

## HL 47: Frontiers of electronic structure theory: Organics and materials

Time: Wednesday 10:30–13:30

Location: MA 004

**Invited Talk**

HL 47.1 Wed 10:30 MA 004

**Transport and excitations in biased nano-junctions: DFT-based simulations** — ●MADS BRANDBYGE — Dept. of Micro and Nanotechnology, DTU-Nanotech, and Center for Nanostructured Graphene (CNG) Technical University of Denmark, Build. 345 east, 2800 Kongens Lyngby, DENMARK

In nano-junctions the electronic current is forced through a bottleneck down to the single molecular or atomic level. The highly non-equilibrium electronic system in such junctions results in various excitations such as phonons or plasmons. The phonon interaction directly yield signals in the current which can be probed in current-voltage spectroscopy, while the plasmon interaction can result in light emission which seems to be related to the current fluctuations/noise at finite frequency. The low frequency shot noise can provide information about the elastic transport channels and underlying spin-dependent electronic structure of the junctions. We will discuss how theory based on non-equilibrium Greens functions in combination with density functional theory or beyond, can be compared to experimental results, and provide important insights into excitations, the underlying transport channels, and electronic structure of the junctions. The electronic current will not only excite phonons. Energy non-conserving current-induced forces may control the resulting heat flow and heat distribution in the junctions, and in some cases lead to a break-down of the harmonic approximation.

HL 47.2 Wed 11:00 MA 004

**Role of atomic multiplets in intermediate valence  $\text{SmB}_6$  and  $\text{PuB}_6$  systems** — ●ALEXANDER B. SHICK<sup>1</sup>, ALEXANDER I. LICHTENSTEIN<sup>2</sup>, and MIKHAIL I. KATSNELSON<sup>3</sup> — <sup>1</sup>Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic — <sup>2</sup>Institute of Theoretical Physics, University of Hamburg, Hamburg, Germany — <sup>3</sup>Radboud University Nijmegen, The Netherlands

The materials with strong electron correlations are important because of the fundamental properties, and the technological applications. Recently,  $\text{SmB}_6$  (as well as  $\text{PuB}_6$ ) was proposed as 3D topological insulator [1]. The electronic structure calculations are performed combining the LDA with an exact diagonalization of the Anderson impurity model [2] for  $[\text{Sm},\text{Pu}]\text{B}_6$ . For the Sm atom in  $\text{SmB}_6$ , intermediate valence ground state (GS) is found with the  $f$ -shell occupation ( $n_{4f}$ ) = 5.6. The GS is a singlet, and the first excited triplet state  $\sim 3$  meV higher in the energy. The  $f$ -orbital density of states is in agreement with experimental PE spectra.  $\text{SmB}_6$  is a narrow band insulator already in LDA, with the direct band gap of  $\sim 10$  meV. The electron correlations increase the band gap which now becomes indirect. For the Pu atom in  $\text{PuB}_6$ , we also find intermediate valence ( $\langle n_{5f} \rangle = 5.5$ ) singlet GS. The calculations illustrate that many-body effects are relevant to form the indirect band gap, and support the idea of "topological Kondo insulator" in  $\text{SmB}_6$ . [1] M. Dzero *et al.*, Phys. Rev. Lett. **104**, 106408 (2010); [2] A. B. Shick *et al.*, Phys. Rev. B **87**, 020505(R) (2013).

HL 47.3 Wed 11:15 MA 004

**Transition paths and cohesive energies in alpha-sexithiophene polymorphs** — ●BERNHARD KLETT, CATERINA COCCHI, and CLAUDIA DRAXL — Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Like many organic crystals, oligothiophenes display polymorphism. Different molecular orientations and stacking arrangements are known to influence electronic and transport properties. An in-depth theoretical understanding of the energetics in these systems is crucial to control their growth and fully exploit their potential. In fact, their outstanding opto-electronic features make oligothiophenes excellent candidates for a number of technological applications, ranging from thin-film transistors to photovoltaic cells. We investigate alpha-sexithiophene in view of the transition between the high-temperature (HT) and low-temperature (LT) phase. With the full-potential all-electron density-functional theory code exciting [1], we analyse the cohesive properties of the two polymorphs. Our results indicate HT as the most stable phase, in agreement with previous molecular-dynamics simulations [2]. We also explore a transition path between the two polymorphs, suggesting different reaction coordinates. Our findings allow for estimating the energy barrier between the two phases, hence gaining

