

## O 5: Focused Session: Frontiers of Electronic Structure Theory I (jointly with HL and TT)

Organizers: R. Drautz (Ruhr-Universität Bochum), N. Marzari (EPFL, Lausanne), Matthias Scheffler (FHI, Berlin)

Time: Monday 10:30–13:15

Location: H36

### Topical Talk

O 5.1 Mon 10:30 H36

**Fully ab initio determination of free energies: Basis for high-throughput approaches in materials design** — ●JOERG NEUGEBAUER, FRITZ KORMANN, MARTIN FRIAK, BLAZEJ GRABOWSKI, and TIMANN HICKEL — MPI für Eisenforschung, Düsseldorf, Germany

A key requirement in developing systematic tools to design novel materials on the computer is the availability of accurate computational tools determining energies not only at  $T = 0$  K but also under realistic conditions, i.e., at finite temperature. Combining accurate first principles calculations with mesoscopic/macroscopic thermodynamic and/or kinetic concepts allows now to address this issue and to determine free energies and derived thermodynamic quantities such as heat capacity, thermal expansion coefficients, and elastic constants with an accuracy that often rivals available experimental data.

In the talk we will show how novel sampling strategies in configuration space together with highly converged density-functional theory calculations allow an unbiased and accurate determination of all relevant temperature dependent free energy contributions. The flexibility and the predictive power of these approaches and the impact they can have in developing new strategies in materials design will be discussed for modern high strength steels and light weight metallic alloys.

O 5.2 Mon 11:00 H36

**Fast screening of perovskites' phase stability using AIDA, a materials' informatics platform for materials design and discovery** — ●GIOVANNI PIZZI<sup>1</sup>, ANDREA CEPELLOTTI<sup>1</sup>, BORIS KOZINSKY<sup>2</sup>, MARCO FORNARI<sup>3</sup>, and NICOLA MARZARI<sup>1</sup> — <sup>1</sup>Theory and Simulation of Materials, EPFL (CH) — <sup>2</sup>Robert Bosch LCC Research and Technology Center, Cambridge (USA) — <sup>3</sup>Dept. of Physics, Central Michigan University (USA)

Many perovskite systems display a high-temperature cubic phase with zero net polarization, whose microscopic nature is still debated. We perform a systematic study of this phase for representative  $ABO_3$  perovskites, showing that there is not a unique microscopic model for it. Some systems are consistent with a displacive or an order/disorder model; others can sustain a stable displacement pattern of B-site cations in supercells, preserving zero net polarization. In such high-throughput searches, a key challenge is the need of a "materials' informatics" infrastructure to automatically prepare, execute and monitor workflows of calculations for large classes of materials, and then retrieve, store and analyze the results. To this aim, we are developing an open-source platform for high-throughput (AIDA—"Automated Infrastructure and Database for Ab-initio design"). Using AIDA free-energy workflows, we studied the phase stability of  $BaTiO_3$ , evaluating the critical temperatures between the cubic, tetragonal, orthorhombic, and rhombohedral phases.

O 5.3 Mon 11:15 H36

**Fast ab-initio screening of magnetic properties applied to the design of new hard magnetic materials** — ●NEDKO DREBOV<sup>1</sup>, CHRISTIAN ELSÄSSER<sup>1</sup>, LOTHAR KUNZ<sup>2</sup>, ALBERTO MARTINEZ<sup>2</sup>, TAKASHI SHIGEMATSU<sup>3</sup>, and THOMAS ECKL<sup>2</sup> — <sup>1</sup>Fraunhofer IWM, Freiburg, Germany — <sup>2</sup>Robert Bosch GmbH, Stuttgart, Germany — <sup>3</sup>Bosch Corporation, Tokyo, Japan

We present a fast computational ab-initio screening method which we use for the identification of new permanent magnetic materials based on rare-earth (RE) and transition-metal (TM) elements.

The candidates for new hard magnetic phases with specific structures and compositions are selected from ab-initio screening of their magnetic properties by using the TB-LMTO-ASA method. This procedure considers a large variety of possible combinations of RE and TM elements. At rather low computational costs one can get sufficiently accurate magnetic moments and exchange coupling parameters to be subsequently used in the process of virtual material design.

The results for selected candidate phases are further refined with a more accurate ab-initio method without potential-shape approximation. The Curie temperatures of the phases can be estimated from the calculated magnetic moments and exchange coupling by means of Monte Carlo simulations.

Acknowledgement: This work was supported by the Co-Operative Project 'Suche nach neuen hartmagnetischen Phasen mit hoher Energiedichte (REleaMag)' funded by the BMBF.

O 5.4 Mon 11:30 H36

**Designer Single-Band Hubbard Materials** — ●SINEAD GRIFFIN and NICOLA SPALDIN — ETH Zurich, Switzerland

The low-energy physics of the High-Tc superconducting cuprates is believed to be encompassed in a single-band Hubbard model. Much work focuses on the computational solutions of the Hubbard model with a view to understanding the complex nature of metal-insulator transitions, superconductivity and strong-correlations physics in general.

