

O 55: Density functional theory and beyond for real materials II

Time: Wednesday 15:00–17:15

Location: H34

O 55.1 Wed 15:00 H34

Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential — ●FABIEN TRAN and PETER BLAHA — Institute of Materials Chemistry, Vienna University of Technology, Vienna, Austria

Recently, Becke and Johnson [1] proposed a semilocal exchange potential which reproduces very well the shape of the exact exchange potential constructed from the optimized effective potential. We showed that this semilocal potential improves (albeit moderately) over the LDA and PBE potentials for the band gap of solids [2]. In order to have further improvement in the results for band gaps, we modified the Becke-Johnson potential (MBJ) [3]. This new potential leads to agreement with experiment which is very good for all types of solids we considered (e.g., wide band gap insulators, sp semiconductors, and strongly correlated 3d transition-metal oxides) and is of the same order as the agreement obtained with the hybrid functionals (e.g., HSE) or the GW methods. This semilocal exchange potential, which recovers the LDA for a constant electron density, mimics very well the behavior of orbital-dependent potentials and leads to calculations which are barely more expensive than LDA calculations. Therefore, it can be applied to very large systems in an efficient way.

[1] A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **124**, 221101 (2006). [2] F. Tran, P. Blaha, and K. Schwarz, *J. Phys.: Condens. Matter* **19**, 196208 (2007). [3] F. Tran and P. Blaha, *Phys. Rev. Lett.* **102**, 226401 (2009).

O 55.2 Wed 15:15 H34

Spectral properties of actinide materials: Charge density self-consistent LDA+Hubbard I method in FP-LAPW basis — ●JINDRICH KOLORENC^{1,2}, ALEXANDER B. SHICK¹, LADISLAV HAVELA³, and ALEXANDER I. LICHTENSTEIN² — ¹Institute of Physics ASCR, Prague, Czech Republic — ²University of Hamburg, Hamburg, Germany — ³Charles University, Prague, Czech Republic

We provide a numerically efficient procedure to perform LDA + Hubbard I calculations including self-consistency over the charge density in the FP-LAPW basis [1]. The method is applied to Pu, Am, and PuAm and PuCe alloys. Our results for valence photoemission spectra (PES) agree with experimental data and with previous LDA+DMFT calculations [2]. Analysis of the $J=5/2$ and $J=7/2$ contributions to the f -occupation supports the intermediate-coupling picture of f -states in heavy actinides. The electronic specific heat coefficient is calculated for PuAm and PuCe alloys in reasonable agreement with recent experiments. We show that Pu atoms keep their mixed-valence character in these alloys. Next, we study electronic and spectral properties of Pu-based superconductor PuCoGa₅ and obtain good agreement with experimental PES [3]. Finally, we analyze surface effects. In Pu monolayer, we find substantial modification of PES due to $5f$ -electron localization consistent with experimental observations [4].

- [1] A. B. Shick et al., *Phys. Rev. B* **80**, 085106 (2009).
 [2] J. H. Shim et al., *Phys. Rev. Lett.* **101**, 126403 (2008).
 [3] J. L. Sarrao et al., *Nature (London)* **420**, 297 (2002).
 [4] L. Havela et al., *Phys. Rev. B* **65**, 235118 (2002).

O 55.3 Wed 15:30 H34

Self-doping Effects at a 45° Grain Boundary in YBa₂Cu₃O₇ — ●U. SCHWINGENSCHLÖGL¹ and C. SCHUSTER² — ¹KAUST, PCSE Division, P.O. Box 55455, Jeddah 21534, Saudi Arabia — ²Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany

The charge redistribution at grain boundaries determines the applicability of high- T_c superconductors in electronic devices because the transport across the grains can be hindered considerably. We investigate the local charge transfer and the modification of the electronic states in the vicinity of the grain-grain interface by ab-initio calculations for a normal-state 45° [001] grain boundary in YBa₂Cu₃O₇. Our results explain the suppressed interface transport and the influence of grain boundary doping in a quantitative manner, in accordance with the experimental situation. The charge redistribution is found to be strongly inhomogeneous, which has a substantial effect on transport properties since it gives rise to a self-doping of 0.10 ± 0.02 holes per Cu atom. Reference: *Phys. Rev. Lett.* **102**, 227002 (2009).

O 55.4 Wed 15:45 H34

All-electron GW calculations for perovskite 3d transition-metal oxides LaTMO₃ — ●ANDREAS GIERLICH, CHRISTOPH FRIEDRICH, and STEFAN BLÜGEL — Institut für Festkörperforschung and Institute for Advanced Simulation, Forschungszentrum Jülich, 52425 Jülich, Germany

The LaTMO₃ family of compounds, where TM is a 3d transition metal, shows a large variety of electronic and magnetic properties. It comprises Mott and band insulators, antiferromagnets, and metals. The rich diversity of properties originates from the interplay between the localization of the 3d electrons and their hybridization with O 2p states in the presence of crystal fields and Hund's rule physics. Standard density-functional calculations within the local-spin-density approximation often fail even qualitatively in describing the electronic structure of these correlated materials. To treat the band structure and electronic correlation on the same footing from first principles we employ the GW approximation for the electronic self-energy. We use our recently developed implementation (<http://www.flapw.de/spex>) in the all-electron full-potential linearized-augmented-plane-wave (FLAPW) method. Within this method a large variety of materials can be treated, including d - and f -electron systems, oxides and magnetic systems, and thus it is particularly suited for the LaTMO₃ family. We present and discuss first results.

