

## DS 4: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge I (joint session O/TT/ CPP/DS)

First-principles electronic structure calculations have become an indispensable tool in many research areas where materials surfaces or interfaces play a central role. Corresponding calculations provide insight into catalytic mechanisms, interfacial ionic and charge transport in batteries or solar cells, materials degradation through corrosion or wear, and many other highly relevant application areas. Despite this prolific use, corresponding calculations face multiple issues. While the invited lectures will have a focus on this interface challenge, the symposium will also cover the general field of computational materials science and electronic-structure theory.

Organizers: Jens Nørskov (Technical University of Denmark), Karsten Reuter (Technical University Munich), and Matthias Scheffler (Fritz Haber Institute of the Max Planck Society, Berlin)

Time: Monday 10:30–13:00

Location: H9

### Topical Talk

DS 4.1 Mon 10:30 H9

**Scaling relations and beyond for kinetic Monte Carlo models in heterogeneous catalysis** — •MIE ANDERSEN — Theoretical Chemistry, Technische Universität München, Germany

Heterogeneous catalysis typically operates at the interface between a gas or liquid and a solid catalytic material. In my talk, I will discuss mean-field and kinetic Monte Carlo models for the operating catalyst. These often rely on input data calculated using either first principles or more approximate methods, e.g. scaling relations, which use only selected adsorption energies as descriptors for the catalyst function [1,2]. I will also discuss recent work [3] where we used compressed sensing methods to identify new low-cost and accurate descriptors that allow to predict adsorption energies for a wide range of adsorbates, multi-metallic transition metal surfaces and facets. The descriptors are expressed as non-linear functions of intrinsic properties of the clean catalyst surface, e.g. coordination numbers and  $d$ -band moments. From a single DFT calculation of these properties, we predict adsorption energies at all potential surface sites, and thereby also the most stable geometry. Compared to previous approaches such as scaling relations, we find our approach to be both more general and more accurate for the prediction of adsorption energies on alloys with mixed-metal surfaces, already when based on training data including only pure metals.

[1] M. Andersen *et al.*, *Ang. Chem. Int. Ed.* **55**, 5210 (2016)

[2] M. Andersen *et al.*, *J. Chem. Phys.* **147**, 152705 (2017)

[3] M. Andersen *et al.*, submitted

DS 4.2 Mon 11:00 H9

**The Teacher and the Student: Exchange-Correlation Energy Densities from Quantum Chemistry and Machine-Learning** — •JOHANNES T. MARGRAF, CHRISTIAN KUNKEL, and KARSTEN REUTER — Chair for Theoretical Chemistry, Technische Universität München, Germany

(Semi-)local density functional approximations (DFAs) are the workhorse electronic structure methods in condensed matter theory and surface science. Central to defining such DFAs is the exchange-correlation energy density  $\epsilon_{xc}$ , a spatial function that yields the exchange-correlation energy  $E_{xc}$  upon integration.

Unlike  $E_{xc}$ ,  $\epsilon_{xc}$  is not uniquely defined. Indeed, there are infinitely many functions that integrate to the correct  $E_{xc}$  for a given electron density  $\rho$ . The challenge for constructing a useful DFA is to find a systematic connection between  $\rho$  and  $\epsilon_{xc}$ . While several empirical and rigorous approaches to this problem are known, there has been little innovation with respect to the fundamental functional forms of DFAs in recent years.

Herein, we discuss two less explored routes to constructing DFAs. Specifically, a recipe for deriving  $\epsilon_{xc}$  directly from many-body wavefunctions is compared to a machine learning (ML) approach that infers the optimal  $\epsilon_{xc}$  for a given functional form. We find that local DFAs based on the many-body  $\epsilon_{xc}$  are not transferrable between systems because the underlying energy densities are inherently non-local. In contrast, the ML  $\epsilon_{xc}$  is by construction as local as possible. The extension of both approaches to non-local DFAs will be discussed.