Here we take the opposite approach of designing a real material which has the Hamiltonian of a 'single-band Hubbard model' material using first-principles electronic structure theory. By combining crystal field splitting with chemistry, we engineer a class of candidate materials with a single d-electron band at the Fermi level. We report the results of ab initio calculations of the electronic and magnetic structure of these new designer materials and discuss the possibilities for experimental synthesis.

O 5.5 Mon 11:45 H36

**The stability of Bi-Sb-Te layered structures: a first-principles study** — ●KIRSTEN GOVAERTS<sup>1</sup>, MARCEL H.F. SLUITER<sup>2</sup>, BART PARTOENS<sup>3</sup>, and DIRK LAMOEN<sup>1</sup> — <sup>1</sup>EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium — <sup>2</sup>Department of Materials Science and Engineering, 3mE, Delft University of Technology, Mekelweg 2, 2628 CD, Delft, The Netherlands — <sup>3</sup>CMT group, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

Using an effective one-dimensional cluster expansion in combination with first-principles electronic structure calculations we have studied the energetics and electronic properties of Bi-Sb-Te layered systems. Our modified, quintuple based cluster expansion explicitly accounts for the Bi and Sb bilayer formation which is due to a Peierls instability. With this new method, groundstates of Bi-Sb-Te can be found without making the dataset of ab initio calculated structures unreasonably large. Groundstates are found within the binary alloys X-Te, with X corresponding to Bi or Sb, for a Te concentration between 0 and 60 at.%. They form an almost continuous series of (meta)stable structures consisting of consecutive X bilayers next to consecutive  $X_2Te_3$  units. Another binary groundstate is the BiSb structure, consisting of alternating Bi and Sb layers, again forming pairs. Groundstates of ternary compounds all consist of consecutive units of  $Bi_2Te_3$ ,  $Sb_2Te_3$  and  $TeSbTeBiTe$ .

O 5.6 Mon 12:00 H36

**RPA Correlation Potential in the Adiabatic Connection Fluctuation-Dissipation formalism** — ●STEFANO DE GIRONCOLI<sup>1</sup>, NICOLA COLONNA<sup>1</sup>, and NGOC LINH NGUYEN<sup>1,2</sup> — <sup>1</sup>Scuola Internazionale Superiore di Studi Avanzati (SISSA), via Bonomea 265, I-34136 Trieste, Italy — <sup>2</sup>Theory and Simulation of Materials, École Polytechnique Fédérale de Lausanne (CH)

Calculations of correlation energies within the formally exact Adiabatic Connection Fluctuation-Dissipation (ACFD) formalism, within the Random Phase Approximation (RPA) for the exchange-correlation kernel, have been recently carried out for a number of isolated and condensed systems. The efficiency of such calculations has been greatly improved by exploiting iterative algorithms to diagonalize RPA dielectric matrices [1]. However for several systems correlation energies may significantly depend about the choice of input single particle wavefunctions [2]. We derive an expression for the RPA self-consistent potential based on Density Functional Perturbation theory and we present self-consistent RPA calculations for weakly bound molecular dimers, including the controversial case of Beryllium dimer. In this case the self-consistent determination of RPA potential is crucial to determine the stability of the system which however results to be unstable toward dissociation in separated fragments.

[1] H.-V. Nguyen and S. de Gironcoli, Phys. Rev. B 79, 205114 (2009);

H. F. Wilson, F. Gygi, and G. Galli, Phys. Rev. B 78, 113303 (2008).

[2] Huy-Viet Nguyen and G. Galli, J. Chem. Phys. 132, 044109 (2010).

O 5.7 Mon 12:15 H36

**The bond-breaking and bond-making puzzle: many-body perturbation versus density-functional theory** — ●F. CARUSO<sup>1</sup>, D. ROHR<sup>2</sup>, M. HELLGREN<sup>3</sup>, X. REN<sup>1</sup>, P. RINKE<sup>1</sup>, A. RUBIO<sup>4,1</sup>, and M. SCHEFFLER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut, Berlin, Germany — <sup>2</sup>Rice University, Houston, USA — <sup>3</sup>SISSA, Trieste, Italy — <sup>4</sup>Universidad del Pais Vasco, Donostia, Spain

Diatomic molecules at dissociation provide a prototypical situation in which the ground-state cannot be described by a single Slater determinant. For the paradigmatic case of H<sub>2</sub>-dissociation we compare state-of-the-art many-body perturbation theory in the GW approximation and density-functional theory (DFT) in the exact-exchange plus random-phase approximation for the correlation energy (RPA). Results from the recently developed renormalized second-order perturbation theory (rPT2) are also reported. For an unbiased comparison and to prevent spurious starting point effects both RPA and GW are iterated to full self-consistency (i.e. sc-RPA and sc-GW). Both include topologically identical diagrams for the exchange and correlation energy but are evaluated with a non-interacting Kohn-Sham and an interacting GW Green function, respectively. This has profound consequences for the kinetic and the correlation energy. GW and rPT2 are both accurate at equilibrium, but fail at dissociation, in contrast to sc-RPA. This failure demonstrates the need of including higher order correlation diagrams in sc-GW. Our results indicate that RPA-based DFT is a strong contender for a universally applicable electronic-structure theory. F. Caruso *et al.* arxiv.org/abs/1210.8300.

