SYEC 2: Exact-exchange and hybrid functionals meet quasiparticle energy calculations II

Time: Thursday 14:00–17:00 Location: A 053

SYEC 2.1 Thu 14:00 A 053

Range separated hybrid density functionals: the importance of middle-range Hartree-Fock exchange — •Artur F. Izmaylov[1], Thomas M. Henderson[1], Gustavo E. Scuseria[1], and Andreas Savin[2] — [1]Department of Chemistry, Rice University, Houston, Texas 77005, USA — [2]Laboratoire de Chimie Théorique, CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, F-75252 Paris, France

In spite of the great success of regular hybrid density functionals, there are still at least two major problems with their application: first, they become computationally intractable when applied to small band-gap periodic systems, and second, properties that heavily depend on the right asymptotic behavior of the exchange-correlation potential suffer from the potential's wrong representation with hybrid functionals. In this work we show that both of these problems can be substantially resolved by introducing range separation of the Coulomb operator into short-, middle-, and long-range parts, and neglecting short- and long-range Hartree-Fock exchange contributions. We demonstrate how addition of middle-range Hartree-Fock exchange to the Perdew-Burke-Ernzerhof (PBE) functional affects thermochemistry and barrier heights in molecules, and band gaps, polarizabilities, and excitation energies in solids.

SYEC 2.2 Thu 14:15 A 053

Applications of the exact-exchange functional in current density functional theory — •Stefan Kurth[1], Stefano Pittalis[1], Sangeeta Sharma[1,2], Nicole Helbig[3], and Eberhard K.U. Gross[1] — [1]Institute for Theoretical Physics, Free University Berlin, Germany — [2]Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany — [3]Donostia International Physics Center (DIPC), San Sebastian, Spain

The proper description of many-electron systems in the presence of magnetic fields within density-functional theory (DFT) requires the current density to be used as basic variable besides the electron and magnetization densities. Applications of this current-DFT (CDFT) formalism have been limited because electron-gas-based approximations for the CDFT exchange-correlation functional have serious pathologies which make them awkward to use in practical calculations.

As an alternative, we present a CDFT version of the optimized effective potential method which allows for the use of explicitly orbital-dependent functionals and which also provides a natural framework to treat non-collinear current and magnetization densities. Results obtained with the exact exchange functional are presented for the spurious energy splittings of degenerate ground states of open-shell atoms as well as for orbital magnetic moments and spin-orbit induced band-splittings in solids.

SYEC 2.3 Thu 14:30 A 053

First-principles approach to Non-Collinear Magnetism: Towards Spin Dynamics — •Sangeeta Sharma[1,2], J Kay Dewhurst[3], Stefan Kurth[2], Stefano Pittalis[2], and E. K. U Gross[2] — [1]1 Fritz Haber Institute of the Max Planck Society, Berlin, Germany. — [2]Institut fur Theoretische Physik, Freie Universität Berlin, — [3]School of Chemistry, University of Edinburgh, Edinburgh, UK

The exact treatment of exchange within the Kohn-Sham formulation of DFT has been one of the most interesting developments of ab-initio theory in recent years. Recently (PRL 98, 196405) we have extended this exact exchange method to describe non-collinear magnetism. The equations for the effective Kohn-Sham scalar potential and magnetic field are derived within the optimized effective potential framework. This is of particular importance for the future ab-initio approach to describe spin dynamics since the most widely used exchange-correlation (XC) approximations (like the LSDA/GGA) rely on the magnetization and XC magnetic field being made locally collinear, rendering these approximations improper for the study of spin-dynamics. This is a serious limitation. With an example of a magnetically frustrated Cr-monolayer and with the help of an accurate full-potential LAPW implementation of our newly derived equations we show that there is a strong local non-collinearity between the magnetization and exchange-correlation magnetic field making future time dependent extensions of this method highly suitable contenders for the ab-initio study of spin dynamics.

SYEC 2.4 Thu 14:45 A 053

Fingerprints of discontinuity in the exchange-correlation energy functional in the subband electronic structure of semiconductor quantum wells — •César R. Proetto and Santiago Rigamonti — Centro Atómico Bariloche and Instituto Balseiro, S. C. de Bariloche, Argentina

One of the basic properties of exact Density Functional Theory, is the derivative discontinuity of the exchange-correlation (xc) energy functional, as the number of electrons in an atom, molecule, or solid changes from N to N+1, with N representing the total number of electrons in a closed shell (atoms and molecules), or in a filled band (semiconductors and insulators). Continuum approximations to the xc energy functional, fail to produce the correct value for this discontinuity, resulting in an important underestimation of the fundamental gap of most semiconductors and insulators. Using an ab initio generated xc functional, which includes exchange exactly and correlation in an exact partial way, we will discuss how this derivative discontinuity arise naturally in the subband spectra of semiconductor quantum wells, each time a subband becomes slightly occupied [1]. Exchange and correlation give opposite contributions to the discontinuity, with correlation overcoming exchange. The associated jump in the intersubband energy is in excellent agreement with experimental data.

