

DS 31: Frontiers of Electronic Structure Theory: Focus on Topology and Transport II (Joint session of DS and O, organized by O)

Time: Wednesday 10:30–13:00

Location: H24

DS 31.1 Wed 10:30 H24

Coupled-Cluster approach for both molecules and solids in the numeric atom-center orbital framework — •TONGHAO SHEN, ARVID CONRAD IHRIG, IGOR YING ZHANG, and MATTHIAS SCHEFFLER — *Fritz-Haber-Institut der MPG, Berlin.*

For a quantitative prediction of material properties, an advanced description of electronic correlation is crucial. As the "gold standard" correlation method in quantum chemistry, the coupled-cluster (CC) ansatz with singles, doubles and perturbative triples (CCSD(T)) is starting to gain attention in materials science[1]. At present, the CCSD(T)-quality description of the correlation effects in solids can be achieved by either studying the cluster-size convergence toward the bulk in real space[1] or implementing CCSD(T) for extended systems in reciprocal space[2]. In order to investigate and compare these approaches on an equal footing, it is essential to have a computational platform that enables CCSD(T) simulations to be carried out using both cluster and periodic models in a single computational environment. In this report, we present a CCSD(T) implementation for both molecules and solids in the all-electron full-potential code FHI-aims[3] with numeric atom-center orbital (NAO) basis sets. A special memory-distribution strategy is designed to significantly reduce the inter-CPU communication, which is the main challenge for the parallelization of wave-function methods. The accuracy and efficiency are demonstrated for a group of molecules, 1D-, 2D- and 3D-periodic materials. [1] C. Müller, *et al.*, PCCP. **14**, 7605 (2012); [2] A. Grüneis, *et al.*, JCTC **7**, 2780 (2011); [3] V. Blum, *et al.*, CPC **180**, 2175-2196 (2009).

DS 31.2 Wed 10:45 H24

Surface adsorption energetics at the "gold standard": Small molecule binding to TiO₂(110) — •DANIEL BERGER^{1,2}, A. KUBAS³, D. MANGANAS³, H. OBERHOFER¹, F. NEESE³, and K. REUTER¹ — ¹TU München — ²University of California, Los Angeles — ³MPI für chemische Energiekonversion, Mülheim an der Ruhr

Adsorption energies at oxide surfaces are central quantities required for catalysis, energy and a multitude of other application areas. At present, the by far dominant computational method to obtain such energetics is density-functional theory (DFT). Unfortunately, systematic benchmarking of such energetics against accurate reference numbers from correlated wave-function theory as known from molecular systems is scarce, largely owing to the fact that the latter techniques are often not available for standard periodic boundary condition supercell calculations.

We address this situation with a solid-state QM/MM embedded cluster approach, in which the adsorbate and immediate surrounding surface atoms are described quantum mechanically, while the long-range electrostatic interactions are accounted for through a polarizable force field. This yields a numerically highly efficient approach that enables use of the recently developed domain-based local pair natural orbital coupled cluster method with single-, double- and perturbative triple-excitations (DLPNO-CCSD(T)) in the quantum region. We exploit corresponding "gold standard" adsorption energies for a set of prototypical small molecules interacting with the rutile TiO₂(110) surface for a systematic benchmark of DFT numbers.

DS 31.3 Wed 11:00 H24

Water adsorption on surfaces from many-body perturbation theory — •THEODOROS TSATSOUKIS and ANDREAS GRÜNEIS — Max-Planck-Institute for Solid State Research, Stuttgart

The accurate description of the interaction of molecules with surfaces is of crucial importance for a wide range of phenomena. While Kohn-Sham density functional theory is one of the most widely-used methods for describing the electronic structure of surfaces, many local and semi-local functionals are often not able to produce accurate molecular adsorption energies. Quantum chemical wave-function based methods such as Møller-Plesset perturbation theory (MP2) and coupled-cluster methods promise controllable accuracy, however, at much higher computational costs. Large part of the latter is due to the number of virtual states. We consider an approach whereby the occupied orbitals are converged in a plane wave basis, whereas the virtual space is then constructed using pseudized Gaussian orbitals expanded in plane waves, leading to reduced computational cost. In particular we study

water adsorption on bulk LiH and h-BN sheets at the level of MP2 theory within the projector-augmented-wave method as implemented in VASP [1]. The results are compared to state-of-the-art methods such as hybrid functionals and diffusion Monte Carlo [2].

