O 6: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - I

Monday 10:30–13:00 GER 38

Talk O 6.1 Mon 10:30 GER 38

DFT wants U: Embedded-cluster calculations of surface oxygen vacancies at TiO_2 with Hubbard-corrected DFT — •Matthias Kick, Karsten Reuter, and Harald Oberhofer — Technische Universität München

Surface oxygen vacancies, in particular their nature as charge trapping centers, play an inportant 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 TiO_2 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.

Full DFT+U functionality has been implemented in the all-electron electronic structure code FHI-aims. Combined with the solid state (QM/MM) embedding functionality in FHI-aims, this yields a numerically most efficient approach to treat aperiodic aspects at oxide surfaces. We illustrate this by calculating neutral and charged states of the surface oxygen vacancy at rutile TiO_2 (110). We systematically assess the reliability and computational efficiency by comparing to hybrid-level DFT calculations and calculations performed in conventional supercells.

Talk O 6.2 Mon 10:45 GER 38

Hubbard interactions from density-functional perturbation theory — •Iurii Timrov, Matteo Cococcioni, and Nicola Marzari — Theory and Simulation of Materials (THEOS), and NCCR-MARVEL, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

DFT+U, together with its V and J extensions, is a simple and powerful tool to model systems containing partially-filled manifolds of localized states [1]. However, the Hubbard parameters are often - and in our view incorrectly - treated semi-empirically. Conceptual and practical methods to determine e.g. the Hubbard U parameter have nevertheless been introduced long ago, based either on the constrained random-phase approximation (cRPA) or on linear-response theory [2]. These approaches make DFT+U a fully first-principles and self-contained method, but are often overlooked due to their cost or complexity. Here, we introduce a computationally inexpensive and straightforward approach to determine the linear-response U, hitherto obtained from the difference between bare and self-consistent inverse electronic susceptibilities evaluated from supercell calculations. By recasting these calculations in the language of density-functional perturbation theory we remove the need of supercells, and allow for a fully automated determination of susceptibilities and Hubbard parameters. Such developments open the way for deployment in high-throughput studies, while providing the community with a simple tool to calculate consistent values of U for any system at hand. [1] V. Anisimov et al., PRB 44, 943 (1991), [2] M. Cococcioni et al., PRB 71, 035105 (2005).

Talk O 6.3 Mon 11:00 GER 38

Time-evolution using full configuration interaction quantum Monte Carlo — •Kai Guther[1], Werner Dobrautz[1], Olle Gunnarsson[1], and Ali Alavi[1,2] — [1]Max-Planck Institute for Solid State Research, Stuttgart, Germany — [2]University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom

We report on a new method to perform real-time quantum evolution of a fermionic system using the full configuration interaction quantum Monte Carlo method [1]. To stabilize the algorithm, a slow simultaneous imaginary-time evolution is performed, yielding properties for times slightly rotated into the complex plane.

We employ this technique to compute Green's functions and therefore by means of analytic continuation also spectral weight functions. We demonstrate the applicability of the algorithm using the examples of the 2D-Hubbard model and the carbon dimer, showing that the algorithm can in principle be used as an Anderson solver for DMFT and is capable of obtaining photoemission spectra of ab-initio systems.

[1] G.H. Booth, A.J.W. Thom and A. Alavi, J. Chem. Phys. 131, 054106 (2009)

Talk O 6.4 Mon 11:15 GER 38

Laplace-transformed MP2 with localized Resolution of Identity for molecular and periodic systems — •Arvid Ihrig, Igor Ying Zhang, and Matthias Scheffler — Fritz-Haber-Institut, Berlin, Germany

The self-interaction error is a well-known problem in (semi)local functionals in density-functional theory (DFT) and to a lesser extend also in hybrid functionals. It leads to a quantitatively and sometimes even qualitatively wrong description. One possible remedy is the 2nd order Moller-Plesset perturbation theory (MP2) and the double-hybrid DFT methods based on it. However, the time and memory requirements prevent their routine-usage for large molecular and condensed-matter systems.

In this work we combine our localized Resolution of Identity (RI-LVL) [1] and its favourable memory requirements with the low-order scaling of the Laplace-transformed MP2 (LT-MP2) [2]. Our highly parallelizable LT-MP2 implementation in a numeric atom-centered orbital (NAO) framework allows us to treat both cluster and periodic models in the same computational environment. We demonstrate the accuracy and other features of our implementation for examples of water clusters and TiO_2 surfaces with small absorbed molecules. We furthermore present a way how the distance-dependent integral screening [3] from the Ochsenfeld group can be generalized to periodic systems.

[1] Ihrig et al., New J. Phys. 17, 093020 (2015)
[2] P. Ayala et al., J. Chem. Phys. 110, 3660 (1999)
[3] S. Maurer et al., J. Chem. Phys. 136, 144107 (2012)

Talk O 6.5 Mon 11:30 GER 38

Bond Disproportionation in Rare-Earth Nickelates: Describing Lattice Distortions within DFT+DMFT — •Alexander Hampel and Claude Ederer — Materials Theory, ETH Zürich, Switzerland

Perovskite rare-earth nickelates, $R\mathrm{NiO_3}$, display a rich and only partially understood phase diagram, where all compounds with R from Pr to Lu undergo a metal-insulator transition (MIT), that is accompanied by a structural distortion. This distortion breaks the symmetry between formerly equivalent Ni sites and can (in the simplest picture) be understood as a charge disproportionation of the Ni^{3+} cations into Ni^{2+} and Ni^{4+}. Here, we use density functional theory (DFT) and its extensions (DFT+U, DFT+DMFT) combined with symmetry-based distortion mode analysis to explore the interplay between lattice distortions, magnetic order and electronic correlation effects in rare-earth nickelates. Thereby, we want to explore the capabilities of the DFT+DMFT method to describe complex materials with coupled electronic and structural degrees of freedom by comparing with DFT+U results and available experimental data.

Talk O 6.6 Mon 11:45 GER 38

Density matrix embedding theory for coupled fermion-boson systems — •Teresa E. Reinhard[1], Uliana Mordovina[1], Heiko Appel[1], Joshua S. Kretchmer[2], Garnet K. L. Chan[2], and Angel Rubio[1,3] — [1]Max Planck Institut für Struktur und Dynamik der Materie, Hamburg — [2]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena — [3]Nano-bio Spectroscopy Group and ETSF, Departamento de Fisica de Materiales, Universidad del Pais Vasco UPV/EHU, San Sebastian

We analyze strongly correlated fermion-boson systems by extending Density Matrix Embedding Theory (DMET) from the purely electronic case [1] to coupled fermion-boson systems. DMET is a novel embedding theory which uses the Schmidt decomposition to divide the treated system into an impurity and a bath part. We project the bath part into the part of the Fock space that contains the entanglement with the impurity region and then solve this much smaller entangled system with exact diagonalization and DMRG.

With this technique, we treat lattice systems of Hubbard-Holstein type, where fermions and bosons are coupled by a bilinear Froehlich coupling. As we choose coherent states for the bosonic basis set, it is convenient to apply our approach to electron-phonon as well as to electron-photon systems.

By using a DMRG solver for the DMET algorithm, an accurate treatment of 2 dimensional systems becomes feasible.

[1] G. Knizia, G. K.-L Chan, Phys. Rev. Lett 109, 186404, (2012)

Talk O 6.7 Mon 12:00 GER 38

Vertex function of homogeneous electron gas — •Yaroslav Pavlyukh — Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, P.O. Box 3049, 67653 Kaiserslautern, Germany — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

We present a systematic study of the vertex function correction in homogeneous electron gas at metallic densities [1]. Contrary to a popular belief the vertex function not only provides corrections to the well known plasmon or particle-hole pair scatterings, but also gives rise to new physical processes such as generation of two plasmon excitations or the transformation of the initial one-particle state into a two-particles-one-hole state. Using a merger of the many-body perturbation and scattering theories, which is a distinct feature of our method, it is shown that additional scattering channels are responsible for the bandwidth reduction (as observed in photoemission experiments on bulk sodium), appearance of the secondary plasmonic satellite below the Fermi level and lead to a substantial modification of the electron spectral function.

[1] Y. Pavlyukh, A.-M. Uimonen, G. Stefanucci, R. van Leeuwen, Phys. Rev. Lett. **117**, 206402 (2016)

Talk O 6.8 Mon 12:15 GER 38

Coupled-Cluster approaches for molecules and solids in the numeric atom-center orbital framework — •Tonghao Shen, Igor Ying Zhang, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, DE

As a well-established and successful wave-function theory hierarchy in quantum chemistry, the coupled-cluster (CC) ansatz is attracting increasing attention in computational materials science [1]. However, compared to traditional density-functional approximations, CC approaches face much greater challenges regarding numerical implementation, bassis-set accuracy and efficiency, in particular for solids [2]. In this report, we present a highly parallel implementation of the CC approaches with singles, doubles and perturbative triples, CCSD(T), in the numeric atom-center orbital (NAO) framework. This implementation allows CCSD(T) simulations to be carried out using both cluster and periodic models in a single computational environment. Taking some popular quantum-chemistry test sets (S22, ISO34, and CYCONF), we demonstrate that CCSD(T) with correlation-consistent NAO basis sets [3] can provide accurate reference data for molecular properties. Our solid-state examples include elemental and binary crystals, as Ne (fcc), C, Si (diamond), LiF, MgO (rocksalt), and BN (zincblende).

Talk O 6.9 Mon 12:30 GER 38

Implementation of the SU(2) Symmetry in FCIQMC using the Graphical Unitary Group Approach — •Werner Dobrautz[1] and Ali Alavi[1,2] — [1]Max-Planck-Institut für Festkörperforschung — [2]Department of Chemistry, University of Cambridge

The Full Configuration Interaction Quantum Monte Carlo (FCIQMC) algorithm [1] is a projector QMC method, previously formulated in the total anti-symmetric space of Slater Determinants, based on the imaginary-time Schrödinger equation to obtain the ground state of a system in the long-time limit.

By formulating the method in eigenfunctions of the $\hat{S}^2$ spin-operator via the Graphical Unitary Group Approach [2] we can make use of the block-diagonal form of spin-preserving, non-relativistic Hamiltonians for different values of the total spin. This allows us to lift possible near degeneracies of low-lying excitations of different spin sectors, calculate spin-gaps more easily and obtain the physical correct ground-state, without spin-contamination, and identify its total spin quantum number.

Our method does not rely on expanding the spin-eigenfunctions in linear combinations of Slater Determinants and thus does not hit an exponential bottle neck and can be applied to system sizes larger than previously reachable with similar approaches.

[1] G. Booth, A. Thom and A. Alavi, J. Chem. Phys. **131**, 054106 (2009)
[2] I. Shavitt, Int. J. Quantum Chem. Symp., **11:** 131 (1977); Int. J. Quantum Chem. Symp., **12:** 5 (1978)

Talk O 6.10 Mon 12:45 GER 38

A study of the dense uniform electron gas with high orders of coupled cluster — •Verena Andrea Neufeld and Alex James William Thom — University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom

We used the recently developed stochastic coupled cluster method [Phys. Rev. Lett. (2010) 105, 263004 and J. Chem. Phys. (2016) 144, 084108] to benchmark the dense uniform electron gas (UEG). The aim was to make predictions about what truncation level of coupled cluster is needed to reach sufficient accuracy in electronic correlation energies for a range of electron densities. This will aid our future studies of solids with stochastic coupled cluster.

We take advantage of sparsity in wavefunctions by doing coupled cluster stochastically. In this study, we used coupled cluster truncation levels up to CCSDTQ5, that includes single, double, triple, quadruple and quintuple excitations directly. We considered the 14 electron UEG with Wigner-Seitz radius in the range 0.5 to 5.0 a.u.. We applied coupled cluster truncations from CCSD to CCSDTQ5 and extrapolated to the complete basis set size limit. By comparing the differences in energy calculated with CCSD to CCSDTQ5, we learn what truncation level is necessary for sufficient accuracy. What truncation level is needed, is dependent on the level of correlation, which decreases with electron density. We are therefore able to relate the degree of correlation linked to electron density to the level of coupled cluster needed for accuracy. This information will prove valuable when tackling periodic solids that can be approximated by the UEG.