insight into the microscopic mechanisms ruling polymorphism in organic crystals. [1] A. Gulans, *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014). [2] R. G. Della Valle, *et al.*, J. Phys. Chem. A, **112**, 6715 (2008).

HL 47.4 Wed 11:30 MA 004

**Importance of the reorganization energy barrier in computational design of porphyrin-based solar cells with cobalt-based redox mediators** — ●KRISTIAN BARUËL ØRNSØ, ELVAR ÖRN JÓNSSON, JUAN MARIA GARCIA-LASTRA, KARSTEN WEDEL JACOBSEN, and KRISTIAN SOMMER THYGESEN — Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

The shift from iodide based redox mediators in dye sensitized solar cells towards octahedral cobalt complexes has led to a significant increase in the efficiency. However, due to the nature of this type of complexes the driving force required for the regeneration of the dye is very high and this limits the achievable efficiency. Here we show that the large driving force is a direct consequence of the large reorganization energy of the dye regeneration reaction. The reorganization energies for charge transfer between a simple zinc porphyrin dye and two popular cobalt based redox mediators is calculated using ab-initio molecular dynamics with explicit solvent. These results are then combined with a Marcus based extrapolation scheme to obtain the reorganization energies of more than five thousand porphyrin based dyes. We propose a scheme for scoring the performance of the porphyrin dyes which is able to identify already known high-performance dyes in addition to a number of even better candidates. Our analysis shows that large internal reorganization energy of the Co-based redox mediators is a main bottleneck for achieving higher efficiencies.

HL 47.5 Wed 11:45 MA 004

**Ab initio Simulation of Optical Limiting: The Case of Metal-Free Phthalocyanine** — ●CATERINA COCCHI<sup>1,2</sup>, DEBORAH PREZZI<sup>2</sup>, ALICE RUINI<sup>2,3</sup>, ELISA MOLINARI<sup>2,3</sup>, and CARLO ANDREA ROZZI<sup>2</sup> — <sup>1</sup>Physics Department and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany — <sup>2</sup>Centro S3, CNR Istituto-Nanoscienze, Modena, Italy — <sup>3</sup>Dipartimento di Scienze Fisiche, Informatiche, Matematiche, University of Modena and Reggio Emilia, Italy

Optical limiting (OL) is a nonlinear process that is relevant for an entire class of devices related to the protection of light-sensitive elements, including the human eye, from intense light sources. While extensively studied experimentally, an accurate theoretical investigation of this phenomenon is still missing. In the framework of time-dependent density-functional theory, we present a fully ab initio, non-perturbative description of OL properties of a metal-free phthalocyanine, a prototypical macrocyclic organic compound. By applying a broadband electric field of increasing intensity, we confirm that reverse saturable absorption is the leading mechanism for OL phenomena in this class of systems, and reveal that a number of dipole-forbidden excitations are populated by excited-state absorption at more intense external fields. The excellent agreement with the available experimental data supports our approach as an effective and powerful tool to describe and predict OL [1]. [1] C. Cocchi *et al.*, Phys. Rev. Lett. **112**, 198303 (2014).

