O 57: New Methods: Theory

Time: Wednesday 16:15–18:00 Location: MA 043

O 57.1 Wed 16:15 MA 043

Periodic coupled-cluster theory for the ground and excited states with atom-centered basis functions

— •Evgeny Moerman[1], Felix Hummel[2], Andreas Irmler[2], Alejandro Gallo[2], Andreas Grüneis[2], and Matthias Scheffler[1] — [1]The NOMAD Laboratory at the FHI-MPG, Berlin — [2]Inst. for Th. Phys., TU Wien, Vienna

Periodic coupled-cluster (CC) theory promises to be a reliable, highly accurate electronic structure method in materials science [1]. The all-electron code FHI-aims [2], which employs numeric atom-centered orbitals (NAOs), has been interfaced to the Cc4s code [3,4], making CC theory for both the ground and excited states accessible to FHI-aims. For molecules, the equation-of-motion-CC (EOM-CC) method predicts quasi-particle energies more accurately than the GW approximation[5], and we expect that this will also hold for bandstructures of solids. Like most correlated wave function methods, CC methods exhibit excessively slow convergence with the size of the super cell. So far, no efficient approach to address this problem exists for NAOs. We present the current state of the CC theory framework available in FHI-aims and possible avenues to address the finite-size error.

[1] G. Booth *et al.*, *Nature*, **493**, 365-370 (2013)
[2] The FHI-aims web page, https://fhi-aims.org
[3] F. Hummel *et al.*, *JCP*, **146**, 124105 (2017)
[4] E. Moerman *et al.*, *JOSS*, **7**, 4 (2022)
[5] M. Lange *et al.*,*JCTC*, **14**, 4224-4236 (2018)

O 57.2 Wed 16:30 MA 043

Efficient and Accurate Calculation of Tunneling Conductance in Molecular Junctions Using Density Functional Theory

— •Enrique Montes and Héctor Vázquez — Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, Prague 162 00, Czech Republic

We present a novel method for the calculation using density functional theory (DFT) of tunneling conductance in molecular junctions for thousands of junction structures. Conductance is estimated within a single scaling parameter by examining clusters where a molecule is bonded to one Au atom at each end and employing unconstrained ab initio molecular dynamics simulations [1]. This method yields accurate DFT-based conductance values across a wide range of geometries.

We investigate two junctions involving conjugated molecules. By examining scenarios where the central benzene ring can freely rotate or is constrained by chemical design [2], we uncover trends in transport properties and establish a clear mapping between molecular structure and junction conductance. Additionally, we evaluate the robustness of our methodology under varied conditions by employing different chemical linker groups (coupling regime) and metallic electrodes [3].

This method overcomes computational limitations, providing reliable conductance evaluation while reducing computational costs by a factor ∼400× as compared to DFT-NEGF transport calculations.

[1] H. Vázquez, J. Phys. Chem. Lett., 13, 9326 (2022).
[2] Y. S. Park, et al. J. Am. Chem. Soc., 131, 10820 (2009).
[3] T. A. Su, et al. Nat. Rev. Mater., 1, 16002 (2016).

O 57.3 Wed 16:45 MA 043

STM simulations with asymmetric/tilted tips: the case of Cu and CO on Cu(111)

— Ivan Abilio[1,2] and •Krisztián Palotás[1,2] — [1]Wigner Research Center for Physics, Budapest, Hungary — [2]Institute of Physics, Budapest University of Technology and Economics, Budapest, Hungary

The correct interpretation of experimental scanning tunneling microscopy (STM) images is very important. The presence of asymmetric/tilted tips complicates this procedure and results in reduced symmetry of the STM images. There are only a few theoretical methods, which are able to treat arbitrary tilting of the tip in STM simulations [1,2,3,4]. In the present work, we employ the revised Chen's derivative rules [4] to study the effect of tilted tips on the STM imaging of a Cu adatom and a CO molecule on a Cu(111) surface. Apart from obtaining good agreement with published experimental images [5], our method enables an analysis of the tunneling current in terms of tip orbital contributions, and thus provides a deeper theoretical understanding of the STM contrast formation. We point out important differences between pure and CO-functionalized metal (symmetric and tilted) STM tips. [1] G. Mándi et al., J. Phys. Condens. Matter 25, 445009 (2013). [2] G. Mándi et al., J. Phys. Condens. Matter 26, 485007 (2014). [3] G. Mándi et al., Prog. Surf. Sci. 90, 223 (2015). [4] G. Mándi and K. Palotás, Phys. Rev. B 91, 165406 (2015). [5] A. Gustafsson et al., Phys. Rev. B 96, 085415 (2017).

