

MM 57: Methods in Computational Materials Modelling (methodological aspect, numerics)

Advances in Electronic Structure Calculations

Time: Thursday 11:45–13:15

Location: TC 006

MM 57.1 Thu 11:45 TC 006

DFT+U for molecular orbitals — ●CHRISTOPH FREYSOLDT and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40273 Düsseldorf

Density functional theory with Hubbard-U corrections (DFT+U) is a standard technique to perform electronic-structure calculations for correlated materials at relatively low computational cost. Standard implementations use projection onto localized atomic orbitals, e.g., the d-orbitals for transition metals or f-orbitals for lanthanides. However, for materials containing superoxide ions (O_2^-), the correlated sites are the molecular π^* orbitals (MOs) of the O_2 unit rather than the p-orbitals of single O atoms. I will present our implementation of DFT+U for molecular sites in the SPHInX code[1]. It is based on projectors for the atomic orbitals and a subsequent geometry-defined contraction to MO space. This setup allows to derive analytical forces with only minor additions to a standard DFT code, and therefore makes the approach available for standard simulation protocols such as geometry optimization, molecular dynamics, or cluster expansion.

[1] <https://sxrepo.mpie.de>

MM 57.2 Thu 12:00 TC 006

Assessment of the GLLB-SC potential for solid-state properties and attempts of improvement — ●FABIEN TRAN, SOHAIB EHSAN, and PETER BLAHA — Vienna University of Technology, Vienna, Austria

Based on the work of Gritsenko *et al.* (GLLB) [Phys. Rev. A **51**, 1944 (1995)], the method of Kuisma *et al.* [Phys. Rev. B **82**, 115106 (2010)] to calculate the band gap in solids was shown to be much more accurate than the common methods of the local density approximation (LDA) and generalized gradient approximation (GGA). The main feature of the GLLB-SC potential (SC stands for solid and correlation) is to lead to a nonzero derivative discontinuity that can be conveniently calculated and then added to the Kohn-Sham band gap for a comparison with the experimental band gap. In this work, a thorough comparison of GLLB-SC with other methods, e.g., the modified Becke-Johnson (mBJ) potential [F. Tran and P. Blaha, Phys. Rev. Lett. **102**, 226401 (2009)], for electronic, magnetic, and density-related properties is presented. It is shown that for the band gap, GLLB-SC does not perform as well as mBJ for systems with a small band gap and strongly correlated systems, but is on average of similar accuracy as hybrid functionals. The results on itinerant metals indicate that GLLB-SC overestimates significantly the magnetic moment (much more than mBJ does), but leads to excellent results for the electric field gradient, for which mBJ is in general not recommended. In the aim of improving the results with the idea of GLLB, variants of the GLLB-SC potential are also tested.

MM 57.3 Thu 12:15 TC 006

Basis Set Selection for Advanced Density Functionals and Quantum Chemistry via Compressed Sensing — ●NIKLAS MENZEL¹, LUCA M. GHIRINGHELLI¹, GITTA KUTYNIOK², and MATTHIAS SCHEFFLER^{1,3} — ¹Fritz-Haber-Institut der MPG, Berlin, DE — ²Technische Universität, Berlin, DE — ³UC Santa Barbara, USA

The selection of basis functions is an important issue in density functional theory and quantum chemistry. The main task is to minimize the computational costs while maintaining the accuracy. Commonly used basis sets are not sufficiently accurate to represent the eigenfunctions for advanced exchange-correlation treatments. This leads to basis set extensions, such as the correlation-consistent basis sets by Dunning [JCP **90**, 1007 (1989)]. We propose a new method based on Compressed Sensing (CS), a recently developed signal processing technique. In CS, sparse signals are recovered using ℓ_0 -norm or ℓ_1 -norm regularization. Similarly, the key component of our approach is to find sparse real-space representations of self-consistently converged eigenfunctions (reference orbitals). We have developed a method for the selection of continuously parametrized basis functions (like Gaussian- or Slater-type basis functions). For the reference orbitals we used numeric atom-centered orbital basis functions. The reference orbitals are

generated for the free atom and homonuclear dimers.

With our new approach we can robustly determine accurate basis sets for all atoms.

MM 57.4 Thu 12:30 TC 006

A Compressed Sensing Approach to Kohn-Sham Density Functional Theory — ●INGO ROTH¹, ADRIAN STEFFENS^{1,2}, CHRISTIAN KRUMNOW¹, LUCA GHIRINGHELLI², MATTHIAS SCHEFFLER², and JENS EISERT¹ — ¹Dahlem Center for Complex Quantum Systems, FU Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

In density-functional theory calculations, the choice of basis sets plays a crucial role, determining the accuracy and computational cost of the simulation. The use of standardized basis sets and schemes which exploit the locality of the problem explicitly by assuming the Fock matrix to be banded often restrict the allowed states too much. Moreover, choosing an optimal basis set is a nontrivial task for many systems of interest, and large basis sets to compensate for this do not only increase computational time, but may also lead to numerical instability. In a more flexible approach, we propose a scheme that employs central notions of compressed sensing, a signal processing paradigm that has revolutionized the recovery of signals by efficiently identifying their underlying sparsity patterns, which makes it possible to massively under-sample, yet fully recover a signal. In this spirit, we have developed an algorithm based on multi-task regularized Stiefel-manifold optimization that enforces sparsity basis function coefficients, thus identifying those basis functions that carry the most relevant information of the system.

MM 57.5 Thu 12:45 TC 006

Full Configuration Interaction Quantum Monte Carlo study of the spin polarized three dimensional uniform electron gas — ●MICHELE RUGGERI¹, PABLO LOPEZ RIOS^{1,2}, and ALI ALAVI^{1,3} — ¹Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany — ²Theory of Condensed Matter Group, Cavendish Laboratory, J. J. Thomson Avenue, Cambridge CB3 0HE, UK — ³University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, UK

The uniform electron gas is system consisting in electrons in a uniform positive background, which can be used to model electrons in a metal and to study electronic correlations. Quantum Monte Carlo methods, especially DMC with the fixed node approximation, proved to be a powerful tool to study the uniform electron gas, but due to the sign problem these QMC results are only variational. It is however possible to obtain essentially exact estimates of the energy of electronic systems using Full Configuration Interaction Quantum Monte Carlo (fcqmc).

We compare fixed node DMC and fcqmc energies for the three dimensional spin polarized uniform electron gas in the high density regime ($r_s = 0.5$ and 1.0) for different system sizes ($N = 7$ to 33 electrons), giving an estimate of the fixed node error. We show that it is possible to improve the fixed node energies using multi-determinant trial wave functions, obtaining results in agreement with fcqmc if a large enough number of determinants is used. Twist averaged boundary conditions are in use to reduce finite size effects.

MM 57.6 Thu 13:00 TC 006

Vibrational modes, phonons, and atomic relaxation in Diffusion Monte Carlo — YU YANG LIU, ●BARTHOLOMEW ANDREWS, and GARETH CONDUIT — University of Cambridge, Cambridge, United Kingdom

Diffusion Monte Carlo methods are a prime candidate for high-accuracy electronic structure calculations. Determining atomic forces and the matrix of force constants is important for relaxing structures, calculating vibrational properties, and performing molecular dynamics simulations. We develop a quantum mechanical expectation value to evaluate the matrix of force constants directly in Diffusion Monte Carlo. The proposed formalism captures the full Van der Waals force, and thus opens new applications to molecules and solids in condensed matter.