O 13: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - II

Monday 15:00–18:15 GER 38

Invited Talk O 13.1 Mon 15:00 GER 38

Towards efficient orbital-dependent density functionals for weak and strong correlation — •Igor Ying Zhang[1], Patrick Rinke[1,2], John P. Perdew[3], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut, Berlin, Germany — [2]Aalto University, Finland — [3]Temple University, USA

We present a new paradigm for the design of exchange-correlation functionals in density-functional theory [1]. Electron pairs are correlated explicitly by means of the recently developed second order Bethe-Goldstone equation (BGE2) approach [2]. Here we propose a screened BGE2 (sBGE2) variant that efficiently regulates the coupling of a given electron pair. sBGE2 correctly dissociates H_2 and H_2^+, a problem that has been regarded as a great challenge in density-functional theory for a long time [3]. The sBGE2 functional is then taken as a building block for an orbital-dependent functional, termed ZRPS, which is a natural extension of the PBE0 hybrid functional. While worsening the good performance of sBGE2 in H_2 and H_2^+, ZRPS yields a remarkable and consistent improvement over other density functionals across various chemical environments from weak to strong correlation. [1] IY Zhang et al., Phys. Rev. Lett. 117, 133002 (2016); [2] IY Zhang et al., New J. Phys. 18 073026 (2016); [3] AJ Cohen et al., Chem. Rev. 112 289 (2011).

Talk O 13.2 Mon 15:30 GER 38

Towards a functional for strong correlation via semiclassical model for the indirect energy and local interpolation along the adiabatic connection — •Stefan Vuckovic and Paola Gori-Giorgi — Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling, FEW, Vrije Universiteit, De Boelelaan 1083, 1081HV Amsterdam, The Netherlands

Finding an approximate XC functional that is able to capture strong correlation effects is a big, unsolved DFT challenge. Even a bigger challenge is to find a functional able to treat any correlation regime successfully. We attempt to construct an XC functional that has no bias towards a particular correlation regime by using a local interpolation along the adiabatic connection between the weak and the strong coupling limit of DFT. [1] In addition to this approach, I will also present our semiclassical model for accurate indirect energies. I will

discuss how this model can be used for a construction of XC functionals, exploiting its XC energy density in the conventional gauge, the one of the electrostatic potential of the XC hole.

1. Stefan Vuckovic, Tom J. P. Irons, Andreas Savin, Andrew M. Teale, and Paola Gori-Giorgi, Journal of Chemical Theory and Computation 2016, 12 (6), 2598-2610

Talk O 13.3 Mon 15:45 GER 38

Benchmark of *GW* approaches for the *GW*100 test set — •Patrick Rinke[1], Matthias Dauth[2], Fabio Caruso[3], and Michiel van Setten[4] — [1]COMP Centre of Excellence, Aalto University, Finland — [2]University of Bayreuth, Germany — [3]University of Oxford, England — [4]Université Catholique de Louvain, Belgium

Many-body theory in the *GW* approach has become the method of choice for calculating charged excitations in solids. Now it is increasingly being applied to molecules, but fundamental questions regarding its *modus operandi* and its accuracy remain. To address both of these aspects, we present a comprehensive assessment of different *GW* methodologies for the recent *GW*100 test set [1] of molecular ionization energies [2]. We compare our *GW* calculations to coupled-cluster singles, doubles, and perturbative triples [CCSD(T)] reference data for *GW*100. We find ionization energies of fully self-consistent *GW* and quasiparticle self-consistent *GW* in excellent agreement with CCSD(T), with discrepancies typically smaller than 0.3 eV and 0.2 eV, respectively. For partially self-consistent and perturbative *GW* the deviation from CCSD(T) is strongly dependent on the starting point. An optimal starting point is found by minimizing the deviation from the straight-line error [3], which concomitantly yields a systematic improvement of the ionization energies. [1] M. J. van Setten, P. Rinke, *et al.*, J. Chem. Theory Comput. **11**, 5665 (2015), [2] F. Caruso, M. Dauth, M. J. van Setten, and P. Rinke, J. Chem. Theory Comput. **12**, 5076 (2016), [3] M. Dauth, F. Caruso, S. Kümmel, and P. Rinke, Phys. Rev. B **93**, 121115(R) (2016).

Talk O 13.4 Mon 16:00 GER 38

Addressing electron-hole correlation in core excitations of solids: A first-principles all-electron approach based on many-body perturbation theory — •Christian Vorwerk, Caterina Cocchi, and Claudia Draxl — Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

In the framework of an all-electron implementation of many-body perturbation theory, we investigate K, $L_{2,3}$, and M_4 absorption edges of three exemplary solids, spanning a broad range of transition energies from a few hundred to several thousands eV. We find that transitions from deep core states, such as the Ti 1*s* states in TiO_2 and the Pb 3*d* states in PbI_2, are ruled by the long-range electron-hole attraction. Spin-orbit coupling and local fields play only a minor role for these excitations, which occur at several keV. The exchange interaction between the excited electron and the core hole becomes more relevant for smaller transition energies, as exemplified with the Ca $L_{2,3}$ edge in CaO. The overlap between Ca 2*p* and 3*d* states calls for a careful treatment of local field effects in order to describe these excitations. Our results, in good agreement with the available experimental data, are thoughtfully analyzed with advanced visualization tools in order to further gain insight into the electronic contributions and the spatial extension of the resulting electron-hole pairs.

Talk O 13.5 Mon 16:15 GER 38

Non-linear-screening contributions to photoemission spectra — •Marilena Tzavala[1,2], Claudia Rödl[1,2,3], and Lucia Reining[1,2] — [1]Laboratoire des Solides Irradiés, École polytechnique, CNRS, CEA, Université Paris-Saclay, 91128 Palaiseau, France — [2]European Theoretical Spectroscopy Facility (ETSF) — [3]Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

The state-of-the-art approach to calculate photoemission spectra of a broad range of materials is many-body perturbation theory in the *GW* approximation, sometimes combined with a cumulant expansion. The effective interaction that appears in these approaches is screened within the linear-response approximation. However, the photoemission of a core electron or a localized valence electron may be a strong perturbation, which suggests that non-linear screening effects could be important. We propose a formulation of the functional relations between the one-body Green's function and the screened interaction which is an alternative to Hedin's equations and which explicitly displays non-linear screening. Using a simple model, we show that exchange-correlation contributions are crucial in order to capture the non-linear effects. We also discuss how to apply the scheme to real materials using time-dependent density-functional theory (TDDFT).

Talk O 13.6 Mon 16:30 GER 38

Dynamic LDA for electronic excitations — •Marco Vanzini[1,2], Matteo Gatti[1,2,3], and Lucia Reining[1,2] — [1]Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA, Université Paris-Saclay, 91128 Palaiseau, France — [2]European Theoretical Spectroscopy Facility (ETSF) — [3]Synchrotron SOLEIL, L'Orme des Merisiers, BP 48 Saint-Aubin, 91192 Gif sur Yvette, France

Density Functional Theory is an extremely useful tool for dealing with ground state properties such as the density or total energy. Kohn–Sham eigenvalues are often considered as approximated electronic excitations, but the resulting spectra are poor.

We propose a generalization of the Kohn–Sham approach to address in an exact framework electron addition and removal spectra. They can be measured by photoemission experiments, and can be evaluated using a computationally expensive non–local Self Energy. Our method is instead based on a frequency–dependent *local* potential [1], which significantly reduces the computing time of an ab–initio calculation.

To find this spectral potential in practice, we propose a jellium–based *dynamical* local density approximation (dynLDA): it relates the unknown potential to its homogeneous counterpart, via a non–trivial connector in space and frequency, which is based on physical insight.

In this talk, I will discuss the achievements and the limits of dynLDA, using models and real solids.

[1] M. Gatti et al., Phys. Rev. Lett. **99**, 057401 (2007).

Talk O 13.7 Mon 16:45 GER 38

Recent developments of the Sternheimer-GW method — •Martin Schlipf[1], Henry Lambert[1,2], and Feliciano Giustino[1] — [1]Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom — [2]Department of Physics, King's College London, London WC2R 2LS, United Kingdom

The GW many-body perturbation method is an important tool to access accurate band gaps from first principles calculations. The conventional implementation determines the Green's function and the screened Coulomb interaction by a summation over unoccupied states tedious to converge. Giustino et al. demonstrated an alternative method to obtain these quantities by solving Sternheimer linear response equations. In this poster, we present our Sternheimer-GW software implemented in the Quantum Espresso framework and highlight some recent advances regarding the precision and stability of the method. We present our results for a small set of semiconducting materials and compare these to results obtained with conventional GW codes. We illustrate on selected examples the complete frequency dependent self energy, which is a natural product of the Sternheimer-GW method, and can be directly compared to experimental angle-resolved photoemission spectroscopy (ARPES) experiments.

Talk O 13.8 Mon 17:00 GER 38

Calculating electronic correlations in the CASTEP ab initio code — •Vincent Sacksteder[1] and Evgeny Plekhanov[2] — [1]W155 Wilson Building, Royal Holloway University of London, Egham Hill, Egham, TW20 0EX, — [2]Kings College London

We present new DMFT and GW features in the CASTEP DFT code. These features are designed to provide more accurate treatment of correlations between localized orbitals, of electronic screening, and of excited states. In present benchmarks on Cerium Oxide, the gamma phase of Cerium, and Silicon. We discuss the calculation of atomic forces within the GW framework.

Talk O 13.9 Mon 17:15 GER 38

Efficient G_0W_0 using localized basis sets: a benchmark for molecules — •Peter Koval[1,2], Mathias Per Ljungberg[1], and Daniel Sánchez Portal[1,2] — [1]Donostia International Physic Center, San Sebastian, Spain — [2]Centro de Fisica de Materiales, San Sebastian, Spain

Electronic structure calculations within Hedin's *GW* approximation are becoming increasingly accessible to the community. In particular, as it has been shown earlier and we confirm by calculations using our **MBPT_LCAO** package [1], the computational cost of the so-called G_0W_0 can be made comparable to the cost of a regular Hartree-Fock calculation. In this work, we study the performance of our new G_0W_0 implementation based on a contour deformation technique to reproduce the ionization potentials of all 117 closed-shell molecules belonging to the G2/97 test set, using a pseudo-potential starting point provided by the popular density-functional package **SIESTA** [2]. Moreover, the ionization potentials and electron affinities of a set of 24

acceptor molecules [3] are compared to experiment and to reference all-electron calculations.

[1] http://mbpt-domiprod.wikidot.com; [2] Soler J. M., *etal* J. Phys.: Condens. Matter **14** (2002) 2745; [3] Knight J. W., *etal* J. Chem. Theory Comput., **12** (2016) 615.

Talk O 13.10 Mon 17:30 GER 38

A dynamic exchange correlation kernel derived from recent results for the homogeneous electron gas — •Martin Panholzer, Matteo Gatti, and Lucia Reining — Laboratoire des Solides Irradies UMR 7642, CNRS-CEA/DSM, Ecole Polytechnique, Palaiseau, France

Time-Dependent Density Functional Theory (TDDFT) is a method of choice to calculate the dynamic structure factor of a wide range of materials. Even in the simplest Adiabatic Local Density Approximation (ALDA), plasmon spectra are generally well described. However, several shortcomings remain. In particular, the onset energy of the spectrum is underestimated [1], and dynamical effects such as lifetime damping and double plasmon excitations are absent [2].

In this work we investigate recent results for the dynamic response of the homogeneous electron gas (HEG)[3] to extract an exchange correlation kernel for TDDFT. In order to get an estimate of the validity of such an approach we compare our results for the dynamic kernel $f_{xc}(q,\omega)$ for the HEG with different kernels and known exact properties. We implemented this kernel with the simplest connection between the HEG and the real material, the mean density approximation. We compare results on simple metals, such as Na and Al, with experiments and ALDA. In order to explore the validity of such an approach we also applied the kernel to Si.

