

O 28: Electronic Structure Theory: General I

Time: Tuesday 10:30–13:15

Location: MA 141

O 28.1 Tue 10:30 MA 141

ELPA-AEO: improvements to the eigensolver targetting electronic-structure theory — ANDREAS MAREK¹, HERMANN LEDERER¹, CHRISTIAN CARBOGNO², MATTHIAS SCHEFFLER², LYDIA NEMEC³, CHRISTOPH SCHEURER³, and KARSTEN REUTER³ — ¹MPCDF, MPG, Garching — ²Fritz-Haber Institut, MPG, Berlin — ³Theoretical Chemistry, TUM, Garching

ELPA is a leading state-of-the-art library of massively parallel, highly scalable direct eigensolver routines.[1,2] It is heavily used by many application programs, e.g. from electronic-structure theory, such as FHI-aims, VASP, Quantum Espresso, or CP2K.

The ongoing ELPA-AEO project (BMBF 01IH15001) joins groups from numerical mathematics, computer science, high-performance computing, electronic structure theory, and theoretical chemistry and physics to develop algorithmic extensions and optimizations with an impact at the application level.[3] In this contribution we report on recent achievements and changes to the library. Application-level showcases with the electronic-structure code FHI-aims are presented and an outlook on new functionality is given.

[1] <http://elpa.mpcdf.mpg.de>

[2] A. Marek et al., J. Phys.: Condens. Matter 26 (2014), 213201
DOI: 10.1088/0953-8984/26/21/213201

[3] <http://elpa-ao.mpcdf.mpg.de>

O 28.2 Tue 10:45 MA 141

An adaptive approach to solid-state QM/MM embedding — JAKOB FILSER, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

QM/MM embedding in crystals [1,2] is a powerful approach to the simulation of non-periodic phenomena such as defects, as it eliminates issues like spurious self-interaction that are present in periodic boundary condition (PBC) supercell calculations. On the other hand, the performance of an embedding model depends crucially on the treatment of the QM/MM boundary and the long-range electrostatics in the MM region. Static setups that employ fixed effective core potentials (ECPs) to prevent charge leakage at the QM/MM boundary and fixed formal charges in the MM region are a common approach as both ECPs and formal charges are readily available [2]. However, such setups do not ensure correct reproduction of the electrostatic potential inside the QM region. We revisit this from an adaptive perspective, aiming to reproduce properties of reference density-functional theory PBC calculations in embedded defect-free supercells. Instead of fixed ECPs we optimize pseudo-potentials with an evolutionary algorithm to reproduce the charge distribution and energetics inside the QM region, providing a proof of concept that ECPs are indeed not the best choice for this purpose. For the MM region we propose a procedure to adapt the point charges to recover the long-range electrostatic potential.

[1] P. Sherwood *et al.*, J. Mol. Struct. - Theochem. 623, 1 (2003).

[2] D. Berger *et al.*, J. Chem. Phys. 141, 024105 (2014).

O 28.3 Tue 11:00 MA 141

A new design principle for embedded cluster models? Embedded-cluster calculations of surface oxygen vacancies at TiO₂. — MATTHIAS KICK, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

Surface oxygen vacancies, in particular their nature as charge trapping centers, play an important role for many oxide materials properties. However, addressing them with first-principles density-functional theory (DFT) computations remains a challenge. At least Hubbard corrected DFT+U is required to achieve an appropriate electron localization. At the same time, the large dielectric constant of polarizable oxides like TiO₂ leads to a strong polarization response. As a result supercells of increasing size are necessary in order to avoid spurious interactions between periodic images in case of charged defects, rendering the conventional periodic boundary condition supercell approach impractical. We combine the solid state (QM/MM) embedding functionality in FHI-aims with DFT+U, yielding a numerically most efficient approach to treat the aperiodic aspects at oxide surface. Systematic calculations of neutral and charged states of the surface oxygen vacancy at rutile TiO₂ (110) show that the shapes of the embedded cluster models are crucial for a proper description of surface phenomena. We assess this problem by proposing a new design principle for

embedded clusters.

O 28.4 Tue 11:15 MA 141

On the Nature of Self-Consistency in Density Functional Theory — NICK WOODS¹, MIKE PAYNE¹, and PHIL HASNIP² — ¹Theory of Condensed Matter, University of Cambridge — ²Condensed Matter Physics, University of York

Density functional theory (DFT) within the Kohn-Sham (KS) framework is a popular method for predicting the electronic structure of materials. The self-consistent field (SCF) method is an iterative procedure used to obtain a particle density that solves KS DFT (a ‘self-consistent’ particle density). Density mixing is a particular class of these methods which combines the particle densities of past iterations in such a way that drives each iterative density closer to solving KS DFT. We begin by discussing the various difficulties presented by solving KS DFT from the point of view of achieving self-consistency with density mixing. Then, we present a systematic study of various density mixing methods proposed in literature, which are examined by utilising a representative test suite of over twenty input systems. These example systems involve cases ranging from simple to nearly pathological. The purpose of this work is to highlight where and why certain schemes perform particularly well. Secondly, we discuss how model dielectrics can be used to accelerate and stabilise convergence of density mixing schemes, and propose a scheme whereby a density-dependent (inhomogeneous) model dielectric can be posited and used to assist convergence.

