

O 92: Electronic Structure Theory

Time: Friday 10:30–12:45

Location: H5

O 92.1 Fri 10:30 H5

Defining the Correlated Subspace in Hubbard-Corrected DFT using Boys Projector Functions — ●HANNA TÜRK, MATTHIAS KICK, GEORG MICHELITSCH, KARSTEN REUTER, and HARALD OBERHOFER — Technical University of Munich

Hubbard-corrected density-functional theory (DFT+U) is an effective self-interaction correction method for DFT, which gained its current popularity particularly due to its high computational efficiency compared to other correction schemes. Applications of DFT+U rest, on the one hand, on a meaningful choice of the effective correction parameter U , a topic widely discussed in literature. On the other hand, though, the performance of the DFT+U scheme also critically depends on the choice of the projector operator, which determines the states the correction is applied to. Unfortunately, this aspect has received much less attention so far, even though a wrong choice of projector can lead to highly unphysical results.

In this contribution, we present a new projector for DFT+U implemented in the electronic structure code FHI-aims. It is based on Boys localized states, which are able to represent delocalized electrons of hybridized molecules better than other projectors based e.g. on localized atomic basis functions. We test the performance of the new Boys projector on an iron porphyrin molecule and compare it to atomically localized projector functions. Thereby, we demonstrate the effects of the choice of projector functions on the accuracy of DFT+U results and discuss the system specific suitability of different projectors.

O 92.2 Fri 10:45 H5

First-Principles Study of Cation Distribution and Electron Solvation in Alkali-Metal Doped Zeolites — ●DEBALAYA SARKER¹, MATTHIAS SCHEFFLER¹, and SERGEY V LEVCHENKO^{1,2,3} — ¹Fritz-Haber-Institut der MPG, Berlin, DE — ²Skolkovo Innovation Center, Moscow, RU — ³NUST MISIS, Moscow, RU

Zeolites are nanoporous aluminosilicates with extraframework cations M^+ , $M=\text{Na, K, Cs}$. Additional doping of M results in M clusters inside the zeolite pores [1], making them potential basic catalysts. Despite extensive experimental efforts, the size, charge state, and stability of the clusters, and in particular how the electrons provided by the M dopants are distributed (solvated) are still debated. By varying the Si:Al ratio, M type, and doping amount, we have studied the M distributions and electron solvation in faujasite-zeolites using van der Waals corrected [2] DFT with semilocal (PBE) and hybrid (HSE06) functionals. A cluster-expansion model is trained to explore the configurational space of the M distribution at finite temperatures. We find that the amount of exact exchange α in HSE06 has no effect on geometry and relative energies. At Si:Al \approx 2.4, for all α the solvated electrons are localized within ~ 3 Å around the M_4^{3+} clusters formed inside smaller β cages, but for Si:Al=5 and $\alpha \lesssim 0.1$ delocalization over the unit cell occurs. Moreover, the equilibrium distribution of framework Al is found to be different for K- and Na-exchanged zeolites, affecting the M clustering in the zeolitic pores.

[1] J. A. Rabo *et al.*, Discuss. Faraday Soc. **41**, 328 (1966).

[2] A. Tkatchenko, M. Scheffler, Phys. Rev. Lett. **102**, 73005 (2009).

O 92.3 Fri 11:00 H5

All-electron FLAPW Realization of DFPT: 2nd-order Quantities and Dynamical Matrix — ●CHRISTIAN-ROMAN GERHORST, MARKUS BETZINGER, DANIEL AARON KLÜPPELBERG, GUSTAV BIHLMAYER, and STEFAN BLÜGEL — Peter Grünberg Institut and Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