[1] G. Onida et al., Rev. Mod. Phys. 74, 601 (2002)
[2] M. Cazzaniga et al., Phys. Rev. B 84, 075109 (2011)
[3] H. M. Böhm et al., Phys. Rev. B 82, 224505 (2010)

Talk O 13.11 Mon 17:45 GER 38

Benchmark calculations of the electronic structure for molecules from the second-Born self-energy — •Michael Schüler[1] and Yaroslav Pavlyukh[1,2] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany — [2]Department of Physics and Research Center OPTIMAS, University of Kaiserslautern, P.O. Box 3049, 67653 Kaiserslautern, Germany

The non-equilbrium Green's function (NEGF) formalism provides a state-of-the-art tool for modeling modern spectroscopic experiments. In particular, time-dependent problems can be treated based on the Kadanoff-Baym equations. The underlying approximation to the self-energy has to be consistent with the treatment of the initial state - as captured by the Matsubara formalism - in order to guarentee the basic conservation laws. One of simplest non-trivial approximation to the self-energy is the second-Born approximation (2BA), which has been employed in numerous time-dependent studies. Systematic tests on the accuracy of the 2BA for various molecules has, however, been lacking so far. In our contribution we fill this gap by benchmark calculations for the 2BA for small molecules from the well established G2 test set. We demonstrate that the accuracy of the 2BA for predicting ionization potentials and electron affinities can compete with accurate quantum chemistry methods such as the Møller-Plesset perturbation theory and the coupled-cluster method. We also apply our method to a class of larger molecules, the diamonoids, which are in the focus of recent experiments and theoretical studies.

Talk O 13.12 Mon 18:00 GER 38

Performance of the GW approximation at reproducing key features in exact Kohn-Sham potentials — •Jack Wetherell[1], Leopold Talirz[1], Matt Hodgson[2], and Rex Godby[1] — [1]University of York, York, United Kingdom — [2]Max Planck Institute of Microstructure Physics, Halle, Germany

One of the major goals of the GW method is to improve the accuracy of charge densities produced by density functional theory (DFT). In this work we test the applicability of one-shot GW from various DFT starting Kohn-Sham orbitals. Also we implement and test the fully self-consistent GW method. We test the applicability of these methods by using them to compute densities for simple model 1D systems from which the exact density can be obtained by the direct solution of the Schrodinger Equation. We choose a set of test systems that are either dominated by exchange or correlation, or contain non-local steps in the exact exchange-correlation potential. Also we analyse systems dominated by electronic interaction. We can also investigate how accurate the exchange-correlation potentials associated with the GW densities are, using our reverse-engineering algorithm.

O 30: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - III

Tuesday 10:30–13:00 GER 38

Invited Talk O 30.1 Tue 10:30 GER 38

Including spin effects in the strong-coupling limit of DFT — •Paola Gori-Giorgi[1], Juri Grossi[1], Derk Pieter Kooi[1], Klaas Giesbertz[1], Michael Seidl[1], Aron Cohen[2], and Paula Mori-Sanchez[3] — [1]Vrije Universiteit Amsterdam, The Netherlands — [2]University of Cambridge, UK — [3]Universidad Autonoma de Madrid, Spain

The exact strong-coupling limit of density functional theory (DFT) reveals a different mathematical structure with respect to the one of traditional approximations for the exchange-correlation (xc) functional: instead of the local density, local density gradients, or quantities related to the Kohn-Sham orbitals, some integrals of the density appear in this limit. In the recent years, xc functionals directly inspired to this mathematical structure have been constructed and implemented in an efficient way. However, the leading terms (exact or approximate) in the strong-coupling limit of DFT are intrinsically semiclassical and, as such, do not incorporated the spin dependence. In this talk, I will present the first study on the incorporation of the spin-dependence in the exact strong-coupling limit in simple one-dimensional cases. I will then discuss approximations for our findings and routes to the construction of spin-dependent xc functionals for strong coupling. Comparison with exact calculations for the Hohenberg-Kohn functional in the strong-coupling regime confirms the accuracy of our expressions for the leading terms.

Talk O 30.2 Tue 11:00 GER 38

Strong correlation from the Random Phase Approximation and beyond — •Thomas Olsen and Kristian Thygesen — Department of Physics, Technical University of Denmark

We assess the performance of the Random Phase Approximation (RPA) for strongly correlated systems and discuss different routes to venture beyond RPA. It is well-known that RPA reproduces the dissociation curve of molecular H2 correctly and thus accurately captures the strong static correlation inherent in the dissociation limit. It is thus natural to ask whether RPA is able to describe the strongly correlated Mott insulators as well. In particular, the accurate description of antiferromagnetic systems is complicated by the fact that the magnetic order often emerges from a detailed interplay between direct exchange and super-exchange couplings, which are respectively exchange and correlation effects. Whereas DFT+U, semi-local and hybrid functionals are often capable of describing either exchange or super-exchange accurately, RPA is shown to give an accurate account of both. We will finally show that RPA can be improved by either including non-local kernel in the framework of TDDFT or including electron-hole interactions in the irreducible response function. Only the latter approach improves the description of strong correlation, whereas the former approach improves atomization energies significantly compared to RPA.

Talk O 30.3 Tue 11:15 GER 38

Surface and adsorption energy calculations within the random phase approximation — •Per Schmidt and Kristian Thygesen — Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

The application of density functional theory (DFT) to the calculation of adsorption and surface energies is ever increasing and as a theory, it has the potential to e.g. guide experiments in the search of better catalysts. However, a previous study[1] shows that with standardly used semi-local functionals, DFT is not able to accurately predict surface and adsorption energies simultaneously. By tuning the functional, either the predicted surface or adsorption energies can be improved

at the expense of the other. For a few cases however, it has been shown[1] that the many-body approach, the random phase approximation (RPA), yields both excellent surface and adsorption energies.

In this work we expand the use of the RPA method to eight adsorption reactions over 20 transition metal surfaces using the electronic structure code GPAW. We report the difference in surface and adsorption energies compared with the standard DFT functionals: PBE, RPBE and BEEF-vdW. We find that RPA does in general predict less stable surfaces, in better agreement with experiments and the average change in adsorption energies varies between ± 0.5 eV. The RPA values could be used to guide construction of new density-functionals aimed at improving surface science calculations.

[1] L. Schimka, J. Harl, A. Stroppa, A. Grüneis, M. Marsman, F. Mittendorfer, and G. Kresse, Nature Materials 9, 741 (2010).

Talk O 30.4 Tue 11:30 GER 38

Large-scale cubic-scaling RPA correlation energy calculations using a Gaussian basis — •Jan Wilhelm and Jürg Hutter — University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

The random phase approximation (RPA) for computing the electron correlation energy has emerged as an accurate tool for predicting the properties of molecules and condensed phase systems. RPA combines a number of attractive features, most importantly that long-range van der Waals interaction is included, in contrast to semilocal density functionals. The drawback connected with RPA is the computational cost: For canonical implementations of RPA, the numerical effort grows as quickly as $O(N^4)$ with the system size N. We present an algorithm for computing the RPA correlation energy in a Gaussian basis requiring $O(N^3)$ operations and $O(N^2)$ memory. The cubic-scaling RPA method is based on the resolution of the identity (RI) with the overlap metric, a reformulation of RI-RPA in the Gaussian basis and imaginary time as well as the use of sparse linear algebra. We report a massively parallel implementation which is the key for the application to large systems. As first benchmark of the method, we show the RPA correlation energy of thousands of water molecules in a high-quality cc-TZVP basis. For a comparison, the canonical RPA method is restricted to 500 water molecules using the whole Piz Daint supercomputer for two hours. Our RPA algorithm enables the application of RPA to large systems where van der Waals interactions play an important role, e.g. for predicting the adsorption energy of large molecules on surfaces.

Talk O 30.5 Tue 11:45 GER 38

Semi-local exchange functionals showing ultranonlocal response: the hope to replace exact exchange — •Thilo Aschebrock and Stephan Kümmel — Theoretical Physics IV, University of Bayreuth, D-95440 Bayreuth, Germany

The widespread success of Density Functional Theory (DFT) is based on a favorable ratio of accuracy to computional cost, especially with semi-local approximations to the exchange-correlation energy. However, functionals such as the local density approximation (LDA), generalized-gradient approximations (GGA) or meta-generalized-gradient approximations (meta-GGA), typically miss important exact exchange features related to the derivative discontinuity. These are essential for accurately describing long-range charge transfer processes. The electrical response of molecular chains, which is dramatically overestimated by local and semi-local density functionals, is a prime example. The key to its correct description is a term in the Kohn-Sham exchange potential that counteracts the external field and has been named "ultranonlocal". We here present how these field-counteracting properties can be incorporated into semi-local DFT on the meta-GGA level. Thereby we show that by utilizing the kinetic-energy-density, it is possible to model ultranonlocal effects in the Kohn-Sham potential by virtue of a semi-local energy expression.

Talk O 30.6 Tue 12:00 GER 38

(De)stabilizing dispersion interactions via external electric charges — •Andrii Kleshchonok[1] and Alexandre Tkatchenko[1,2] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — [2]Physics and Materials Science Research Unit, University of Luxembourg, L-1511 Luxembourg

Van der Waals (vdW) or dispersion interactions play a central role in the structure, stability, and reaction mechanisms in large variety of molecules and materials. However, in many situations of interest in material science and biophysics, vdW interactions should account for the coupling with external (in)homogeneous electric fields. In this work we address the effect of external static charge field on long-range electron correlations. By using the quantum Drude oscillator model, we derive analytical expressions of the charge induced dipole-quadrupole dispersion energy, that is accounted neither in standard DFT methods, nor in popular vdW correction schemes. Analysing the scaling laws of this dispersion term, we conclude that positive charge stabilizes dispersion interactions, while a negative charge has an opposite effect. Benchmark over S22 molecular dataset estimates the induced dispersion to be in the range of 20-300 % of conventional electrostatic energy. Our findings could have broad potential implications, including exfoliation of 2D materials, chemical reaction rates in charged droplets, and biological membranes.

Talk O 30.7 Tue 12:15 GER 38

An optimisability proof for self-consistent constrained DFT, and its implications for constraint-based 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.

We develop the connection between constrained DFT energy derivatives and response functions, providing a rigorous assessment of the uniqueness and character of cDFT stationary points while accounting for electronic interactions and screening [1]. In particular, we provide a non-perturbative proof that stable stationary points of linear density constraints occur only at energy maxima with respect to their Lagrange multipliers, generalizing the proof of Ref. [2]. We demonstrate that multiple solutions, hysteresis, and energy discontinuities may occur in cDFT, and we provide necessary conditions for the optimizability of multi-constraint cDFT. We show that the applicability of cDFT in automating symmetry-preserving self-interaction error corrections is limited by a fundamental incompatibility with non-linear constraints. We circumvent this by utilizing separate linear and quadratic correction terms, which may be interpreted either as distinct constraints, each with its own Hubbard U type Lagrange multiplier, or as the components of a generalized, two-parameter DFT+U functional [3]. [1] Phys. Rev. B **94**, 035159 (2016). [2] Phys. Rev. A **72**, 024502 (2005). [3] Phys. Rev. B Rapid Comms., Accepted (2016), arXiv:1608.07320.

Talk O 30.8 Tue 12:30 GER 38

Density-based local hybrid functional for interfaces — •Pedro Borlido[1], Silvana Botti[1], and Miguel Marques[2] — [1]Institu für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743, Jena, Germany — [2]Instiut für Physik, Martin-Luther-Universität Halle Wittenberg, D-06099 Halle, Germany

Hybrid functionals in density functional theory have become the state-of-the-art for the calculation of electronic properties of solids. The key to their performance is how and in which amount a part of Fock exchange is mixed with semi-local exchange-correlation functionals. We propose here a material dependent and local mixing parameter which is a functional of the electron density alone, through an estimator of the local dielectric function inspired by the work done in *Phys. Rev. B* 83, 035119 (2011). This new functional is by construction an approximation of the *GW* self-energy and it enables therefore calculations of quasiparticle energy levels of comparable quality as *GW*, but at the reduced cost of a hybrid density functional. In contrast with other recent self-consistent schemes for the mixing parameter, our approach does not require to calculate the dielectric function and leads to a negligible increase of the computation time.