[1] S. Rigamonti and C. R. Proetto, Phys. Rev. Lett. 98, 066806 (2007).

SYEC 2.5 Thu 15:00 A 053

Exchange-energy functionals for finite two-dimensional systems — •Stefano Pittalis[1,3], Esa Rasanen[1,3], Nicole Helbig[2,3], and E.K.U. Gross[1,3] — [1]Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany — [2]Unité de Physico-Chimie et de Physique des*Matériaux, Université Catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium — [3]European Theoretical Spectroscopy Facility (ETSF)

Implicit and explicit density functionals for the exchange energy in finite two-dimensional systems are developed following the approach of Becke and Roussel [Phys. Rev. A 39, 3761 (1989)]. Excellent agreement for the exchange-hole potentials and exchange energies is found when compared with the exact-exchange reference data for the two-dimensional uniform electron gas and few-electron quantum dots, respectively. Thereby, this work significantly improves the availability of approximate density functionals for dealing with electrons in quasi-two-dimensional structures, which have various applications in semiconductor nanotechnology.

SYEC 2.6 Thu 15:15 A 053

Wigner crystallization in exact exchange theory: calculation of the persistent current in a quantum ring — •Marc Siegmund and Oleg Pankratov — Lehrstuhl für Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstr. 7/B2, 91058 Erlangen

A pinned Wigner crystal is a correlated many-body state with electrons localized at discrete lattice sites. At low electron densities such a crystalline state supersedes the Fermi liquid state as the Coulomb repulsion dominates over the kinetic energy. The electron crystal can be pinned by the arbitrarily weak localized potential which would have no effect on the Fermi liquid state. Hence the Wigner crystallization should result in a drastic “collective” localization of electrons provided a pinning potential is applied.

We use the DFT-OEP method (in KLI approximation) to calculate the electron persistent current induced by magnetic flux through the quantum ring. The current is calculated as a function of the interaction parameter r_S in the density range where the system undergoes Wigner transition. At high densities (small r_S) the current is independent of r_S whereas below some critical density the current drops exponentially indicating a transition to the localized Wigner state. We find the critical $r_\mathrm{S}^\mathrm{c} \approx 2.05$.

The amplitude of the electron density oscillations shows a clear square root dependence on $r_\mathrm{S} - r_\mathrm{S}^\mathrm{c}$, indicating a second-order character of the phase transition. This is a natural consequence of the mean-field-type DFT-OEP approach.

SYEC 2.7 Thu 15:30 A 053

The relativistic optimized potential method for solids implemented within the multiple scattering KKR method — •D Ködderitzsch[1], H Ebert[1], and H Akai[2] — [1]Ludwig-Maximilians-Universität München, Department Chemie und Biochemie, Physikalische Chemie, Butenandtstraße 11, D-81377 München, Germany — [2]Department of Physics, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

We present the first implementation of a *spin-polarized relativistic* optimized potential method (ROPM) for solids in the framework of spin-density functional theory. We have reformulated the ROPM in terms of Green's functions and sketch our subsequent implementation within the framework of the KKR multiple-scattering theory for solids. This method is an all electron, basis set free approach. All quantities are expanded in a fully relativistic spin-angular representation; spin-orbit coupling is treated *non*-perturbatively. Core-core interactions are determined along the lines of the method presented in Ref. [1], core-valence (band states) and valence-valence interactions are expressed in terms of the relativistic multiple-scattering representation. We used exact exchange (EXX) as a first step towards a complete exchange correlation functional. Results for semi-conductors and transition-metals are discussed.

[1] D. Ködderitzsch, H. Ebert, E. Engel, submitted to PRB

SYEC 2.8 Thu 15:45 A 053

Hybrid functional and GW calculations on defects in semiconductors: from quantitative to qualitative changes of defect levels and states compared to standard DFT methods — •Adam Gali[1], Peter Deák[2], Bálint Aradi[2], and Riccardo Rurali[3] — [1]Department of Atomic Physics, Budapest University of Technology and Economics, Budapest, Budafoki út 8, H-1111, Hungary — [2]Bremen Center for Computational Materials Science, University of Bremen, D-28359 Bremen, Germany — [3]Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

The state-of-the-art method to calculate defect properties in semiconductors is density-functional theory (DFT) in a supercell geometry. Standard implementations of DFT, like the local density or the generalized gradient approximation, suffer from the underestimation of the band gap, which may lead to erroneous defect level positions. We applied and compared hybrid functional and model GW method to correct the one-electron DFT defect levels in various semiconductors. We show i) the very simple scissor correction may work for vacancy defects but fails for interstitial defects ii) the standard DFT method can predict even qualitatively wrong description of the defect states iii) the correct description of the defect state can lead to different geometry of the defect, therefore, the self-consistent correction of the total energy and forces is also necessary. Finally, we compare hybrid functional and GW method on bare and defective semiconductor nanostructures.