HL 47.6 Wed 12:00 MA 004

**High-throughput Screening of Perovskite Oxides and Related Compounds for Light Harvesting Applications** — ●IVANO E. CASTELLI<sup>1</sup>, NICOLA MARZARI<sup>1</sup>, KRISTIAN S. THYGESEN<sup>2</sup>, and KARSTEN W. JACOBSEN<sup>2</sup> — <sup>1</sup>Theory and Simulation of Materials, and EPFL National Center for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, Lausanne, Switzerland — <sup>2</sup>Center for Atomic-scale Materials Design, Technical University of Denmark, Kgs. Lyngby, Denmark

Solar energy harvesting in a photoelectrochemical (PEC) cell, where water is split into hydrogen and oxygen, is an attractive and renewable contribution to our global needs of increasing energy demand and storage. We explore the possibility of identifying novel photocatalysts for PECs with the use of high-throughput quantum mechanical simulations. We devise inexpensive approaches to calculate systematically the structural and electronic properties of 19000 cubic ABX<sub>3</sub> perovskites, obtained by combining 52 possible metals as A- or B-

cations, together with oxygen, nitrogen, sulfur and fluorine as anions. Using the screening criteria of stability and bandgap, 20 promising materials have been identified for visible-light harvesting [1]. The problem of corrosion has been addressed, determining the Pourbaix diagrams of the candidates through a combination of experimental and computational data [2]. We also suggest a handful of lower symmetry layered and rare-earth perovskites for further theoretical and experimental investigation. References: [1] I. E. Castelli et al., *Energy Environ. Sci.* 5, 9034 (2012). [2] I. E. Castelli et al., *Topics in Catalysis* 57, 265 (2014).

HL 47.7 Wed 12:15 MA 004

**Understanding and designing novel materials for energy** — ●SILVANA BOTTI — Friedrich-Schiller-Universität Jena, Germany

I will present an overview of our most recent theoretical/computational developments and some examples of their application to calculate from first-principles the structural and electronic properties of materials for energy production, storage, and saving.

The systems we are interested in are varied, ranging from thin-films absorbers and transparent conductive oxides for solar cells, to thermoelectrics, light-weight materials for constructions, complex hydrides for on-board hydrogen storage.

Nowadays, ab initio approaches based on density functional theory ally accuracy and efficiency, which make them suitable for understanding the physics not only of simple bulk crystals, but also of nanostructures, crystals with defects, doped crystals, interfaces, alloys, etc. As a consequence, ab initio calculations are finally able to analyze the "real" samples measured in experiments, allowing accurate comparisons of both ground-state and excited-state properties.

Moreover, ab initio methods can be used together with structural prediction algorithms and evolutionary algorithms to solve the inverse problem, i.e. find the best material for a specific application, providing a precious guide for experimental search of novel materials.

HL 47.8 Wed 12:30 MA 004

**Accurate density-functional theory calculation of bulk properties of 65 elemental solids** — ●SVEN LUBECK<sup>1</sup>, ANDRIS GULANS<sup>1,2</sup>, and CLAUDIA DRAXL<sup>1</sup> — <sup>1</sup>Humboldt-Universität zu Berlin, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Density-functional theory (DFT) is a common method for calculating various properties of molecules and solids. While a large part of errors in DFT calculations stems from approximations to the exchange-correlation functional, there are additional not well controlled errors introduced by numerical implementation of electronic structure codes. In this work, we present accurate benchmark calculations of equation of state for 65 non-magnetic elemental solids. The data have been obtained using the full-potential augmented-plane-waves (APW) code `exciting` [1]. High accuracy has been achieved by constructing a converged APW+lo basis set, which yields consistent bulk properties of considered solids for a range of augmentation sphere sizes. Using methodology suggested in Ref. [2], we compare our results to those obtained with WIEN2k [2] and find the average and maximum  $\Delta$ -values of 0.3 meV/atom and 2.1 meV/atom, respectively.

[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).

[2] K. Lejaeghere, V. Van Speybroeck, G. Van Oost and S. Cottenier, *Critical Reviews in Solid State and Materials Sciences* 39, 1-24 (2014).