Talk O 30.9 Tue 12:45 GER 38

On the hunt for better functionals in DFT: a new quantum embedding scheme — •Uliana Mordovina[1], Teresa E. Reinhard[1], Heiko Appel[1], and Angel Rubio[1,2] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — [2]Nano-bio Spectroscopy Group and ETSF, Departamento de Fisica de Materiales, Universidad del Pais Vasco UPV/EHU, San Sebastian, Spain

We propose a new systematic technique to derive functionals for standard density functional theory (DFT) in an ab-initio fashion. This technique origins in the recently developed density-matrix embedding theory (DMET) [1]. DMET is a quantum-in-quantum embedding method, which is based on finding a projection between the high-dimensional wave function of the full system and a lower-dimensional wavefunction living in the active space of the embedded system, which is then solved exactly. In the original DMET scope, the projection is improved via optimization of the reduced one-body density matrix. We replace this optimization by a density inversion, exploiting the one-to-one mapping between electronic density and Kohn-Sham potential.

Not only the DMET scheme is improved by the uniqueness of the

density-potential mapping, the proposed density-embedding also allows for finding accurate Kohn-Sham potentials. Moreover, unlike in usual DFT, we can systematically improve the description by increasing the size of the active space.

We show benchmark results of our method for molecules in 1D.

[1] G. Knizia, G. K.-L Chan, Phys. Rev. Lett 109, 186404, (2012)

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

Tuesday 18:30–20:30 P2-OG4

Poster 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.

Poster 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.

Poster O 65.3 Tue 18:30 P2-OG4

Conceptual problemsof 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)

Poster 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)

Poster 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.

Poster 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.

Poster 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 carbon 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).

Poster 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)

Poster 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 (□) are treated on the same footing, through a cluster expansion (CE) in the quasi-ternary Ge/Ni/□ 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.

Poster 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).

Poster 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

Poster 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 $\Sigma_{\text{eph}} = -i\frac{\hbar}{2\tau}$ we are able to compute the dressed propagator G by solving Dyson's equation $G = G_{\text{ref}} + G_{\text{ref}} \cdot \left(\Delta V + \Sigma_{\text{eph}}\right) \cdot G$, 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.

O 71: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - IV

Wednesday 10:30–13:00 GER 38

Invited Talk O 71.1 Wed 10:30 GER 38

Electronic excitations in 2D materials and heterostructures — •Kristian Sommer Thygesen — Technical University of Denmark, Lyngby, Denmark

Atomically thin two-dimensional (2D) materials have recently emerged as a new class of materials with unique and highly tunable optoelectronic properties. Different 2D crystals can be stacked to form van der Waals heterostructures (vdWH) where the individual 2D layers are held together by weak van der Waals forces leading to atomically well-defined interfaces. This fascinating scenario opens up the possibility of designing heterostructures with tailored electronic or optical properties. I will give a general introduction to the electronic properties of 2D materials, including characteristic features of their dielectric screening and collective excitations with special emphasis on the challenges related to their ab-initio description. I will show how the dielectric function of a given 2D material can be controlled by embedding it into a vdWH, and how this in turn can be used to control the band structure, exciton binding energies or the plasmon dispersion in 2D materials.

Talk O 71.2 Wed 11:00 GER 38

Charge and energy transport at the nanoscale: A DFT perspective — •Florian G. Eich, Fabio Covito, and Angel Rubio — Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, D-22761 Hamburg, Germany

Understanding the interplay between charge and energy transport at the nanoscale paves the way for novel thermoelectric devices, which may prove useful for the development for sustainable energy sources. However, concepts, such as heat flow, temperature and entropy are only well-established at the macroscopic level for slow dynamics. This raises the question about whether these concepts can be employed for small length and short time scales. We will present our recent efforts to use a time-dependent density-functional theory framework, dubbed nonequilibrium thermal DFT, in order to generalize temperature and heat or energy flow to the microscopic regime. To this end we will highlight the analogy of the formally exact microscopic equations of motion for charge density and energy density in thermal DFT to the macroscopic equations of motion of hydrodynamics. Furthermore, we will present first result using our approach to compute transient energy energy currents induced by a temperature gradient and show that in the steady-state limit persistent temperature oscillations develop.

Talk O 71.3 Wed 11:15 GER 38

Conductance of aromatic and antiaromatic molecular circuits — Narendra P. Arasu and •Héctor Vázquez — Inst. of Physics, Academy of Sciences of the Czech Rep., CZ

Molecular structures with delocalized conjugated orbitals play an essential role in molecular transport due to their high conductance and small attenuation factors. While much work has been done on aromatic molecules, some studies have shown that conductance actually decreases with aromaticity [1].

In this talk I will discuss the effect of (anti)aromaticity on conductance. I will show results of first-principles transport calculations for an aromatic-antiaromatic pair of molecules and compare with experiment. Conductance is calculated using DFT and NEGF including corrections to the DFT level positions. The corrected conductance values are in very good agreement with experiment. We find that the conductance of the antiaromatic molecule is much higher than that of its aromatic counterpart. Calculations show this to be a consequence of the smaller HOMO-LUMO gap of the antiaromatic complex as well as on the molecular level alignment at the junction [2].

[1] W. Chen, H. Li, J.R. Widawsky, C. Appayee, L. Venkataraman, and R. Breslow, J. Am. Chem. Soc. 136 918 (2014).

[2] S. Marqués-González, S. Fujii, J.-Y. Shin, H. Shinokubo, N.P. Arasu, H. Vázquez and M. Kiguchi, (to be submitted).

Talk O 71.4 Wed 11:30 GER 38

Current-induced cooling of Carbene-based molecular junctions: role of electrodes structure — •Giuseppe Foti and Héctor Vázquez — Institute of Physics, Czech Academy of Sciences Cukrovarnicka 10, Prague 6

In this talk I will present our first principles calculations based on density functional theory (DFT) plus Nonequilibrium Green's functions (NEGF) of the current-induced heating and cooling dynamics of a series of Carbene-based molecular junctions [1]. I will show how the atomistic details of electrode terminations have a strong impact on the heating dynamics of the junctions and how they can maximize the cooling of the system. In the cases where the molecule is attached to blunt leads and the electronic coupling to bulk states is strong the cooling efficiency of the most active vibrational modes decreases monotonically as bias increases. This results in the heating of the junction. On the other hand, when the molecule is connected to sharp electrode terminations such as chain-like structures, which can be formed experimentally when the metal-molecule bond is mechanically strong, and the electronic coupling to electrode states is weak, the cooling efficiency shows a non-monotonic behavior. It first decreases as a function of voltage but then increases at relatively high biases, effectively cooling down the junction [2]. These results reveal the important role of the atomistic structure of metal-molecule interface in the current-induced damping of localized molecular vibrations.

[1] Foti, G.; Vázquez, H. Nanotechnology 2016, 27, 125702.

[2] Foti, G.; Vázquez, H. submitted

Talk O 71.5 Wed 11:45 GER 38

DFTB-based recursive Green's function algorithms for electron transport in quasi-1D systems — •Fabian Teichert[1,2,4], Andreas Zienert[3,4], Jörg Schuster[4], and Michael Schreiber[2] — [1]Dresden Center for Computational Materials Science (DCMS), Dresden, Germany — [2]Institute of Physics, Technische Universität Chemnitz, Chemnitz, Germany — [3]Center for Microtechnologies (ZfM), Technische Universität Chemnitz, Chemnitz, Germany — [4]Fraunhofer Institute for Electronic Nano Systems (ENAS), Chemnitz, Germany

Within the last decades, quantum transport theory and density functional theory have become very important for predicting the electronic properties of new materials and future electronic devices.

We focus on the problem of improving quantum transport algorithms for large quasi-1D systems which are enormously time-consuming today. We combine the density functional tight binding (DFTB) approach with the recursive Green's function formalism (RGF), which is very effective for such systems. First, we show how to improve the RGF for the case of randomly distributed real defects. For this, we use the steps of the renormalization decimation algorithm (RDA), which is part of the electrode calculation. Second, we show how to improve the calculation of the surface Green's functions of electrodes which have a long unit cell. Here, we employ the decimation technique to reduce the dimensionality of the periodic Hamiltonian matrix, leading to effective matrices, which are treated by the RDA. Finally, we apply these algorithms to carbon nanotubes and present our results.

Talk O 71.6 Wed 12:00 GER 38

Conditions for formation of two-dimensional electron gas at the $LaFeO_3/SrTiO_3$ — •Igor Maznichenko[1], Sergey Ostanin[1], Arthur Ernst[2], Ingrid Mertig[1,2], Katayoon Mohseni[2], Holger L. Meyerheim[2], Eberhard K.U. Gross[2], Pengfa Xu[3], Wei Han[3], Philip M. Rice[3], Jaewoo Jeong[3], Mahesh G. Samant[3], and Stuart S.P. Parkin[2,3] — [1]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany — [3]IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, USA

The formation of a conducting two dimensional electron gas (2DEG) at the interface between two insulating oxide layers was explained theoretically for atomically and chemically abrupt interfaces via polar discontinuity.

Here we show that a 2DEG is formed at the interface between thin layers of lanthanum ferrite, $LaFeO_3$ (LFO), that are more than 3 unit cells thick, when grown epitaxially on $SrTiO_3$ (STO) (001). The interface property highly depends on the surface property of TiO_2 terminated STO. The interface is conducting if the STO is not annealed in an oxygen environment prior to the LFO growth, while insulating if the STO is annealed.

First principles calculations reveal that a 2DEG should be realized for an ideal interface but that modest chemical intermixing suppresses it. These calculations also show that the presence of oxygen vacancies supports 2DEG formation due to electronic doping.

Talk O 71.7 Wed 12:15 GER 38

Thermal Renormalization of the Electronic Structure: Trends across Chemical and Structural Space — •Honghui Shang[1], Christian Carbogno[1], Patrick Rinke[2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [2]Aalto University, Helsinki, Finland

Advances in electronic structure theory now allow us to compute the renormalization of the electronic structure due to thermal nuclear motion from first principles [1]. In this work, we present a systematic computational assessment of this renormalization for 82 octet binaries in both the zincblende and the rocksalt structure. After validating our computational approach that is based on finite-differences [2] and Fröhlich-type corrections [3] for polar materials, we discuss and analyze the observed trends: For instance, we find that most materials exhibit the expected band-gap reduction upon temperature increase; however, some materials (e.g. CuCl and CdO) do not follow this trend and exhibit the opposite behavior. We discuss the underlying electronic mechanism as well as its dependence on the chemical composition and structure of the material. In this context, also the sensitivity of such calculations with respect to the chosen basis set and exchange-correlation functional (LDA, PBE, HSE06) are critically investigated.

[1] F. Giustino, arXiv:1603.06965 (2016).
[2] G. Antonius, *et al. Phys. Rev. Lett.* **112**, 215501 (2014).
[3] J. P. Nery and P. B. Allen, *Phys. Rev. B* **94**, 115135 (2016).

Talk O 71.8 Wed 12:30 GER 38

Spin-wave excitations and electron-magnon scattering from many-body perturbation theory — •Mathias C.T.D. Müller, Christoph Friedrich, and Stefan Blügel — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

We study the spin excitations and the electron-magnon scattering in bulk Fe, Co, and Ni within the framework of many-body perturbation theory as implemented in the full-potential linearized augmented-plane-wave method. Starting from the *GW* approximation we obtain a Bethe-Salpeter equation for the magnetic susceptibility treating single-particle Stoner excitations and magnons on the same footing. Due to approximations used in the numerical scheme, the acoustic magnon dispersion exhibits a small but finite gap at Γ. We analyze this violation of the Goldstone theorem and present an approach that implements the magnetic susceptibility using a renormalized Green function instead of the non-interacting one, leading to a substantial improvement of the Goldstone-mode condition [1]. Finally, we employ the solution of the Bethe-Salpeter equation to construct a self-energy that describes the scattering of electrons and magnons. The resulting renormalized band structures exhibit strong spin-dependent lifetime effects close to the Fermi energy. We also see kinks in the electronic bands, which we attribute to electron scattering with spatially extended spin waves.

[1] Müller *et al.*, Phys. Rev. B **94**, 064433 (2016).

