O 63: Focussed session: Frontiers of electronic structure theory: Strong correlations from first principles IV (jointly with TT)

Time: Thursday 10:30–13:15   Location: HE 101

Topical Talk   O 63.1   Thu 10:30   HE 101
Random phase approximation and GW for correlated systems — •Patrick Rinke — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

In the quest for finding an "optimal" first principles electronic structure method, that combines accuracy and tractability with transferability across different chemical environments and dimensionalities (e.g. molecules, wires/tubes, surfaces, solids), the treatment of exchange and correlation in terms of "exact-exchange plus correlation in the random-phase approximation (EX+cRPA)" offers a promising avenue. Likewise one can express the same level of theory in the Green's function context through the GW approximation, which has the additional advantage that quasiparticle spectra as measured by direct and inverse photoemission become accessible. For lanthanide and actinide oxides as prototypical f-electron solids, I will demonstrate that GW calculations yield spectral properties in good agreement with experiment, provided a suitable starting point like density-functional theory in the local-density approximation augmented by Hubbard U corrections (LDA+U) is used [1]. For the f-electron metal Cerium, for which (semi)local DFT functionals fail to reproduce the isostructural α-γ phase transition, EX+cRPA calculations based on hybrid functionals yield a double minimum in the total energy versus volume curve, indicative of the phase transition. For correlations in molecular systems, I will contrast EX+cRPA with GW and discuss recent schemes that go beyond cRPA [2]. [1] H. Jiang, *et al.*, Phys. Rev. Lett. **102**, 126403 (2009), [2] J. Paier *et al.*, arXiv:cond-mat/1111.0173

O 63.2   Thu 11:00   HE 101
Renormalized second-oder perturbation theory for the electron correlation energy: concepts and benchmarks — •Xinguo Ren[1], Patrick Rinke[1], Gustavo E. Scuseria[2] und Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Rice University, Houston, USA

We present a renormalized second-oder perturbation theory (R2PT) for the electron correlation energy that combines the random-phase approximation (RPA), second-order screened exchange (SOSEX) [1], and renormalized single excitations (rSE) [2]. These three terms all involve a summation of certain types of diagrams to infinite order, and can be viewed as a "renormalizationöf the direct, the exchange and the single excitation (SE) term of 2nd-order Rayleigh-Schrördinger perturbation theory based on an (approximate) Kohn-Sham reference state. A preliminary version of R2PT has been benchmarked for covalently-bonded molecular systems and chemical reaction barrier heights [3] and shows an overall well balanced performance. We have extended this, by including "off-diagonal" diagrams into the rSE term and expect this refined version of R2PT to be more generally applicable to electronic systems of different bonding characteristics. Extended benchmarks of van-der-Waals-bonded molecules and crystalline solids will be presented. [1] A. Grüneis *et al.*, J. Chem. Phys. **131**, 154115 (2009). [2] X. Ren *et al.*, Phys. Rev. Lett. **106**, 153003 (2011). [3] J. Paier *et al.*, arXiv:cond-mat/1111.0173.

O 63.3   Thu 11:15   HE 101
Energetics of LDA+DMFT(CTQMC) in a fully charge self-consistent pseudopotential formulation — •Daniel Grieger, Christoph Piefke, Oleg E. Peil, and Frank Lechermann — 1. Institut für Theoretische Physik, Universität Hamburg, Germany

In recent years, the combination of the local-density approximation (LDA) to density functional theory with the dynamical mean-field theory (DMFT) has proven to be a powerful and reliable tool to describe explicit strong electronic correlations in realistic materials. In order to obtain information about observables like equilibrium lattice constants, bulk moduli, phase stability and many more, it is essential to calculate total energies in this formalism in a consistent and physically sound way. A key step is to converge the correlated charge density within a comprehensive LDA+DMFT interface (charge self-consistency). We use a mixed-basis pseudopotential implementation of DFT and a numerically exact hybridisation-expansion continuous-time QMC solver for DMFT, so that we can combine the highest possible accuracy with a minimum of further approximations. Besides illuminating the crucial parts of the theoretical total-energy formalism, we will present the

application of the method to calculate details of the phase diagram of several realistic materials in the realm of intermediate to strong electronic correlations.

