatter with spin fluctuations and form quasiparticles as a result or more complex many-body states. To calculate this effect, a \mathbf{k} -dependent self-energy describing the scattering of electrons and magnons is constructed from the solution of a Bethe-Salpeter equation for the T matrix. Partial self-consistency is achieved by the alignment of the chemical potentials. We discuss details of the implementation and illustrative results. The renormalized electronic band structures exhibit strong spin-dependent lifetime effects close to the Fermi energy, which are strongest in Fe. The renormalization gives rise to a band anomaly at large binding energies in iron, which results from a coupling of the quasihole with Stoner excitations.

Talk O 11.4 Mon 15:45 H9
Dielectric function of homogeneous electron gas from Bethe-Salpeter equation — ●JAAKKO KOSKELO^{1,2}, MARTIN PANHOLZER^{2,3}, LUCIA REINING^{1,2}, and MATTEO GATTI^{1,2,4} — ¹Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA, Université Paris-Saclay, F-91128 Palaiseau, France — ²ETSF — ³Institute for Theoretical Physics, Johannes Kepler University, Linz, Austria — ⁴Synchrotron SOLEIL, France

The homogeneous electron gas (HEG) is one of the most important model systems in condensed matter physics, and it has been subject of a great number of studies. Some properties of HEG such as total energy and static correlation functions can be obtained from quantum Monte Carlo simulations with great accuracy, but for dynamical correlation functions only very few results are available.

Methods based on the Bethe-Salpeter equation (BSE) have been very successful in semiconductors and insulators, but metals have been less studied. In this contribution, we use the BSE in its standard approximations, including a statically screened electron-hole interaction, to study the dielectric function of HEG. We find significant differences in static screening and spectra compared to other approaches. In particular, the BSE in its current approximations fails to reproduce the negative static screening in the low-density HEG, which is related to a so-called ghost exciton. We also use the time-dependent mean-density approximation [1] in order to compare our results to experimental loss spectra of sodium.

[1] M. Panholzer et al, Phys. Rev. Lett. **120**, 166402 (2018).

Talk O 11.5 Mon 16:00 H9
DFT study of electronic and optical properties of SrTiO_{3-δ} including many-body effects — ●VIJAYA BEGUM, MARKUS E GRUNER, and ROSSITZA PENTCHEVA — Faculty of Physics and Centre for Nanointegration (CENIDE), University of Duisburg-Essen, Duisburg.

The electronic and optical properties of SrTiO₃ (STO), a perovskite material of key importance in the field of oxide electronics, are explored in the framework of density functional theory including many-body effects within the GW approximation and excitonic corrections by solving the Bethe-Salpeter equation (BSE). We further analyse the origin of the strong excitonic effects, in particular a peak at ≈ 6.5 eV, by decomposing the BSE eigenvectors obtained from GW+BSE to extract the leading electron-hole pair contribution for the particular BSE eigenstate following the approach of Bokdam *et al.* [Scientific Reports **6**, 28618 (2016)]. Alternatively, we use the model-BSE (mBSE) which utilises a parametrised analytical model for the static screening. For STO, the mBSE spectrum closely reproduces the one from GW+BSE, which allows to reduce the computational effort by circumventing the intermediate time-consuming GW step. We further proceed to describe the effect of oxygen defects on the electronic and optical properties in STO.

Funding by DFG- SFB1242, project C02 is gratefully acknowledged.

Talk O 11.6 Mon 16:15 H9
Second-order Møller-Plesset perturbation theory and beyond for the band gap and single-particle excitations of solids — ●MARIA DRAGOUMI¹, SERGEY V. LEVCHENKO^{2,1,3}, IGOR YING ZHANG^{4,1}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der

Max-Planck-Gesellschaft, Berlin, DE — ²Skolkovo Innovation Center, Moscow, RU — ³NUST MISIS, Moscow, RU — ⁴Fudan University, Shanghai, CN

Calculations of the fundamental band-gap and the low-energy excitations of solids are still a challenge for electronic-structure theory. The computationally efficient Kohn-Sham (KS) density functional theory (DFT) with the widely used local or semi-local approximations provides a KS band gap which is much smaller than the fundamental gap. Many-body perturbation theory, on the other hand, addresses the fundamental gap directly. We present here an efficient scalable implementation of Møller-Plesset second order perturbation theory (MP2) for quasi-particle energies [1,2]. By solving the Dyson equation of the single-particle Green's function, considering self-energy up to second order, we go beyond MP2. The new approach shows a competitive or even superior performance in comparison to the current state-of-the-art methods such as hybrid functionals and GW approximation, where second order exchange is missing. We present numerical results for the band-gap of a wide range of semiconductors and insulators.

[1] J. Sun and R. J. Bartlett, J. Chem. Phys. **104**, 8553 (1996).

[2] A. Grüneis, et.al, J. Chem. Phys. **133**, 074107 (2010).

Talk O 11.7 Mon 16:30 H9
Accelerating GW Calculations within the LAPW Framework — ●SVEN LUBECK, ANDRIS GULANS, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Germany

The GW approach of many-body perturbation theory is an indispensable method for calculating the electronic band structure of solids. Its implementation in computer programs using the linearized augmented plane-wave + local orbital (LAPW+LO) method allows for obtaining numerically precise results. Unfortunately, high precision comes at the price of a large number of LAPWs and LOs. In this work, we accelerate GW calculations by optimizing the use of LAPWs and LOs in the computer package `exciting` [1]. On the one hand, we introduce a systematic way of obtaining a minimal set of LOs. On the other hand, we perform a basis transformation from the plane-wave part of the LAPWs to different types of basis functions, exploring the efficiency of numeric atom-centered orbitals, Gaussian type orbitals, and Kohn-Sham orbitals. Presenting band gaps of two exemplary materials, zincblende ZnO and hexagonal monolayer BN, we illustrate that our optimization schemes reduce the computational cost down to values as low as 15% without compromising the precision.

[1] A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, J. Phys.: Condens. Matter **26**, 363202 (2014).

Talk O 11.8 Mon 16:45 H9
Ab-initio description of transient ion formation of NO on Au(111) — DANIEL CORKEN, NICHOLAS D. M. HINE, and ●REINHARD J. MAURER — Departments of Physics and Chemistry, University of Warwick, United Kingdom

Gaining a fundamental understanding of the interactions of molecules on metal surfaces is essential for the development of novel heterogeneous catalysts. An interesting feature of gas-surface reactions at metal surfaces is that the Born-Oppenheimer approximation breaks down. Vibrationally excited and translationally hot molecules can transfer energy to the electrons of a metal via excitation of electron-hole pairs (EHP). In case of NO on Au(111), [1] this nonadiabatic energy loss is believed to stem from the transient generation of charged ion species at the surface. A computationally feasible and accurate description of such a molecule-metal charge-transfer state represents a challenge and several methods have been proposed. Upon a review of existing experimental evidence, we will present our approach to this problem. We use linear expansion-Delta-Self-Consistent-Field Density Functional Theory (le Δ SCF-DFT) [2] to model the anionic resonance of NO on Au(111). The le Δ SCF-DFT method enforces the electronic configuration of reference molecular states while solving the Kohn-Sham equations self-consistently. By comparison to experiment and other models, we assess the methods' ability to describe the ground- and excited-states during molecular scattering. We further explore avenues to extract nonadiabatic couplings and to construct model Hamiltonians based on this method. [1] JCP **130**, 174716, [2] JCP **139**, 014708;