O 57.4 Wed 17:00 MA 043

Sub-nanometer depth profiling of native metal oxide layers within single fixed-angle X-ray photoelectron spectra

— •Martin Wortmann[1], Klaus Viertel[2], Michael Westphal[1], Dominik Graulich[1], Yang Yang[1], Maik Gärner[1], Jan Schmalhorst[1], Natalie Frese[3], and Timo Kuschel[1] — [1]Bielefeld University, Bielefeld, Germany — [2]Bielefeld University of Applied Sciences, Bielefeld, Germany — [3]University of Hawaii, Honolulu, USA

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here, we propose a simple and accessible approach for the depth profiling of ultrathin oxide layers within single fixed-angle XPS spectra. Instead of using only one peak in the spectrum, as is usually the case, we utilize all peaks within the energy range of a standard lab device, thus resembling energy-resolved XPS without the need for a synchrotron. We derived and tested new models that allow the calculation of depth-resolved concentration profiles at the oxide-metal interface, which are also valid for angular- and energy-resolved XPS. The proposed method not only improves the accuracy of earlier approaches but also paves the way for a more holistic understanding of the XPS spectrum.

O 57.5 Wed 17:15 MA 043

Adapting Explainable Machine Learning to Study Mechanical Properties of 2D Hybrid Perovskites

— •Yuxuan Yao[1,2], Dan Han[3,4], Hubert Ebert[4], Aron Walsh[5], David O. Scanlon[3], and Harald Oberhofer[2] — [1]Chair for Theoretical Chemistry, Technical University of Munich — [2]Chair for Theoretical Physics VII, University of Bayreuth — [3]School of Chemistry, University of Birmingham — [4]Department of Chemistry and Center for NanoScience, University of Munich — [5]Department of Materials, Imperial College London

The fast increase of power conversion efficiency (PCE) and low-cost preparation of lead-based halide perovskite photovoltaics are of great interest for use in optoelectronic devices. 2D hybrid organic and inorganic perovskites (HOIPs) have been used as capping layers on top of 3D perovskites to increase the stability and PCE. On the other hand, the soft and stable HOIPs are attractive in sustaining flexible electronic devices. In our work, we utilize explainable machine learning (ML) techniques to accelerate the in silico prediction of elasticities of 2D perovskites, as indicated by their Young's moduli. Our ML models allow us to distinguish between stiff and nonstiff HOIPs and to extract the materials' features most strongly influencing the Young's modulus. The Pb-halogen-Pb bond angle emerges as the dominant physical feature with an inverse correlation to the structural non-stiffness. Furthermore, the cations' steric effect index (STEI) was found to yield rough estimates of non-stiffness. Finally, the deformation of the octahedra strongly affects the mechanical properties, allowing us to perform transfer learning from single layered to multi-layered 2D perovskites.

O 57.6 Wed 17:30 MA 043

Enhanced Sampling of Rare Events Using Boltzmann Generators

— •David Greten[1], Karsten Reuter[1], and Johannes T. Margraf[1,2] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]University of Bayreuth

The kinetics of catalytic processes in surface chemistry are determined by rare events such as bond breaking or bond forming reactions. These events are highly challenging to describe in atomistic simulations because brute-force molecular dynamics (MD) simulations would require an unfeasible number of time steps to observe them. Biased MD methods like Metadynamics or Umbrella Sampling represent the most rigorous approach to overcome this limitation. Such enhanced sampling methods are thus the gold standard for the computation of free energy barriers. Nonetheless, they inherit some of the drawbacks of conventional MD, namely long equilibration periods and correlation between samples along the trajectory. In this context, generative machine learning models (such as Boltzmann Generators, BGs) may offer significant advantages, as they can directly generate statistically independent samples from the Boltzmann distribution. In this contribution, we explore how BGs can be used in enhanced sampling simulations of rare events.

O 57.7 Wed 17:45 MA 043

Surface segregation in high-entropy alloys from alchemical machine learning — •Arslan Mazitov and Michele Ceriotti — Laboratory of Computational Science and Modeling, Institute of Materials, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

High-entropy alloys (HEAs), containing several metallic elements in near-equimolar proportions, have long been of interest for their unique bulk properties. More recently, they have emerged as a promising platform for the development of novel heterogeneous catalysts, because of the large design space, and the synergistic effects between their components. In this work we use a machine-learning potential that can model simultaneously up to 25 transition metals to study the tendency of different elements to segregate at the surface of a HEA. We show that, thanks to the physically-inspired functional form of the model, a small amount of data is sufficient to extend a potential that was previously developed using exclusively crystalline bulk phases, so that it can also accurately model defective configurations and surfaces. We then present several computational studies of surface segregation, including both a simulation of a 25-element alloy, that provides a rough estimate of the relative surface propensity of the various elements, and targeted studies of CoCrFeMnNi and IrFeCoNiCu, which provide further validation of the model, and insights to guide the modeling and design of alloys for heterogeneous catalysis.