TT 57: Focused Session: Frontiers of Electronic Structure Theory 6 (jointly with HL and O)

Time: Thursday 10:30–13:15   Location: H36

Topical Talk   **TT 57.1   Thu 10:30   H36**
Atomic-scale design of energy materials — •KARSTEN W. JA-COBSEN — CAMD, DTU Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

The design of new materials for more efficient production and use of sustainable and clean energy is of utmost importance for the standard of living all over the World the coming years. In the talk I shall describe some computational efforts to design new materials related to solar energy in particular to the conversion of light into hydrogen fuel through water splitting. We have employed computational screening to search for stable semiconductor materials with an appropriate bandgap, band edge alignment, and with sufficient stability to be relevant for light-induced water splitting. In particular we have focused on materials in the cubic perovskite structure but also more generally materials in the ICSD database. The screening of bandgaps is performed using the so-called GLLB-functional which is shown to give reasonable estimates of light absorption for a number of different systems. The stability of the materials towards dissolution in water is investigated through the construction of Pourbaix diagrams combining DFT calculations and experimental information about solution energies.

The talk will also cover some recent efforts in using machine-learning techniques to develop new electronic density functionals. The functional construction uses Tikhonov regularization to obtain smooth functionals and employs bootstrapping to avoid overfitting. The new functionals are named Bayesian Error Estimation Functionals (BEEF) because they automatically offer error estimation on calculated results.

TT 57.2   Thu 11:00   H36
A new computational screening approach for co-catalysts for water splitting:
Disentangling electron and proton transfer. — •HARALD OBER-HOFER, DANIEL BERGER, RAN JIA, and KARSTEN REUTER — TU München, Germany

Recently, computational screening techniques have made great progress in the identification and classification of promising new materials for (photo-)catalytic water splitting. Yet, contributions of so called co-catalysts—nano-sized particles enhancing the reaction kinetics—have so far not been addressed. In our contribution we present a novel first-principles thermodynamic approach based on earlier work by Nørskov and Rossmeisl [J. Phys. Chem. B **108**, 17886 (2004)] to gauge the efficiency of co-catalyst particles and search for favourable combinations of catalyst surface and co-catalyst particle. Additionally, we study reaction pathways other than the commonly assumed proton-coupled electron transfer. Our results show that these uncoupled paths can lead to new, unexpected behaviour: Catalysts predicted to have a good reactivity considering only coupled mechanisms might actually get stuck in charged intermediates, while others can be much more reactive than anticipated.

TT 57.3   Thu 11:15   H36
An extended Pareto approach to computational materials design — •KURT LEJAEGHERE[1], STEFAAN COTTENIER[1,2], and VERONIQUE VAN SPEYBROECK[2] — [1]Center for Molecular Modeling, Ghent University, Zwijnaarde, Belgium — [2]Department of Materials Science and Engineering, Ghent University, Zwijnaarde, Belgium

Because of competing design criteria, it is often hard to decide on one particular material as the best solution for a given need. A multidimensional optimization strategy can already narrow down the initial large set of candidates to a much smaller number of promising materials, the Pareto-optimal set. Quite often, however, this set contains more materials than can be afforded for further systematic examination. An ordering within this set, highlighting the most promising candidates, would be very useful to expedite the design process. Conventional Pareto approaches cannot offer such a ranking. We present an algorithm to do exactly this.

This procedure is applied to a set of binary tungsten alloys to look for a candidate first-wall material for nuclear fusion purposes. Because of the harsh operating conditions inside (future) fusion reactors, materials selection is a critical aspect there. Tungsten is a promising first-wall material, but several issues, such as room-temperature brittleness, are still to be resolved. Alloying tungsten with other elements is one possible way of overcoming these problems. By combining a

computational screening study (at the DFT-PBE level) with our extended Pareto analysis, a select number of alloys is presented as most promising candidates for further experimental investigation.