Talk O 71.9 Wed 12:45 GER 38

Charged supercells revised: Small Polarons in Oxides with proper account for long-range polarization — •Sebastian Kokott, Sergey V. Levchenko, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, DE

Formation of small polarons (excess charges localized within one unit cell) often determines charge mobility and optical absorption in oxide materials. In this work, we address two important challenges in the DFT description of small polarons: sensitivity to the errors in exchange-correlation (XC) treatment and finite-size effects in supercell calculations. The polaron properties are obtained using a modified neutral potential-energy surface (PES) [1]. Using the hybrid HSE functional and considering the whole range $0 \leq \alpha \leq 1$ of exact exchange, we show that the modified PES model significantly reduces the dependence of the polaron level and binding energy in MgO and TiO_2 on the XC treatment. It does not eliminate the dependence on supercell size. Based on Pekar's model [2], we derive the proper long-range behavior of the polaron and a correction that allows to obtain the polaron properties in the dilute limit (tested for supercells containing up to 1,000 atoms). The developed approach reduces drastically the computational time for exploring the polaron PES, and gives a consistent description of polarons for the whole range of α. It allows us to find a self-trapped hole in MgO that is noticeably more stable than reported previously.—[1] B. Sadigh *et al.*, PRB **92**, 075202 (2015); [2] S.I. Pekar, ZETF **16**, 335 (1946). This work received funding from the Leibniz ScienceCampus "GraFOx".

O 78: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - V

Wednesday 15:00–18:15 GER 38

Talk O 78.1 Wed 15:00 GER 38

First-principle Linear Response in Real Space — •Honghui Shang[1], Danilo S. Brambila[1], Christian Carbogno[1], Patrick Rinke[2], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — [2]Aalto University, Helsinki, Finland

Density-functional perturbation theory (DFPT) has developed into an important computational tool for assessing the linear electronic response of crystalline solids to perturbations, e.g., from electric fields or nuclear displacements [1]. In this work we present a full real-space reformulation of DFPT and its implementation [2] in the all-electron, numeric atom-centered orbital electronic structure theory code FHI-aims. We discuss the specific contributions, e.g., relativistic effects and Pulay terms, that arise in such a formulation and validate our implementation by systematically comparing with the finite-difference approach for various extended systems. The computational efficiency is then analyzed via scaling and scalability tests on massively parallel architectures (CRAY and IBM x86 clusters). Finally, we show that this real-space formalism enables an arbitrarily dense sampling of the Brillouin zone by numerically cheap Fourier transformations, which in turn facilitates an efficient evaluation of the electron-phonon coupling matrix elements. We demonstrate the efficiency by computing the relaxation time of hot carriers in Si.

[1] X. Gonze and C. Lee, *Phys. Rev. B* **55**, 10355, (1997).
[2] H. Shang, *et al.*, *Comp. Phys. Comm. (accepted)*, arXiv:1610.03756.

Talk O 78.2 Wed 15:15 GER 38

Anharmonic Vibrations in Solids: Why and When Going Beyond Perturbative Treatments is Necessary — •Hagen-Henrik Kowalski, Maja-Olivia Lenz, Christian Carbogno, and Matthias Scheffler — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

In *ab initio* theory, the nuclear motion is typically assessed using a truncated second order Taylor expansion for the potential energy (harmonic approximation). Recent computational and methodological advancements [1] allow to extend this expansion to the third order so to approximately treat also anharmonic effects. Little is known, however, about the role of higher order terms. In this contribution, we systematically compare how a third-order expansion performs with respect to techniques that are able to capture higher degrees of anharmonicity, e.g., the quasi-harmonic approximation and fully anharmonic molecular dynamics. For this purpose, anharmonic properties such as the thermal expansion and the Grüneisen parameters are computed for a set of materials with increasing degree of anharmonicity (Si, Mg_2Si, CuCl, and ZrO_2). This reveals that a third order expansion can still lead to quantitative and even qualitative errors at elevated temperatures and/or in highly anharmonic systems. Eventually, we discuss the impact of the chosen exchange-correlation functionals on these calculations and the implications of these findings for the computation of thermal conductivities [2].

[1] D. A. Broido, *et al.*, *Appl. Phys. Lett.* 91, 231922 (2007).
[2] C. Carbogno, R. Ramprasad, and M. Scheffler, *ArXiv:* 1608.06917.

Talk O 78.3 Wed 15:30 GER 38

Anharmonic and Quantum Fluctuations in Molecular Crystals from Ab Initio Simulations — •Mariana Rossi[1] and Michele Ceriotti[2] — [1]Fritz Haber Institute of the Max Planck Society, Berlin — [2]École Polytechnique Fédérale de Lausanne, Switzerland

Molecular crystals often exist in multiple competing polymorphs which are challenging to be predicted computationally, but show significantly different physicochemical properties. This challenge is not due only to the combinatorial search space, but also to the complex interplay of subtle effects determine the relative stability of different structures.

Here we estimate all contributions to the free energies of these systems with density-functional theory, including the oft-neglected anharmonic contributions and nuclear quantum effects, by using a series of different flavors of thermodynamic integration. As an example, for the two most stable forms of paracetamol we find that anharmonic contributions, different descriptions of van der Waals interactions, and nuclear quantum effects **all** matter to quantitatively determine the stability of different phases [1]. Our studies indicate that anharmonic free energies could play an important role for molecular crystals composed by large molecules and opens the way for a systematic inclusion of these effects in order to obtain a predictive screening of structures. [1] Rossi, Gasparotto, Ceriotti, *PRL* **117**, 115702 (2016).

Talk O 78.4 Wed 15:45 GER 38

Exact solutions and approximations in the exact factorization of the electron-nuclear wavefunction — •Graeme Gossel and Neepa Maitra — Department of Physics and Astronomy, Hunter College of the City University of New York, 695 Park Avenue, New York, NY 10065.

"Recently it was shown how a molecular wavefunction may be written exactly as a single product of a nuclear and an electronic wavefunction, with a pair of corresponding equations of motion [1]. This exact factorization provides a new and rigorous starting point for developing intuitive and physical approximations to the exact coupled system. Strikingly, in this factorized picture the electronic Hamiltonian is not strictly Hermitian. Nevertheless, the norm is conserved so long as certain terms persist. This, and other constraints, inform the approximations we apply to make the process numerically feasible. In parallel we present numerical self-consistent solutions of the exact factorization equations devoid of approximations to assess accuracy and behaviour of different terms. Finally, we discuss how a well characterized and robust single-product-picture such as this may be used in TDDFT calculations.

[1] A Abedi, NT Maitra, and EKU Gross, PRL 105 (12), 123002, 2010

Talk O 78.5 Wed 16:00 GER 38

Insight into time-propagation TDDFT excitations via Kohn–Sham decomposition — •Tuomas P. Rossi[1], Mikael Kuisma[2,3], Martti J. Puska[1], Risto M. Nieminen[1], and Paul Erhart[2] — [1]Aalto University, Espoo, Finland — [2]Chalmers University of Technology, Gothenburg, Sweden — [3]University of Jyväskylä, Jyväskylä, Finland

The real-time-propagation formulation of time-dependent density-functional theory (RT-TDDFT) is an efficient method for calculating optical excitations of large molecules and nanoparticles. However, within RT-TDDFT, the analysis of the response is often limited to photoabsorption spectra and induced densities, in contrast to linear-response formulations of TDDFT, such as the Casida method, in which one can obtain further understanding on the basis of the Kohn–Sham electron-hole decomposition of the excitations.

In this work, we show that the Kohn–Sham decomposition can be equivalently obtained from RT-TDDFT calculations. We demonstrate the approach for the optical response of organic molecules and large metallic nanoparticles. The focus is especially on plasmonic applications, for which the method enables the analysis in terms of transition contribution maps [1]. By using the decomposition, we can shed light on the microscopic origin of plasmon resonances and their damping via plasmon–single-electron coupling, while retaining the favorable scaling of RT-TDDFT compared to linear-response formulations.

[1] S. Malola *et al.*, ACS Nano **7**, 10263 (2013).

Talk O 78.6 Wed 16:15 GER 38

Gauge-invariant Magnetic Properties from Time-Dependent Current-Density-Functional Theory — •Nathaniel Raimbault[1], Paul de Boeij[3], Pina Romaniello[2], and Arjan Berger[1] — [1]Laboratoire de Chimie et Physique Quantiques, IRSAMC, Université Toulouse III - Paul Sabatier — [2]Laboratoire de Physique Théorique, CNRS, IRSAMC, Université Toulouse III - Paul Sabatier — [3]University of Twente, Faculty of Science and Technology, Physics of Interfaces and Nanomaterials

Standard formulations of magnetic response properties are often plagued by gauge dependencies, which can lead to unphysical results, and to a slow convergence with basis-set size. In this talk we present a novel method for obtaining magnetic properties from the current density [1]. This alternative scheme is fully gauge-invariant, numerically efficient, and can be applied to any method from which the current density can be obtained. To illustrate our method, we applied it to time-dependent current-density-functional theory (TDCDFT). While different types of magnetic properties can be calculated in this way, we here emphasize the calculation of circular dichroism spectra, which are notably important in order to characterize secondary structures in biomolecules. The circular dichroism spectra we thus obtain for methyloxirane, dimethyloxirane and α-pinene are in good agreement with experiment [2]. [1] N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, PRL 114, 066404 (2015); [2] N. Raimbault, P.L. de Boeij, P. Romaniello, and J.A. Berger, JCTC 12, 3278 (2016)

Talk O 78.7 Wed 16:30 GER 38

Calculation of charge transfer integrals using constrained-DFT — •Tobias Lettmann and Nikos Doltsinis — Institut für Festkörpertheorie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Deutschland

For the investigation of charge transport properties of organic semiconductor materials, the fast and accurate calculation of charge transfer integrals (or transition matrix elements) is desirable. It has been suggested that the transfer integrals depend on a universal linear function of the corresponding wavefunction overlap, which can then be used to approximate the integral at a reduced computational cost[1].

We have calculated transfer integrals for dimers of poly(3-hexylthiophene) (P3HT) and diperylene bisimide (DiPBI), which are used in organic solar cells, in a large variety of intra- and intermolecular conformations and polymer lengths using a constrained-DFT approach[2]. Our results show, that there is indeed a universal relation between transfer integral and wavefunction overlap. However this relation is (i) nonlinear for large overlaps and (ii) only holds true if the transfer integral is rescaled by the number of electrons of the respective system.

[1] F. Gajdos et al.: *J. Chem. Theory Comput.*, 2014, **10**, 4653
[2] H. Oberhofer, J. Blumberger: *J. Chem. Phys.*, 2010, **133**, 244105

Talk O 78.8 Wed 16:45 GER 38

Towards ultra long-range ab-initio calculations — •Tristan Müller[1], Sangeeta Sharma[1,2], Eberhard K.U. Gross[1], and John K. Dewhurst[1] — [1]Max-Planck-Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany — [2]Department of physics, Indian Institute for Technology-Roorkee, 247997 Uttarkhand, India

We propose a generalization of the Bloch state which involves an additional sum over a finer grid in reciprocal space around each k-point. This allows for ab-initio calculations of ultra long-range modulations in the density which may involve millions of unit cells but with an efficiency rivaling that of a single unit cell. This is due to a new algorithm developed specifically for solving the particular eigenvalue problem that this ansatz requires. Thus physical effects on the micron length scale, which nevertheless depend on details of the electronic structure on nanometer length scales, can be computed exactly within density functional theory.

Talk O 78.9 Wed 17:00 GER 38

Local density fitting within a Gaussian and plane waves scheme for large-scale density functional theory calculations — •Dorothea Golze[1,2], Marcella Iannuzzi[1], and Jürg Hutter[1] — [1]Aalto University, Otakaari 1, 02150 Espoo, Finland — [2]University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

A local resolution-of-identity (LRI) approach is introduced in the Gaussian and plane waves (GPW) scheme to enable large-scale Kohn-Sham (KS) density functional theory calculations. The construction of the KS matrix in GPW scales already linearly with respect to system size by using a plane wave expansion of the density for the evaluation of the Coulomb term in combination with a local basis. The intention is to retain the linear scaling of the GPW approach, while reducing the prefactor for computing the KS matrix. The locality of the density fitting ensures an $O(N)$ scaling and is implemented by approximating the atomic pair density by an expansion in one-center fit functions. The prefactor is smaller with LRI since the computational demands for the grid-based operations become negligible, while they are dominant in GPW. We observe a speed-up of the self-consistent field (SCF) procedure by a factor of up to 30 for periodic systems dependent on the symmetry of the simulation cell and the grid cutoff. The accuracy of LRIGPW is assessed for different systems and properties. Generally, total energies, reaction energies, intramolecular and intermolecular structure parameters are well reproduced. LRIGPW yields also high quality results for extended condensed phase systems such as liquid water, ice XV and molecular crystals.

