

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

Time: Monday 10:30–13:00

Location: GER 38

O 6.1 Mon 10:30 GER 38

**DFT wants U: Embedded-cluster calculations of surface oxygen vacancies at TiO<sub>2</sub> 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 important role for many oxide materials properties. However, addressing them with first-principles density-functional theory (DFT) computations remains a challenge. At least Hubbard corrected DFT+U is required to achieve an appropriate electron localization. At the same time, the large dielectric constant of polarizable oxides like TiO<sub>2</sub> 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<sub>2</sub> (110). We systematically assess the reliability and computational efficiency by comparing to hybrid-level DFT calculations and calculations performed in conventional supercells.

O 6.2 Mon 10:45 GER 38

**Hubbard interactions from density-functional perturbation theory** — ●IURI TIMROV, MATTEO COCCIONI, 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).

O 6.3 Mon 11:00 GER 38

**Time-evolution using full configuration interaction quantum Monte Carlo** — ●KAI GUTHER<sup>1</sup>, WERNER DOBRAUTZ<sup>1</sup>, OLLE GUNNARSSON<sup>1</sup>, and ALI ALAVI<sup>1,2</sup> — <sup>1</sup>Max-Planck Institute for Solid State Research, Stuttgart, Germany — <sup>2</sup>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)

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 extent 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<sub>2</sub> surfaces with small adsorbed 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)

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, RNiO<sub>3</sub>, 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<sup>3+</sup> cations into Ni<sup>2+</sup> and Ni<sup>4+</sup>. 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.

O 6.6 Mon 11:45 GER 38

**Density matrix embedding theory for coupled fermion-boson systems** — ●TERESA E. REINHARD<sup>1</sup>, ULIANA MORDOVINA<sup>1</sup>, HEIKO APPEL<sup>1</sup>, JOSHUA S. KRETCHMER<sup>2</sup>, GARNET K. L. CHAN<sup>2</sup>, and ANGEL RUBIO<sup>1,3</sup> — <sup>1</sup>Max Planck Institut für Struktur und Dynamik der Materie, Hamburg — <sup>2</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena — <sup>3</sup>Nano-bio Spectroscopy Group and ETSF, Departamento de Física de Materiales, Universidad del País 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)

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)

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, basis-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).

O 6.9 Mon 12:30 GER 38

**Implementation of the SU(2) Symmetry in FCIQMC us-**

**ing the Graphical Unitary Group Approach** — ●WERNER DOBRAUTZ<sup>1</sup> and ALI ALAVI<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institut für Festkörperforschung — <sup>2</sup>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)

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.