Talk O 11.9 Mon 17:00 H9
Luminescence of β -SiAlON:Eu²⁺ phosphors: DFT study — ●SALEEM AYAZ KHAN¹, ONDREJ ŠÍP¹, ROBIN NIKLAUS², WOLFGANG SCHNICK², and JAN MINAR¹ — ¹University of West Bohemia, Pilsen, Czech Republic — ²LMU Munich, Germany

Highly efficient phosphor-converted light-emitting diodes (pc-LEDs) are popular in lighting and high-tech electronics applications [1]. Among them β -SiAlON:Eu²⁺ stands out as a promising narrow-band green phosphor for white-LEDs applications exhibiting good thermal and chemical stabilities. Photoluminescent properties of this material can be tuned by introducing the disorder at various sublattices. To understand the mechanism behind this effect, we performed a systematic study of electronic structure and photoluminescence properties of β -SiAlON:Eu²⁺. The calculations were done within the *ab-initio* fully relativistic full-potential framework. The disorder was treated by employing both the supercell approach and the coherent potential approximation (CPA). The Stokes shifts were calculated from differences of total energies of the ground and excited states of β -SiAlON:Eu²⁺. The main focus is on monitoring how the Al and O content and Eu²⁺ activator concentrations influence the local β -Si₃N₄ electronic structure and how this may be used to tune photoluminescence properties.

[1] Z. Wang, W. Ye, Iek-H. Chu, and S. P. Ong, *Chem. Mater.*, **28**, 8622 (2016).

Talk

O 11.10 Mon 17:15 H9

Spin fluctuations in itinerant ferromagnets: Computing the dynamic transverse spin susceptibility with TDDFT and PAW — •THORBJØRN SKOVHUS and THOMAS OLSEN — Technical University of Denmark

We present a numerical scheme for computing the dynamic transverse spin susceptibility using time-dependent density functional theory which allows us to study magnons in itinerant ferromagnets. The scheme is based on a real-space grid implementation of the projected augmented wave method and use a simple plane wave representation of the response function. Employing the adiabatic local density approximation for the exchange-correlation kernel, calculations of the magnon spectra in bulk transition metals iron and nickel are presented. In the context of the present implementation, the influence from the choice of numerical scheme on the violation of the Goldstone theorem is investigated.

O 25: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge III (joint session O/ CPP/DS/TT)

Tuesday 10:30–13:00

H9

Topical Talk

O 25.1 Tue 10:30 H9

Addressing the structure and dynamics of weakly-bonded interfaces — •MARIANA ROSSI — Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin

Interfaces between different materials constitute the basis of technological devices. Incorporating organic components within different architectures opens the path for creating more versatile interfaces with a wide range of properties at a reduced cost. However, the large conformational space that organic components can explore at finite temperatures and the inherent anharmonicity of their intra and intermolecular interactions brings further challenges to first-principles simulations. In this talk, I will discuss our recent efforts to address these challenges, based on developments within density functional theory an *ab initio* (path integral) molecular dynamics. I will present strategies for conformational space sampling of organic/inorganic interfaces, discuss the relationship between atomic and electronic structure including the effect of different functionals, present techniques to include anharmonicity in vibrational fingerprints and machine learning tools to calculate these at reduced costs, and our recent methodological developments that allow the inclusion of quantum nuclear effects in high-dimensional systems (especially weakly bonded interfaces) using path integral molecular dynamics.

Talk

O 25.2 Tue 11:00 H9

Elucidating the Nuclear Quantum Dynamics of Intramolecular Double Hydrogen Transfer in Porphycene — •YAIR LITMAN¹, JEREMY O. RICHARDSON², TAKASHI KUMAGAI¹, and MARIANA ROSSI¹ — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²ETH, Zurich, Switzerland

We address the double hydrogen transfer (DHT) dynamics of the porphycene molecule: A complex paradigmatic system where the making and breaking of H-bonds in a highly anharmonic potential energy surface requires a quantum mechanical treatment not only of the electrons but also of the nuclei [1]. We combine density-functional theory calculations, employing hybrid functionals and van der Waals corrections, with recently proposed and optimized path-integral ring-polymer methods for the calculation of vibrational spectra and reaction rates. Our simulations predict the position and width of the N-H stretching band of porphycene and DHT rates in excellent agreement with experiments, thus confirming our determination of the tunneling pathways and the anharmonic mode couplings that play a role in this reaction. They also provide quantitative information about the usually ignored competition between concerted and stepwise DHT pathways at different temperature. These results show that our theoretical approach can describe hydrogen transfer dynamics in different environments, for example when porphycenes are adsorbed on surfaces in prototype molecular switch architectures [2]. [1] Y. Litman, Richardson, J. O., Kumagai, T., Rossi, M. *arXiv:1810.05681*. [2] T. Kumagai, et al., *J. Chem. Phys.*, **148**, 102330 (2018).

Talk

O 25.3 Tue 11:15 H9

Interplay of quantum nuclear fluctuations and the electronic

structure of the cyclohexane/Rh(111) interface — •KAREN FIDANYAN and MARIANA ROSSI — Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, Berlin

Cyclohexane (C₆H₁₂) adsorbed on metal surfaces can participate in catalytic dehydrogenation reactions, which show good potential for hydrogen storage. It has been observed experimentally that C₆H₁₂ adsorbed on the Rh(111) surface shows an isotope effect on the work function change and the adsorption energy upon deuteration [1]. The physical origin of this puzzling isotope effect on the electronic structure has not been fully resolved. We employ density-functional theory (PBE functional with van der Waals corrections) and *ab initio* path-integral molecular dynamics at 150 K to characterize the underlying physics of this phenomenon. We perform these simulations almost at classical-nuclei cost by making use of the spatially-localized ring-polymer contraction scheme proposed in Ref. [2]. The harmonic approximation to zero-point-energy in the adsorption energy is not able to capture the isotope effects observed experimentally. We thus include anharmonic corrections through the dynamics and identify the temperature-dependent electronic level broadening and renormalization due to the interaction with phonons in this system.

[1] T. Koitaya and J. Yoshinobu, *Chem. Rec.* **14** 848-856 (2014).

[2] Y. Litman, D. Donadio, M. Ceriotti and M. Rossi, *J. Chem. Phys.* **148** 102320 (2018).

Talk

O 25.4 Tue 11:30 H9

Quantum-Nuclear Effects in Anharmonic Thermal Transport of Organic Materials — •HAGEN-HENRIK KOWALSKI, MARIANA ROSSI, MATTHIAS SCHEFFLER, and CHRISTIAN CARBOGNO — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

To date, an accurate computational assessment of thermal transport in organic compounds still constitutes a considerable challenge for first principles theory, since the vibrations in such compounds are to a large extent governed by quantum-nuclear (QN) *and* strongly anharmonic (SA) effects [1]. Perturbative approaches account for QN, but not for SA effects, whereas Molecular Dynamics (MD) approaches [2] with classical nuclei account for SA, but neglect QN effects. To overcome this limitation, we here present a framework capable of accounting for both QN and SA effects by sampling the vibrational motion via Thermostatted Ring Polymer Molecular Dynamics (TRPMD). The lattice thermal conductivity is assessed through the Green-Kubo formalism and the auto-correlation of the heat flux. To obtain this quantity, we extend the *ab initio* heat-flux definition proposed in Ref. [2] from MD to TRPMD, in order to include QN effects. We critically discuss the approach, its accuracy, and numerical cost for several materials, ranging from toy-models, e.g., solid Argon, to recently discussed organic materials, in which both QN and SA effects are non-negligible.

