

## HL 11: Frontiers of electronic structure theory - Non-equilibrium phenomena at the nano-scale I (organized by O)

Non-equilibrium processes such as charge and heat transport are central to electronic and thermoelectric applications. Understanding these phenomena at the nanoscale challenges both theory and experiment. Basic theoretical issues are related to the role of quantum mechanics, the interplay of ballistic, diffusion and hopping processes, the importance of dissipation, the effect of electronic correlation, and the signatures of unusual quantum states. On the experimental side devising measurements to unravel these phenomena in a controlled way poses severe difficulties. In this regard, optical lattices of cold atoms are emerging as a powerful laboratory to test theoretical models and discover unforeseen phenomena.

This symposium will cover current issues in the field by bringing together scientists working in different specific areas with the aim of fostering interdisciplinary discussion, assessing current theoretical understanding, and indicating future goals with emphasis on electronic structure theory.

Organizers: Roberto Car (Princeton), Kristian S. Thygesen (Lyngby) and Matthias Scheffler (Berlin)

Time: Monday 10:30–13:15

Location: TRE Ma

### Topical Talk

HL 11.1 Mon 10:30 TRE Ma

**Molecular junction transport: some theoretical and computational considerations** — ●MARK RATNER<sup>1</sup> and MATTHEW REUTER<sup>2</sup> — <sup>1</sup>Chemistry, Northwestern University, Evanston Illinois 60208 USA — <sup>2</sup>Chemistry, Northwestern University, Evanston Illinois 60208 USA

Following the development of break junction techniques, and very elegant measurements by many labs worldwide, the understanding of the community for single molecule transport junctions on the experimental side has been very nicely unified. While there are still challenges, interpretations of the transport (and indeed of some second-order response properties) is now quite sophisticated.

There have been major advances in the computational approaches also, and in many cases, computations and measurements can be compared quantitatively. But there are some remaining difficulties in the computational and theoretical approaches, and this talk will discuss a few of them.

The topics addressed will be: single molecule aspects, histograms and their usage, time-dependence of the transport, and ghost transmission and computational accuracy.

HL 11.2 Mon 11:00 TRE Ma

**On the description of biased nanocontacts from ab initio** — ●STEVEN ACHILLES<sup>1</sup>, JÜRGEN HENK<sup>1</sup>, MICHAEL CZERNER<sup>2</sup>, CHRISTIAN HELLIGER<sup>2</sup>, and INGRID MERTIG<sup>1</sup> — <sup>1</sup>Institute of Physics, Martin Luther University Halle-Wittenberg, D-06099 Halle, Germany — <sup>2</sup>I. Physikalisches Institut, Justus Liebig University, D-35392 Giessen, Germany

A suitable description of arbitrary shaped and biased nanocontacts is very important for investigating and predicting physical effects of materials on the nanometer scale. In particular, the electronic transport properties under finite bias voltages are of great interest.

To account for systems under finite bias we extended our Korrington-Kohn-Rostoker Green's function method [1] to the Keldysh formalism [2]. The method was developed for different types of geometries, i.e. planar junctions [3] and embedded real-space clusters [4]. Both implementations include a self-consistent treatment of the electronic structure under external bias using the nonequilibrium density.

We present ab initio results of voltage drops, the charge relaxation under finite bias voltage and current-voltage characteristics for different types of geometries.

[1] R. Zeller, P.H. Dederichs, B. Ujfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B 52, 8807 (1995); P. Zahn, I. Mertig, R. Zeller, and P.H. Dederichs, Mat. Res. Soc. Symp. Proc. 475, 525 (1997).

[2] L.V. Keldysh, Sov. Phys. JETP 20 (4), 1018-1026 (1965).

[3] S. Achilles et al., Phys. Rev. B 88 (12), 125411 (2013).