Talk O 78.10 Wed 17:15 GER 38

From the Electron Localization Function to a Coalescent-Pair Locator — •Stefano Pittalis[1], Daniele Varsano[1], Alain Delgado[2,3], and Carlo Andrea Rozzi[1] — [1]Istituto Nanoscienze, Consiglio Nazionale dellle Ricerche, Via Campi 213a, 41125 Modena, Italy — [2]Department of Physics, University of Ottawa, Ottawa, ON K1N 6N5, Canada — [3]Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear, Calle 30 # 502, 11300 La Habana, Cuba

The Electron Localization Function (ELF), as proposed originally by Becke and Edgecombe, uses the information on the distribution of pairs of electrons with parallel spins. The ELF has been widely adopted as a descriptor of atomic shells and covalent bonds, but it is not useful to visualize the bond in H_2 – the simplest neutral molecule in the universe. Here we propose a complementary descriptor which also works for H_2 by exploiting the information on pairs of electrons with opposite spins. Remarkably, only quantities derived from occupied single-particle orbitals are required in the calculations. If time allows, implications for developing improved approximate density functionals will also be discussed.

Talk O 78.11 Wed 17:30 GER 38

Band structure interpolation via maximally localized Wannier functions implemented in LAPW+lo basis — •Sebastian Tillack, Andris Gulans, and Claudia Draxl — Institut für Physik, Humboldt-Universität zu Berlin, 12489 Berlin

The band structure is one of the most fundamental quantities of any solid that carries a lot of information about the material's properties. Obtaining a smooth dispersion from density-functional theory (DFT) and especially from the *GW* approximation of many-body perturbation theory may be very expensive. To this extent, we have implemented a method for generating maximally localized Wannier functions (WF) [1] from Kohn-Sham wavefunctions in the full-potential all-electron code `exciting` [2] using a (linearized) augmented plane-waves plus local-orbitals basis. These WF are used for interpolating wavefunctions and corresponding eigenenergies for arbitrary **k**-points in a computationally cheap post-processing step. The interpolated Kohn-Sham and *GW* bands of conventional and two-dimensional semiconductors and insulators are also used as an input to calculations of optical-excitation spectra.

[1] N. Marzari and D. Vanderbilt, *Phys. Rev. B* ***56***, 12847 (1997)
[2] A. Gulans, et al. *J. Phys.: Condens. Matter* ***26***, 363202 (2014)

Talk O 78.12 Wed 17:45 GER 38

Chemical insight from Fermi-Löwdin orbitals — •Torsten Hahn[1], Sebastian Schwalbe[1], Simon Liebing[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 correcting the self-interaction error in Density Functional Theory (FLO-SIC DFT) [1,2,3] is briefly introduced. Contrary to standard DFT approaches, where only auxiliary Kohn-Sham orbitals are available, FLO-SIC DFT delivers a set of well-defined, localised Fermi-Löwdin orbitals. These localised orbitals together with their optimised reference positions yield an inherently 'chemical' representation of bonding details in molecules that resembles remarkably well Lewis concept of lone and binding electron pairs. For complex examples, the method provides detailed insights into the bonding situation in terms of multi-center many-electron bonds in a natural, chemically-intuitive fashion.

[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).

Talk O 78.13 Wed 18:00 GER 38

Conditions for describing triplet states in reduced density matrix functional theory — Iris Theophilou[1], Nektarios N. Lathiotakis[2], and •Nicole Helbig[3] — [1]Max Planck Institute for the Structure and Dynamics of Matter, Luruper Chaussee 149, 22761 Hamburg, Germany — [2]Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48, GR-11635 Athens, Greece — [3]Peter-Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich, D-52425 Jülich, Germany

We consider necessary conditions for the one body-reduced density matrix (1RDM) to correspond to a triplet wave-function of a two electron system. The conditions concern the occupation numbers and are different for the high spin projections, $S_z = \pm 1$, and the $S_z = 0$ projection. Hence, they can be used to test if an approximate 1RDM functional yields the same energies for both projections. We employ these conditions in reduced density matrix functional theory calculations for the triplet excitations of two electron systems. In addition, we propose that these conditions can be used in the calculation of triplet states of systems with more than two electrons by restricting the active space. We assess this procedure in calculations for a few atomic and molecular systems. We show that the quality of the optimal 1RDMs improves by applying the conditions in all the cases we studied.

O 88: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - VI

Thursday 10:30–13:45 GER 38

Talk O 88.1 Thu 10:30 GER 38

Implicit solvation functionality in FHI-aims: Kirkwood multipole expansion model — •Markus Sinstein, Karsten Reuter, and Harald Oberhofer — Technische Universität München, Germany

Implicit solvation models describe a liquid environment in form of a dielectric continuum. Used within first-principles calculations for the solute such models provide a numerically most efficient way to effectively capture solvation effects. To this end we have implemented the multipole expansion (MPE) model introduced originally by Kirkwood into the full-potential density-functional theory (DFT) code FHI-aims. This implementation fully exploits the optimized multi-center multi-pole decomposition of the density performed within FHI-aims and therewith leads generally to an insignificant overhead as compared to the underlying DFT calculation for the solute.

Aiming to minimize the number of free parameters inevitably connected with such implicit models, we use an iso-density definition of the solvent cavity. As to the other parameters, we present an efficient parametrization scheme based on experimentally measured hydration energies of small organic molecules. Finally, we discuss extensions of the solvation model to address extended solid-liquid interfaces.

Talk O 88.2 Thu 10:45 GER 38

Using Dipsersion-Corrected Density Functional Theory to Understand the Phase Diagram of Alkanethiolates on Gold — •Joakim Löfgren, Henrik Grönbeck, Kasper Moth-Poulsen, and Paul Erhart — Chalmers University of Technology, Gothenburg, Sweden

A key challenge in modern computational materials chemistry is the description of van der Waals interactions in density functional theory simulations, where the failure of conventional exchange-correlation functionals is well-known. While, in the recent years, several methods have been proposed for overcoming these difficulties, the applications are becoming increasingly more demanding as well. An important example is that of ligand-protected nanoparticles, which typically feature metallic, covalent as well as dispersive interactions that should all, ideally, be treated on an equal footing. In this work we show that significant progress can be made in this direction: with the aid of the recently-developed vdW-DF-cx functional we study the phase diagram of self-assembled monolayers of alkanethiolates on gold. This system is important for practical applications and as a general representative of self-assembly at a metal surface. In particular, a quantitative description of the dispersion-driven phase transition between a lying-down and a standing-up monolayer is obtained using an ab inito thermodynamics framework. The results are shown to be in good agreement with experimental data and highlight that accurately accounting for dispersive interactions is both feasible and a crucial part of modeling self-assembled systems.

Talk O 88.3 Thu 11:00 GER 38

Finite-temperature properties of the thermoelectric clathrate

$Ba_8Al_xSi_{46-x}$ — •Maria Troppenz, Santiago Rigamonti, and Claudia Draxl — Humboldt-Universität zu Berlin

Intermetallic clathrate compounds are promising candidates for high-efficiency thermoelectric (TE) applications. Here, we study $Ba_8Al_xSi_{46-x}$ in the composition range $x \in [6, 16]$ [1]. Recent theoretical studies [2] show a strong dependence of the electronic properties on configuration, i.e. the atomic arrangement of the substitutional Al atoms in the crystal framework. At the Zintl composition (x = 16), the ground-state configuration is semiconducting. However, configurations higher in energy are metallic. Understanding this metal-semiconductor transition is essential, as semiconducting behavior is a prerequisite for TE applications. In this work, we employ the cluster expansion technique combined with Monte-Carlo simulations and the Wang-Landau method [3] to access finite-temperature properties. We find that the transition is driven by a partial order-disorder transition of the substituents. Most importantly, it is found that the transition temperature (~ 800 K) at the Zintl composition is close to the typical temperatures at which the figure of merit of TE clathrates is maximal. Signatures of the transition in the entropy, order parameter, specific heat, and canonical distribution are analyzed for the full composition range.

[1] J. H. Roudebush *et al.*; *Inorg. Chem.* **51**, 4161 (2012)
[2] M. Troppenz, S. Rigamonti and C. Draxl; preprint.
[3] F. Wang and D. P. Landau, *Phys. Rev. Lett.* **86**, 2050 (2001)

Talk O 88.4 Thu 11:15 GER 38

Electronic structure and solid-state optical properties of indigo from time-dependent optimally tuned range-separated hybrid functional theory — •Bernd Kollmann[1], Arun Kumar Manna[2], Daniel Lüftner[1], Leeor Kronik[2], and Peter Puschnig[1] — [1]Institute of Physics, NAWI Graz, University of Graz, Austria — [2]Department of Materials and Interfaces, Weizmann Institute of Science, Israel

Indigo is a natural dye with a long history in organic chemistry. Recent applications of indigo as a functional building block for organic electronics, like in solar cells or field effect transistors, have renewed the interest in the chemical and physical properties of this molecule. We report on its electronic structure for the isolated molecule as well as for the alpha- and beta- bulk molecular crystal phases. Further we investigate the optical properties of the bulk molecular crystal phases. For the molecule we employ an optimally tuned range-separated hybrid functional (OT-RSH) within density functional theory. Comparing the theoretical results obtained with different levels of theory and with experiment emphasizes the need for going beyond simple semi-local DFT-functionals in order to obtain the correct orbital ordering. For the bulk crystals we take into account the screening in the bulk by using an optimally tuned screened range-separated hybrid (OT-SRSH) approach. Regarding the optical properties of the bulk molecular phases we employ time-dependent density functional theory (TDDFT) to calculate the absorption spectra, whereby TDDFT represents an accurate low-cost substitute to many-body perturbation theory.

Talk O 88.5 Thu 11:30 GER 38

Thermodynamic properties from ab-initio calculations - Ti as a case study — •Guy Makov — Materials Dept, Ben-Gurion University of the Negev, Beer Sheva, Israel

Ab-initio calculations of thermophysical properties and of phase stability as a function of pressure and temperature are considered in titanium as a case study. Ti is of interest due to its multiple phases and unusual thermophysical properties. At low temperatures Ti has been reported to exhibit negative anisotropic thermal expansion. In addition, there have been reports of two additional phases at high pressure and room temperature, and a possible transition to a bcc phase at very high pressures.

Despite extensive studies there remains both experimental and theoretical uncertainty in determining the phase diagrams and selected properties. Density Functional Theory total energy calculations complemented by Density Functional Perturbation Theory (DFPT) calculations of phonon spectra are obtained as a function of pressure. The free energy and thermal properties (heat capacity and thermal expansion) of Ti phases, phase equilibria and high pressure phase sequence are determined. The contribution of phonon modes to the thermal expansion is analyzed and the negative thermal expansion is shown to be dominated by negative mode Gruneisen parameters at specific points on the Brillouin zone boundaries. The elastic (Debye) theory for negative thermal expansion is shown to be irrelevant for these phenomena. Uncertainties in the calculated results are discussed in light of experimental observations & motivating further experimental studies.

Talk O 88.6 Thu 11:45 GER 38

Molecular orbitals in the bismuth perovskites — •Kateryna Foyevtsova[1,2], Arash Khazraie[1,2], Ilya Elfimov[1,2], and George A. Sawatzky[1,2] — [1]Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada V6T 1Z1 — [2]Stewart Blusson Quantum Matter Institute, Vancouver, BC, Canada V6T 1Z4

The bismuth perovskites $SrBiO_3$ and $BaBiO_3$ become superconducting upon hole doping, with the transition temperatures as high as 30 K. The origin of the superconductivity in these compounds has remained unidentified for more than three decades. The BCS mechanism alone is not sufficient to account for such a high T_c due to the small electron-phonon coupling that is being consistently found in numerous experimental and theoretical studies. Further effects must therefore be of key importance, such as, for example, formation of bipolarons.