[1] Marsman *et al.*, The Journal of Chemical Physics, **130**, 184103 (2009)

[2] Al-Hamdani *et al.*, The Journal of Chemical Physics, **142**, 181101 (2015)

DS 31.4 Wed 11:15 H24

Photo-isomerization in azobenzene-functionalized self-assembled monolayers: The impact of many-body effects — •CATERINA COCCHI and CLAUDIA DRAXL — Institut für Physik und IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

Self-assembled monolayers (SAMs) of azobenzene-functionalized alkanethiols on gold suffer from hindered photo-isomerization, as observed experimentally [1]. While this behavior is generally ascribed to strong intermolecular coupling, a clear microscopic understanding of this phenomenon is still missing. In order to address this question, we perform a first-principles study of the excited-state properties of azobenzene-functionalized SAMs. In the framework of many-body perturbation theory (GW approximation and Bethe-Salpeter equation), as implemented in the all-electron full-potential code exciting [2], we investigate the optical absorption spectra of these materials, inspecting the influence of packing density and functionalization of the azobenzene molecules with different end groups. Through a systematic analysis of the character of the excitations, we clarify the role and interplay of screening and local-field effects, which strongly impact light absorption and hence photo-isomerization in these systems.

[1] C. Gahl *et al.* J. Am. Chem. Soc. **132**, 1838 (2010). [2] A. Gulans *et al.* J. Phys.: Condens. Matter **26**, 363202 (2014).

DS 31.5 Wed 11:30 H24

Laplace-transformed MP2 with localized Resolution of Identity -efficient in-memory MP2 for large systems — •ARVID CONRAD IHRIG¹, PATRICK RINKE², IGOR YING ZHANG¹, and MATTHIAS SCHEFFLER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Aalto University, Helsinki, Finland

A well-known problem in local and semi-local density functional approximations and to a lesser extend also in hybrid functionals is the one-electron self-interaction error, which can lead to a qualitatively wrong description for applications like charge-transfer systems. One possible remedy is the 2nd order Møller-Plesset perturbation theory (MP2), which does not suffer from this error. However, the time and memory requirements for MP2 prevent it routine-use for large molecular and periodic systems. The Laplace-transformed MP2 (LT-MP2) [1] can significantly reduce the computational time, but requires the usage of intermediate variables stored on disk, resulting in an inefficient usage of computational resources. In this work we combine the LT-MP2 with our localized Resolution of Identity (RI-LVL) [2] approach to eliminate the disk-storage bottleneck and fully exploit massive parallelization strategies. RI-LVL expands the basis function pairs in the electron repulsion integrals in local auxiliary basis sets. For the example of water clusters, we demonstrate the favourable memory scaling (at worst N^2) of our new MP2 implementation, which facilitates the in-memory calculation of large systems at high accuracies.

[1] P. Ayala *et al.*, J. Chem. Phys. **110**, 3660 (1999)

[2] Ihrig *et al.*, New J. Phys. **17**, 093020 (2015)

DS 31.6 Wed 11:45 H24

GW singles contributions for the random phase approximation correlation energies — •JIRI KLIMES¹, MERZUK KALTAK², EMANUELE MAGGIO³, and GEORG KRESSE³ — ¹J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic — ²Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY — ³University of Vienna, Faculty of Physics, Vienna, Austria

The random phase approximation (RPA) to the correlation energy yields often very accurate results for condensed matter systems. However, a general tendency to underbind has been observed for systems such as molecular solids or for adsorption. One of the ways that have been proposed to improve the accuracy of RPA are the so-called sin-

gles corrections of Ren and coworkers [1]. We present our derivation of the singles corrections using the assumption that the electron density changes when going from the reference to the interacting system [2]. This leads to a very compact expression for the corrections. Moreover, the singles formula can be easily modified to account for screening effects, giving the GW singles. We assess the effect of both the original and modified singles on covalently and metallically bonded systems as well as on simple weakly bonded systems. Finally, we show that adding the singles corrections leads to considerably improved adsorption energies and lattice energies of molecular solids.

[1] Ren, Tkatchenko, Rinke, Scheffler, Phys. Rev. Lett **106**, 153003 (2010).

[2] Klimeš, Kaltak, Maggio, Kresse, J. Chem. Phys. **143**, 102816 (2015).

DS 31.7 Wed 12:00 H24

Long-range corrected DFT meets GW: vibrationally resolved photoelectron spectra from first principles — •THOMAS KÖRZDÖRFER — Institut für Chemie, Universität Potsdam, D-14476 Potsdam

We introduce an entirely non-empirical and computationally efficient scheme to calculate highly reliable vibrationally resolved photoelectron spectra for molecules from first principles.[1] To this end, we combine non-empirically tuned long-range corrected hybrid functionals with non-self-consistent many-body perturbation theory in the G_0W_0 approximation and a Franck-Condon multi-mode analysis based on DFT-calculated frequencies. The vibrational analysis allows for a direct comparison of the GW-calculated spectra to gas-phase ultraviolet photoelectron measurements of neutral and anionic molecules, respectively. In addition, vertical IPs and EAs were benchmarked against other GW methods and basis-set extrapolated CCSD(T) results for a recently introduced test set of 24 molecules frequently used in organic electronics.[2] $G_0W_0@LRC$ -DFT yields mean absolute errors on the order of 0.1 eV for IPs, EAs, and fundamental gaps, clearly outperforming commonly used G_0W_0 approaches as well as partially and fully self-consistent GW methods.