[1] M. Rossi, P. Gasparotto, M. Ceriotti, *Phys. Rev. Lett.* **117**, 115702, (2016).

[2] C. Carbogno, R. Ramprasad, and M. Scheffler, *Phys. Rev. Lett.* **118**, 175901, (2017).

Talk

O 25.5 Tue 11:45 H9

Electronic Conduction in Metal Junctions with Multi-Heme Proteins — ●ZDENEK FUTERA¹, XIUYUN JIANG¹, JAN ELSNER², and JOCHEN BLUMBERGER^{1,3} — ¹Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom — ²University of Cambridge, Robinson College, Grange Road, Cambridge CB3 9AN, United Kingdom — ³Institute for Advanced Study, Technische Universität München, Lichtenbergstrasse 2 a, D-85748, Garching, Germany

Multi-heme proteins such as STC or MtrF are membrane proteins facilitating long-range electron transfer (ET) across cell membrane in metal-reducing bacteria. We have used classical molecular dynamics (MD) together with electronic-structure calculations based on density functional theory (DFT) to show that in native environment the conducted electrons are transferred by incoherent hopping between the heme cofactors. However, recent experimental measurements of current-voltage (I-V) curves suggested that the ET mechanism changes to coherent electron tunneling in vacuum when the protein is electronically coupled with metal electrodes. To investigate such conditions, we performed MD simulations in accurate gold/protein interaction force field to identify adsorption of STC and MtrF between two gold electrodes. By large-scale DFT calculations of the whole interfacial structure we identified the conduction channels formed predominantly by delocalized heme iron states. Finally, we apply Landauer formalism to compute I-V curves on STC junction using the DFT electronic states corrected for band alignment and discuss the ET mechanism.

Talk O 25.6 Tue 12:00 H9
Elastic and lattice-dynamical properties of titanium-based compounds — ●PETER WEBER, PASQUALE PAVONE, and CLAUDIA DRAXL — Humboldt-Universität zu Berlin, Physics Department and IRIS Adlershof, Germany

Titanium is the basic element of a variety of compounds with very different electronic, mechanical, and thermal properties. While, for instance, the rocksalt crystals TiC and TiN are well known for their hardness, allotropes of TiO₂ show much softer elastic behaviour. In this work we present the results of an *ab-initio* investigation of the elastic and lattice-dynamical properties of these compounds under pressure. The elastic-constant tensor is calculated up to the third order. Pressure effects on the lattice-dynamical properties of these compounds are evaluated in terms of the mode Grüneisen parameter at the Brillouin zone center. The calculations are performed using density-functional theory as implemented in the full-potential all-electron software package **exciting** [1]. Linear and nonlinear elastic constants are obtained using the **ElaStic** tool [2].

- [1] A. Gulans *et al.*, J. Phys.: Condens. Matter **26** (2014) 363202
[2] R. Golezorkhtabar *et al.*, Comp. Phys. Commun. **184** 1861 (2013)

Talk O 25.7 Tue 12:15 H9
Understanding the electron transport through NiSi₂-Si in-

terfaces — ●FLORIAN FUCHS^{1,2,3,4}, SIBYLLE GEMMING^{1,2,3}, and JÖRG SCHUSTER^{2,4} — ¹Institute of Physics, Technische Universität Chemnitz, Chemnitz, Germany — ²Center for Advancing Electronics Dresden (cfaed), Dresden, Germany — ³Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Dresden, Germany — ⁴Fraunhofer Institute for Electronic Nano Systems (ENAS), Chemnitz, Germany

Metal-semiconductor interfaces are of huge importance for applications and can be found in various field-effect transistors. We study the interface between NiSi₂ and silicon on the basis of density functional theory and the NEGF formalism. Different crystal orientations and strain states are investigated systematically.

We focus on the tunneling phenomena of carriers through the Schottky contact at the interface, which are crucial for the on-current in transistors. The on-current is found to be strongly dependent on strain and orientation. It will be shown that the height of the Schottky barrier determines the tunneling current. However, not all changes in the current can be traced back to the barrier height. The modification of the electronic structure matter as well, which can be modeled based on the effective mass of the tunneling carriers. We have also extracted work functions of the isolated materials which we relate to the extracted Schottky barrier heights. It will be shown that the Schottky-Mott model fails for this material system. Better approaches will be discussed in our contribution.

Talk O 25.9 Tue 12:45 H9
Discovering a novel nanometric cubic phase in monochalcogenide semiconductors - Theory meets experiment — ●GUY MAKOV^{1,2}, URI ARGAMAN¹, ELAD SEGEV², RAN ABUTBUL^{1,2}, and YUVAL GOLAN^{1,2} — ¹Dept. of Materials, Ben-Gurion University, Beer-Sheva, Israel — ²Ilse Katz Institute of nanoscience, Ben-Gurion University, Beer-Sheva, Israel

A new nanometric cubic binary phase with a low-symmetry 64-atom cubic structure was recently discovered in tin monosulfide. Subsequently, this phase was synthesized and identified in tin monoselenide and posited to exist in germanium monosulfide and monoselenide based on density functional theory total energy calculations. A series of computational and experimental studies have identified promising optical properties due to the larger bandgap and non-centrosymmetric structure of the crystal. The structure, atomic positions, band gaps and vibrational spectra of these phases were determined by *ab-initio* density functional calculations and found to be in very good agreement with experimental measurements. The phases were determined to be mechanically stable from *ab-initio* phonon spectra and energetically close to competing structures such as rhombohedral and orthorhombic. Surface energy calculations indicate that the particles must be stabilized by ligand adsorption. Ligand surface properties are explored to explain the nanocrystal growth mechanisms. This talk will focus on the results of our calculations on surface and bulk properties and their interplay with experimental studies.

O 32: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge IV (joint session O/CPP/DS/TT)

Tuesday 14:00–16:45

H9

Topical Talk O 32.1 Tue 14:00 H9
The Data Revolution in Materials Science, Through the Lens of the Materials Project — ●KRISTIN PERSSON — University of California, Berkeley, USA

Advanced materials are essential to economic and societal development, with applications in multiple industries, from clean energy, to national security, and human welfare. Historically, novel materials exploration has been slow and expensive, taking on average 18 years from concept to commercialization. Due to the tremendous improvements in computational resources, coupled with software development during the last decades, real materials properties can now be calculated from quantum mechanics much faster than they can be measured. A new era of computational materials prediction and design has been born. A result of this paradigm change are databases like the Materials Project which is harnessing the power of supercomputing together with state of the art quantum mechanical theory to compute the properties of all known inorganic materials and beyond, design novel materials and offer the data for free to the community together with online analysis and design algorithms. We leverage the rich data from the Materials Project for machine learning; accelerating materials design, character-

ization and finally synthesis of materials. This talk will survey this rapidly evolving and exciting paradigm in science, showcasing the possibilities and iteration between ideas, computations, insight and new materials development.