O 5.8 Mon 12:30 H36

**Density-Functional Theory Applied to Rare Earth Metals: Approaches Based on the Random-Phase Approximation** — ●MARCO CASADEI<sup>1</sup>, XINGUO REN<sup>1</sup>, PATRICK RINKE<sup>1</sup>, ANGEL RUBIO<sup>1,2</sup>, and MATTHIAS SCHEFFLER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, Germany — <sup>2</sup>University of the Basque Country UPV/EHU, Donostia, Spain

The description of the volume collapse exhibited by some *rare earth* metals poses a great challenge to density-functional theory (DFT) since local/semilocal functionals (LDA/GGA) fail to produce the associated phase transitions. We approach this problem by treating all electrons at the same quantum mechanical level, using both hybrid functionals (e.g. PBE0 and HSE06) and exact-exchange plus correlation in the random-phase approximation (EX+cRPA). We also assess the performance of recently developed beyond RPA schemes (e.g. rPT2 [1]). The calculations are performed for cerium and praseodymium, that display a volume collapse, and neodymium, in which the volume collapse is absent. The isostructural  $\alpha$ - $\gamma$  phase transition in cerium is the most studied. The exact exchange contribution in PBE0 and HSE06

is crucial to produce two distinct solutions that can be associated with the  $\alpha$  and  $\gamma$  phases, but quantitative agreement with the extrapolated phase diagram requires EX+cRPA [2]. [1] Ren *et al.*, J. Mater. Sci. 47, 7447 (2012). [2] M. Casadei *et al.*, Phys. Rev. Lett. 109, 14642 (2012).

O 5.9 Mon 12:45 H36

**Thermodynamics of the  $\alpha \rightleftharpoons \gamma$  transition in cerium from first principles** — ●JORDAN BIEDER and BERNARD AMADON — CEA, DAM, DIF, F-91297 Arpajon, France

The Dynamical Mean Field Theory (DMFT) combined with density functional theory has been successful to describe strongly correlated materials [1]. However, the computation of the ground state properties requires a good accuracy from both the DFT and the DMFT side. We use thus a strong coupling Continuous Time Quantum Monte Carlo (CT-QMC) solver, which is fast and able to reach low temperatures, in combination with a projector augmented wave (PAW) DMFT implementation.

Extensive calculations using this implementation allows us to carefully reassess the ground state properties and thermodynamics of the  $\alpha \rightleftharpoons \gamma$  phase transition in Cerium at low temperatures. In particular, stochastic noise is small enough to avoid any ambiguity on the interpretation of energy versus volume curves. The DMFT picture is put in perspective with recent DFT calculations [2] and recent experimental investigations [3,4].

[1] G. Kotliar *et al.* Rev. Mod. Phys. 78, 865(2006)

[2] M. Casadei *et al.* Phys. Rev. Lett. 109, 146402(2012)

[3] F. Decremps *et al.* Phys. Rev. Lett. 106, 065701(2011)

[4] M. J. Lipp *et al.* Phys. Rev. Lett. 109, 195705 (2012)

O 5.10 Mon 13:00 H36

**Exciton dispersion in wide-gap insulators: there and back again** — ●FRANCESCO SOTTILE<sup>1,2</sup> and MATTEO GATTI<sup>1,2</sup> — <sup>1</sup>LSI, Ecole Polytechnique, Palaiseau, France — <sup>2</sup>European Theoretical Spectroscopy Facility

We present ab initio calculations of exciton dispersion of wide-gap insulators, like LiF and solid Argon. With the help of the Bethe-Salpeter equation (recently extended to describe full coupling finite momentum excitonic effects) we calculate the momentum dispersion of the first low-lying excitons, both visible and dark. Their particular behaviour (the exciton shows up, lower down, shows up again, to finally disappear) is analyzed with respect to: direction of the momentum dispersion, the coupling effect, real space exciton distribution and many-body interference effects. The results [1] are finally compared with recent inelastic X-ray scattering experiments [2,3] for what concerns LiF, while they constitutes a completely ab initio prediction for solid Ar.

[1] The Bethe-Salpeter calculation are carried out with the EXC code (<http://www.bethe-salpeter.org/>) [2] P. Abbamonte *et al.*, PNAS 105, 12159 (2008) [3] C.-C. Lee *et al.* arXiv:1205.4106v1