O 63.4   Thu 11:30   HE 101
Unraveling the α-γ phase transition in Ce from first principles — •Marco Casadei[1], Xinguo Ren[1], Patrick Rinke[1], Angel Rubio[1,2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG (TH), Berlin, Germany — [2]UPV/EHV, San Sebastian (Fisica Materiales), Spain

The presence of localized, partially occupied f-electron states dictates many of the peculiar physical properties of rare-earth materials. In particular, the description of the isostructural α-γ phase transition in Cerium poses a great challenge to density-functional theory (DFT) based approaches since local/semilocal functionals (LDA/GGA) fail to produce the phase transition. We approach this problem by treating all electrons (including the f-electrons) at the same quantum mechanical level. The calculations are performed using both hybrid functionals (e.g. PBE0), that incorporate a portion of exact-exchange, and full exact-exchange plus correlation at the level of the random phase approximation (EX+cRPA). The PBE0 hybrid functional predicts the correct magnetic properties of both phases and yields a double minimum in the total energy versus volume curve, indicative of the phase transition, although with the wrong energetic order. EX+cRPA is then essential to capture the right energetic ordering of the minima. Our results suggest a hypothetical persistence of the phase transition to zero temperature, the driving mechanism being the change of the hopping amplitude between f-type orbitals.

O 63.5   Thu 11:45   HE 101
Electron correlation effects in americium metal under pressure — •Alexander Shick[1,2], Jindrich Kolorenc[2], and Roberto Caciuffo[1] — [1]European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe — [2]Institute of Physics ASCR, Prague

Evolution of the electronic structure of elemental americium due to the lattice compression is investigated. We make use of a version of the LDA+DMFT method based on the "exact diagonalization" of the multi-orbital Anderson impurity Hamiltonian with the full Coulomb interaction matrix and the spin-orbit coupling [1]. Also, we include the charge density self-consistency [2]. We observe only a relatively minor modifications of the electronic structure with compression, which appears to be in accord with the RXES and XANES spectra at the L_3 edge that were recently determined experimentally [3]. Neither these experiments nor our calculations support the earlier theoretical proposal that the f-electron occupation should increase with compression, leading eventually to a mixed-valence ($5f^6 + 5f^7$) behavior [4].
[1] A. B. Shick, J. Kolorenc, V. Janis, A. I. Lichtenstein, Phys. Rev. **B 84**, 113112 (2011). [2] A. B. Shick, J. Kolorenc, L. Havela, A. I. Lichtenstein, Phys. Rev. **B 80**, 085106 (2009). [3] S. Heathman, J.-P. Rueff, L. Simonelli, M. A. Denecke, J.-C. Griveau, R. Caciuffo, G. H. Lander, Phys. Rev. **B 82**, 201103 (2010). [4] S. Y. Savrasov, K. Haule, G. Kotliar, Phys. Rev. Lett. **96**, 036404 (2006).

O 63.6   Thu 12:00   HE 101
DFT and beyond-DFT derived tight-binding parameters for RMnO$_3$ using the VASP2WANNIER90 interface — •Sowmya Sathyanarayana Murthy[1], Roman Kovacik[2], Martijn Marsman[1], Cesare Ederer[2], Georg Kresse[1], and Cesare Franchini[1] — [1]Faculty of Physics, University of Vienna and Center for Computational Materials Science, A-1090 Wien, Austria — [2]School of Physics, Trinity College Dublin, Dublin 2, Ireland

By combining the Vienna ab initio simulation package with the wannier90 code we have constructed maximally localized Wannier functions (MLWFs) for the Jahn-Teller/GdFeO$_3$ distorted insulating perovskites RMnO$_3$ (R=La, Pr, Nd, Sm and Eu) at different levels of approximation for the exchange-correlation kernel (PBE, HSE and GW)[1]. By suitably mapping the MLWFs onto an effective e_g tight-binding (TB) Hamiltonian[1,2] we have computed a complete set of TB parameters using two alternative model parameterizations, with and without an explicit treatment of the electron-electron interaction. The

so obtained set of tabulated TB parameters provide band dispersion in excellent agreement with the underlying *ab initio* and MLWF bands. The evolution of the structural and electronic properties of RMnO$_3$ as a function of the atomic radius of R[3] is discussed in terms of the corresponding changes in the TB parameters and MLWFs properties.

References:
[1] C. Franchini *at. al* arXiv:1111.1528 (2011).
[2] R. Kovacik & C. Ederer Phys. Rev. B **81** 245108 (2010).
[3] T.Kimura *et al.* Phys. Rev. B **68** 060403(R) (2003).