TT 57.4   Thu 11:30   H36
Automated system for massive sets of first-principles calculations — •ATSUSHI TOGO and ISAO TANAKA — Department of Materials Science and Engineering, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto, Japan

Large systematic sets of first principles calculations can provide information that cannot be obtained merely by a single calculation. Computation of phonon, cluster expansion, and data mining are typical examples that require massive sets of calculations. If each of single calculation is independent to the others, it is trivial to handle massive calculations consecutively. However it is annoying if a calculation has to wait for the previous calculations to finish. We have been developing an automated system. This system is composed of an automation algorithm and interfaces for a first-principles calculation code (VASP) and a batch-queuing system (grid engine). Small tools are prepared to handle crystal symmetry and dynamical properties. As an application, an algorithm for crystal structure search is implemented. The automation algorithm is as follows. We define 'task'. A task is made of 'task elements', where each task element is designed to be also a task. A task may be composed of a series of task elements. In this case, each task element waits for the previous task element to finish. A task may be composed of task elements that are mutually independent. In this case, all task elements are distributed into computers at the same time. By describing each kind of task in a similar manner, a task is easily built into the other task as a task element.

TT 57.5   Thu 11:45   H36
Bandgap Engineering via Nanoporosity in ZnO — ILKER DEMIROGLU[1], SERGIO TOSONI[1], FRANCESC ILLAS[1], and •STEFAN BROMLEY[1,2] — [1]Departament de Química Física and Institut de Química Teòrica i Computacional, Universitat de Barcelona (IQTCUB), 08028 Barcelona, Spain — [2]Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain

Following previous studies [1-3], we have mined databases of 4-connected nets to generate novel nanoporous ZnO structures. Using density functional theory and GW calculations, we calculate the energetic stability and band gaps of >80 distinct nanoporous ZnO solids. We find that the degree and type of nanoporosity is inextricably linked with band gap magnitude. Increasing the degree of nanoporosity tends reduce energetic stability and increase the band gap. Within this tendency, we also find significant variations in band gap (~0.5 eV) for structures with very similar densities or energetic stabilities but different types of nanoporosity (e.g. pore size). We estimate that altering the degree/type of nanoporosity could allow tailored band gap values up to ~4.2 eV. This proposed nanomorphological approach to band gap engineering potentially opens the door to optoelectronically tunable sensors, solar cells and other unforeseen devices which could take advantage of this versatile combination.

[1] J. Carrasco, F. Illas and S. T. Bromley, PRL 99, 235502 (2007). [2] M. A. Zwijnenburg, F. Illas and S. T. Bromley, PRL 104, 175503 (2010). [3] D. Stradi, F. Illas, S. T. Bromley, PRL 105, 045901 (2010).

TT 57.6   Thu 12:00   H36
Phonon-mediated quantum processes in materials — •EMMANOUIL KIOUPAKIS — University of Michigan, Ann Arbor, MI, USA

Higher-order quantum processes enabled by the coupling of charge carriers to lattice vibrations can play an important role in the operation of modern electronic and optoelectronic devices. First-principles calculations based on density functional theory can provide insight into the fundamental nature of phonon- assisted quantum processes in materials and their impact on device performance. In this talk, I will discuss our recent work on phonon-assisted quantum processes with first-principles techniques. I will show how phonon- assisted Auger recombination gives rise to the observed efficiency loss in nitride light-emitting diodes. Moreover, I will demonstrate that first-principles techniques can accurately reproduce the phonon-assisted optical absorption spectrum of silicon. Last, I will show that phonon-mediated

free-carrier absorption leads to optical loss in transparent conducting oxides and semiconductor lasers. The developed techniques are general and can be applied to study phonon-assisted quantum processes in any material. This work was done in collaboration with C. G. Van de Walle, P. Rinke, K. Delaney, A. Schleife, F. Bechstedt, D. Steiauf, H. Peelaers, J. Noffsinger, S. G. Louie, and M. L. Cohen.

TT 57.7   Thu 12:15   H36

Electron-hole puddles in the absence of charged impurities — •Marco Gibertini[1,2], Andrea Tomadin[2], Francisco Guinea[3], Mikhail I. Katsnelson[4], and Marco Polini[2] — [1]Theory and Simulations of Materials, École Polytechnique Fédérale de Lausanne, Station 12, 1015 Lausanne, Switzerland — [2]NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, I-56126 Pisa, Italy — [3]Instituto de Ciencia de Materiales de Madrid (CSIC), Sor Juana Inés de la Cruz 3, E-28049 Madrid, Spain — [4]Radboud University Nijmegen, Institute for Molecules and Materials, NL-6525 AJ Nijmegen, The Netherlands

It is widely believed that carrier-density inhomogeneities ("electron-hole puddles") in single-layer graphene on a substrate such as quartz are due to charged impurities located close to the graphene sheet. In this talk we demonstrate by using a Kohn-Sham-Dirac density-functional scheme that corrugations in a real sample are sufficient to determine electron-hole puddles on length scales that are larger than the spatial resolution of state-of-the-art scanning tunneling microscopy.

