Symposium Exact-exchange and hybrid functionals meet quasiparticle energy calculations (SYEC)

jointly organized by
Surface Science Division (O),
Semiconductor Physics Division (HL),
Dielectric Solids Division (DF), and
Low Temperature Physics Division (TT)

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Overview of Invited Talks and Sessions

(lecture rooms A 053 and A 151; Poster F)

Invited Talks

SYEC 1.1	Thu	9:30–10:00	A 151	**Nonlocal exact exchange: range separation, hybridization, and local variants** — •Gustavo Scuseria
SYEC 1.2	Thu	10:00–10:30	A 151	**Magnetization-current density-functional theory** — •Andreas Görling
SYEC 1.3	Thu	10:30–11:00	A 151	**GW and hybrid functionals applied to extended systems** — •Georg Kresse
SYEC 1.4	Thu	11:00–11:30	A 151	**Electronic properties of solids within a GW-based DFT scheme: Local versus non-local hybrid functionals** — •Angel Rubio
SYEC 1.5	Thu	11:30–12:00	A 151	**The Quasiparticle Self-Consistent GW Approximation** — •Mark van Schilfgaarde
SYEC 1.6	Thu	12:00–12:30	A 151	**Ab-initio Many-Body Perturbation Theory of Electrons, Holes, Excitons, and their Dynamics** — •Michael Rohlfing

Sessions

SYEC 1.1–1.6	Thu	9:30–12:30	A 151	**Exact-exchange and hybrid functionals meet quasiparticle energy calculations I**
SYEC 2.1–2.12	Thu	14:00–17:00	A 053	**Exact-exchange and hybrid functionals meet quasiparticle energy calculations II**
SYEC 3.1–3.7	Thu	18:30–19:30	Poster F	**Exact-exchange and hybrid functionals meet quasiparticle energy calculations III - Poster (joined by SYMS posters)**
SYEC 4.1–4.9	Fri	10:15–12:30	A 151	**Exact-exchange and hybrid functionals meet quasiparticle energy calculations IV**

SYEC 1: Exact-exchange and hybrid functionals meet quasiparticle energy calculations I

Time: Thursday 9:30–12:30 Location: A 151

Invited Talk SYEC 1.1 Thu 9:30 A 151

Nonlocal exact exchange: range separation, hybridization, and local variants — •Gustavo Scuseria — Rice University, Houston, Texas, USA

This presentation will address our current efforts to develop more accurate exchange-correlation forms for density functional theory. There are two leading themes in our current work: range separation and local weights. On the first theme, we will present a three-range hybrid functional and discuss the rationale for the success of screened functionals like HSE and LC-wPBE. On the second theme, the emphasis will be on new metrics for local hybridization and local range separation.

Invited Talk SYEC 1.2 Thu 10:00 A 151

Magnetization-current density-functional theory — •Andreas Görling — Lehrstuhl für Theoretische Chemie, Egerlandstr. 3, 91058 Erlangen, Germany

A magnetization current density-functional theory is introduced that represents a framework for a unified treatment of magnetic effects, noncollinear spin, spin-orbit interactions, and currents of the electron density as well as of the magnetization. A corresponding exact-exchange magnetization-current density functional is presented and used in an implementation of the new approach. This implementation employs plane wave basis sets and pseudopotentials that take into account spin-orbit coupling. First results for atoms and molecules are presented.

Refs.: S. Rohra and A. Görling, Phys. Rev. Lett. 97, 013005 (2006). S. Rohra, E. Engel, and A. Görling, submitted; arXiv:cond-mat/0608505.

Invited Talk SYEC 1.3 Thu 10:30 A 151

GW and hybrid functionals applied to extended systems — •Georg Kresse — Faculty of Physics, University of Vienna

GW calculations are presented for small gap and large gap systems, comprising typical semiconductors (Si, SiC, GaAs, GaN, ZnO, ZnS, CdS and AlP), insulators (C, BN, MgO, LiF) and noble gas solids (Ar, Ne). The general finding is that single shot G0W0 calculations using wavefunctions obtained by conventional density functional theory calculations yield too small band gaps, whereas G0W0 calculations following hybrid Hartree-Fock density functional calculations tend to overestimate the band gaps. This is at first sight astonishing, since hybrid functionals themselves yield very good band gaps. The contradiction is resolved by showing that the a proper treatment of the attractive electron-hole interaction (excitonic effects) is required to obtain good static and dynamic dielectric functions using hybrid functionals. The corrections are incorporated in GW using vertex corrections, and the inclusion of these vertex corrections rectifies the predicted band gaps.

