

## CPP 23: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge III (joint session O/CPP/DS/TT)

Time: Tuesday 10:30–13:00

Location: H9

### Topical Talk

CPP 23.1 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.

CPP 23.2 Tue 11:00 H9  
**Elucidating the Nuclear Quantum Dynamics of Intramolecular Double Hydrogen Transfer in Porphycene** — ●YAIR LITMAN<sup>1</sup>, JEREMY O. RICHARDSON<sup>2</sup>, TAKASHI KUMAGAI<sup>1</sup>, and MARIANA ROSSI<sup>1</sup> — <sup>1</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany — <sup>2</sup>ETH, 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).

CPP 23.3 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 (C<sub>6</sub>H<sub>12</sub>) adsorbed on metal surfaces can participate in catalytic dehydrogenation reactions, which show good potential for hydrogen storage. It has been observed experimentally that C<sub>6</sub>H<sub>12</sub> 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 renormaliza-

tion 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).

CPP 23.4 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).

CPP 23.5 Tue 11:45 H9  
**Electronic Conduction in Metal Junctions with Multi-Heme Proteins** — ●ZDENEK FUTERA<sup>1</sup>, XIUYUN JIANG<sup>1</sup>, JAN ELSNER<sup>2</sup>, and JOCHEN BLUMBERGER<sup>1,3</sup> — <sup>1</sup>Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom — <sup>2</sup>University of Cambridge, Robinson College, Grange Road, Cambridge CB3 9AN, United Kingdom — <sup>3</sup>Institute 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.

CPP 23.6 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 TiO<sub>2</sub> 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. Pres-

sure 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)

CPP 23.7 Tue 12:15 H9

**Understanding the electron transport through NiSi<sub>2</sub>-Si interfaces** — •FLORIAN FUCHS<sup>1,2,3,4</sup>, SIBYLLE GEMMING<sup>1,2,3</sup>, and JÖRG SCHUSTER<sup>2,4</sup> — <sup>1</sup>Institute of Physics, Technische Universität Chemnitz, Chemnitz, Germany — <sup>2</sup>Center for Advancing Electronics Dresden (cfaed), Dresden, Germany — <sup>3</sup>Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Dresden, Germany — <sup>4</sup>Fraunhofer 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 NiSi<sub>2</sub> 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.

CPP 23.8 Tue 12:30 H9

**Impact of Lattice Screening on Wannier-Mott Excitons** — •CLAUDIA RÖDL — Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

Optical properties of materials are most relevant for a large variety of technological applications, ranging from photovoltaics over various spectroscopy techniques to LEDs and displays. In optical spec-

tra, microscopic quantum many-body effects like excitons, i.e. coupled electron-hole-pair excitations, are measurable at a macroscopic scale and crucially determine the materials properties. Hence, a deep understanding of exciton physics constitutes an indispensable driving force for innovation in optics and optoelectronics.

The state-of-the-art parameter-free theoretical description of excitons is based on the Bethe-Salpeter equation of many-body perturbation theory. The present theoretical standard approach takes only the static electronic screening of the electron-hole-pair interaction into account. The coupling of excitons to phonons and, hence, polaronic screening contributions are omitted. However, the exciton-phonon coupling is crucial for the qualitative and quantitative understanding of exciton spectra in materials with strong polaronic effects, such as many technologically highly relevant oxides. We will tackle this problem and explore routes towards the inclusion of the polaronic screening contributions into the Bethe-Salpeter framework. As test systems, we study simple two-atomic bulk semiconductors and insulators.

CPP 23.9 Tue 12:45 H9

**Discovering a novel nanometric cubic phase in monochalcogenide semiconductors - Theory meets experiment** — •GUY MAKOV<sup>1,2</sup>, URI ARGAMAN<sup>1</sup>, ELAD SEGEV<sup>2</sup>, RAN ABUTBUL<sup>1,2</sup>, and YUVAL GOLAN<sup>1,2</sup> — <sup>1</sup>Dept. of Materials, Ben-Gurion University, Beer-Sheva, Israel — <sup>2</sup>Ilse 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.