TT 57.8   Thu 12:30   H36

Ab-initio transport calculations of functionalized graphene flakes — •Michael Walz, Alexei Bagrets, and Ferdinand Evers — Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), D-76021 Karlsruhe, Germany

These days, nanoelectronics is focused on molecular systems such as single organic molecules, graphene ribbons, functionalized graphene flakes, carbon nanotubes.

In our project, we calculate the transmission and the local current density in graphene flakes which are functionalized by adsorbed atoms. We are especially interested in current patterns associated with the functionalized carbon atoms and the role of quantum interference effects.

Performing such calculations starting from first principles is challenging because of high computational costs. On this account, we work with the parallelized *ab-initio* framework FHI-aims, on top of which we implement our own transport calculations using non-equilibrium Green's functions (NEGF) techniques with standard functionals [1,2]. Such *ab-initio* transport studies already exist for the field of Molecular Electronics. Our effort presents a first step towards the broader scope of meso-sized molecular materials in general.

[1] V. Blum *et al.*, Comput. Phys. Commun. **180**, 2175 (2009).
[2] A. Arnold *et al.*, J. Chem. Phys. **126**, 174101 (2007).

TT 57.9   Thu 12:45   H36

Thermionic emission from metal surfaces: A first principles study — •Johannes Voss[1], Sharon Chou[1], Aleksandra Vojvodic[1,2], Igor Bargatin[3], Roger Thomas Howe[1], and Frank Abild-Pedersen[2] — [1]Stanford University, USA — [2]SLAC National Accelerator Laboratory, USA — [3]University of Pennsylvania, USA

The ability to lower the temperatures required for sufficient electronic emission from hot cathodes would lead to more efficient thermionic energy converters and electron guns. Thermionic emission of electrons from metal surfaces is governed by the work function and tunneling probabilities. While the former can be extracted easily from ab initio band structure calculations, for the latter, scattering properties of the surface need to be taken into account.

Here, we present density functional theory calculations of thermionic emission currents based on a non-equilibrium Green's function approach. We compare these results to experiments both for clean and coated metal surfaces. Based on an analysis of interactions in the coating layers, we suggest design pathways for new materials with higher emission current densities.

TT 57.10   Thu 13:00   H36

Comparative computational study of Li, Na, and Mg diffusion in bulk Si: influence of cooperative effects, vibrations, and atom-centered bases — •Sergei Manzhos[1], Oleksandr Malyi[1], and Teck L. Tan[2] — [1]Department of Mechanical Engineering, National University of Singapore, Blk EA #07-08, 9 Engineering Drive 1, Singapore 117576 — [2]Institute of High Performance Computing, A*STAR, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632

Si is one of the most efficient anode materials for Li ion batteries. At the same time, for bulk storage and/or high energy density applications, Na and Mg are advantageous due to low cost and abundance of Na and high energy density in the case of Mg. Yet the performance of Si as anode material for Na and Mg batteries is still understudied. We present a comprehensive computational study of diffusion barriers of Li, Na, and Mg in Si including cooperative effects (influence of neighboring metal atoms on the barrier). Interactions between metal atoms in Si cause a significant lowering of the diffusion barrier; this effect is increasing when going from Li to Na to Mg. Zero-point vibrations (ZPE) affect migration barriers strongly and differently for different metals, increasing the barrier for Li diffusion, having little effect on Na, and decreasing the barrier for Mg. Most calculations to date for metal ion diffusion in battery electrodes were done using plane-wave based codes. We present an analysis of the effects due to atomic-centered basis selection. To the best of our knowledge, this is the first study of the effects of ZPE and atomic-centered bases on the computed properties of battery electrodes.