Talk O 32.2 Tue 14:30 H9
High-throughput simulations of complex band structure — ●EMANUELE BOSONI and STEFANO SANVITO — School of Physics and CRANN, Trinity College Dublin, College Green, Dublin 2

The Complex Band Structure (CBS) generalizes the conventional band structure of a material by considering wave-vectors with complex components. The CBS extends the description of the allowed states of a material beyond the bulk propagating states, including in the picture the evanescent wave-functions that grow or decay from one unit cell to the next. Even though these latter states are forbidden by translational symmetry, they become important when this is broken via, for example, an interface. In the past, many studies made use of CBS calculations in order to confirm or motivate experimental findings, but only recently we see some efforts to give an unified perspective to the study of this quantity [1]. Moreover, the growth in recent years of high-

performance computational resources available at relatively low cost opens the possibility to make a systematic, high-throughput, study of the CBS within the Density Functional Theory (DFT) framework.

In this contribution we will present our implementation of the Transfer Matrix Method [1] for the calculation of the CBS within the DFT code Siesta [2] and we will explain challenges and benefits of the high-throughput approach. We will present a proof of concept example in which we calculated the CBS for a set of materials and we will conclude explaining the relevance of our project in the field of spintronics.

[1] Reuter M. G., J. Phys.: Condens. Matt. 29, 053001 (2017)

[2] J. M. Soler et al., J. Phys.: Condens. Matt. 14, 2745 (2002)

Talk O 32.4 Tue 15:00 H9

First-principles Modelling of Solid-Solid Interfaces in all Solid-State Batteries — ●BORA KARASULU¹, JAMES P. DARBY¹, CLARE P. GREY², and ANDREW J. MORRIS³ — ¹Dept. of Physics, Univ. of Cambridge, UK — ²Dept. of Chemistry, Univ. of Cambridge, UK — ³School of Metallurgy and Materials, Univ. of Birmingham, UK

All solid-state batteries (ASSBs) can potentially mitigate the safety issues known for conventional Li-ion batteries, and provide enhanced energy densities, by replacing the organic electrolyte solutions with solid inorganic equivalents. Mechanical and (electro)chemical incompatibilities between the ASSB solid components, however, lead to high resistances, curtailing the Li-ion transport at their interfaces. In this talk, we introduce a high-throughput ab initio modelling approach towards the rational design of electrolyte/electrode interfaces in ASSBs. First, we obtain phase diagrams of sulfide-based electrolytes with diverse compositions, phases, vacancies and doping using the Ab Initio Random Structure Searching (AIRSS) method. Next, the stable and low-lying metastable phases are screened for their ionic conductivity using ab initio molecular dynamics simulations. Finally, diverse surfaces of the selected electrolyte phases are interfaced with the surfaces of electrodes or other interfacial (e.g. solid electrolyte interphase, SEI) layers to determine the stable combinations using an automated procedure (INTERFACER). The devised approach will be demonstrated in action for a collection of interfaces, e.g. Li-P-S electrolytes with LiCo₂, Li-metal electrodes and alike.

Talk O 32.5 Tue 15:15 H9

New Insights into Amorphous Materials and their Surfaces by Combining Machine Learning and DFT — ●VOLKER DERINGER — University of Cambridge, Cambridge, UK

Understanding links between atomic structure, chemical reactivity, and physical properties in amorphous solids is a long-standing challenge. DFT-based atomistic simulations have played important roles in this, but come at high computational cost. Novel interatomic potentials based on machine learning (ML) achieve close-to DFT accuracy, but require only a small fraction of the cost. In this talk, I will argue that such ML-based potentials are particularly useful for studying amorphous solids.

First, I will describe a Gaussian Approximation Potential (GAP) for amorphous carbon, which we recently used to simulate the deposition of tetrahedral amorphous carbon (*ta-C*) films, one atom at a time. These simulations reproduced the experimentally observed count of sp³ atoms and gave new insight into the microscopic growth mechanism. I will then discuss how ML-based potentials can be combined with density-functional methods to yield new insights into surface functionalization (specifically, hydrogenation and oxidation) of *ta-C*. Finally, I will present recent work on amorphous silicon, another prototypical non-crystalline material that ML-driven simulations can describe with high accuracy. Looking ahead, these studies suggest that ML-based potentials may become more widespread tools for the realistic modelling and understanding of the amorphous state.

Talk O 32.6 Tue 15:30 H9

Harvesting from unbiased sampling of open systems: phase diagrams and property maps of surfaces and clusters in reactive atmosphere — ●YUANYUAN ZHOU, MATTHIAS SCHEFFLER, and LUCA M. GHIRINGHELLI — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Numerous processes that occur at surfaces of materials play a critical role in the manufacture and performance of functional materials, e.g., electronic, magnetic, and optical devices, sensors, catalysts, and coatings. A prerequisite for analyzing and understanding the electronic properties and the function of surfaces is detailed knowledge of the atomic structure, i.e., the surface composition and geometry under realistic condition. We introduce a Replica-Exchange (RE) Grand-Canonical (GC) Monte-Carlo algorithm. By means of the coupled sam-

pling at several chemical potentials (i.e., partial pressures) of a reactive gas atmosphere and temperatures, the REGC scheme enables the unbiased calculation of (*p, T*) phase diagrams of surfaces, nanoparticles, or clusters in contact with reactive atmosphere, where all anharmonic contributions are included. Moreover, the multi-canonical sampling yields the temperature-pressure dependence (map) of all equilibrium observables that can be measured within the given model Hamiltonian. For instance, structural parameters such as the radial distribution function, or the fundamental electronic gap. This allows for rational design, where *operando* condition are taking fully into account. We demonstrate the approach for model Lennard-Jones surfaces as well as Si clusters and surfaces in a hydrogen atmosphere.

Talk O 32.7 Tue 15:45 H9

DFT Predicted XAS Spectra for the Solid Electrolyte Interphase — ●ANGELA F. HARPER¹ and ANDREW J. MORRIS² — ¹Department of Physics, University of Cambridge, JJ Thomson Ave, Cambridge CB3 0HE, UK — ²School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, UK

The future of large-scale energy storage relies heavily on the ability of Li-ion batteries to have high capacity and long-term stability. Si is a widely used high capacity anode for Li-ion batteries which offers around 3000 mAh/g of capacity per charge. However, it is limited by the severe volume expansion upon lithiation [1]. To suppress this expansion and avoid permanent destruction of the solid electrolyte interphase (SEI), artificial coating materials such as alumina are used to limit volume expansion and aid with lithiation. In this work, I will show how density functional theory can be used to understand the structure and morphology of the Si interface with artificial SEI [2,3]. By calculating the XAS spectra of different SEI bulk phases as well as the interface, it is then possible to compare these results to experiment. Future studies will then lithiate these phases to study their electrochemical properties as possible battery anode coatings.