The dynamical properties of atoms in the harmonic approximation are obtained by solving an eigenvalue problem of the dynamical matrix, which is related to the second-order variation of the total energy with respect to the atom displacement. We determine the dynamical matrix employing the all-electron full-potential linearized augmented plane-wave (FLAPW) method, as realized in the FLEUR (www.flapw.de) code, using the density functional perturbation theory (DFPT). The formulation and realization of the DFPT in the LAPW basis is a non-trivial task, as it entails a much more sophisticated formalism compared to plane-wave codes. Due to the atom-position dependence and the discontinuities at the boundaries of the domain-wise defined LAPW basis, so-called Pulay and surface terms emerge making the realization

of DFPT in FLAPW a challenge. In this contribution, we start from a brief presentation of these terms within the self-consistent solution of the Sternheimer equation, which delivers all required first-order quantities for the dynamical matrix. We will put an emphasis on how to treat the second-order changes of the external potential, the second-order variations of the wavefunction, as well as the basis-induced Pulay terms in the dynamical matrix setup, and show first results.

O 92.4 Fri 11:15 H5

Exploring the Molecular Density-Density Response Function for Inter-Molecular Interactions — ●CHRISTIAN DRESSLER, ARNE SCHERRER, and DANIEL SEBASTIANI — Chemistry Department, MLU Halle-Wittenberg, 06120 Halle(Saale), Germany

The molecular density-density response function yields the linear response of the molecular electronic charge density to arbitrary external perturbations. This motivates its application to molecular dynamics simulations, where the inter-molecular interaction potentials are constantly changing. We aim to explore this application of the molecular response function to the efficient modeling of inter-molecular interactions. Our starting point is an explicit representation of the molecular density-density response function in terms of its spectral decomposition[1]. From this representation, we devise a low rank approximation that allows to separate the contributions to the electronic response density from different multipole moments of the perturbation [2, 3]. This maximally condenses the physically relevant information of the full response function required for inter-molecular interactions. For its application to molecular dynamics simulations, we further generalize this explicit representation to arbitrary molecular geometries [4].

[1] D. Lu, F. Gygi and G. Galli., Phys. Rev. Lett. **100** 147601 (2008); [2] A. Scherrer and D. Sebastiani, J. Comput. Chem. **37** 665 (2016); [3] P. Ahlert, A. Scherrer, C. Dreßler and D. Sebastiani, Eur. Phys. J. B, **91** 94 (2018); [4] A. Scherrer, C. Dreßler, P. Ahlert and D. Sebastiani, J. Chem. Phys. **144** 144111 (2016)

O 92.5 Fri 11:30 H5

Electronic and conducting properties of single molecules with N-heterocyclic carbene terminations — ENRIQUE MONTES and ●HECTOR VAZQUEZ — Inst. of Physics, Academy of Sciences of the Czech Rep., CZ

N-heterocyclic carbenes (NHCs) have been recently shown to be a feasible alternative to thiol linker groups on Au due to their remarkable thermal and chemical stability. Here we demonstrate electron transport across single NHC-bonded single molecule circuits for the first time [1].

We investigate a series of NHC-terminated molecules by means of Density-Functional Theory and Non-Equilibrium Green's Functions, in collaboration with synthesis and experiments. We study the electronic structure and electron transport properties of a series of molecules of different length on Au electrodes. Molecules synthesized with the NHC group bonded to different metal precursors (Au, Ag, Cu) showed a modulation of conductance. Calculations reveal the effect of the NHC termination on the spectral properties of the junction [2,3] and establish the strong metal-molecule electronic coupling provided by the NHC unit.

[1] E.A. Doud, M.S. Inkpen, G. Lovat, E. Montes, D.W. Paley, M.L. Steigerwald, H. Vázquez, L. Venkataraman and X. Roy, JACS **140**, 8944 (2018).

[2] G. Foti and H. Vázquez, Nanotechnology **27**, 125702 (2016).

[3] G. Foti and H. Vázquez, J. Phys. Chem. C **121**, 1082 (2017).

