O 65: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond

Time: Tuesday 18:30–20:30   Location: P2-OG4

O 65.1   Tue 18:30   P2-OG4

Angular projection potentials for density functional calculations — •Rudolf Zeller — Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Development of advanced 21st century applications benefits from a quantum-mechanical understanding of material properties by density-functional theory. However, because the Kohn-Sham-Schrödinger equation must be solved numerically, for all but the smallest systems considerable computer resources are needed which makes very precise calculations difficult. In order to overcome this problem numerous techniques have been developed in the past to make the calculations affordable.

It is my aim to present a novel approach based on non-local potentials which act as projection potentials in the space of spherical harmonics. I will explain the unconventional mathematical techniques that can be used to prove that the Kohn-Sham-Schrödinger equation for these potentials can be solved exactly in the angular variables and, in view of the present computing capabilities, practically exactly in the radial variables. I will discuss the advantage of the use of angular projection potentials for precise total-energy calculations. The advantage arises from the fact that, as a consequence of the practically exact calculable density, the stationarity property of the total-energy functional with respect to the potential can be exploited to full extent.

O 65.2   Tue 18:30   P2-OG4

DFPT within the All-Electron FLAPW Method: Application to Phonons — •Christian-Roman Gerhorst, Markus Betzinger, Gustav Bihlmayer, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

In all-electron methods based on Density Functional Theory, typically the Finite Displacement approach is employed when describing the effect of a phonon perturbation on an electronic many-particle system. In difference to this common procedure, we implement the considerably more effective Density Functional Perturbation Theory (DFPT) into our full-potential linearized augmented plane-wave (FLAPW) code FLEUR; i.e. an all-electron code avoiding any approximation to the shape of the potential including the $1/r$ singularity. This is a non-trivial problem, because we have to tackle a position-dependent basis set generating additional Pulay and surface terms beyond the contributions known for force calculations when atoms are displaced. In this contribution, we report about the key challenge to the realization of the DFPT, which is the self-consistent solution of the Sternheimer equation providing the linear response of the electron density to a phonon perturbation. In a next step, we will use these results to construct the Dynamical Matrix encoding all relevant phonon information to shed light on the phonon-related properties of electronic many-particle systems.

O 65.3   Tue 18:30   P2-OG4

Conceptual problems of self-interaction corrections — •Charlotte Vogelbusch, Ronald Starke, and Lenz Fiedler — TU Freiberg, Institute for Theoretical Physics, Germany

Electronic structure calculations with density functional theory usually include the so-called self-interaction error which occurs due to the approximation of the exchange-correlation functional.

A corresponding self-interaction correction has first been introduced by J. P. Perdew and A. Zunger. This poster deals with the main aspects and problems of their method. In particular, we discuss the recent modification of the Perdew-Zunger self-interaction correction proposed by M. R. Pederson [2].

[1] J. P. Perdew, A. Zunger, Phys. Rev. B 23, 5048 (1981)
[2] M. R. Pederson et al., J. Chem. Phys., vol. 140, 121103 (2014)

O 65.4   Tue 18:30   P2-OG4

Numerical improvements of Fermi-Löwdin orbital self-interaction correction — •Lenz Fiedler, Torsten Hahn, Charlotte Vogelbusch, and Jens Kortus — TU Freiberg, Institute for Theoretical Physics, Germany

Electronic structure theory calculations based on density functional

theory (DFT) using semilocal approximations for exchange and correlation are subjected to the self-interaction error. The recently proposed Fermi-Löwdin orbital method for self-interaction correction (FLOSIC) is based on sets of localized orbitals, that are a unitary invariant transformation of the Kohn-Sham orbitals [1,2]. The practical application of this method is however still numerically costly because one needs to determine the Fermi orbital descriptors that minimize the total energy. Numerical improvements to this optimization will drastically improve the performance of the whole FLOSIC DFT method.