[1] Ogata, K. et al Nat. Comm. 5, 3217 (2014)

[2] Morris, A. et al Comp. Phys. Comm. 185, 5, 1477 (2014)

[3] Nicholls, R. et al J. Phys.: Conf. Ser. 371 012062 (2012)

Talk O 32.8 Tue 16:00 H9

Constructing Accurate Machine Learning Force Fields for Flexible Molecules — ●VALENTIN VASSILEV-GALINDO, IGOR POLTAVSKY, and ALEXANDRE TKATCHENKO — Physics and Material Science Research Unit, University of Luxembourg, Luxembourg

State-of-the-art machine learning (ML) models can reproduce potential energy surfaces (PES) for molecules containing up to a few tens of atoms with the accuracy comparable to the most exact ab initio methods. This provides a unique tool for computing different thermodynamic properties that would require millions of CPU years otherwise. For instance, a recently developed sGDML[1,2] model predicts forces and energy with CCSD(T) accuracy using just a few hundreds of configurations for training. However, up to now ML has been mainly applied to rather rigid molecules. In this regard, our objective is to test ML for flexible molecules and out-of-equilibrium configurations along transition paths. For this, we select molecules (e.g. azobenzene, stilbene) with relatively complex transition paths, which result from an interplay between long- and short-range interactions. Then, different paths connecting PES minima are tested using sGDML. This allows us to define optimal descriptors and the most appropriate strategies for choosing the training sets, which is crucial for ML models relying on a limited number of training points. Our results open an avenue for efficiently calculating transport pathways, transition rates and other out-of-equilibrium properties with previously unattended accuracy.

[1] Chmiela, S. et al., Sci. Adv. 3, e1603015 (2017).

[2] Chmiela, S. et al., Nat. Commun. 9, 3887 (2018).

Talk O 32.9 Tue 16:15 H9

Calculating critical temperatures for magnetic order in two-dimensional materials — ●DANIELE TORELLI — CAMD, Department of Physics, Technical University of Denmark, 2820 Kgs. Lyngby, Denmark

Recent observation of ferromagnetic out-of-plane order in two-dimensional (2D) CrI₃ highlights the importance of a microscopic understanding of magnetic anisotropy (MA) in ground state magnetic systems. Single-ion anisotropy and anisotropic exchange coupling comprise crucial ingredients to escape the Mermin-Wagner theorem which implies that rotational symmetry cannot be spontaneously broken at any finite temperature in 2D and thus prevents magnetic order.

In the present work we investigate the variation of critical temperature in Heisenberg model systems using classical Metropolis Monte

Carlo simulations. A fit for square, hexagonal and honeycomb lattices leads to a simple expression for the critical temperatures as a function of MA and exchange coupling constants.

Based on a new developed computational 2D materials database, we predict 2D structures with high critical temperatures and high thermodynamic and dynamic stability for future experimental investigations. As testing system, relevant Heisenberg exchange couplings and MA energies in mono-layer CrI₃ are obtained from first principle calculations and energy mapping analysis, yielding to an estimation of Curie temperature in good agreement with experimental results.

Talk O 32.10 Tue 16:30 H9
Amino-acids on metallic surfaces: searching conformational space — ●DMITRII MAKSIMOV, CARSTEN BALDAUF, and MARIANA ROSSI — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
 Organic-inorganic interfaces are challenging for computational model-

ing, in particular regarding the prediction of stable configurations at the interface, which determine the electronic properties of the system as a whole. The amino acid arginine is a flexible molecule in the gas phase and experiments show its self-assembly into dimers, rings, and chains on Ag(111) and Au(111) surfaces. For two protonation states (neutral Arg and charged ArgH⁺), we perform systematic structure searches by placing known gas-phase minima in different orientations on top of the surfaces, followed by full relaxation within long-range dispersion corrected density-functional theory (DFT). In the analysis, we aim at understanding the alterations of the conformational space from the gas phase to surface adsorption by means of a dimensionality-reduced representation based on a combination of the Smooth Overlap of Atomic Positions (SOAP) and the Sketchmap techniques [1]. The favorable interaction with the metallic surface reduces the number of accessible conformations for neutral Arg. For the adsorption of charged ArgH⁺, the number of local minima increases due to surface-dependent partial charge screening. [1] S. De et al., *J. Cheminform.*, **9**:6 (2017)

O 51: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge V (joint session O/CPP/DS/TT)

Wednesday 10:30–13:15

H9

Topical Talk O 51.1 Wed 10:30 H9
Theoretical Investigations of Electrochemical CO₂ Reduction — ●KAREN CHAN — Department of Physics, Technical University of Denmark

The electroreduction of CO₂ has the potential to store energy from intermittent renewable sources and to produce carbon-neutral fuels and chemicals; In this talk, I will discuss new developments in modeling the electrochemical interface. I will then present the application of these models of the interface to CO₂ reduction: the determination of reaction pathways and kinetics on transition metals, field and solvation effects, pH effects on C₂ product selectivity, and implications for catalyst design.

Topical Talk O 51.2 Wed 11:00 H9
First-principles approach to model electrochemical reactions at the solid-liquid interface — ●MIRA TODOROVA, SUDARSAN SURENDRALAL, and JÖRG NEUGEBAUER — MPI für Eisenforschung, Düsseldorf

Processes at solid-liquid interfaces are at the heart of many present day technological challenges related to the improvement of battery materials, electro-catalysis, fuel cells, corrosion and others. Describing and quantifying the underlying fundamental mechanisms is equally challenging for experimental and theoretical techniques.

Utilizing concepts from semiconductor physics, we have developed a novel potentiostat design, which enables us to perform ab initio calculations under controlled bias conditions. Easily applied in standard density functional theory codes, it controls the electrode potential of the system by tuning the excess charge of the working electrode and allows us to obtain direct insight into key mechanisms of electrocatalysis and corrosion. As a prototype example, we consider one of the most corrosive systems under wet conditions - Mg. Using the new approach we solve a 150-year-old problem, which links H-evolution under anodic conditions to Mg dissolution [1].

[1] S. Surendralal, M. Todorova, M.W. Finnis and J. Neugebauer, *Phys. Rev. Lett.* **120**, 246801 (2018).

Talk O 51.3 Wed 11:30 H9
Towards out of the box implicit solvation at liquid-liquid interfaces — ●JAKOB FILSER¹, MARKUS SINSTEIN¹, CHRISTOPH SCHEURER¹, SEBASTIAN MATERA², KARSTEN REUTER¹, and HARALD OBERHOFER¹ — ¹Technische Universität München — ²Freie Universität Berlin

Implicit solvation models are widely used to incorporate solvent effects in electronic structure theory. Treating the solvent as a structureless dielectric continuum, they lift the necessity to explicitly sample solvent degrees of freedom. However, even state of the art models currently cannot treat solvation at technically highly important dielectric interfaces, e.g. between two immiscible liquids.

As a remedy, we modify the multipole expansion (MPE) model to also account for liquid-liquid interfaces, specifically focusing on the electrostatics of mutually interacting dielectric regions. Non-electrostatic free energy contributions thereby are treated with a sim-

ple linear model, fitted to experimental free energies of solvation in the two liquids. We demonstrate the efficacy of this approach for small molecules at a water–1-octanol interface, which show the correct qualitative behaviour with respect to orientation and position at the interface.

Future, quantitative applications of our new implicit solvation interface methods are clearly possible but will necessitate both improvements to the non-electrostatic free energy terms and a more exhaustive parameterization effort for a wide range of solvents.