DS 4.3 Mon 11:15 H9

**Self-Interaction Corrected SCAN for Molecules and Solids: All-Electron Implementation with Numerical Atom-Centered Basis Functions** — •SHENG BI, IGOR YING ZHANG, CHRISTIAN CARBOGNO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

Electronic self-interaction is the most severe cause of inaccuracies in all semilocal density-functional approximations (DFAs), including the promising meta-GGA “strongly constrained and appropriately normed” (SCAN) functional [1]. This error can be alleviated via localized orbital scaling corrections [2] or via self-interaction corrections (SIC) based on Fermi-orbitals [3]. In this contribution, we follow the latter concept which involves solving a set of SIC constraints. Here, we present an all-electron implementation of the self-consistent SIC for semilocal DFAs, including SCAN. We first validate our implementation by inspecting certain properties (HOMO and dissociation energies) for a molecular test set, showing that SIC improves SCAN calculations. Furthermore, we compare the performance of SCAN-SIC and SCAN $\alpha$ , i.e., SCAN with a fraction of exact exchange, in predicting the broken symmetry in pentacene – note that standard semilocal DFAs always favor symmetric solutions. Eventually, we discuss the extension of our SIC approach to periodic solids.

[1] J. Sun *et al.*, *Phys. Rev. Lett.* **115**, 036402 (2015).

[2] N. Q. Su *et al.*, *Proc. Natl. Acad. Sci.* **115**, 9678 (2018).

[3] Z. Yan *et al.*, *Phys. Rev. A* **95**, 052505 (2017).

DS 4.4 Mon 11:30 H9

**Progress in Fermi-Löwdin orbital self-interaction correction to DFT** — •TORSTEN HAHN, SEBASTIAN SCHWALBE, and JENS KORTUS — Institute for Theoretical Physics, Freiberg, Germany

The accuracy of density functional theory (DFT) calculations is limited by the so called self-interaction error [1]. The recently proposed Fermi-Löwdin orbital based method [2,3,4] for self-interaction correction (FLO-SIC) is a unitary invariant and size extensive approach to overcome this error. We present the current state of the method and discuss selected applications. In addition we discuss strategies to improve the thermochemical and numerical performance of the FLO-SIC approach in combination with state-of-the-art exchange-correlation functionals.

[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)

[3] M. R. Pederson, *J. Chem. Phys.*, vol. 142, 064112 (2015)

[4] S. Schwalbe *et al.*, *J. Comp. Chem.*, vol. 39, 2463 (2018).

DS 4.5 Mon 11:45 H9

**Time evolution of the natural occupation numbers** — •CARLOS BENAVIDES-RIVEROS and MIGUEL A. L. MARQUES — Martin-Luther Universität Halle Wittenberg

Reduced density matrix functional theory (RDMFT) is based on the Gilbert theorem, which asserts that the ground-state wave function can be written as a functional of the one-body reduced density matrix. Since RDMFT accounts for fractional natural occupation numbers, it captures quite well static (strong) electron correlation (unlike DFT, RDMFT correctly predicts the insulating behavior of Mott-type insulators). Yet the time-dependent extension of RDMFT suffers from various shortcomings. Chief among them, the current status of the theory does not allow the fermionic occupation numbers to evolve in time. It is known that this deficiency is connected to the failure of RDMFT to account for relative phases at the level of the two-body reduced density matrix. Based on recent results on fermionic exchange symmetry, we propose a new equation for the time evolution of the fermionic occupation numbers.

DS 4.6 Mon 12:00 H9

**Nonempirical hybrid functionals constructed through ad-**

**justable potential probes for band gap predictions of extended systems** — •THOMAS BISCHOFF, IGOR RESHETNYAK, and ALFREDO PASQUARELLO — Chaire de Simulation à l'Echelle Atomique (CSEA), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

We describe a nonempirical procedure for achieving accurate band gaps of extended systems through the insertion of suitably defined potential probes. By enforcing Koopmans' condition on the resulting localized electronic states, we determine the optimal fraction of Fock exchange to be used in the adopted hybrid functional. As potential probes, we consider native defects, the extrinsic hydrogen impurity, and various adjustable potentials that allow us to vary the energy level of the localized state in the band gap and its degree of localization. By monitoring the delocalized screening charge, we achieve a measure of the hybridization with the band states, which can be used to improve the band gap estimate. Application of this methodology to AlP, C and MgO yields band gaps differing by less than 0.2 eV from experiment.