In order to remove the dependency on the initial wavefunctions, self-consistent GW calculations are presented, again including a many body treatment of vertex corrections. The results are in excellent agreement with experiment, with a few percent deviations for all considered materials. Finally an outlook on total energy calculations based on GW methods is given and the shortcommings of hybrid functionals are discussed in this light.

Invited Talk SYEC 1.4 Thu 11:00 A 151

Electronic properties of solids within a GW-based DFT scheme: Local versus non-local hybrid functionals — •Angel Rubio — European Theoretical Spectroscopy Facility (ETSF), Dpto Fisica de Materiales, Universidad del Pais Vasco, Centro Mixto CSIC-UPV, San Sebastian, Spain

In this talk we will show alternative treating of correlation effects within a density-functional-based approach based on the adiabatic-connection fluctuation-dissipation theorem (ACFDT) and the linearise Sham-Schlüter. In this context we have calculated the RPA energies as well as the structural properties of simple solids (Si, NaCl). As expected, there are minor differences between the KS-LDA and the RPA results. However, in model layered systems, where layer-layer interactions are very weak, there are evident discrepancies due to the presence of long-ranged correlations. We will discuss the implications for the gap and optical properties in a KS and generalised KS formalisms.

Work done in collaboration with M. Gruning, A. Marini and P. Garcia-Gonzalez. References: Advanced Correlation Functionals: Application to Bulk Materials and Localized Systems P. Garcia-González, J.J. Fernandez, A. Marini and A. Rubio, J. Phys. Chem. B , (2007); First-Principle Description of Correlation Effects in Layered Materials; A. Marini, P. García-González and A. Rubio Phys. Rev. Letts 96,); Density functionals from many-body perturbation theory: the bandgap for semiconductors and insulators M. Grüning, A. Marini and A. Rubio J. Chem. Phys. 124, (2006), and Effect of spatial nonlocality on the density functional band gap, Phys. Rev. B 74, (2006)

Invited Talk SYEC 1.5 Thu 11:30 A 151

The Quasiparticle Self-Consistent GW Approximation — •Mark van Schilfgaarde — Arizona State University, Tempe AZ

In many-body perturbation theory, the self-energy Σ is constructed in a perturbation expansion in some noninteracting quasiparticles, generated by a noninteracting hamiltonian H_0 or Green's function G_0. The perturbation theory generates an interacting Green's function G. We introduce the idea of a self-consistent perturbation, where G_0 is chosen to be as close as possible to G, to minimize the size of the perturbation. We have implemented the idea in the GW approximation, which we call the quasiparticle self-consistent GW (QSGW) approximation. QSGW handles both itinerant and correlated electrons on an equal footing, in a true *ab initio* manner. It describes optical properties in a wide range of materials rather well, including cases where the local-density and LDA-based GW approximations fail qualitatively. Self-consistency dramatically improves agreement with experiment, and is sometimes essential. Weakly correlated materials such as Na, and *sp* semiconductors are described with uniformly high accuracy. QSGW reliably treats many aspects of correlated materials. Spin wave spectra in Fe, MnO, NiO and MnAs are uniformly well described.

QSGW avoids some formal and practical problems encountered in the LDA-based and self-consistent GW, which will be discussed. Discrepancies with experiments are highly systematic and increase with localization of the eigenfunctions. We will present results for several materials classes to illustrate this, and offer arguments to show what extra diagrams must be included to account for the discrepancies.

Invited Talk SYEC 1.6 Thu 12:00 A 151

Ab-initio Many-Body Perturbation Theory of Electrons, Holes, Excitons, and their Dynamics — •Michael Rohlfing — Fachbereich Physik, Universität Osnabrück, Osnabrück, Germany

Excited electrons, holes, and correlated electron-hole pairs are of prime importance for the spectral properties of condensed matter. They are described by many-body perturbation theory (MBPT), which sytematically includes electronic exchange-correlation effects. The most common realization of this approach is Hedin's GW approximation to the electron self-energy operator, combined with solving the Dyson equation of quasiparticles (electrons and holes) and the Bethe-Salpeter equation (BSE) of electron-hole pairs. This GW+BSE method has turned into a standard procedure for many systems, from bulk crystals to defects, surfaces, polymers, molecules, and adsorbate systems.

We will present the GW+BSE method and its relation to other approaches and discuss a number of prototypical systems and results. Particular emphasis will be put on the dynamics related to electronic excitations. On the one hand, the excited state on its own may be subject to femtosecond dynamics of the electronic degrees of freedom. On the other hand, the dependence of the total energy on the geometry may be different in the excited state, causing structural relaxation, spectral broadening, and Stokes shifts. In particular, we discuss prototypical excitations at surfaces, like charge-transfer processes at molecules on insulators [CO:MgO(001)] and particle expulsion from insulator surfaces [KI(001)] and semiconductor surfaces [H:Si(001)].