Talk O 51.4 Wed 11:45 H9
Continuum models of the electrochemical diffuse layer in electronic-structure calculations — ●FRANCESCO NATTINO¹, OLIVIERO ANDREUSSI², and NICOLA MARZARI¹ — ¹Theory and Simulations of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland — ²Department of Physics, University of North Texas, Denton, TX 76207, USA

The electrical diffuse layer is a structure that spontaneously forms at essentially any solvated interface, such that its presence in electrochemistry is ubiquitous. While first-principles methods are desirable to describe any process occurring at the surface, fully-atomistic models of electrolyte solutions suffer from computational limitations. In this context, continuum models represent a practical tool to bypass these difficulties and to account for the presence of the diffuse layer at electrified interfaces. However, despite the increasing popularity of continuum models in the field of materials science, even relatively simple observables such as the differential capacitance (DC) of single-crystal electrode surfaces remain challenging to model quantitatively. I will present and discuss the performance of a hierarchy of continuum diffuse-layer models that we have implemented and coupled to an atomistic first-principles description of a charged metal surface. In particular, I will compare computed DC values for the prototypical Ag(100) surface in an aqueous solution to experimental data, and validate in this way the accuracy of the models considered.

Talk O 51.5 Wed 12:00 H9
Ab initio molecular dynamics of Pt(111)/H₂O interfaces in an electrolytic cell setup — ●SUDARSAN SURENDRALAL, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany.

Recently, we developed a novel scheme to perform density functional theory (DFT) simulations of electrochemical interfaces under conditions of constant applied voltage utilizing charge transfer from a semiconductor counter electrode [1]. We use a fractionally doped Ne counter electrode because of its inertness, wide band gap, and low deformation potential. Our DFT based molecular dynamics calculations of the Pt(111)/H₂O interface in this setup reveals that we are able to accurately reproduce macroscopic observables like the potential of zero charge (PZC). We discuss the work function drop at the interface at the PZC, due to the charge polarization by the non-dissociative chemisorption of water molecules at the Pt surface. Possible pitfalls

due to the choice of the DFT exchange-correlation functional, non-converged computational parameters and confinement effects due to the presence of the counter electrode will also be discussed.

[1] S. Surendralal, M. Todorova, M. W. Finnis, and J. Neugebauer, *Phys. Rev. Lett.* **120**, 246801 (2018).

Talk O 51.6 Wed 12:15 H9
Swipe left for water molecules? - Implicit vs explicit descriptions of liquid water at interfaces. — ●NICOLAS HÖRMANN¹, OLIVIERO ANDREUSSI², and NICOLA MARZARI¹ — ¹Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, CH-1015 Lausanne, Switzerland — ²Department of Physics, University of North Texas, Denton, TX 76207, USA

We present a study of relevant electrochemical interfaces, such as semiconductor-water and metal-water interfaces based on periodic density functional theory (DFT) calculations with the interface modelled with different degrees of complexity. Water at metallic surfaces is modelled within the self-consistent continuum solvation scheme (SCCS) [1] with explicit application of a potential which allows the comparison of pH dependent properties with experimental results [2,3]. In the case of semiconductors, different amounts of interfacial water are substituted with implicit solvent and observables such as the measured band alignment are obtained from thermal averaging over molecular dynamics snapshots. We find that it is necessary and sufficient to include strongly bound interfacial water molecules (dissociated or not) explicitly and replace the rest with an implicit model, in order to obtain consistent results with all-explicit simulations [4]. Based on these results we simulate the surface Pourbaix diagrams of the most stable surfaces of GaAs, GaN, GaP, CdS and anatase and rutile TiO₂.

[1] *J. Chem. Phys.* **136**, 064102 (2012); [2] *Nat Commun.* **9**, 3117 (2018). [2,3] NH (2018) submitted

Talk O 51.7 Wed 12:30 H9
Transition metal oxide nanoparticles as efficient catalysts for proton exchange membrane electrolyzers: morphology, activity and stability — ●DANIEL OPALKA, YONGHYUK LEE, JAKOB TIMMERMANN, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technische Universität München

Transition metal oxides such as RuO₂ and IrO₂ are currently the best known electrocatalysts for the oxygen evolution reaction from liquid water in proton exchange membrane (PEM) electrolyzers. However, dynamic load operation of PEM cells induces transformations of the catalyst morphology leading to metal dissolution and catalyst degradation. We present a computational model to predict the morphology, activity and stability from *ab initio* electronic structure theory and fundamental thermodynamic principles. Based on this model, we have explored novel strategies to reduce material expenses and improve catalyst stability while preserving high catalytic activity via nanoparticles with a core-shell design. From an analysis of different surface coverages with oxygen, hydroxyl and hydroxo species, voltage-dependent phase

diagrams for catalyst surfaces are presented which correlate with characteristic features observed in cyclovoltammetric measurements. Results from atomistic models of selected nanoparticles on the basis of Wulff's Theorem show negligible size effects, but a strong influence of the facet terminations on the surface relaxation.

Talk O 51.8 Wed 12:45 H9
Modelling the fingerprint of chemical reactions on catalytic surfaces in core-electron binding energies — ●JOHANNES LISCHNER and JUHAN MATTHIAS KAHK — Imperial College London

Core-electron X-ray photoemission spectroscopy is a powerful experimental technique to gain information about chemical reactions on catalytic surfaces. Interpreting experimental spectra, however, is often challenging and theoretical modelling of core-electron binding energies is required to meaningfully assign peaks to adsorbate species. In this talk, I will present a novel first-principles modelling strategy to calculate core-electron binding energies of molecules on metallic surfaces. Specifically, we combine plane-wave/pseudopotential DFT calculations of surface slab models for geometry optimizations with all-electron Delta-SCF calculations on cluster models for determining accurate core-electron binding energies. This approach is computationally efficient and yields good agreement with experimental measurements for a wide range of adsorbates on copper(111) surfaces.

Talk O 51.9 Wed 13:00 H9
What Makes a Successful Photoanode? - The Role of the Semiconductor-Catalyst Interface — ●FRANZISKA SIMONE HEGNER¹, BENJAMIN MOSS², JAMES DURRANT², SIXTO GIMENEZ³, JOSÉ-RAMÓN GALÁN-MASCARÓS¹, and NÚRIA LÓPEZ¹ — ¹Institute of Chemical Research of Catalonia (ICIQ) — ²Imperial College London — ³Institute of Advanced Materials, Castellón

A large scale implementations of artificial photosynthesis is still limited by the low efficiencies of the employed photoelectrochemical systems. A common strategy to improve performance is to deposit a co-catalyst on the light-harvesting photoanode. However, the role of the catalyst is controversial; is it acting as a true catalyst, i.e. transferring charges, or is it merely influencing the electronic structure of the semiconductor?[1]

The semiconductor-catalyst interface is key to catalytic performance, but its accurate description is limited since linear scaling relationships no longer apply. Herein the function of the co-catalyst (cobalt hexacyanoferrate) is discussed on two photoanode interfaces, Fe₂O₃ and BiVO₄. Density Functional Theory and time-resolved spectroscopy were used to shed light on the underlying charge-transfer processes. Taking into account the advantages and disadvantages of all applied techniques, a relationship between electronic structure alignment, interface morphology, and photocatalytic efficiency is proposed.[2]

[1] D. R. Gamelin, *Nat. Chem.*, **4** (2012), 965-967. [2] F. S. Hegner, D. Cardena-Moscoros, S. Gimenez, N. López, J. R. Galán-Mascarós. *ChemSusChem*, **10** (2017) 4552-4560.