We present the implementation of a preconditioned conjugate gradient [3] and a quasi-Newton L-BFGS algorithm [4] that draw on approximations of the analytical Hessian of the energy function. For a set of small molecules, benchmarks are done for different approximated Hessians. We here discuss the influence of different methods to approximate the Hessian and the usage of off-diagonal Hessian elements on the optimization performance.

[1] M. R. Pederson et al., J. Chem. Phys., vol. 140, 121103 (2014)
[2] J. Perdew, A. Zunger, Phys. Rev. B 23, 5048 (1981)
[3] D. Liu, J. Nocedal, Math. Prog. B 45, 503 (1989)
[4] W. Hager, H. Zhang, SIAM J. Optim., 16-1, 170 (2005)

O 65.5   Tue 18:30   P2-OG4

Electronic and Magnetism Properties of Vacancy-Defected, Fluorine Doped and Adsorption upon MO3 (M= Cr, Mo, W) Surface: a first-principles study — •Masoud Mansouri[1,2] and Tahereh Mahmoodi[1] — [1]Department of Physics, Mashhad Branch, Islamic Azad University, Mashhad 9187147578, Iran — [2]Computational Science Unit, Research Center for Applied Biology, Mashhad Branch, Islamic Azad University, Mashhad, Iran

In this work, a systematic DFT calculation was carried out to investigate the effects of various kinds of dopants on the electronic structure of MO3 (M= Cr, Mo, W) Surface. The possibility to obtain magnetic phase from native defects in pure bulk is investigated. We found that vacancies can induce a magnetic phase of *2 μB with a local magnetic moment, whereas corresponding M vacancies (VM) provides the transition of the insulating MO3 into a metallic-like phase and changes the electronic transport. Moreover, We find that Fluorine (F) doping improves the metallic phase MO3*x Fx (x= 0.04, 0.08, 0.16), where the near Fermi states are formed mostly from M d-orbital and admixture of O-2p orbitals. Next, we present results on the influence of the common gas molecules (Ch4, H2S and NO2) on the electrical resistivity. The most stable configurations, magnetism, adsorption energies, Fermi surface and electronic properties are thoroughly discussed.

O 65.6   Tue 18:30   P2-OG4

An Investigation of Group V dopants in Silicon using Linear Scaling DFT — •Jack Poulton and David Bowler — London Centre for Nanotechnology, 19 Gordon St, London, WC1H 0AH

The aim of our work is to model the incorporation and properties of group V element dopants in silicon using linear scaling density functional theory. In doing so we hope to learn how to incorporate new impurities and make predictions as to how the behaviour of these impurities for comparison with experimental data. This will then allow us to determine the suitability of certain dopants for usage as qubits in a silicon based solid state quantum computer.

O 65.7   Tue 18:30   P2-OG4

Deciphering chemical bonding with Fermi-Löwdin orbitals — •Torsten Hahn[1], Sebastian Schwalbe[1], Jens Kortus[1], and Mark Pederson[2] — [1]Institute for Theoretical Physics, TU Freiberg, Germany — [2]Department of Chemistry, Johns Hopkins University, Baltimore Maryland (MD), US

The recently developed Fermi-Löwdin orbital based method for the correction of the self-interaction error within Density Functional Theory (FLO-SIC) [1,2] does provide improved orbital eigenvalues and more realistic level ordering [3]. We demonstrate the versatility of this method to provide details of chemical bonding by applying it to several systems featuring both localized and delocalized multi-center chemical bonding.

We present results on systems with varying structural complexity: Boron clusters, compounds containing planar tetra-coordinated car-

bon as well as several aromatic and anti-aromatic molecules. The FLO-SIC method yields an inherently 'chemical' representation of bonding in terms of Lewis-type lone and binding electron pairs as well as delocalized multi-center, many-electron bonds. We anticipate that this parameter free methodology becomes a reliable tool to obtain insights into fundamental bonding details especially in situations where standard DFT fails.

[1] M. R. Pederson et.al, JCP 140, 121103 (2014).
[2] M. R. Pederson, JCP 142, 064112 (2015).
[3] T. Hahn et al., JCP 143, 224104 (2015).