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 $r_S^c \approx 2.05$.

The amplitude of the electron density oscillations shows a clear square root dependence on $r_S - r_S^c$, 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 3*d* 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 3*d* orbitals of transition metals, such as the 6 eV satellite in the photoemission spectrum of nickel. Furthermore, exchange splittings and 3*d* 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 3*d* 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 3*d* 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 **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.

SYEC 3: Exact-exchange and hybrid functionals meet quasiparticle energy calculations III - Poster (joined by SYMS posters)

Time: Thursday 18:30–19:30 Location: Poster F

SYEC 3.1 Thu 18:30 Poster F

Implementation of exact exchange in a real-space DFT code using the projector augmented wave method — •Carsten Rostgaard and Jens Jørgen Mortensen — Center for Atomic-scale Materials Design, Technical University of Denmark, Denmark

The projector augmented wave (PAW) method for density-functional theory (DFT) calculations, offers a formally well defined linear transformation from the sharply featured all-electron wave function to the smooth pseudo wave function, thus enabling a computationally efficient approach to solving the Kohn-Sham equations, while retaining the accuracy of a full potential (frozen core) calculation.

As DFT calculations with orbital dependent exchange-correlation functionals probe the core region of the wave function, the PAW scheme is ideally suited for such functionals. For exact exchange calculations in PAW, one needs to determine the action of the non-local Fock operator on the smooth pseudo wavefunctions. The Fock operator can then be applied directly, as is done in most hybrid functionals, of it can be 'localized' (i.e. made multiplicative) by some appropriate scheme, like OEP, LHF, KLI, etc.

We have implemented the Fock operator in the real-space PAW-DFT code gpaw, and a benchmark test of the atomization energies and HOMO-LUMO gaps of a number of small molecules has been performed, and compared to calculations done in VASP and Gaussian, using the PBE0 hybrid functional. We find that the effect of the valence-core exchange interaction, available in the PAW framework, can be substantial.

SYEC 3.2 Thu 18:30 Poster F

Study of electronic properties and point defects in UO_2 using local hybrid exchange-correlation functionals — •Doru Torumba[1], Jean-Paul Crocombette[1], and François Jollet[2] — [1]CEA Saclay, DEN/DMN/SRMP, 91191 Gif-Sur-Yvette, France — [2]Département de Physique Théorique et Appliquée, CEA-DAM, Bruyères-le-Châtel, France

The new computational methods, as the local hybrid exchange-correlation functionals, require a careful benchmarking of their performance on many different systems in order to asses their reliability.

In the present contribution the local version of the hybrid PBE0 exchange-correlation functional is used for calculating the structural and magnetic properties of uranium dioxide. The results are compared to the ones obtained using the more common functionals: GGA and LDA+U. Additionally, the results of an ongoing study on the charge and the structure of point defects in uranium dioxide will be presented.

SYEC 3.3 Thu 18:30 Poster F

Role of emerging methods in advanced DFT study of novel compounds with high-efficiency photovoltaic applications — •Pablo Palacios[1,2], Perla Wahnon[1], Kefren Sanchez[1], Irene Aguilera[1], Julio Juan Fernandez[1], and Jose Carlos Conesa[2] — [1]Universidad Politecnica de Madrid, Madrid, Spain — [2]Consejo Superior de Investigaciones Cientificas, Cantoblanco, Spain

An exhaustive study of compounds with unusual electronic structure used as new efficient photovoltaic materials is presented. These intermediate band materials obtained by selective substitution of atoms of a host semiconductor by transition metals present a narrow, partially-filled band inside the semiconductor band-gap, separated from host valence and conduction bands. Therefore additional current carriers can be obtained from the absorption of low energy photons enabling electrons to get the conduction band through the intermediate band.

Although standard DFT is a suitable tool for our purposes, in order to enhance prediction capabilities for these new materials there are some features, i.e. host semiconductor gap, which can be improved with advanced methods let be GW, exact exchange or hybrid functionals.

Exact exchange studies have been done in several candidates for intermediate band material as well as advanced analysis of the correlation effect. Exact exchange method was implemented in our group within SIESTA. For the moment these studies have contributed to support the reliability of the prediction of intermediate band materials to such an extent that experimental samples are being grown. State-of-the-art techniques could complement the results obtained to date.