O 57: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge VI (joint session O/CPP/DS/TT)

Wednesday 15:00–17:45

H9

Talk O 57.1 Wed 15:00 H9
First-principles quantum transport simulations including strong correlation effects — ANDREA DROGHETTI¹, ●WILHELM APPELT², LIVIU CHIONCEL², MILOS RADONJIĆ³, ENRIQUE MUÑOZ⁴, STEFAN KIRCHNER⁵, DAVID JACOB¹, DIETER VOLLHARDT², ANGEL RUBIO⁶, and IVAN RUNGGER⁷ — ¹University of the Basque Country (Spain) — ²University of Augsburg (Germany) — ³University of Belgrade (Serbia) — ⁴Pontificia Universidad Católica de Chile — ⁵Zhejiang University (China) — ⁶Max Planck Institute for the Structure and Dynamics of Matter (Germany) — ⁷National Physical Laboratory (UK)

When magnetic molecules are brought into contact with metals the electron-electron interaction leads to the appearance of the correlated Kondo state. In this talk we will present the results of first-principles calculations for the electronic structure and the linear-response conductance of radical molecules adsorbed on metallic surfaces in the Kondo regime [*Phys. Rev. B* **95**, 085131 (2017), *Nanoscale* **10**, 17738 (2018)]. In particular we will outline the methodological approach

as implemented in the Smeagol electron transport code and we will benchmark the results against experiments. The method relies in the first place on the combination of Density Functional Theory with the Green's functions technique. We will explain how a molecular device is projected onto an effective Anderson impurity problem, which is then solved either by continuum time quantum Monte Carlo or numerical renormalization group. Finally, we will describe some work-in-progress aimed at computing transport properties beyond linear-response.

Talk O 57.2 Wed 15:15 H9
Density functional theory for transport through correlated systems — ●STEFAN KURTH — Univ. of the Basque Country UPV/EHU, San Sebastian, Spain — IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — Donostia International Physics Center DIPC, San Sebastian, Spain

A recently proposed density functional formalism to describe electronic transport through correlated systems in the steady state uses both the density on the junction and the steady current as basic variables. The corresponding Kohn-Sham system features two exchange-correlation

(xc) potentials, a local xc potential and an xc contribution to the bias, which are universal functionals of the basic variables.

A recent parametrization of the xc potentials for the single-impurity Anderson model correctly incorporates both the Kondo and Coulomb blockade regimes. It allows for calculation of currents and differential conductances at arbitrary bias and temperature at negligible numerical cost but with the accuracy of sophisticated renormalization group methods. A time-local version of this functional is used to study the Anderson model under the influence of both DC and AC biases. We observe interaction-induced shifts of the photon-assisted conductance peaks, suppression of the Kondo plateau at zero temperature and lifting of Coulomb blockade at finite temperature.

Talk O 57.4 Wed 15:45 H9
Many-body spectral functions from steady state density functional theory — ●DAVID JACOB^{1,2} and STEFAN KURTH^{1,2,3} — ¹Dpto. de Física de Materiales, Universidad del País Vasco UPV/EHU, San Sebastián, Spain — ²IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — ³DIPC, San Sebastián, Spain

We present a scheme to extract the true many-body spectral function of an interacting many-electron system from an equilibrium density functional theory (DFT) calculation [1]. To this end we devise an ideal STM-like setup and employ the recently proposed steady-state DFT formalism (i-DFT) which allows to calculate the steady current through a nanoscopic region coupled to two biased electrodes [2]. In our setup one of the electrodes serves as a probe ("STM tip"). In the ideal STM limit of vanishing coupling to the tip, the system to be probed is in quasi-equilibrium with the "substrate" and the normalized differential conductance yields the exact equilibrium many-body spectral function. Moreover, from the i-DFT equations we derive an exact relationship which expresses the interacting spectral function in terms of the Kohn-Sham one. Making use of i-DFT xc functionals that capture Coulomb blockade as well as Kondo physics, the method yields spectral functions for Anderson impurity models in good agreement with NRG calculations. It is thus possible to calculate spectral functions of interacting many-electron systems at the cost of an equilibrium DFT calculation.

References: [1] D. Jacob and S. Kurth, *Nano Lett.* **18**, 2086 (2018) [2] G. Stefanucci and S. Kurth, *Nano Lett.* **15**, 8020 (2015)

Talk O 57.5 Wed 16:00 H9
Magnetic phase transitions induced by pressure and magnetic field: the case of antiferromagnetic USb₂ — ●LEONID SANDRATSKII — Max Planck Institute of Microstructure Physics, Halle, Germany

Fascinating phenomena observed under applied pressure and magnetic field are currently attracting much research attention. Recent experiments have shown that application of the pressure or magnetic field to the USb₂ compound induce the transformations of the ground-state antiferromagnetic (AFM) up-down-down-up structure to, respectively, ferromagnetic (FM) or ferrimagnetic configurations. Remarkably, the magnetic critical temperature of the FM state, induced by pressure, is more than two times smaller than the Neel temperature of the ground state. We performed density-functional theory (DFT) and DFT+U studies to reveal the origin of the unusual magnetic ground-state of the system and the driving mechanisms of the phase transitions. We investigate both the magnetic anisotropy properties and the parameters of the interatomic exchange interactions. To study pressure-induced effects we carry out calculations for reduced volume and demonstrate that the AFM-FM phase transformation indeed takes place but depends crucially on the peculiar features of the magnetic anisotropy. We also explain why the magnetic field that couples directly to the magnetic moments of atoms leads to the phase transition to the ferrimagnetic state whereas the pressure that does not couple directly to magnetic moments results in the FM structure.

Talk O 57.6 Wed 16:15 H9
Charge localization at a weakly coupled molecule-metal system studied by linear expansion Δ -self-consistent field density-functional theory (Δ SCF-DFT) — ●HADI H. AREFI^{1,2}, DANIEL CORKEN³, REINHARD MAURER³, F. STEFAN TAUTZ^{1,2}, and CHRISTIAN WAGNER^{1,2} — ¹Peter Grünberg Institut (PGI-3), Forschungszentrum Jülich, Germany — ²JARA-Fundamentals of Future Information Technology — ³Department of Chemistry, University of Warwick, Coventry, United Kingdom

Predicting the charge arrangements at the interface between molecules and metals represents a formidable challenge for semi-local approximations to Density Functional Theory (DFT). This could become even

more critical when molecules are only weakly coupled to the metal. Single-molecular devices based on such weak coupling have recently been created by molecular manipulation with a scanning probe microscope (SPM), where a single PTCDA (perylene-tetracarboxylic dianhydride) molecule was placed in a free-standing upright configuration either on a SPM tip [1] or on a pedestal of two adatoms on the Ag(111) surface [2]. There are indications that the mechanism stabilizing these unexpected configurations is linked to an integer charge transfer creating a singly occupied molecular orbital. We use the Δ SCF-DFT method [3] to confine charge on the LUMO of the PTCDA and study the consequences with vdW-corrected DFT.

