

O 64: Focussed session: Theory and computation of electronic structure: new frontiers V (jointly with HL, DS)

Time: Thursday 11:15–13:00

Location: TRE Phy

Topical Talk

O 64.1 Thu 11:15 TRE Phy
Electronic excitations in thin-film materials for solar cells: beyond standard density functional theory — ●SILVANA BOTTI — LSI, École Polytechnique, CNRS, CEA-DSM, Palaiseau, France — LPMCEN, Université Claude Bernard Lyon 1, CNRS, Villeurbanne, France — European Theoretical Spectroscopy Facility

Cu(In,Ga)(Se,S)₂ (CIGS) thin-film solar cells have emerged as a technology that can challenge the current hegemony of silicon solar panels. CIGS conserve to a very high degree their electronic properties in a large non-stoichiometric range and are remarkably insensitive to radiation damage or impurities. Kesterites Cu₂ZnSe(S,Se)₄ have very similar electronic properties. Unlike CIGS, they are composed of abundant, non-toxic, less expensive chemical elements.

The origin of the exceptional electronic properties of these complex materials is still not completely understood, despite the large amount of experimental and theoretical work dedicated to that purpose. In particular, standard density functional theory (DFT) yields band structures in quantitative and qualitative disagreement with experiments. This is a serious problem when it comes to designing new materials for more efficient photovoltaic energy conversion.

I will discuss which theoretical approaches beyond standard DFT are reliable at a reasonable computational cost, together with the new physical insight that they allow to obtain.

O 64.2 Thu 11:45 TRE Phy

What is the G^0W^0 band gap of ZnO? — MARTIN STANKOVSKI¹, ●GABRIEL ANTONIUS^{2,1}, DAVID WAROQUIERS¹, ANNA MIGLIO¹, HEMANT DIXIT³, PATRICK RINKE⁴, HONG JIANG⁴, MATTEO GIANTOMASSI¹, XAVIER GONZE¹, MICHEL CÔTÉ², and GIAN-MARCO RIGNANESE¹ — ¹IMCN-NAPS, Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium — ²Département de physique, Université de Montréal, Montréal, Canada — ³CMT-EMAT, Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020, Antwerpen, Belgium — ⁴Fritz-Haber-Institut, Berlin-Dahlem, Germany

Zinc oxide is known to be a challenging system for G^0W^0 calculations. Its theoretical description has been widely discussed recently, and authors do not agree on the value of the band gap one should obtain from the G^0W^0 method. In an attempt to clarify the situation, we study the accuracy and the convergence properties of many schemes or approximations used at each level of the calculation, and show how different procedures may lead to very different conclusions. We first invest the sensitivity of the final band gap on the initial exchange-correlation potential used to generate the Kohn-Sham structure. We then study the behaviour of various plasmon pole models used to reproduce the dynamical properties of the dielectric matrix and discuss their validity for this particular system. Finally, the pseudopotential approach is compared to the PAW formalism, equivalent to an all-electrons calculation.

O 64.3 Thu 12:00 TRE Phy

Global exploration of the energy landscape of solids on the ab initio level — ●KLAUS DOLL^{1,2}, ANIKET KULKARNI¹, DEJAN ZAGORAC¹, J. CHRISTIAN SCHÖN¹, and MARTIN JANSEN¹ — ¹Max Planck Institute for Solid State Research, D-70569 Stuttgart — ²Institut für Math. Phys., TU Braunschweig, D-38106 Braunschweig

In the first step of rational synthesis planning, one needs to identify targets, i.e. (meta)stable crystal structures [1]. Simulated annealing has been shown to be one possibility to explore the respective energy landscape [2]. Our approach consists of a global search for structure candidates based on (up to very recently) empirical potentials, and subsequently a high accuracy local optimization. In order to overcome the limitation of employing potentials, ab initio energies are now used in all the stages [3-7].

After LiF [4] and BN [5], GeF₂ has been studied as an example of a system with stereochemically active lone pairs. Chain-like structures have been found. Further examples include CaC₂ with newly predicted structures at zero pressure as well as at high pressure [6], and PbS [7].

