SYEC 4: Exact-exchange and hybrid functionals meet quasiparticle energy calculations IV

Time: Friday 10:15–12:30   Location: A 151

SYEC 4.1   Fri 10:15   A 151

GW Method for f-electron Systems: Applications to CeO_2 and ThO_2 — •Hong Jiang[1], Ricardo I. Gomez-Abal[1], Xinzheng Li[1], Patrick Rinke[1,2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]University of California at Sant Barbara, CA 93106

Understanding the physics of f-electron systems is regarded as a great challenge in condensed-matter physics today. In many of these materials the strong localization of the f-electrons gives rise to large many-body exchange and correlation effects and in addition leads to severe self-interaction errors in the local-density approximation (LDA). Many-body perturbation theory in the GW approximation offers both a quasiparticle perspective and an exact treatment of exchange. It is therefore a promising approach for investigating these systems. In this work we apply the G_0W_0 method to CeO_2 and ThO_2, the "simplest" f-electron systems for which the LDA provides a qualitatively correct description, but underestimates band gaps significantly. For both materials, G_0W_0 based on LDA provides an accurate description for the fundamental $(p\text{-}d)$ band gap. In CeO_2, the highly localized f-states fall within the p-d gap; the G_0W_0 correction increases the p-f gap and reduces the f-band width considerably. The resultant density of states is in good agreement with experiments. In ThO_2, the $5f$-states are more delocalized and overlap with the Th-$6d$ bands; the G_0W_0 correction shifts the $5f$-bands more than $6d$-bands, changing the density of unoccupied states considerably. Implications for general f-electron systems with partially filled f-shell are discussed.

SYEC 4.2   Fri 10:30   A 151

All-electron G_0W_0 study of IIb-VI semiconductors and group III nitrides — •Xinzheng Li[1], Hong Jiang[1], Ricardo I. Gomez-Abal[1], Claudia Ambrosch-Draxl[2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195, Berlin — [2]Materials Physics Department, University of Leoben, A-8700, Leoben, Austria

IIb-VI semiconductors and group III nitrides are technologically important materials in optical applications due to their wide band gaps. From the theoretical point of view, the presence of the semicore d states from the cation makes them an interesting subject of study. Using our newly developed all-electron G_0W_0 code based on the FP-(L)APW+lo method, we have studied their electronic structure. Particular emphasis is put on: 1) the interaction between electrons in the semicore shell of the cation, and 2) the influence of deep core states on the G_0W_0 results. Our results show that the exchange interaction between electrons within the semicore shell is of crucial importance for a good description of the d-states in these systems. The influence of deep core states on the d-band positions is significant, which emphasizes the importance of the all-electron treatment. Although G_0W_0 results clearly improve over the LDA values, comparison with experiments shows that discrepancies of up to 3 eV in the d-band positions and 0.7 eV in the fundamental band gaps still remain, a clear indication that efforts beyond LDA based G_0W_0 are required.

SYEC 4.3   Fri 10:45   A 151

Total and self-energies beyond LDA and GGA: exact-exchange, GW and MP2 united by numeric atom-centered orbitals — •Andrea Sanfilippo[1], Xinguo Ren[1], Alexandre Tkatchenko[1], Patrick Rinke[1,2], Volker Blum[1], Karsten Reuter[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut, Faradayweg 4-6, D-14195, Berlin (Germany) — [2]University of California at Santa Barbara, CA 93106 (USA)

Well known deficiencies of present-day exchange-correlation functionals in density-functional theory (DFT) comprise the spurious self-interaction, the absence of non-local correlation (van der Waals, image interactions), and the absence of the derivative discontinuity with respect to changes in the electron number. We present a unified framework to overcome these deficiencies by many-body perturbation theory in the bare (Hartree-Fock, MP2) and the screened Coulomb interaction (Hedin's GW approximation). Using numeric atomic-centered orbitals as basis sets, the efficiency of our formulation relies on the representation of intermediate quantities like the polarizability, and bare and screened Coulomb potentials by a second, auxiliary set of

atom-centered basis functions. For an extended set of finite systems spanning individual atoms, small molecules (water dimer, methane, silane, benzene), metal clusters (Na_n), and biomolecules (alanine) we demonstrate that our implementation in the new DFT code FHI-aims [1] is significantly more efficient than existing formulations based on traditional plane wave or Gaussian basis sets.

[1] V. Blum *et al.*, The FHI-aims project, www.fhi-berlin.mpg.de/aims/

SYEC 4.4   Fri 11:00   A 151

Accurate description of the bonding of C_6H_6 at noble metal surfaces, using a local exchange-correlation correction scheme — •Erik McNellis, Karsten Reuter, and Matthias Scheffler — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin (Germany)

The adsorption of benzene (C_6H_6) at the close-packed Cu(111) surface is a much studied model system for the interaction of larger π-conjugated molecules with solid surfaces. At first glance a rather simple system, the suspected predominantly van der Waals type bonding at the extended metal surface poses a severe challenge for accurate first-principles calculations. Density-Functional Theory (DFT) with local and semi-local exchange-correlation (xc) functionals is uncertain to properly account for this type of bonding, while the system sizes required to correctly grasp the metallic band structure quickly become computationally untractable with correlated wave function techniques. We overcome these limitations with a recently introduced "local xc correction" scheme [1], correcting the deficiencies in the adsorption energetics from present-day DFT xc functionals with hybrid functional and Møller-Plesset perturbation theory calculations for small clusters. From the obtained convergence of the xc correction with cluster size we can disentangle the short-range and dispersion type contributions to the bonding of the molecule at different heights above the surface. This enables us to qualify the role played by the two contributions in determining the binding energetics and geometry. [1] Q.-M. Hu, K. Reuter, and M. Scheffler, PRL **98**, 176103 (2007) and **99**, 169903 (2007); C. Tuma and J. Sauer, CPL **387**, 388 (2004).