O 28.5 Tue 11:30 MA 141

The Kohn-Sham gap as example for an explicit density functional — MARTIN PANHOLZER^{1,3}, MATTEO GATTI^{2,3}, and LUCIA REINING^{2,3} — ¹Johannes Kepler University, Linz, Austria — ²Laboratoire des Solides Irradiés, Ecole Polytechnique, CNRS, CEA, Université Paris-Saclay, F-91128 Palaiseau, France — ³European Theoretical Spectroscopy Facility (ETSF)

It is well known that the density fully characterizes the ground state of a system. The use of the total energy as a functional of the density led to the usual implementation of Kohn-Sham(KS)-DFT. But other quantities, apart from the total energy, are rarely investigated. In this work we examine the KS-gap as a functional of the density. Numerically the inversion of the KS-equation is done iteratively. Different schemes are compared.

A purpose of the work is to investigate the sensitivity of a system to inaccuracies in the density, especially in view of a subsequent calculation of excited state properties. The KS-gap acts here as an easily accessible indicator.

We also use the density-functional formulation for the band gap to discuss the relation between the Kohn-Sham gap and the electron addition and removal gap.

O 28.6 Tue 11:45 MA 141

Calculation of molecular conductance “on the fly” for thousands of junction geometries — HECTOR VAZQUEZ — Inst. of Physics, Academy of Sciences of the Czech Rep., CZ

Single molecule circuits, where an electrical current is passed across a molecule placed between two electrodes, are ideal systems for studying a range of quantum phenomena[1]. Ab-initio transport calculations based on DFT-NEGF give a detailed description of transmission but their computational cost restricts this approach to a few structures.

In this talk I will describe an approximate method to calculate molecular conductance from a small cluster including the molecule. The reduced computational cost of this approximation enables the calculation of thousands of junction structures. When combined with Molecular Dynamics simulations, the evolution of junction structure and conductance can be simultaneously calculated. I will discuss this approximation to conductance and its implementation in the SIESTA code[2]. I will present results for several conjugated systems for tens of thousands of geometries[3] and analyze the relationship between molecular structure and conductance.

[1] T.A. Su, M. Neupane, M.L. Steigerwald, L. Venkataraman and C. Nuckolls, Nature Rev. Mater. 1 16002 (2016).

[2] J.M. Soler, E. Artacho, J.D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys. Cond. Matt. 14, 2745

(2002).

[3] H. Vazquez, R. Skouta, S. Schneebeli, M. Kamenetska, R. Breslow, L. Venkataraman and M.S. Hybertsen, *Nature Nanotechnol.* 7 663 (2012).

O 28.7 Tue 12:00 MA 141

Band alignment at insulator/semiconductor interfaces through advanced electronic-structure calculations

— •THOMAS BISCHOFF, IGOR RESHETNYAK, and ALFREDO PASQUARELLO — Chaire de Simulation à l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Insulator/semiconductor interfaces are encountered in a broad variety of modern electronic devices. The precise understanding of their properties are of great fundamental and practical importance.

For an accurate description of such systems the band gaps of the consisting materials as well as their offsets must be predicted in an appropriate way. Unfortunately the calculation of these quantities in standard semi-local DFT suffer from the well-known self-interaction error. Advanced methods for electronic-structure calculation like the many-body perturbation theory and hybrid functionals can partially overcome this deficiency. However, these methods tend to position the band edges differently even when they give the same band gap [1]. This phenomenon which is not yet fully understood has direct implications on the band offsets in heterostructures [2].

In this work a representative set of insulator/semiconductor heterostructures is considered through various levels of theory. In particular, we focus on interfaces between materials with different bonding character.

[1] W. Chen et al., *Phys. Rev. B* 86, 035134 (2012)

[2] K. Steiner et al., *Phys. Rev. B* 89, 205309 (2014)

O 28.8 Tue 12:15 MA 141

Electronic and transport properties of the thermoelectric Mg_2X ($\text{X}=\text{Si}, \text{Ge}, \text{Sn}$) substitutional alloys

— •JUAN GUERRA, CARSTEN MAHR, MARCEL GIAR, MICHAEL CZERNER, and CHRISTIAN HEILIGER — Justus Liebig University Giessen, Institut für Theoretische Physik, Giessen, Germany

Due to recent research interest in Mg_2X based binary substitutional alloy systems for thermoelectric applications, we present an ab initio description of electronic properties in the cases of $\text{X}=\text{Si}$, Ge , and Sn . We model these systems using the coherent potential approximation (CPA) implementation in the Korringa, Kohn and Rostoker Green's functions formalism in the full relativistic approach. Within this formalism, we use the Bloch spectral density function to obtain all physical observables. The change of structural parameters with composition deviates from Vegard's law and fits a cubic polynomial function. Relevant alloying effects on bands have been found thus affecting electronic states and effective masses. In the entire compositional range, we present a comprehensive analysis of some important physical quantities for transport, i.e., energy gaps (direct, indirect, and between the low-lying conduction bands), spin-orbit splitting energy, and parabolic band effective masses along different directions and at different symmetry points of the Brillouin zone.