[1] L. Gallandi and T. Körzdörfer, JCTC **11**, 5391 (2015).

[2] L. Gallandi, N. Marom, P. Rinke, and T. Körzdörfer, JCTC accepted for publication (2015).

DS 31.8 Wed 12:15 H24

LDA-1/2 as a starting point for G_0W_0 calculations — •RONALDO RODRIGUES PELA^{1,2}, UTE WERNER¹, DMITRII NABOK¹, and CLAUDIA DRAXL¹ — ¹Humboldt-Universität zu Berlin, Institut für Physik and IRIS Adlershof, Berlin, Germany — ²Instituto Tecnológico de Aeronáutica, São José dos Campos, Brazil

For many semiconductors and insulators, LDA represents a bad starting point for G_0W_0 calculations. Hybrid functionals improve upon LDA, but at the price of increasing computational cost of about 2 orders of magnitude. An alternative starting-point for the single-shot G_0W_0 can be the LDA-1/2 method [1], because it approximately includes the self-energy of quasi-particles within a generalized Kohn-Sham scheme, leading to improved band-gaps over the LDA ones, but without being computationally more involved. In this work, we systematically compare 3 starting-points for G_0W_0 calculations: LDA, PBE0, and the LDA-1/2 method. A selection of semiconductors (C, Si, SiC, AlP, LiF, MgO, Ne, Ar, GaN, GaAs, CdS, ZnS, and ZnO) is chosen for this benchmark. We demonstrate that LDA-1/2 is a good choice in most cases, reducing the root mean square error in band-gap

predictions by 50% when compared to G_0W_0 on top of LDA or PBE0. With the exception of large band gap materials, LDA-1/2 predictions are already close to the experimental band gaps, and thus G_0W_0 has minor effects.

Reference [1]: Phys. Rev. B **78**, 125116 (2008).

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DS 31.9 Wed 12:30 H24

DFT+U within a numeric atom-centered orbital basis — •MATTHIAS KICK, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München

Materials like transition metal oxides (TMOs) still challenge a description through first-principles density-functional theory (DFT). Appropriately capturing the electron localization in TMOs generally requires at least hybrid exchange-correlation functionals. Such higher-rung functionals come with appreciable computational cost, which limits their use in large supercell calculations. For such applications effective and numerically less intense approaches are therefore still a much sought alternative.

One such method is the DFT+U approach, where the on-site Coulomb correlation effects are treated using a model Hamiltonian, while remaining interactions are treated on the level of semi-local DFT. Full DFT+U functionality including nuclear gradients (forces) has been implemented in the electronic structure code *FHI-aims*. We account for three common occupation matrix representations, differing in the way how the occupations of the correlated subspaces are determined. We critically discuss their performance and differences in the context of the numeric atomic orbital basis sets employed in *FHI-aims*. The established numerically efficient framework is finally used to address neutral and charged oxygen vacancies at the TiO₂(110) surface within a solid-state embedding approach.

DS 31.10 Wed 12:45 H24

High-throughput Screening and Statistical Learning for Design of Transparent Conducting Oxides — •CHRISTOPHER SUTTON, LUCA M. GHIRINGHELLI, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft

Transparent conducting oxides (TCOs) represent a class of well-developed and commercialized wide-bandgap semiconductors that are crucial for many electronic devices. Ternary Al, Ga, and In-based sesquioxides are investigated as alternative wide-bandgap semiconductors motivated by very intriguing recent experimental work that has demonstrated bandgap engineering in (GayIn_{1-y})₂O₃ from 3.8 eV to ca. 5 eV[1] and ca. 5 eV to 7.5 eV for (Al_{1-x}Gax)₂O₃. [2]

New ternary oxides with the chemical structure of (Al_xGayIn_{1-x-y})₂O₃ have been identified using cluster expansion (CE) models combined with fast stochastic optimization techniques (e.g., Wang-Landau and diffusive nested sampling) in order to efficiently search potential (ordered and disordered) configurations within a given lattice and for different temperatures. Wang-Landau and diffusive nested sampling has also allowed for a consideration of the effect of entropy on the relative stability of ternary oxides. Statistical learning has also been used to identify a structure-property relationship to efficiently identify new wide-band gap TCOs to improve the fundamental chemical and physical properties (e.g., conductivities, mobilities, and optical transparency) by investigating the parameters that control these properties.

[1] F Zhang, et al., Solid State Communications 2014, 186, 28. [2] H Ito, et al., Japanese Journal of Applied Physics 2012, 51, 100207.