In this talk, we will focus on the insulating state of the pristine $SrBiO_3$. Peculiarly, this state is associated with a structural distortion whereby the Bi-O bonds disproportionate, resulting in a three-dimensional array of alternating small and large BiO_6 octahedra. This "breathing" distortion melts away with doping and is believed to be competing with superconductivity. We will show using DFT calculations that the microscopic state in the pristine bismuthates corresponds to a lattice of frozen bipolarons. More specifically, the holes, intrinsically present in the material, condense pairwise into the A_{1g}-symmetric molecular orbitals formed from the O-p_σ atomic orbitals of the small BiO_6 octahedra. This is facilitated by the strong hybridization between the O-2p states and the Bi-6s states.

Talk O 88.7 Thu 12:00 GER 38

Ab initio calculations and strain-dependent scaling of excitons in carbon nanotubes — •Christian Wagner[1,3], Jörg Schuster[2], Michael Schreiber[3], and André Schleife[4] — [1]Center for Microtechnologies, TU Chemnitz, Germany — [2]Fraunhofer Institute ENAS, Chemnitz, Germany — [3]Institute of Physics, TU Chemnitz, Germany — [4]Department for Materials Science, UIUC, USA

Optical transitions in carbon nanotubes (CNTs) show a strong strain sensitivity, which makes them suitable for optical strain sensing at the nano-scale and for strain-tunable emitters. The origin of this effect is the band-gap change, depending on strain and chirality, which is well explored. However, there is no quantitative model for the strain dependence of optical transitions — as they are subject to strong excitonic effects due to the quasi one-dimensional structure of CNTs.

One approach towards such a model is the scaling relation of CNT excitons with respect to dielectric constant, reduced mass, and CNT radius given by Perebeinos *et al.* However, the description of screening in this model is insufficient, since for CNTs, a one-dimensional wave-vector dependent dielectric function $\epsilon(q)$ is needed instead of an effective-medium dielectric constant ϵ_0.

We achieve this by combining the scaling relation with the wave-vector dependent screening model by Deslippe *et al.* The strain-dependent scaling is fitted to electronic-structure calculations within many-body perturbation theory as a reference. This enables us to quantitatively predict the strain dependence of optical transitions for any CNT.

Talk O 88.8 Thu 12:15 GER 38

Dzyaloshinskii-Moriya-interaction energy, where it is located? Real and reciprocal spaces views. — •Leonid Sandratskii — Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Recently Dzyaloshinskii-Moriya interaction (DMI) attracted new wave of intense attention stimulated by its role in the stabilization and fast dynamics of skyrmions. Numerous approaches have been suggested for the estimation of the the DMI parameters. Many efforts are devoted to reveal the electronic properties responsible for the strength of the DMI and, in this way, to help to engineer the materials with desired DMI characteristics. Although there is full consensus with respect to the most fundamental reasons of the DMI, the SOC and broken inversion symmetry, in details the physical pictures suggested by different authors differ strongly. In particular, this concerns the role of the avoiding crossings in the electronic structure, the spatial location of the DMI energy, the role of the orbital moments. This stimulated us to perform detailed study of the DMI in CoPt bilayer focusing on the open questions. We used both the approximate calculations for spin spirals with arbitrary wave vectors and more precise but also more time and resources consuming full relativistic calculations for supercells with the magnetic structures of opposite chirality. The results of the calculations are presented and analyzed.

Talk O 88.9 Thu 12:30 GER 38

***Ab-initio* study of the Raman spectra of strained graphene** — •Albin Hertrich, Caterina Cocchi, Pasquale Pavone, and Claudia Draxl — Department of Physics, Humboldt-Universität zu Berlin, Germany

Raman spectroscopy is an important non-destructive method for characterizing graphene-based materials. The main features of Raman spectra of pristine graphene are the first-order G-band at $\approx 1580\,\mathrm{cm}^{-1}$ and the dispersive second-order 2D-band at $\approx 2700\,\mathrm{cm}^{-1}$. In this work, we perform a systematic analysis on the effect of strain on both bands. All calculations are done using the full-potential all-electron code `exciting` [1]. Phonon properties are computed within the frozen-phonon approximation, the frequency-dependent dielectric tensor within the random-phase approximation. Raman-scattering intensities are calculated from vibrational matrix elements and derivatives of the dielectric tensor with respect to the phonon normal coordinates [2]. Under biaxial strain both Raman bands are shifted, while uniaxial strain leads to a splitting of the G-band by lifting the degeneracy of the optical in-plane Γ-point phonons. Further, we explore the effect of different types of inhomogeneous strain on the optical phonon frequencies and Raman-scattering intensities.

[1] A. Gulans *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014).
[2] C. Ambrosch-Draxl *et al.*, Phys. Rev. B **65**, 064501 (2002).

Talk O 88.10 Thu 12:45 GER 38

DFT meets Landau Theory: The High Pressure Phase Transition of Lead Titanate — •Andreas Tröster — Vienna University of Technology, Institute of Material Chemistry, Getreidemarkt 9 A-1060 Wien, Austria

Landau theory (LT) coupled to infinitesimal strain is a cornerstone of the theory of structural phase transitions. At high pressures, however, this approach breaks down due to the appearance of large strains and the accompanying nonlinear elastic energy contributions. In density functional theory (DFT), on the other hand, stress and strain are easy to control, but entropic effects are difficult to incorporate since DFT is a genuine zero temperature method. Recently we have shown how to combine the strengths of these two antipodal approaches by constructing a high pressure extension of conventional LT with the help of DFT. Essential for the success of this approach is the ab initio calculation of pressure-dependent elastic constants. This theory yields a concise numerical description of the high pressure phase transition in strontium titanate, and also allows to resolve a number of severe and long-standing discrepancies between the experimental data and the theoretical description of the ferroelectric high pressure phase transition of the perovskite lead titanate, a material which is also of considerable technological interest.

Talk O 88.11 Thu 13:00 GER 38

Ground-State and Excitation Properties of Orthorhombic $MAPbI_3$ — •Claudia Rödl and Silvana Botti — Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

Hybrid organic-inorganic halide perovskites are one of the most promising candidates for the next generation of photovoltaic devices with high power-conversion efficiencies. Despite the amazing progress in device fabrication, many of the fundamental properties of these materials are not yet understood. The flexibility in composition of hybrid perovskites permits to tune physical properties like band gap, dielectric constant, or optical absorption which renders them interesting also from a fundamental point of view and for applications beyond photovoltaics. The most intensively studied compound, methylammonium lead iodide ($MAPbI_3$), condenses in a low-temperature orthorhombic phase which undergoes a phase transition to a tetragonal structure at 162.2 K and transforms into a cubic high-temperature phase above 327.4 K. These phase transitions go along with a change in the optical properties. Here, we focus on the orthorhombic phase of $MAPbI_3$. We have studied the ground-state atomic structure, and in particular the orientation of the MA^+ ion within the inorganic cage, within density-functional theory. We investigate the one-particle excitation properties (band gap, photoemission spectrum) within the GW approximation of many-body perturbation theory. Moreover, we calculate optical and loss spectra using time-dependent density-functional theory and solving the Bethe-Salpeter equation.

Talk O 88.12 Thu 13:15 GER 38

Structure, nonstoichiometry, and geometrical frustration of α-tetragonal boron — •Jens Kunstmann[1], Naoki Uemura[2], Hagen Eckert[1], and Koun Shirai[2] — [1]TU Dresden, Germany — [2]Osaka University, Japan

It is currently believed that boron in the α-tetragonal structure is not an elemental crystal. Here we contradict this view and resolve the structural and thermodynamic characteristics of pure α-tetragonal boron via density functional theory calculations. The conditions for stable covalent bonding are almost fulfilled at a stoichiometric composition B_{52}. This phase is an elemental crystals with geometrical frustration. Furthermore, our thermodynamic considerations show that small, positive deviations from the stoichiometric composition occur at finite temperatures. [Uemura, Shirai, Eckert, Kunstmann, Phys. Rev. B 93, 104101 (2016)]

Talk O 88.13 Thu 13:30 GER 38

Magnetic response properties of thin films using Kubo's linear response formalism — •Andreas Held, Sebastian Wimmer, Sergiy Mankovsky, and Hubert Ebert — Department Chemie, Ludwig-Maximilians-Universität München

We have applied the fully relativistic spin-polarized Korringa-Kohn-Rostoker method to investigate various magnetic response properties of two-dimensional systems such as free-standing mono- and multilayers, surfaces and thin films on surfaces. Our approach is based on an implementation of Kubo's linear response formalism within the tight-binding (or screened) KKR framework that allows introducing layer-resolved response coefficients τ_{ij}^{IJ}. Extending previous work [1] focusing on the symmetric part of the electrical conductivity tensor, we are able to describe the full response tensors connected to charge and spin transport, Gilbert damping, spin-orbit torque and the Edelstein effect. An implementation of the Coherent Potential Approximation for layered systems allows the treatment of disorder effects including the Vertex Corrections to the response coefficients [2]. This can be used to study chemical disorder in alloys but also to include the effect of finite temperatures. For the latter the so-called Alloy-Analogy Model [3] is employed to treat vibrations and spin fluctuations.

[1] W.H. Butler *et al.*, *Phys. Rev. B* **52**, 13399 (1995). [2] W.H. Butler, *Phys. Rev. B* **31**, 3260 (1985); K. Palotás *et al.*, *Phys. Rev. B* **67**, 174404 (2003). [3] H. Ebert *et al.*, *Phys. Rev. B* **91**, 165132 (2015).

O 99: Electronic Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond - VII

Thursday 16:00–18:30 GER 38

Invited Talk O 99.1 Thu 16:00 GER 38

Spectacular success of DFT in predicting novel topological phases — •Arun Bansil — Northeastern Univ, Boston USA

The revolutionary discovery of topological insulators has turned out to be the proverbial tip of the much larger iceberg of exotic phases of quantum matter driven by spin-orbit coupling effects. The consideration of electronic states protected by time-reversal, crystalline and particle-hole symmetries has led to the prediction of many novel materials that can support Weyl, Dirac and Majorana fermions, and to new types of topological crystalline and Kondo insulators, and quantum spin Hall insulators with large band gaps. The first-principles DFT-based band theory paradigm has been a key player not only in this discovery process but also in identifying salient characteristics of topological states, enabling direct and sharpened confrontation between theory and experiment. [1] I will discuss our recent theoretical work aimed at predicting topological materials and identify cases where the materials have been realized successfully. [2-10] I will also comment on the potential of topological materials as next generation platforms for manipulating spin and charge transport and other applications.

[1] Bansil, Lin and Das, Rev. Mod. Phys. 88, 021004 (2016). [2] Chang et al, Sci. Adv. 2, e1600295 (2016). [3] Huang et al., PNAS 113, 1180 (2016). [4] Zheng et al., ACS Nano 10, 1378 (2016). [5] Xu et al., Science 349, 613 (2015). [6] Zeljkovic et al., Nat. Mat. 14, 318 (2015). [7] He et al., Nat. Mat. 14, 577 (2015). [8] Xu et al., Nat. Phys. 11,

748 (2015). [9] Crisostomo et al., Nano Lett. 15, 6568 (2015). [10] Xu et al., Sci. Adv. 1, e1501092 (2015).

Talk O 99.2 Thu 16:30 GER 38

Interlayer excitons and Band Alignment in MoS_2/hBN/WSe_2 van der Waals Heterostructures — •Simone Latini — Technical University of Denmark, Copenhagen, Denmark

Van der Waals Heterostructures (vdWHs) are a unique platform for the realization of novel (opto)-electronic devices with embedded multifunctionality. Combining two-dimensional (2D) semiconductors with misaligned band edges can lead to the formation of photo-excited electrons and holes localized in distinct layers, which result into interlayer excitons. Understanding the energetics behind the formation of interlayer excitons is the first step towards the engineering of charge separation processes in photovoltaic devices and photodetectors. The contribution of our work is then twofold. (I) We calculate, for the first time, the interlayer exciton binding energies in complex vdWHs, specifically MoS_2/hBN/WSe_2 heterostructures, using a first-principles approach. The binding energy is of extreme technological importance as it is a measure of how strongly the electron-hole pair is bound and hence how easily it can be separated. (II) We obtain accurate electronic band edges at the interface between the layers of the vdWHs, a task which could not yet be accomplished with any available state of the art technique. Importantly, the accuracy of our calculated exciton binding energies and band edges is confirmed by a striking agreement with experimental data on photoluminesce of interlayer excitons in MoS_2/hBN/WSe_2 heterostructures.