SYEC 3.4 Thu 18:30 Poster F

Implementation of the non-local exchange potential within the FLAPW method — •M. Betzinger, C. Friedrich, G. Bihlmayer, and S. Blügel — Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Hybrid functionals (e.g. PBE0, B3LYP) are currently explored as a practical approximation to the exchange-correlation functional in density-functional theory (DFT). They yield accurate results for molecules, improve the band gap of semiconductors and insulators as well as the description of strongly correlated systems. So far most of the implementations for periodic systems employ pseudopotentials with a plane-wave basis set, which restricts their range of applicability. We develop an implementation within the full-potential linearized augmented plane-wave method (FLAPW), with which a much wider range of materials can be treated. The crucial step is the evaluation of the non-local exchange potential. Our approach uses a mixed basis-set. After representing the Coulomb interaction in this basis, the exchange matrix elements can be written as a Brillouin-zone (BZ) integral over vector-matrix-vector products. The Coulomb interaction goes to infinity in the center of the BZ leading to a divergence in the integrand. The divergent part is separated from the numerical integration and treated analytically. We show convergence properties of the mixed basis-set and first results for prototype semiconductors and insulators.

Financial support from the Deutsche Forschungsgemeinschaft through the Priority Program 1145 is gratefully acknowledged.

SYEC 3.5 Thu 18:30 Poster F

Two-particle excitations within the Hubbard model — Berlinson Dominikus Napitu[1,2] and •Jamal Berakdar[2] — [1]Martin-Luther-Universität, Halle-Wittenberg,Germany — [2]Max-Planck-Institut für MikrostrukturPhysik, Halle

Remarkable progress has been achieved recently in studying experimentally the two-particle spectrum of surfaces via angular and energy-resolved two-electron emission upon [1,2] a single-photon absorption. We show in this theoretical contribution how these measurements correlate with the particle-particle Green's function and contrast with related spectroscopies such as core-valence-valence (CVV) Auger spectra and appearance potential spectroscopy (APS). Based on the single band Hubbard model [3] we developed a method for the calculations of the corresponding two-particle spectra while the single particle properties are being evaluated within dynamical-mean field theory (DMFT)scheme [4].

[1] Schumann, F.O., Winkler, C., Kirschner, J., Phys. Rev. Lett. 98, 257604(2007); [2] Schumann, F.O., Winkler, C., Kirschner, J., New. Jour. Phys. 9.372/1-14 (2007); [3] Hubbard, J.I., Proc. Roy. Soc. London 276, 238 (1963); [4] Georges, A., et al., Rev. Mod. Phys.68, 13 (1996).

SYEC 3.6 Thu 18:30 Poster F

Optical Excitation of the *F* Center in Calcium Fluoride Within Many-Body Perturbation Theory — •Yuchen Ma and Michael Rohlfing — Fachbereich Physik, Universität Osnabrück, Osnabrück, Germany

As a prototype for defects in insulators, we discuss the optical properties of the *F* center in calcium fluoride (CaF_2), which constitutes a prominent defect of the material. The *F* center of CaF_2 exhibits a defect state deep in the band gap. Its excitation by light (at 3.3 eV excitation energy) is described by *ab-initio* many-body perturbation theory (GW approximation and Bethe-Salpeter equation), including electronic exchange, correlation, and electron-hole interaction effects. The excitation can be regarded as a $1s \rightarrow 2p$ transition. The exciton of the absorption band is strongly localized around the vacancy (within about 2 Å for the hole and 4 Å for the electron), but they induce prominent lattice distrotion around the defect. Constrained density-functional theory can predict reliable geometric relaxation for the localized excitons in ionic insulators. The excitation causes strong relaxation of the defect geometry, leading to significant broadening of the optical spectrum by 0.5 eV and to an large Stokes shift of 1.5 eV.

SYEC 3.7 Thu 18:30 Poster F

Physisorption of Organic Molecules on Noble-Metal Surfaces — •Michael Rohlfing[1], Thomas Bredow[2], and Florian Janetzko[2] — [1]Fachbereich Physik, Universität Osnabrück, Germany — [2]Institute for Physical and Theoretical Chemistry, Universität Bonn, Germany

We discuss the physisorption of organic molecules to noble-metal surfaces due to Van-der-Waals interaction. Different from density-functional theory, we treat the exchange energy explicitly and calculate the correlation part within the random-phase approximation. In here, the response of the metal surface is described by a combination of a jellium surface and local polarizability of the *d* electrons, while the response of the adsorbate is obtained from a DFT calculation. We discuss results for the adsorption of Xe, benzene, and PTCDA on the Ag(111) surface. The obtained adsorption energies and distances are between those of DFT-LDA (which overbinds) and DFT-PBE (which does not bind at all), thus constituting a significant improvement beyond DFT. The correlation energy obtained with RPA is compared to classical R^{-6} correction terms. Although the empirical approach gives qualitatively similar potential curves, RPA better reproduces experimental adsorption energies and distances.

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-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 systematically 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.