O 92.6 Fri 11:45 H5

Adsorption site-selectivity in single-molecule junctions — ●ENRIQUE MONTES and HECTOR VAZQUEZ — Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, Prague, Czech Republic

Knowing the geometry of the metal-molecule interface is of paramount importance in single-molecule junctions as it strongly determines its electron transport properties. This is particularly true for thiol-based junctions, where conductance can change by orders of magnitude. In this work we present a series of density functional theory (DFT) conductance calculations. We demonstrate an adsorption site-selectivity technique by combining these calculations with surface enhanced Ra-

man scattering and current-voltage characteristics [1]. We illustrate the impact of this technique on prototypical aminobenzenethiol (ABT) and benzenedithiol (BDT) molecules connected to Au electrodes. This methodology distinguishes multiple molecular adsorption sites, and uncovers the origin of conductance fluctuations, which had never been detected experimentally up to now. In the case of ABT and BDT single-molecule junctions, electrical conductance can vary by up to a factor 100, hampering the development of reproducible conductance signatures. This study unambiguously monitors changes in molecular adsorption geometry for the first time and demonstrates their significant role on junction conductance fluctuations.

[1] S. Kaneko, E. Montes, S. Suzuki, S. Fujii, T. Nishino, K. Tsukagoshi, K. Ikeda, H. Kano, H. Nakamura, H. Vázquez and M. Kiguchi, Adsorption site recognition in single molecule circuits (submitted).

O 92.7 Fri 12:00 H5

Exact exchange-correlation kernels for optical spectra — ●MIKE ENTWISTLE and REX GODBY — Department of Physics, University of York, and European Theoretical Spectroscopy Facility, Heslington, York YO10 5DD, United Kingdom

Time-dependent Kohn-Sham density functional theory (TDDFT) is in principle an exact theory of excited states in many-electron systems, such as the optical absorption spectrum of molecules and solids, but its application is severely restricted by the limitations of the available approximate functionals for electron exchange and correlation - in particular the exchange correlation kernel, f_{xc} , the functional derivative of the exchange-correlation potential with respect to the electron density. To assist the construction of more powerful approximations for f_{xc} , we calculate the exact $f_{xc}(x, x', \omega)$ for a number of small, prototype systems, and analyse its character, including key aspects in which it differs from the common approximations.

O 92.8 Fri 12:15 H5

Systematic construction of the low-energy effective Hamilto-

nian from first-principles calculations — ●PILKWANG KIM, JI HOON RYOO, and CHEOL-HWAN PARK — Department of Physics, Seoul National University, Seoul 08826, Korea

Low-energy excitations are generally of primary interest in condensed matter physics. While first-principles methods based on density functional theory are the most reliable option, the computational cost of such methods is usually higher than other methods. On the opposite end, low-energy effective Hamiltonian methods have also been widely used as they require relatively smaller basis sets and lower computational costs. In such methods, there are some parameters that can be tuned to mimic low-energy excitations while taking account of the symmetry of the system. In this presentation, we discuss our systematic approach to construct a low-energy effective Hamiltonian that describes the electronic structure obtained from first-principles calculations. We demonstrate our method by applying it to real materials of interest.

O 92.9 Fri 12:30 H5

Atomistic study of the gas hydrates using classical molecular dynamics simulations — ●LAXMAN KUMAR KUNDARAPU and ANOOP KISHORE VATTI — Manipal Institute of Technology, Manipal, Karnataka, India

Gas clathrates are found copiously in permafrost region. In natural gas reservoirs or gas processing field, hydrates are formed by the chemical combination of the water and gas (precisely methane) at temperature above the freezing point of water. Gas clathrates are crystalline solids composed of water (ice) and gas (Methane/Ethane/Propane/CO₂). The most common hydrate structure i.e. sI (structure I) is investigated. These cubic structure forms a combination of polyhedral cages (water) hosting the guest molecule (methane). We performed classical molecular dynamics (MD) simulations to understand the behaviour of gas hydrates using various water models (SPC/TIP3P/TIP4P) under extreme pressure. The structural properties and accuracy of the various water models be discussed.