O 63.7   Thu 12:15   HE 101

A periodic implementation of hybrid functionals for numeric atom-centered orbitals — Sergey Levchenko, Rainer Johanni, Xinguo Ren, Jürgen Wieferink, Patrick Rinke, ●Volker Blum und Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin

Traditional density functional theory based on the electron density and its gradients has a successful track record in condensed matter theory, but is also subject to some well known limitations: For instance, the residual self-interaction of the electrons; or, failure to cover the fundamental band gap of solids. Hybrid density functionals that add some non-local exchange are becoming a *de facto* strategy to remedy such issues; however, evaluating the non-local exchange operator in periodic systems efficiently can be nontrivial. We here describe an implementation of periodic non-local exchange using numeric atom-centered basis functions within the FHI-aims [1] all-electron code. The implementation is based on a localized "resolution of identity" strategy for the Coulomb operator, coupled with efficient integral and density matrix screening operations (in real space) that allow to cover periodic systems up to (currently) $O(100)$ atoms at essentially converged basis set accuracy, and seamlessly in parallel (memory and CPU time, tested up to hundreds of CPUs). We prove the accuracy of our approach for bulk semiconductors and their surfaces, using the PBE0 and HSE density functionals. [1] V. Blum *et al.*, Comp. Phys. Comm. **180**, 2175 (2009).

O 63.8   Thu 12:30   HE 101

Precise all-electron response functions from a combined spectral sum and Sternheimer approach: application to EXX-OEP — ●Markus Betzinger, Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The optimized-effective-potential (OEP) method is used to construct local potentials from non-local, orbital-dependent exchange-correlation functionals, e.g., exact exchange (EXX). The method involves two response functions, which have to be converged to very high precision to obtain smooth and stable local potentials. Usually, this requires an exceptionally large orbital basis, leading to very costly calculations, especially for all-electron methods such as FLAPW [1,2]. In this work, we propose a scheme that combines the usual spectral sum from standard perturbation theory with a radial Sternheimer approach. It also comprises a, albeit small, Pulay-type correction, which refines the results especially for small basis sets. We demonstrate that with this new approach already the conventional minimal LAPW basis set is sufficient to yield precise response functions. Furthermore, very few unoccupied states are required, which reduces the computational cost considerably. The numerically important Sternheimer contribution arises from the potential dependence of the LAPW basis functions and is constructed by solving inexpensive radial differential equations. We show results for complex transition-metal oxides.
[1] M. Betzinger *et al.*, Phys. Rev. B **83**, 045105 (2011)
[2] Fleur code: http://www.flapw.de

O 63.9   Thu 12:45   HE 101

Accurate electronic structure calculation on transition metal defects in SiC by HSE06+U functional — ●Viktor Ivády[1] and Ádám Gali[1,2] — [1]Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, PO Box 49, H-1525 Budapest, Hungary — [2]Department of Atomic Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1111 Budapest, Hungary

Relatively little is known about transition metal impurities in semiconductors. The accurate treatment of these systems require the exact description of strongly correlated partially occupied d and f shells of the impurities in host materials of sp^3 bonds. In our study we investigate the electronic structure of transitional metals (Ti, V and Cr) in 4H-SiC by means of PBE (semi)local functional and HSE06 range separated hybrid functional calculations in 576-atom supercell where experimental data are available for these impurities. While HSE06 functional yielded superior results over (semi)local functionals regarding the Mott-insulators with correlated states our results show that HSE06 are not sufficiently accurate for the chosen isolated transition metal defects. The application of HSE06+U functional allow us to apply orbital dependent corrections on the correlated orbitals in the experimental band gap of SiC. We chose the U to fulfill the generalized Koopmann's and Janak's theorems that is presumably an "exact" functional of the system. Our investigations show that U should be energy dependent and its acutal value depends also on the given defect configuration even for the same type of the impurity. We compare the experimental and calculated transition levels obtained by the "exact" functional.

O 63.10   Thu 13:00   HE 101

Origin of magnetism and qausiparticle properties of Cr-doped rutile and anatase TiO2 — ●Fabiana Da Pieve[1,2,3], Sergio Di Matteo[4], Tonatiuh Rangel[2,3], Matteo Giantomassi[2,3], Gian-Marco Rignanese[2,3], and Xavier Gonze[2,3] — [1]EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium — [2]Unité NAPS, Université Catholique de Louvain,Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium — [3]ETSF, European Theoretical Spectroscopy Facility — [4]Groupe theorique Departement Materiaux et Nanoscience Institut de Physique de Rennes,UMR UR1-CNRS 6251, Université de Rennes 1, F-35042 Rennes Cedex, France

We studied magnetic ground-state properties, band gaps and quasiparticle excitations in the rutile and anatase phases of Cr-doped TiO2, by combining LSDA+U ab-initio calculations and many-body GW perturbative corrections to LSDA+U results. The position of Cr-impurity states and band gaps found by GW on top of LSDA+U is in good agreement with available experimental data. The magnetic ground-state is characterized by a different geometrical coordination of Cr-ions in rutile and in anatase: interestingly, these constraints, due to correlated hopping (superexchange, direct exchange or F-center exchange) lead to ferromagnetic or antiferromagnetic couplings of Cr-ions depending on the number of O vacancies. We suggest two key experiments that could confirm our calculations by measuring directly Cr-t2g states, which play a central role in our model and in optical properties.