[4] S. Achilles et al., to be published

HL 11.3 Mon 11:15 TRE Ma

**Elasticity changes in molecular junctions under bias: an ab-initio study** — ●CLOTILDE S. CUCINOTTA<sup>1</sup>, MELIN BAI<sup>1,2</sup>, IVAN RUNGGER<sup>1</sup>, SHMIN HOU<sup>2</sup>, and STEFANO SANVITO<sup>1</sup> — <sup>1</sup>School of Physics and CRANN, Trinity College Dublin, College Green, Dublin 2, Ireland — <sup>2</sup>Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China

Non-conservative current induced forces are at the origin of a rich variety of dynamical processes, including vibrations, rotations, phonon energy flow, desorption and reactions. The ability to simulate these phenomena paves the way for crucial advances in interface physics and in molecular electronics. New insights into how the presence of non-conservative forces can affect the vibrational spectrum of prototypic Au-H<sub>2</sub>-Au nano-junctions are obtained by the Non Equilibrium Green Functions approach combined with Density Functional Theory as implemented in the Smeagol code [1]. The modification of the phonon spectrum of the junction in the presence of an external bias is for the first time analysed, in terms of charge redistribution caused by the electron flow, potential drop and differences in an average distance collective variable. Phonon modes changes are related to a change in bias of some of the elastic constants. The importance of electric field vs. current effects is compared. The elasticity changes of the molecular junction with bias are interpreted in terms of the current flowing through the system. [1] <http://www.smeagol.tcd.ie/SmeagolDownloads.htm>.

riety of dynamical processes, including vibrations, rotations, phonon energy flow, desorption and reactions. The ability to simulate these phenomena paves the way for crucial advances in interface physics and in molecular electronics. New insights into how the presence of non-conservative forces can affect the vibrational spectrum of prototypic Au-H<sub>2</sub>-Au nano-junctions are obtained by the Non Equilibrium Green Functions approach combined with Density Functional Theory as implemented in the Smeagol code [1]. The modification of the phonon spectrum of the junction in the presence of an external bias is for the first time analysed, in terms of charge redistribution caused by the electron flow, potential drop and differences in an average distance collective variable. Phonon modes changes are related to a change in bias of some of the elastic constants. The importance of electric field vs. current effects is compared. The elasticity changes of the molecular junction with bias are interpreted in terms of the current flowing through the system. [1] <http://www.smeagol.tcd.ie/SmeagolDownloads.htm>.

HL 11.4 Mon 11:30 TRE Ma

**Carbon nanotubes decorated with magnetic clusters: magnetism, electron transport and gas sensing** — ●ZEILA ZANOLLI<sup>1</sup> and JEAN-CHRISTOPHE CHARLIER<sup>2</sup> — <sup>1</sup>Forschungszentrum Juelich, PGI and IAS, Juelich, Germany — <sup>2</sup>IMCN, Université catholique de Louvain (UCL), Belgium

In this work, first-principles techniques and non-equilibrium Green's function approaches are used to investigate magnetism and spin-polarized quantum transport in carbon nanotubes (CNTs) decorated with transition metal magnetic nanoclusters (NC).

For small cluster sizes (< 1 nm), *ab initio* calculations predict a considerable local magnetic moment that induces spin polarization in the host CNT due to a strong mutual interaction with the magnetic NC. Such a huge local magnetic perturbation can be tailored by molecular adsorption on the metallic NC, thus modifying both the magnetization and the spin-dependent conductance of the hybrid CNT-NC system. The adsorption of benzene on Ni- or Pt-decorated metallic CNTs has been investigated as a test case. The *ab initio* simulations demonstrate that the magnetization change due to the absorption of a single C<sub>6</sub>H<sub>6</sub> molecule should be large enough to be detected experimentally using either magnetic-AFM or SQUID magnetometer. Consequently, the present research suggests a novel approach for single molecule gas detection, based on local magnetic moment measurements in CNT-NC hybrid systems [1].

[1] Z. Zanolli, J.-C. Charlier, ACSnano 6 (2012) 10786-10791.

### 15 min. break

### Topical Talk

HL 11.5 Mon 12:00 TRE Ma

**Insight into Charge Transport in Molecular Junctions from Ab Initio Theories of Level Alignment** — ●JEFFREY B. NEATON — Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, USA — Department of Physics, University of California, Berkeley, Berkeley, CA — Kavli Energy Nanosciences Institute, Berkeley, CA

Recent scanning tunneling microscope-based break-junction experiments of molecular junctions – devices formed by trapping organic molecules between macroscopic metallic electrodes – have reported robust conductance, thermopower, switching behavior, quantum in-

terference effects, spin-filtering phenomena, and even nonlinear effects such as rectification, establishing such junctions as unique and revealing windows into the physics of charge transport at the molecular scale. In this talk, I will summarize a predictive approach to compute and understand the transport properties of molecular junctions with good accuracy. Our approach includes important exchange and correlation effects missing in standard DFT Kohn-Sham junction level alignment, building on self-energy corrections within a GW approximation. Advantages and limitations of our approach will be discussed quantitatively in the context of a direct comparison with recent photoemission and transport measurements. I will also describe applications of this approach to select junctions exhibiting novel trends in conductance, thermopower, and nonlinear IV characteristics, where new physical insight is obtained by relating computed transport phenomena to junction structure and chemistry.