SYEC 2.9 Thu 16:00 A 053

Theoretical Spectroscopy of Point Defects in Semiconductors — •M. Bockstedte[1,2], Adam Gali[3], A. Marini[4], A. Rubio[1], and O. Pankratov[2] — [1]ETSF, Univerisdad del País Vasco UPV/EHU, San Sebastián, Spain — [2]Theor. Festkörperphysik, Universität Erlangen-Nürnberg, Erlangen, Germany — [3]Department of Atomic Physics, Budapest University of Technology and Economics, Budapest, Hungary — [4]ETSF, Universit di a Roma Tor Vergata, Roma, Italy

The current theory of point defects in semiconductors is largely based on the density functional theory (DFT) and the local spin density approximation (LSDA). Numerous defect models have been identified with experimental defect centers by predicting quantities related to the defect's electronic structure. However, there are apparent limitations: the position of localized defect levels is affected by the well-known DFT band gap error and the excited states of defects cannot be assessed rigorously. These two fundamental defect properties are accessible via the many body perturbation theory within the GW-approximation and Bethe-Salpeter equation implemented in the program package SELF. We demonstrate the relevance of this approach for the interpretation of optical experiments for well-identified defect centers. As such we considered the carbon vacancy and di-vacancy in SiC. We show that the observed absorption spectra in contrast to the earlier interpretation also involve resonant levels and the ionization of the vacancy in two different charge states. We discuss the origin of the prominent absorption/photo-luminescence line of the di-vacancy, a common compensation center in semi-insulating SiC.

SYEC 2.10 Thu 16:15 A 053

Understanding correlations in vanadium dioxide from first principles — •Matteo Gatti[1,2], Fabien Bruneval[1,2,3], Valerio Olevano[1,4], and Lucia Reining[1,2] — [1]European Theoretical Spectrocopy Facility (ETSF) — [2]LSI - Ecole Polytechnique, Palaiseau, France — [3]Dep. of Chemistry and Applied Biosciences, ETH Zurich, Lugano, Switzerland — [4]Institut Néel, CNRS, Grenoble, France

Vanadium dioxide is a prototype material for the discussion of correlation effects in solids. First-principles density-functional theory does not describe the metal-insulator transition, whereas strongly correlated models reproduce the main features. Here we present a parameter-free GW calculation of VO_2 and show that correlation effects in the band-structure of both the metallic and the insulating phases are correctly reproduced, provided that quasiparticle energies and wavefunctions are calculated self-consistently. Our calculations explain the satellite in the photoemission spectrum of the metal as due to a plasmon resonance in the energy-loss function and show that this feature disappears in the insulator.

SYEC 2.11 Thu 16:30 A 053

Electronic correlation in $3d$ transition metals beyond *GW*: The FLEX method — •Andreas Gierlich[1], Arno Schindlmayr[1], Stefan Blügel[1], and Václav Drchal[2] — [1]Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 18221 Praha 8, Czech Republic

The *GW* approximation is currently the most successful *ab initio* approach to electronic excitations and spectroscopies of semiconductors and simple metals. However, it ignores spectral features resulting from higher-order correlation effects in the localized $3d$ orbitals of transition metals, such as the 6 eV satellite in the photoemission spectrum of nickel. Furthermore, exchange splittings and $3d$ valence band widths of transition metals often deviate from experimental measurements. The fluctuation-exchange (FLEX) method is a diagrammatic technique that describes additional two-particle scattering processes beyond those contained in the *GW* approximation. We have developed a simplified FLEX implementation designed to describe electronic correlation in $3d$ transition metals. Starting from density-functional calculations within the full-potential linearized augmented plane-wave scheme, we apply the FLEX method as a perturbative correction to include the two-particle correlation effects in the self-energy of the $3d$ electrons. The resulting equations are solved self-consistently within dynamical mean-field theory. We have applied this scheme to selected materials with intermediate correlation strength and present illustrative results.

SYEC 2.12 Thu 16:45 A 053

Efficient all-electron implementation of the *GW* approximation within the full-potential linearised augmented-plane-wave method — •Christoph Friedrich, Arno Schindlmayr, and Stefan Blügel — Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

The *GW* approximation for the electronic self-energy yields quasiparticle band structures in very good agreement with experiment, but almost all implementations so far are based on the pseudopotential approach, which limits their range of applicability. We have developed an implementation within the full-potential linearised augmented-plane-wave (FLAPW) method, which treats core and valence electrons on an equal footing. Within this method a large variety of materials can be treated, including d- and f-electron systems, oxides and magnetic systems. Our implementation employs a mixed basis set for the representation of basis-function products in the interstitial and muffin-tin regions. An expansion of the wave functions around the Γ point using $\mathbf{k}\cdot\mathbf{p}$ perturbation theory allows us to treat the divergence of the Coulomb interaction analytically leading to fast convergence with respect to the $\mathbf{k}$-point sampling. The anisotropy of the dielectric screening is fully taken into account. A basis transformation to the eigenfunctions of the Coulomb potential allows a reduction of the basis-set size without compromising the accuracy, which leads to a considerable speed-up in computation time. As a demonstration we show convergence tests and results for selected solids. Financial support from the DFG through the Priority Programme 1145 is gratefully acknowledged.