[1] C. Wagner et al. *Phys. Rev. Lett.* **115**, 026101 (2015) [2] T. Esat et al. *Nature* **558**, 573 (2018) [3] R. J Maurer, K. Reuter, *JCP* **139**, 014708 (2013)

Talk O 57.7 Wed 16:30 H9
Dispersion corrected density functional theory studies on PVDF/hydrated aluminium nitrate composite system — ●RANJINI SARKAR and TARUN KUNDU — Indian Institute of Technology, Kharagpur

Electro-active polymer Polyvinylidene fluoride (PVDF) based ferroelectric composites have gained significant technological importance over conventional ceramic ferroelectrics. This article provides quantum chemical description of PVDF/ hydrated aluminium nitrate salt composite system in the light of density functional theory. Four monomer units of pristine α and β -PVDF, pure Al(NO₃)₃·9H₂O, and PVDF/Al(NO₃)₃·9H₂O structures are optimized using dispersion corrected exchange correlation functional B3LYP-D and 6-311+G(d,p) basis set. Similar to the experimental findings, the current theoretical investigation also suggests that hydrogen bond interaction between PVDF and the hydrated salt molecule plays the major role for the enhancement of ferroelectric properties in this composite system. Non-covalent interaction phenomenon is elucidated on the basis of natural bond orbital analysis, Bader's quantum theory of atoms in molecules and reduced density gradient analysis. Chemical Reactivity and charge transfer mechanisms are explained using atomic-dipole corrected Hirshfeld population analysis, molecular electrostatic potential plot and frontier molecular orbital analyses, respectively.

Talk O 57.8 Wed 16:45 H9
Band-structure effects in vertical layered material heterostructures — ●NICHOLAS D. M. HINE¹, GABRIEL C. CONSTANTINESCU², NELSON YEUNG¹, SIOW-MEAN LOH¹, JOSÉ MARÍA ESCARTÍN², CUAUHTEMOC SALAZAR GONZALEZ¹, and NEIL R. WILSON¹ — ¹Department of Physics, University of Warwick, United Kingdom — ²Cavendish Laboratory, University of Cambridge, 19 JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom

Controlling the properties of layered material heterostructures is crucial to the success of devices based on the novel capabilities of 2D materials, yet theoretical insight has been limited by the large system sizes required to study rotated, incommensurate interfaces. We use linear-scaling DFT calculations with non-local vdW functionals to explore large-scale models of heterostructures of interest for device applications. Results will be presented for heterostructures including MoS₂/MoSe₂, MoSe₂/WSe₂, and other Transition Metal Dichalcogenide pairings, TMDCs with graphene and hBN substrates, and hBN/Phosphorene. Band-structure changes caused by stacking and rotation of the layers are obtained by unfolding the supercell spectral function into the primitive cells, incorporating spin-orbit coupling. Changes in spectral weight and band-structure between the monolayers and heterostructured interfaces show how lattice mismatch (MoS₂/MoSe₂) or spacer layers (Phosphorene/hBN/Phosphorene) can allow the component monolayers to retain more independence in heterostructures than in homo-stacks. Finally, applying electric fields allows the behaviour of gated structures to be predicted and explained.

Talk O 57.9 Wed 17:00 H9
Global Trends in Calcium-Silicate-Hydrate Phases Identified by Infrared Spectroscopy and Density Functional Theory — ●MOHAMMADREZA IZADIFAR, FRANZ KÖNIGER, ANDREAS GERDES, CHRISTOF WÖLL, and PETER THISSEN — Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces (IFG), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Building and construction industry are at the same time the backbone and the driving force of our modern society. Nearly all our today's technical infrastructure is based on cement-based materials. Detailed, spectroscopic investigations of model reactions on well-defined mineral substrates under UHV-conditions are largely lacking, thus prohibiting

a validation of theoretical methods. Eight different Calcium-Silicate-Hydrate (CSH) phases, namely Tobermorite 14Å, Tobermorite 11Å, and Tobermorite 9Å, Wollastonite, Jaffeite, Jennite, γ -C2S, and α -C2SH, are calculated with the help of Density Functional Theory using the Vienna ab initio simulation package (VASP). First, we take care of the mechanical properties of the material. Our results revealed that Jaffeite, γ -C2S, and α -C2SH have a linear bulk modulus due to the monomer structure of silicate tetrahedra. Tobermorite 14Å and Jaffeite have the lowest and highest bulk modulus, respectively. In the second part, the optimized geometries allow for the precise calculations vibrational eigenmodes and frequencies by the force-constant (FC) approach. The proportions of C/S and H/C are major criteria for the classification of the calculated wavenumber of $\nu(\text{Si-O})$ for all phases in our model system.

Talk O 57.10 Wed 17:15 H9
Origin of carbon 1s binding energy shifts in amorphous carbon materials — ●MICHAEL WALTER^{1,4,5}, FILIPPO MANGOLINI², ROBERT W. CARPICK³, and MICHAEL MOSELER^{4,5} — ¹FIT, University of Freiburg, Germany — ²University of Texas at Austin, USA — ³University of Pennsylvania, USA — ⁴Fraunhofer IWM, Freiburg, Germany — ⁵Physikalisches Institut, Universität Freiburg, Germany

The quantitative evaluation of the carbon hybridization state by X-ray photoelectron spectroscopy (XPS) has been a surface-analysis problem for the last three decades due to the challenges associated with the unambiguous identification of the characteristic binding energy values of sp^2 - and sp^3 -bonded carbon. Here, we compute the binding energy values for model structures of various carbon allotropes, including graphite, diamond, doped-diamond, and amorphous carbon (a-C), using density functional theory (DFT). The large band-gap of diamond allows defects to pin the Fermi level, which results in large variations of the C(1s) core electron energies for sp^3 -bonded carbon, in

agreement with the large spread of experimental C(1s) binding energy values for sp^3 carbon. In case of hydrogen-free a-C, the C(1s) core electron binding energy for sp^3 carbon atoms is approximately 1 eV higher than the binding energy for sp^2 -hybridized carbon. However, the introduction of hydrogen hinders the unambiguous quantification of the carbon hybridization state on the basis of C(1s) XPS alone. This work can assist surface scientists in the use of XPS for the accurate characterization of carbon-based materials.

Talk O 57.11 Wed 17:30 H9
Mechanically tuned conductivity of graphene grain boundaries from first-principles calculations — DELWIN PERERA, ●JOCHEN ROHRER, and KARSTEN ALBE — Institut für Materialwissenschaft, Technische Universität Darmstadt, Germany

Nanocrystalline graphene has recently been shown to have a strong piezoresistivity and strain gauge factors that are notably higher compared to single- or microcrystalline graphene [1]. The origin of the enhanced piezoresistivity in nanocrystalline graphene is still not fully understood, but several theoretical works suggest that grain boundaries are the main cause as these can evoke transport gaps.

In our work we test this assumption with density functional theory based transport calculations of graphene bicrystals. In particular, we extend our analysis of the interplay between grain boundary structure and transport properties [2] by including mechanical strain. We compute transmission functions and current-voltage curves and compare them with tight binding calculations. Our findings suggest that the strain-induced transport gap modulation can be fully described by the response of the bulk graphene band structure towards strain.

[1] Riaz *et al.*, Nanotechnology **26**, 325202 (2015)

[2] Perera *et al.*, Phys. Rev. B **98**, 155432 (2018)