O 28.9 Tue 12:30 MA 141

'Hartree-exchange' in ensemble density functional theory: guaranteed single-valued and maximally free from interactions

— •STEFANO PITTALIS¹ and TIM GOULD² — ¹CNR-Istituto di Nanoscienze, Via Campi 213A, I-41125 Modena, Italy — ²Qld Micro- and Nanotechnology Centre, Griffith University, Nathan, Qld 4111, Australia

Ensemble density functional theory is, in principle, a promising framework to simplify the calculation of excitation energies of many-electron systems. But its application has been hampered by difficulties in calculating, and approximating, the exchange energy. We show that a better starting point is a *combined* 'Hartree-exchange' functional, $\mathcal{E}_{\text{HX}}[n]$,

obtained as the right derivative of the universal ensemble density functional taken with respect to the coupling constant at vanishing interaction [Gould and Pittalis, *accepted in Phys. Rev. Lett.*]. This definition ensures that the resulting $\mathcal{E}_{\text{HX}}[n]$ is guaranteed single-valued – a basic prerequisite, which is at risk when dealing with densities from typical degenerate states – and is computable from a constrained minimization over valid non-interacting ensembles. Crucially, here the conventional restriction to single Slater determinants must be abandoned. The aforementioned definition can be finally restated – through use of the Schur-Horn theorem – into a practical expression which is also amenable to approximations. Specialized expressions from the literature can now be regarded as originating from the unifying approach presented here. Prototypical applications will be outlined, if time allows.

O 28.10 Tue 12:45 MA 141

Energy gaps of low-dimensional many-electron systems from Kohn-Sham quantities: Exchange-only approximations

— •ALBERTO GUANDALINI¹, CARLO ANDREA ROZZI², ESA RÄSÄNEN³, and STEFANO PITTALIS² — ¹Dept. FIM, University of Modena and Reggio Emilia, Italy — ²Center S3, CNR - Istituto Nanoscienze, Modena, Italy — ³Dept. of Physics, Tampere University of Technology, Tampere, Finland

The electron addition energies of two-dimensional (2D) quantum dots are commonly obtained from the ground-state (gs) energies of systems with $N - 1$, N , and $N + 1$ electrons [1]. In this work we assess two alternative methods to calculate the addition energies. They resort to (a) the difference of the eigenvalues of the highest-occupied Kohn-Sham (KS) orbitals for systems with N and $N + 1$ electrons [2]; and (b) the KS gap plus the discontinuity of the exchange-correlation potential – through KS quantities for systems with N electrons [3]. While the original definition of the addition energy involves self-consistent gs calculations for three different systems, method (a) involves two of such calculations, and method (b) only one. At the exchange-only level, we analyze the performance of standard semi-local and (direct) potential approximations. We find that method (b) allows us to reduce the computational effort, yet maintaining the accuracy.

[1] Reimann and Manninen *Rev. Mod. Phys.* 74, 1283 (2002) [2] Capelle et al. *Phys. Rev. Lett.* 99, 010402 (2007) [3] Chai and Chen, *Phys. Rev. Lett.* 110, 033002 (2013)

O 28.11 Tue 13:00 MA 141

Importance of spin-orbit and on-site Coulomb interactions on the electronic structure and lattice dynamics of thorium and actinium

— •LUKAS KYVALA and DOMINIK LEGUT — VSB-Technical University of Ostrava, 17. listopadu 15/2172, 708 33 Ostrava, Czech Republic

We investigate electronic structure and lattice dynamics of thorium and actinium within density function theory. Recently, Actinium (Ac) shows excellent potential in radiotherapy and Thorium (Th) appears to be a suitable substitution for uranium in novel nuclear fuels. Therefore, we determined the effect of spin-orbit interaction (SOI) for the electronic, elastic, phonon and thermodynamic properties of number of Ac phases (*hcp*, *bcc*, *fcc*, and *sc*). Similarly, in the case of Th in addition to SOI we investigated also localized versus itinerant behavior of the *f* electrons. Therefore we applied so-called Hubbard parameter U in the range of 0.5-2 eV for the Th *5f* electrons. Next, we calculated the elastic tensor by the linear-response method as implemented in VASP code to determine elastic constants (C_{ij}). Subsequently, the criteria of stability based on C_{ij} were evaluated. Subsequently, we calculated vibrational properties using the direct force-constant method as implemented in the PHONOPY code. Actinium phase transition is discussed within the quasi-harmonic approximation under temperature and pressure. Our calculated mechanical and thermodynamic properties of Th are in good agreement with experimental data and for the Ac element serve as prediction. This work was supported by CSF grant No. 17-27790S and project No. CZ.02.1.01/0.0/0.0/16_013/0001791.