Talk O 99.3 Thu 16:45 GER 38

Trionic effects in graphene nanoribbons and further nanomaterials — •Thorsten Deilmann and Kristian Sommer Thygesen — Center for Atomic-Scale Materials Design (CAMD), Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Among low-dimensional materials armchair-edged graphene nanoribbons are very promising candidates with optical properties which are dominates by excitons. In the presence of additional charges, trions (i.e. charged excitons) can occur in the optical spectrum. With our recently developed first-principle many-body approach [1], we predict strongly bound trions in nanoribbons with decreasing binding energies of 660 to 140 meV for widths of 3.6 to 14.6 Å. We determine their optical spectra and identify several trions by their real-space wave functions. [1] Phys. Rev. Lett. **116**, 196084.

Talk O 99.4 Thu 17:00 GER 38

Interface Structure Prediction using the Ab Initio Random Structure Searching Method — •Georg Schusteritsch and Chris Pickard — Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, U.K.

First-principles structure prediction of bulk materials is now routinely performed, however the field of predicting the atomic structure of interfaces is still in its infancy. A detailed understanding of and ability to predict the atomic structure of interfaces is however of crucial importance for many technologies. Interfaces are very hard to predict due to the complicated geometries, crystal orientations and possible non-stoichiometric conditions involved and provide a major challenge to structure prediction. We present here the ab initio random structure searching (AIRSS) method and how it can be used to predict the structure of interfaces. Our method relies on generating random structures in the vicinity of the interface and relaxing them within the framework of density functional theory. The method is simple, requiring only a small set of parameters, and can be efficiently run on modern parallel computer architectures. We focus here on the prediction of grain boundaries, but application to heterostructure interfaces is straightforward. Examples for several grain boundary defects in technologically important materials will be presented: In particular grain boundaries in graphene, the prototypical two-dimensional material will be discussed, alongside with examples of grain boundaries in transition metal oxides, such as SrTiO3 and TiO2.

Talk O 99.5 Thu 17:15 GER 38

Predicting new materials and their properties with supercomputers: the example of perovskites — •Silvana Botti[1] and Miguel A.L. Marques[2] — [1]Institut für Festkörpertheorie und -optik, Friedrich-Schiller Universität Jena, Max-Wien-Platz 1, 07743 Jena — [2]Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

Can new materials with optimized properties be designed using supercomputers?

I will try to convince you through the example of the search of new perovskites that first-principles calculations can efficiently speed up the discovery of new materials.

Theoretical approaches based and going beyond density functional theory ally today accuracy and efficiency, and are therefore suitable tools for understanding the physics not only of simple perfect crystals, but also of nanostructured materials, doped semiconductors, interfaces, alloys, etc. As a result, ab initio simulations of spectroscopic properties can finally account for the complexity of "real" experimental samples, allowing accurate comparison of calculated and measured structural and excitation properties. The powerful combination of theoretical spectroscopy with high-throughput calculations, structural prediction and machine learning can therefore provide a precious guide to experimentalists in the search of new materials.

Talk O 99.6 Thu 17:30 GER 38

Spectral property prediction with artificial neural networks — •Annika Stuke[1], Milica Todorovic[1], Kunal Ghosh[2], Aki Vehtari[2], and Patrick Rinke[1] — [1]Department of Applied Physics, Aalto University, Finland — [2]Helsinki Institute of Information Technology, Department of Computer Science, Aalto University, Finland

The ability to efficiently design new and advanced optoelectronic materials is hampered by the lack of suitable methods to rapidly and accurately identify yet-to-be-synthesized materials that meet a desired application. To overcome such design challenges, a machine learning model based on a deep multi-task artificial neural network (ANN) is presented that can predict spectral properties of small organic molecules. The ANN is trained and validated on data generated by accurate state-of-the art quantum chemistry computations for diverse subsets of the GDB-13 and GDB-17 datasets [1,2]. The molecules are represented by a simple, easily attainable numerical description based on nuclear charges and cartesian coordinates and are mapped onto multiple excited-state properties simultaneously using a deep ANN trained by gradient descent and error backpropagation [3]. This on-demand prediction model can be used to infer spectral properties of various candidate molecules in an early screening stage for new optoelectronic materials at negligible computational cost, thereby completely bypassing conventional laborious approaches towards materials discovery.

[1] L. C. Blum et al., J. Am. Chem. Soc. 2009, 131, 8732, [2] R. Ramakrishnan et al., Scientific Data 2014, 1, 140022, [3] G. Montavon et al., New J. Phys. 2013, 15, 095003

Talk O 99.7 Thu 17:45 GER 38

Machine-Learning Based Interatomic Potential for Amorphous Carbon — •Volker Deringer and Gábor Csányi — University of Cambridge, Cambridge, UK

Machine-learning based interatomic potentials are currently of growing interest in the solid-state theory communities, as they enable materials simulations with close-to DFT accuracy but at much lower computational cost. Here, we present such an interatomic Gaussian approximation potential (GAP) model for liquid and amorphous carbon. We first discuss the maximum accuracy that any finite-range potential can achieve in carbon structures; then, we show how a hierarchical set of two-, three-, and many-body structural descriptors can be used to fit a GAP that indeed reaches the target accuracy. The new potential yields accurate energetic and structural properties over a wide range of densities; it also correctly captures the structure of the liquid phases, at variance with state-of-the-art empirical potentials. Exemplary applications to surfaces of "diamond-like" tetrahedral amorphous carbon (ta-C) will be presented, including simulations of high-temperature surface reconstructions ("graphitization"). The method appears to be promising for realistic and accurate simulations of nanoscale amorphous carbon structures.

Talk O 99.8 Thu 18:00 GER 38

High-throughput computational search for new high mobility transparent (semi)conducting materials — •Geoffroy Hautier[1], Joel Varley[2], Anna Miglio[1], David Waroquiers[1], Viet-Anh Ha[1], and Gian-Marco Rignanese[1] — [1]Université catholique de Louvain, Louvain-la-Neuve, Belgium — [2]Lawrence Livermore National Laboratory

Transparent conducting oxides (TCMs) are large band gap materials (to favor transparency) doped with electrons (n-type) or holes (p-type). TCMs are essential to many technologies from solar cell to transparent electronics and there is currently a large effort towards the discovery of new TCMs. I will present the results of a high-throughput com-

putational search for new TCMs especially directed at p-type materials. Focusing on low effective masses (leading to high mobility), large band gaps and dopability, I will show how thousands of compounds can be screened using various ab initio techniques (from density functional theory to GW) to find new potential high performance TCMs. I will discuss several unsuspected compounds with promising electronic structures and when available link our findings to experimental results. Beyond the description of those novel TCM candidates, I will chemically rationalize our findings, highlighting several design strategies towards the development of future high mobility TCMs.

Talk O 99.9 Thu 18:15 GER 38

Cross-validation in the cluster expansion method — •Axel Hübner, Santiago Rigamonti, and Claudia Draxl — Humboldt-Universität zu Berlin

The cluster expansion technique allows the construction of model Hamiltonians for an efficient evaluation of the total energy of alloys. This technique relies on a fit to a small set of *ab-initio* calculations for selected atomic configurations. Key aspects to maximize the predictive performance of the model are the selection of a set of basis functions, i.e. clusters, and of configurations. To achieve this, the cross-validation technique is typically used [1]. In this work, an analytical formula for the calculation of the leave-many-out cross-validation score (CV) is derived. This formula exhibits numerical instabilities, whose analytical properties yield a criterion for structure selection in cluster expansions. Moreover, a relation between the noise in the data and the CV is outlined. This leads to a tool which allows us to estimate, for a given noise level, the size of the ab-initio data set upon which no improvements of the model are obtained. These results are exemplified for a cluster expansion of the thermoelectric clathrate alloy $Ba_8Al_xSi_{46-x}$, calculated with the `CELL` package [2].

[1] A. van d. Walle *et al.*, Journal of Phase Equilibria 23 (2002), Aug., Nr. 4

[2] M. Troppenz *et al.*, submitted (2016); S. Rigamonti *et al.*, in preparation.

SYES 1: Frontiers of Electronic-Structure Theory: New Concepts and Developments in Density Functional Theory and Beyond

Friday 10:30–13:00 HSZ 02

Invited Talk SYES 1.1 Fri 10:30 HSZ 02

Going Beyond Conventional Functionals with Scaling Corrections and Pairing Fluctuations — •Weitao Yang — Duke University

Fractional fractional charges and fractional spins provide a clear analysis of the errors of commonly used functionals. We developed a scaling correction scheme by imposing the Perdew-Parr-Levy- Balduz linearity condition. Our novel scheme leads to the significantly improved description of dissociating molecules, transition-state species, and charge-transfer systems. Within many-electron theory, we have formulated the ground-state exchange-correlation energy in terms of pairing matrix linear fluctuations, opening new a channel for density functional approximations. This method has many highly desirable properties. It has minimal delocalization error with a nearly linear energy behavior for systems with fractional charges, describes van der Waals interactions similarly and thermodynamic properties significantly better than the conventional RPA, and captures the energy derivative discontinuity in strongly correlated systems. We also adopted pp-RPA to approximate the pairing matrix fluctuation and then determine excitation energies by the differences of two-electron addition/removal energies. This approach captures all types of interesting excitations: single and double excitations are described accurately, Rydberg excitations are in good agreement with experimental data and CT excitations display correct 1/R dependence.

Invited Talk SYES 1.2 Fri 11:00 HSZ 02

Multi-reference density functional theory — •Andreas Savin — Laboratoire de Chimie Théorique, CNRS and UPMC, Univ. Paris VI, Sorbonne University, Paris, France

It is sometimes said that there is no multi-reference density functional theory. The talk presents a personal viewpoint, and will focus on the following points. 1) There are many ways to introduce multi-determinant wave functions into density functional theory. 2) Several variants have been successfully explored. 3) Difficulties inherent to approximations (both for wave functions and density functionals) persist, but can be attenuated.

Invited Talk SYES 1.3 Fri 11:30 HSZ 02

Density functionals from machine learning — •Kieron Burke — UC Irvine

Machine learning is spreading to all aspects of our lives. A particular method, kernel ridge regression, has proven very useful for fitting and interpolating in high-dimensional spaces.

Several years ago, in collaboration with the group of Klaus-Robert Muller in computer science at TU Berlin, we demonstrated how to construct a machine-learned density functional on a simple toy problem, non-interacting fermions in a box. We showed both its successes and limitations. We have continued to develop this method (PRL, 2012).

I will report on two recent works. In the first (arXiv:1609.02815), we construct the non-interacting kinetic energy functional for small molecules in 3D using a basis. We avoid the challenge of finding functional derivatives by learning the potential to density map directly, thereby bypassing the need to solve the Kohn-Sham equations.

In the second, we learn the interacting functional directly for the first time. In 1D, we model chains of H atoms of different length, and learn F[n] itself, from highly accurate DMRG calculations. With a novel choice of basis for the densities, we are able to learn the functional to chemical accuracy in the thermodynamic limit (arXiv:1609.03705).

Invited Talk SYES 1.4 Fri 12:00 HSZ 02

Taming Memory-Dependence in Time-Dependent Density Functional Theory — •Neepa Maitra — Hunter College of the City University of New York

The exact exchange-correlation functional of time-dependent density functional theory (TDDFT) is known to depend on the history of the densities and the initial states, a dependence which is ignored in almost all of the calculations today that use an adiabatic approximation. The lack of this dependence can sometimes lead to drastically incorrect predictions of the dynamics, as has been shown in several examples recently. We present here a new approach to developing functional approximations that breaks free of the adiabatic approximation, and test the resulting approximations on a number of model systems.

Invited Talk SYES 1.5 Fri 12:30 HSZ 02

Quantum Embedding Theories — •Fred Manby — School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK

Issues of accuracy in density functional theory can be addressed by making more accurate methods (like coupled-cluster theory) more efficient; or by making density functional approximations more accurate. Efforts in both directions are underway in our group, but in this talk I will focus on a third possibility, namely the development of quantum-mechnical multiscale models that enable the use of a high-accuracy method in a small, physically important region coupled to density-functional theory (or other low-cost methods) to describe the molecular environment.