O 65.8   Tue 18:30   P2-OG4

Binding energy curves for diatomic molecules obtained by FLO-SIC DFT — •Simon Liebing[1], Sebastian Schwalbe[1], Torsten Hahn[1], Jens Kortus[1], and Mark Roger Pederson[2] — [1]TU Bergakademie Freiberg, Institute for Theoretical Physics, Germany — [2]Department of Chemistry, Johns Hopkins University, Baltimore, USA

The recently developed Fermi-Löwdin orbital method to correct the self-interaction error within DFT (FLO-SIC) [1,2] is used to study bond dissociation of diatomic molecules (e.g. N_2, O_2 and LiF). Binding energy curves are derived within this FLO-SIC methodology and the obtained results are compared to quantum chemical methods (RHF, UHF and ROHF in combination with CCSD/CCSD(T)). Due to the fact that FLO-SIC DFT recovers the correct $-1/r$ behaviour of the potential, the obtained energies for large (infinite) separations agree well with the quantum chemical results. Further, changing Fermi orbital configurations as a function of the separation distance are observed. These distinct configurations could be interpreted as step-wise breaking of multiple bonds during the stretching of the considered molecule and corresponding alterations of spins within its electronic structure.

[1] M. R. Pederson et al., JCP, vol. 140, 121103 (2014)
[2] T. Hahn et al., JCP, vol. 143, 224104 (2015)

O 65.9   Tue 18:30   P2-OG4

Groundstates of the ternary clathrate $Ba_8Ni_xGe_{46-x-y}\square_y$ **obtained with an iterative cluster expansion approach** — •Martin Kuban, Santiago Rigamonti, Maria Troppenz, and Claudia Draxl — Humboldt-Universität zu Berlin

Intermetallic clathrates are promising candidates for the construction of thermoelectric (TE) devices. These rely on a junction between n- and p-type semiconductors. The clathrate compound $Ba_8Ni_xGe_{46-x-y}\square_y$ is of special interest, as it presents a crossover from p-type to n-type conductivity around $x = 4.0$ [1]. Thus, a junction on the same base material could be tailored. In this work, we perform an *ab-initio* study of the structural stability and electronic properties of this compound in the composition range $0 \leq x \leq 6$ and $0 \leq y \leq 4$. Both the substitutional species (Ni) and vacancies ($\square$) are treated on the same footing, through a cluster expansion (CE) in the quasi-ternary Ge/Ni/$\square$ sublattice. The large size of this sublattice (46 sites) leads to a combinatorial explosion of the number of configurations, i.e. the possible arrangements of the substitutional atoms and vacancies in the lattice. As this prevents the use of standard CE methodology, we make use of an iterative CE technique (iCE) as implemented in the code CELL [2]. The iCE is based on efficient samplings of the configurational space. The structural properties (lattice constants, bond distances, etc.) as well as the electronic bandstructure of the stable structures are analyzed.

[1] U. Aydemir *et al.*; Dalton Trans **44**, 7524 (2015).
[2] S. Rigamonti *et al.*, in preparation.

O 65.10   Tue 18:30   P2-OG4

The inapplicability of exact constraints, and a minimal two-parameter DFT+U generalisation, for self-interaction error correction — •Glenn Moynihan[1], Gilberto Teobaldi[2,3], and David D. O'Regan[1] — [1]School of Physics, CRANN and AMBER, Trinity College Dublin, Ireland. — [2]Stephenson Institute for Renewable Energy and Department of Chemistry, The University of Liverpool, U.K. — [3]Beijing Computational Science Research Center, China.