HL 11.6 Mon 12:30 TRE Ma

**Towards First-Principles Modeling of Solvent Effects in Photo-Catalytic Water Splitting** — ●STEFAN RINGE, HARALD OBERHOFER, SEBASTIAN MATERA, and KARSTEN REUTER — Technische Universität München, Germany

In the context of solar energy conversion the search for new materials for photo-catalytic water splitting has received new impetus. While in general powerful, computational screening approaches are struggling with the complexity of the underlying physical processes at the solid-liquid interface. Recent work points in particular at the necessity to include at least an efficient description of solvent screening effects to compute meaningful descriptors even in simple computational hydrogen electrode approaches. To this end, we present an implementation of the modified Poisson-Boltzmann (MPB) implicit solvation model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. Optimally integrating into this code environment, we solve the MPB equation in a novel approach based on an expansion of the electrostatic potential in the localized basis functions of FHI-aims. In contrast to common numerical multi-grid solvers this approach can directly make use of the optimized integration schemes used to reach self-consistency and removes the need for numerical interpolation between different grids. We demonstrate the approach and its efficiency for a range of molecular test systems, and show first results for catalytic water splitting on gold nano-clusters.

HL 11.7 Mon 12:45 TRE Ma

**Towards a combined QM/MM and implicit solvent descrip-**

**tion of photoelectrochemical processes** — ●MARKUS SINSTEIN<sup>1</sup>, DANIEL BERGER<sup>1</sup>, RAN JIA<sup>2</sup>, VOLKER BLUM<sup>3</sup>, HARALD OBERHOFER<sup>1</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Jilin University, P.R. China — <sup>3</sup>Duke University, USA

Photoelectrochemical systems are widely explored to drive energy-relevant redox reactions like water splitting or CO<sub>2</sub> reduction. The detailed analysis of the involved elementary processes via first-principles calculations is challenged by the necessity to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte. Especially for charge (proton and/or electron) transfer steps traditionally employed periodic boundary condition approaches involve charged supercells with difficult to control finite size errors. To this end, we present a solid state QM/MM embedding approach, in which only a finite cluster model of the photocatalyst surface is treated quantum mechanically and the correct Madelung potential of the periodic system is obtained by embedding into a charge field. For the efficient modeling of photoelectrochemical processes we combine this approach with an implicit solvation scheme within the DFT package FHI-aims. Finally, we also show early test results of the combined QM/MM implicit solvent model.

HL 11.8 Mon 13:00 TRE Ma

**Ab-initio Simulation of Molecular Networks on the Surface of Water** — ●RALPH KOITZ, MARCELLA IANNUZZI, ARI P SEITSONEN, and JÜRIG HUTTER — University of Zurich, Zurich, Switzerland

Molecules adsorbed on surfaces play an important role in catalysis, surface science, and nanotechnology. Traditionally, research has focused on various adsorbates atop metals and metal oxides using computational and surface-science techniques. More recently, however, it was demonstrated that ordered monolayer networks can also be formed on the surface of liquid water by using metal ions to bind together multidentate precursor molecules. As these assemblies are difficult to characterize, computational methods can provide valuable insight into their formation and structure.

In this contribution we present large-scale DFT-based molecular dynamics simulations of the formation of a network of *tris*-terpyridine-derived molecules (TTPB) on a water slab. In particular, we focus on the structure of the molecule on the surface, the mechanism of Zn<sup>2+</sup> ion insertion from the solution and the subsequent linking of molecules into aggregates. We employ the metadynamics method to quantify the free energy surface of the involved processes. Our results provide detailed insight into on-surface and subsurface diffusion in this system and chemical reactions of TTPB on the surface of water.