[1] M. Jansen, *Angew. Chem. Int. Ed.* **41**, 3746 (2002); [2] J. C. Schön and M. Jansen, *Angew. Chem. Int. Ed.* **35**, 1286, (1996); [3] J. C. Schön, K. Doll, M. Jansen, *Phys. Status Solidi (b)* **247**, 23 (2010);

[4] K. Doll, J. C. Schön, M. Jansen, *Phys. Chem. Chem. Phys.* **9**, 6128 (2007); [5] K. Doll, J. C. Schön, M. Jansen, *Phys. Rev. B* **78**, 144110 (2008); [6] A. Kulkarni, K. Doll, J. C. Schön, M. Jansen, *J. Phys. Chem. B* **114**, 15573 (2010); [7] D. Zagorac, K. Doll, J. C. Schön, M. Jansen, in preparation

O 64.4 Thu 12:15 TRE Phy

Ab initio calculations of electronic excitations: Collapsing spectral sums — ●ARJAN BERGER^{1,2}, LUCIA REINING^{1,2}, and FRANCESCO SOTILE^{1,2} — ¹Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA-DSM, 91128 Palaiseau, France — ²European Theoretical Spectroscopy Facility (ETSF)

We present a method for the evaluation of electronic excitations of advanced materials by reformulating spectral sum-over-states expressions such that only occupied states appear. All empty states are accounted for by one effective energy. Thus we keep the simplicity and precision of the sum-over-states approach while speeding up calculations by more than an order of magnitude. We demonstrate its power by applying it to the GW method, where a huge summation over empty states appears twice (screening and self-energy). We show the precision bulk silicon and argon. We then use it to determine the band structure and optical spectrum of the technologically important oxide SnO₂. We will also show how our approach can be used to develop exchange-correlation kernels for time-dependent density-functional theory that are both accurate and computationally efficient.

O 64.5 Thu 12:30 TRE Phy

Oxides – a challenge for (theoretical) spectroscopy — ●PATRICK RINKE¹, HONG JIANG¹, MATTHIAS SCHEFFLER¹, ANDREAS GREULING², MICHAEL ROHLFING², ANDERSON JANOTTI³, EM-MANOUIL KIOUPAKIS³, and CHRIS G. VAN DE WALLE³ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Universität Osnabrück, Osnabrück — ³University of California at Santa Barbara, CA

Oxides are of tremendous technological importance, yet challenging materials to characterize. In many cases the agreement between experimental and theoretical spectroscopy observed for other material classes has not been attained. We use rutile TiO₂ as an example to illustrate some of the problems. Many-body perturbation theory in the G_0W_0 approach based on density-functional theory in the local-density approximation gives a fundamental band gap of 3.3 eV in seemingly good agreement with the 3.3 ± 0.5 eV measured in direct and inverse photoemission [1]. However, the lowest exciton computed in Bethe-Salpeter calculations for the optical spectrum is found at an energy of 3.21 eV, while optical experiments only give 3.03 eV [2]. Polaronic effects, i.e. the renormalization of the band edges due to electron-phonon coupling, reduce the band gap, but it remains a challenge to include the ionic contribution to the dielectric function, which can be substantial in oxides, in the G_0W_0 calculations and to incorporate both effects consistently into Bethe-Salpeter calculations. Another aspect to consider is the role of electron correlations. [1] Y. Tezuka *et al.*, *J. Phys. Soc. Jpn.* **63**, 347 (1994). [2] J. Pascual *et al.*, *Phys. Rev. B* **18**, 5606 (1978).

O 64.6 Thu 12:45 TRE Phy

The surprising accuracy of semilocal functionals within density functional theory (DFT): A study of systems involving point defects — ●RAMPI RAMPRASAD¹, PATRICK RINKE², and MATTHIAS SCHEFFLER² — ¹University of Connecticut, Storrs, USA; Fritz-Haber-Institut der MPG, Berlin, Germany — ²Fritz-Haber-Institut der MPG, Berlin, Germany

The use of screened nonlocal exchange functionals within hybrid DFT computations is becoming practical, providing improved electronic structure descriptions [1]. However, the appropriate amount of nonlocal exchange (α) and the extent of screening (ω) to be used are still being explored. Here, we will focus on two properties relevant for systems containing point defects: charge transition levels and defect formation energies. By making the α and ω as variables, it will be shown that semilocal treatments of the exchange interaction for defects in Si and ZrO₂ yield charge transition levels that are quantitatively competitive with more involved nonlocal treatments, extending notions presented recently [2]. This implies that the difference in formation energies

of neutral and charged defects remains a constant, although the formation energy itself may vary with the type of treatment. We have identified correlations between defect formation energies and features of the electronic structure of the defect-free parent material, allowing

for extrapolations of the formation energy to the “correct” values.

[1] A. V. Krukau, et al, J. Chem. Phys. 125, 224106 (2006). [2] H. Komsa, et al, Phys. Rev. B 81, 205118 (2010).