O 55.5 Wed 16:00 H34

Bridging rare-earth physics and chemistry: a hybrid functional study for Ce — ●MARCO CASADEI¹, XINGUO REN¹, ANGEL RUBIO^{1,2}, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der MPG, 14195 Berlin, Germany — ²Dpt. Fisica Materiales, UPV/EHU, San Sebastian Spain

The presence of localized, partially occupied f electronic states is responsible for many peculiar physical properties of rare-earth materials. Of particular interest is the α - γ phase transition in Ce metal, which poses a big challenge to first principles approaches based on local/semilocal (LDA/GGA) approximations to density functional theory (DFT). Within LDA and GGA, the f electrons tend to be more delocalized than they should, and thus the γ phase with localized f electrons can not be described.

Hybrid functionals provide a way of improving the exchange-correlation functionals climbing the so-called Jacob's ladder in Perdew's sense to the fourth rung. By incorporating a fraction of exact exchange, hybrid functionals reduce the self-interaction error considerably which is the main reason for the failure of LDA/GGA in this case. It is highly interesting to see how quantitatively hybrid functionals work for this renowned problem. To this end we calculated the cohesive energies of the Ce clusters of increased size, cut from Ce bulk, as a function of the lattice constant. For these clusters, we establish that there exists multi-solution behavior at the hybrid functional (here PBE0) level, which is absent for LDA/GGA. We analyze the implication of this behavior to the α - γ phase in Ce bulk.

O 55.6 Wed 16:15 H34

Nonadiabatic electron dynamics in time-dependent reduced-density-matrix functional theory — ●RYAN REQUIST and OLEG PANKRATOV — University of Erlangen-Nuremberg, Erlangen, Germany

Numerical simulation of real-time electron dynamics in strongly-driven molecules and confined environments remains a challenging problem for *ab initio* electronic structure methods. One of the most widely used methods is the adiabatic extension of the local density approximation (ALDA) in TD DFT. Although it often works well in linear response calculations, it performs poorly for charge transfer excitations and is unable to account for excitations of doubly-excited character. Progress toward describing these excitations has been made in time-dependent reduced-density-matrix functional theory, which uses the one-body reduced density matrix as the basic variable. This theory might have advantages for real-time dynamics as well. However, a nontrivial obstacle to applying the adiabatic extension approximation has been identified. Namely, the adiabatic extension of the available ground-state functionals leads incorrectly to time-independent occupation numbers (the eigenvalues of the one-body reduced density matrix). In this talk, we describe an adiabatic approximation [arXiv:0911.0945]

that generates time-dependent occupation numbers. Tests for a model system demonstrate that it captures quite well Landau-Zener transitions and Stueckelberg oscillations, which are canonical nonadiabatic effects in real-time dynamics. Electron correlation is found to play a crucial role.

O 55.7 Wed 16:30 H34

Is there a physical meaning of the natural orbitals? Analysis of exactly solvable models — ●NICOLE HELBIG¹, ILYA V. TOKATLY^{1,2}, JOHANNA I. FUKS¹, and ANGEL RUBIO^{1,3} — ¹Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, San Sebastián, Spain — ²IKERBASQUE, Basque Foundation for Science, Bilbao, Spain — ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Reduced density matrix functional theory provides a set of orbitals, namely the natural orbitals, which are originally defined mathematically as the eigenfunctions of the one-body density matrix. We investigate the suitability of these orbitals as a basis for describing many-body excitations. We analyze to which extent the natural orbitals describe both bound as well as ionized excited states and show that depending on the specifics of the excited state the ground-state natural orbitals yield a good approximation or not.

O 55.8 Wed 16:45 H34

On the way to exact-exchange quality from a semi-local functional — ●ANDREAS KAROLEWSKI and STEPHAN KÜMMEL — Theoretische Physik, Universität Bayreuth, 95440 Bayreuth, Germany

In this talk we discuss an approach for constructing a semi-local “ab initio” exchange functional that promises to incorporate many of the attractive features of exact exchange at low computational cost. A particularly relevant example is predicting the polarizabilities of extended systems. This has been a long-standing problem in density functional

theory. We show that the new approach predicts the polarizabilities of extended conjugated molecules with much better accuracy than typical semi-local functionals.

The common approach of functional development is starting with an expression for the exchange correlation energy and calculating the exchange correlation potential via the functional derivative. In contrast, we start with an effective approximation for the exchange potential and show that it predicts the polarizabilities with much better accuracy than typical semi-local functionals. Furthermore we discuss a way of finding a corresponding energy functional.

O 55.9 Wed 17:00 H34

Exchange and Correlation effects in the electronic properties of transition metal oxides: the example of NiO — ●MATTEO GUZZO^{1,3}, MATTEO GATTI^{2,3}, and LUCIA REINING^{1,3} — ¹LSI - ETSF, Ecole Polytechnique, Palaiseau CEDEX 91128, France — ²Nano-bio group - ETSF, Universidad del País Vasco, San Sebastian, Spain — ³European Theoretical Spectroscopy Facility (ETSF)

The original contributions O 55.9 “Insights in the T-matrix formalism” by Pina Romaniello and O 55.10 “GW without empty states” by Arjan Berger have been withdrawn. Instead, this talk by Matteo Guzzo has been rescheduled from O 10.7 to this slot.

NiO, as a prototype for strongly-correlated materials, has been extensively studied experimentally and theoretically. Its Antiferromagnetic phase is reasonably well described in GW (a many-body approximated approach), but self-consistency is needed to obtain proper wavefunctions for the system. Still, agreement with experiment is not perfect. In particular, the unoccupied d-states result too high in energy by about 1 eV. In the present work we investigate the effects of vertex corrections derived from time-dependent density-functional theory on this result, starting from a simple LDA correction and going to more complex vertices including non-locality.