In approximate DFT, the self-interaction error (SIE) is a ubiquitous systematic inaccuracy responsible for underestimated insulating gaps, inaccurate dielectric properties and reaction barriers. It hinders the predictive applicability of DFT to spectroscopy, photochemistry, electrochemistry, and crystal-structure stability. It is, however, amenable to approximate correction using efficient methods such as DFT+U [1]. A calculation scheme for the Hubbard U parameters by variationally extremising a suitable functional might be desirable. but we show here that such an approach is not readily viable. Specifically, we prove that self-consistent constrained DFT [3] cannot be generalised for the non-linear constraints needed to target SIE [2]. We circumvent this using a generalised DFT+U functional, enabling the simultaneous correction of total-energies and ionization potentials, or either together with Koopmans' condition. For the latter, we outline a practical, approximate first-principles scheme by which the required Hubbard parameter pair, U_1 and U_2, may be estimated. [1] H. J. Kulik, et al., Phys. Rev. Lett. **97**, 103001 (2006). [2] Phys. Rev. B Rapid Comms., Accepted (2016), arXiv:1608.07320. [1] Phys. Rev. B **94**, 035159 (2016).

O 65.11   Tue 18:30   P2-OG4

A Hubbard U based correction method for exciton binding in neutral excitations: TDDFT+U — •Okan K. Orhan and David D. O'Regan — School of Physics, Trinity College Dublin, Ireland.

The DFT+U (density-functional theory + Hubbard U) method is widely used to improve the approximate DFT description of the ground state properties of solids and molecules comprising transition-metal ions. We introduce its generalisation to the time domain in the guise of TDDFT+U (time-dependent DFT+U), intended to extend these improvements to the calculation of neutral excitations. Related methods have been previously discussed [1,2], and here we offer a detailed treatment emphasising single-particle excitations and absorption spectra. Our software implementation is a combination of the linear-scaling DFT+U [3] and linear-response TDDFT [4] functionalities available in the ONETEP code [5]. In a study of small nickel-comprising molecules, we find that the Hubbard U correction to the exchange-correlation kernel acts to partially cancel the effects of the DFT+U term of the underlying ground-state potential, enhancing the exciton binding.
[1] C.-C. Lee, H. C. Hsueh, and W. Ku, Phys. Rev. B **82**, 081106(R) (2010). [2] D. Shin, G. Lee, Y. Miyamoto, and N. Park, J. Chem. Theory Comput., **12** (1), pp 201-208 (2016). [3] D. D. O'Regan, N. D. M. Hine, M. C. Payne, and A. A. Mostofi, Phys. Rev. B **85**, 085107 (2012). [4] T. J. Zuehlsdorff, N. D. M. Hine, M. C. Payne, and P. D. Haynes, J. Chem. Phys. **143**, 204107 (2015). [5] C. K. Skylaris, P. D. Haynes, A. A. Mostofi, and M. C. Payne, J. Chem. Phys., **122** (8), 084119 (2005). For the ONETEP code, see http://www.onetep.org

O 65.12   Tue 18:30   P2-OG4

Implementation of Electron-Phonon Coupling in the KKR Formalism and its Applications to Simple Metals — Carsten Eberhard Mahr, •Michael Czerner, Christian Franz, and Christian Heiliger — Justus-Liebig-University, Giessen, Germany

Electron-phonon coupling is one of the main incoherent inelastic scattering mechanisms in a wide variety of crystalline material systems at room temperature. Therefore, it is necessary to incorporate those effects in any realistic calculation of thermoelectric properties. We do so by extending our density functional theory (DFT) based Korringa-Kohn-Rostocker (KKR) Green's function formalism code.

By approximating the Fröhlich-type interaction with a self-energy $\Sigma_{\mathrm{eph}} = -i\frac{\hbar}{2\tau}$ we are able to compute the dressed propagator G by solving Dyson's equation $G = G_{\mathrm{ref}} + G_{\mathrm{ref}} \cdot (\Delta V + \Sigma_{\mathrm{eph}}) \cdot G$, where G_{ref} is the Green's Function of an arbitrary (though typically repulsive) reference system. The corresponding electron-phonon scattering time τ is extracted from electron linewidth calculations.

We demonstrate the physical validity of the beforementioned calculational scheme for non-equilibrium properties by comparing evaluated temperature dependent resistivity characteristics of transport systems consisting of copper, aluminum and other simple metals to experiment. Further, technical details of the implementation in the KKR basis set are presented.