SYEC 4.5   Fri 11:15   A 151

Large scale GW calculations of Na cluster on the Cu(001) surface — •Yaroslav Pavlyukh and Jamal Berakdar — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Heinrich-Damerow-Str. 4, 06120 Halle

Application of the many-body perturbation theory to realistic systems relies on the knowledge of single- and two-particle correlation functions. The Configuration Interaction (CI) approach widely adopted in quantum chemistry provides information on the excited states of the system and, thus, allows to compute the screened Coulomb interaction (a 2-particle quantity) from first principles. In this way one can systematically go beyond the random phase approximation (RPA). This is beneficial for finite systems such as molecules or clusters where the screening is more complex than in bulk systems. We developed a theory that combines the CI and Green's function methods and applied it to realistic systems. In particular, we studied the screened Coulomb interaction which provides access to the life-times of quasiparticle states. Our investigation of the adsorption of Na_9^+ cluster on a Cu(001) surface shows that the life-times of the hybridized single-particle states drastically depend on the geometry of the system. This indicates a change in electronic correlations upon adsorption and suggests that only *ab initio* methods can provide an adequate description of the experiment.

SYEC 4.6   Fri 11:30   A 151

Duality of the KS and OEP potentials and implementation of OEP in a plane wave code — •Nikitas Gidopoulos[1], Stewart Clark[2], and Keith Refson[3] — [1]ISIS, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, Oxon, OX11 0QX, U.K. — [2]Department of Physics, University of Durham, Science Labs, South Road, Durham DH1 3LE, U.K. — [3]CSE, STFC, Rutherford Appleton Laboratory, HSIC, Didcot, Oxon, OX11 0QX, U.K.

Traditionally, the Kohn-Sham (KS) system is defined as the virtual non-interacting system of electrons with the same ground state density as the interacting system of interest. It is shown that in fact the KS system can also be obtained as the optimal non-interacting system in a straightforward unconstrained energy minimization [1], i.e., an

energy optimization that does not constrain the ground state density in any way. It also turns out that the KS and the Optimised Effective Potential (OEP) systems are closely related by the duality of the variational principles from which they originate. The new point of view allows the natural development of ab initio expressions for the correlation energy and potential in KS theory. Further, we implement the OEP method in the plane wave code CASTEP exploiting the Hylleraas variational principle, which allows us to construct a minimization algorithm in order to obtain efficiently the infinite orbital sums that are necessary to determine OEP. Applications to semiconductor gaps will be presented.

[1] N.I. Gidopoulos, arXiv:cond-mat/0603277

SYEC 4.7 Fri 11:45 A 151

Generalized density functional theory for effective potentials — •Fernando Reboredo and Paul Kent — Oak Ridge National Laboratory, Oak Ridge TN USA

We demonstrate the existence of different density functionals that retain selected properties of the many-body ground state in the non-interacting density functional solution. We focus on diffusion Monte Carlo applications that require trial wave functions with Fermion optimal nodes. The theory can be extended and used to understand current practices in several electronic structure methods [GW-BSE,CI,EPM] within a generalized density functional framework. The theory justifies and stimulates the search of optimal empirical density functionals and effective potentials but also cautions on the limits of their applicability. The theoretical concepts are tested against a near-analytic model that can be solved to numerical precision.

SYEC 4.8 Fri 12:00 A 151

The quality of Müller type functionals in reduced density matrix functional theory — •Nicole Helbig[1,2,4], Nektarios N. Lathiotakis[3,2,4], Ali Akbari[1,4], Angel Rubio[1,4], and E.K.U. Gross[2,4] — [1]Department of Material Science, UPV/EHU, Centro Mixto CSIC-UPV, Centro Joxe Mari Korta, San Sebastián, Spain — [2]Institut für Theoretische Physik, Freie Universität Berlin, Berlin, Germany — [3]Theoretical and Physical Chemistry, National Hellenic Research Foundation, Athens, Greece — [4]European Theoretical Spectroscopy Facility (ETSF)

Reduced density matrix functional theory, which uses the one-body density matrix as its fundamental variable, provides a powerful tool for the description of many-electron systems. While the kinetic energy is known exactly as a functional of the one-body density matrix the correlation energy needs to be approximated. Most approximations that are currently employed are modifications of the Müller functional. The adiabatic extension of these functionals into the time-dependent domain proofs problematic because it leads to time-independent occupation numbers. We assess the general quality of these approximations for an exactly solvable two-electron system as well as for calculations of the fundamental gap. In addition, we address the impact of those functionals for excited state properties in optics.

SYEC 4.9 Fri 12:15 A 151

Closing the gap to reality: non local exchange and correlations in metals — •Gernot Stollhoff — MPI f. Festkörperforschung, Heisenbergstr.1, D 70569 Stuttgart

The Local Ansatz (LA)is the only ab-initio correlation scheme that can be used for metals. Here, it will be demonstrated that non-local exchange and correlation contributions exist that are very relevant for metals but have never been treated before, and are not covered by any of the density functional (DF) schemes either. These contributions aim at reducing the long range charge fluctuations by lattice symmetry reductions, charge density wave instabilities or charge redistributions for the case of degenerate bands. Applications are presented for polyacetylene, Li (bcc, densely packed), Zn, V, Fe. In all cases, the DF results are deficient, and the LA corrections are verified by experiment. These corrections may also strongly influence electron-phonon coupling.