DS 4.7 Mon 12:15 H9

**Quantum-mechanical relation between atomic dipole polarizability and van der Waals radius** — •DMITRY FEDOROV, MAINAK SADHUKHAN, MARTIN STÖHR, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

The atomic dipole polarizability  $\alpha$  and the van der Waals (vdW) radius  $R_{\text{vdW}}$  are two key quantities to describe the ubiquitous vdW forces important for the structure and dynamics of molecules and materials [1]. The commonly assumed relation between them,  $R_{\text{vdW}} \propto \alpha^{1/3}$ , is based on a classical picture of hard-sphere atoms. Employing the quantum Drude oscillator model [2], we reveal [3] the quantum-mechanical relation  $R_{\text{vdW}} = \text{const.} \times \alpha^{1/7}$  which is markedly different from its classical counterpart. Based on the accessible accurate reference data for  $\alpha$  and  $R_{\text{vdW}}$ , we demonstrate that the obtained formula can be used as a unified definition of the vdW radius solely in terms of the atomic polarizability for all chemical elements. Moreover, for vdW-bonded heteronuclear dimers consisting of atoms A and B, the simple combination rule  $\alpha = (\alpha_A + \alpha_B)/2$  provides a remarkably accurate way to calculate their equilibrium interatomic distance. These findings unveil a fundamental relationship between the geometric and electronic properties of atoms. From a practical point of view, they allow us to reduce the empiricism and improve the efficiency of computational models for vdW interactions.

- [1] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
- [2] Jones *et al.*, Phys. Rev. B **87**, 144103 (2013)
- [3] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)

DS 4.8 Mon 12:30 H9

**impact of continuum electronic states on van der Waals dispersion interactions** — •MOHAMMAD REZA KARIMPOUR, DMITRY FEDOROV, and ALEXANDRE TKATCHENKO — University of Luxem-

bourg, Luxembourg, Luxembourg

The ubiquitous van der Waals (vdW) forces play an important role for structure, stability, and dynamics of molecules and materials. Their description on atomistic level is important for molecular physics, crystal chemistry, surface science, structural biology, and pharmacy. To this end, the development of simple yet efficient models is of high importance. Normally, such models focus only on fluctuations to bound electron states, described via quantum harmonic oscillator potentials. However, the polarizability of real atomic and molecular systems has important contributions also from fluctuations to continuum states. To study their influence on the vdW dispersion interactions from a general point of view, here we consider models based on the Dirac delta-function potentials. In one-dimensional case, such a potential provides just one bound state whereas all excited states belong to the continuum electron spectrum. We apply both the atomistic method and the scattering picture representing the van der Waals and Casimir approaches for dispersion interactions, respectively. In the atomistic framework we compare our results to the ones of the quantum oscillator models. Within the other picture, we discuss an obtained new scaling law in comparison to the results known for excited atomic systems.

- [1] Woods *et al.*, Rev. Mod. Phys. **88**, 045003 (2016)
- [2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)

DS 4.9 Mon 12:45 H9

**Relation between the van der Waals radius and higher-order atomic polarizabilities** — •ORNELLA VACCARELLI, DMITRY FEDOROV, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

The atomic polarizabilities and van der Waals (vdW) radii describe the electronic and geometric aspects of the ubiquitous vdW interactions [1, 2], respectively. Normally, these quantities are assumed to be independent. Therefore, they are determined separately from each other. Based on the quantum Drude oscillator model [3], recently we revealed [4] a remarkable direct relationship between the vdW radius and the dipole polarizability. This provides a unified determination of the vdW radius for all chemical elements solely in terms of their dipole polarizabilities. In addition, further relations between the vdW radius  $R_{\text{vdW}}$  and higher-order atomic polarizabilities  $\alpha_n$  ( $n = 1, 2, \dots$ ) were found empirically. Here, we present a physical background for these results. The derivation of the corresponding scaling laws is performed by going beyond the dipole approximation for the Coulomb interaction to obtain higher-order contributions to attractive and repulsive forces acting on atoms in a vdW-bonded homonuclear dimer. We focus on the derivation of the proportionality constants  $C_n$  in the general relation  $R_{\text{vdW}}(\alpha_n) = C_n \alpha_n^{2/7(n+1)}$  unveiling their quantum nature.

- [1] Woods *et al.*, Rev. Mod. Phys. **88**, 045003 (2016)
- [2] Hermann *et al.*, Chem. Rev. **117**, 4714 (2017)
- [3] Jones *et al.*, Phys. Rev. B **87**, 144103 (2013)
- [4] Fedorov *et al.*, Phys. Rev. Lett. **121**, 183401 (2018)