HL 47.9 Wed 12:45 MA 004

**Electronic phase transitions of bismuth under strain from relativistic self-consistent GW calculations** — IRENE AGUILERA, ●CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We present quasiparticle self-consistent GW (QSGW) calculations of

semimetallic bulk Bi. We go beyond the conventional QSGW method by including the spin-orbit coupling throughout the self-consistency cycle. This approach improves the description of the electron and the hole pockets considerably with respect to standard density functional theory (DFT), leading to excellent agreement with experiment. We employ this relativistic QSGW approach to conduct a study of the semimetal-to-semiconductor and the trivial-to-topological transitions that Bi experiences under strain. While DFT predicts that an unphysically large strain is needed for such transitions, we show that the relativistic QSGW description of the electronic structure moves the required strain into a regime that is likely to be realizable in experiment. We acknowledge financial support from the Alexander von Humboldt Foundation and from the Helmholtz Association through the Virtual Institute for Topological Insulators (VITI).

HL 47.10 Wed 13:00 MA 004

**A GW algorithm of reduced complexity for organic crystals** — ●SABER GUEDDIDA<sup>1</sup>, DIETRICH FOERSTER<sup>1</sup>, PETER KOVAL<sup>2</sup>, and DANIEL SANCHEZ-PORTAL<sup>2</sup> — <sup>1</sup>Laboratoire Ondes et Matière d'Aquitaine, University of Bordeaux, France — <sup>2</sup>Donostia International Physics Center, San Sebastian, Spain

Density functional theory (DFT) provides a variational estimate of the electronic structure and geometry of many materials in their ground state. By its construction, DFT is unsuited for a description of the excited states, and particularly so for semi conductors. For these, one resorts to Hedin's GW approximation that gives rather good bands and gaps. A practical limitation of this approach is its computational cost that increases with the fourth power ( $N^{**4}$ ) of the number of atoms  $N$  per unit cell. Starting in 2007 [1], we have developed methods of "reduced complexity" that lower the growth of CPU time in calculations of electronic structure from  $N^{**4}$  to  $N^{**3}$ , both for optical absorption [2] and in the GW approximation for finite systems [3]. Here we report on the extension of our methods to crystals, where we reduce the growth of CPU time again from  $N^{**4}$  to  $N^{**3}$ , with  $N$  now the number of atoms in the unit cell of the crystal. Our work is motivated by organic semiconductors that have too many atoms in their unit cell for  $O(N^{**4})$  algorithms to be practical. Our results should help to improve and optimize organic solar cells. [1] D. Foerster, *J. Chem. Phys.* 128 (34108) 2008. [2] P. Koval, D. Foerster and O. Coulaud, *J. Chem. Theory Comp.* 6 (2654) 2010. [3] D. Foerster, P. Koval, and D. Sánchez-Portal, *J. Chem. Phys.* 135, 74105 (2011).

HL 47.11 Wed 13:15 MA 004

**Modeling anisotropic organic molecules at patterned semiconductor surfaces** — ●NICOLA KLEPPMANN and SABINE H. L. KLAPP — Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Hybrid systems consisting of organic molecules at inorganic semiconductor surfaces are gaining increasing importance as thin film devices for optoelectronics. Their large charge carrier densities and tuneable resonance energies make them ideal candidates for semiconductor devices. However, the efficiency of such devices strongly depends on the self-organized structure formed by the adsorbed molecules, which depends, in turn, on the complex interplay of growth conditions and molecular properties. Recent ab initio calculations and experiments inspire us to examine the growth of sexiphenyl (6P) on ZnO(10-10) as a model system to understand self-organization of highly anisotropic molecules [1]. We develop a coarse-grained interaction hamiltonian of 6P molecules using a Gay-Berne potential and a linear quadrupole interaction term with additional substrate influence. We perform both equilibrium and non-equilibrium (growth) Monte Carlo simulations on a 2D lattice, where the rotational degrees of freedom of the molecules are continuous. We use these simulations to investigate orientational ordering in the condensed state, which is characterized by local descriptors such as order parameters and angular distributions.

[1] N. Kleppmann, and S. H. L. Klapp, submitted to JCP

[2] S. Bommel, N. Kleppmann et al., *Nat Comm* 5, 5388 (2014)