

O 46: New Methods and Developments 3: Theory

Time: Wednesday 15:00–17:00

Location: H6

O 46.1 Wed 15:00 H6

Atomistic and coarse-grained modelling of liquid-liquid and liquid-gas interfaces — ●JAKOB FILSER^{1,2}, KARSTEN REUTER^{1,2}, and HARALD OBERHOFER^{1,3} — ¹Chair of Theoretical Chemistry, TU Munich — ²Theory Department, Fritz Haber Institute Berlin — ³Chair for Theoretical Physics VII, University of Bayreuth

Modelling of dielectric interfaces remains a central challenge in computational chemistry. Liquid-liquid and liquid-gas interfaces have so far received relatively little attention, compared to solid surfaces. We present a new method to incorporate solvation effects into density-functional theory calculations of large organic adsorbates at liquid-liquid and liquid-gas interfaces. Simulating a large number of solvent molecules explicitly at this first-principles level is not computationally tractable. We therefore resort to an implicit solvation approach, treating the solvent as a structureless dielectric medium. Specifically, we advance the multipole-expansion method, in which we model the interface as the boundary of two semi-infinite media with different permittivity. Additionally, we introduce a piecewise expansion of the dielectric response. While the previous version of the MPE method could solve the electrostatic problem only for small solute molecules up to ≈ 10 non-hydrogen atoms, this development now allows us to simulate larger solutes with an overall non-convex hull, with electrostatic interaction energies converged up to few meV. Validating first results of our model for octanoid acid at a water-gas interface by explicit force-field level molecular dynamics simulation provides insight into the role of the atomistic structure of the solvent in the adsorption.

O 46.2 Wed 15:15 H6

Quantum feedback at the solid-liquid interface: flow-induced electronic current and negative friction — ●BAPTISTE COQUINOT^{1,2}, LYDÉRIC BOCQUET¹, and NIKITA KAVOKINE² — ¹Laboratoire de Physique de l'École Normale Supérieure, ENS, Université PSL, CNRS, Paris, France — ²Center for Computational Quantum Physics, Flatiron Institute, New York, NY 10010, USA

An electronic current driven through a conductor can induce a current in another conductor through the famous Coulomb drag effect. Similar phenomena have been reported at the interface between a moving fluid and a conductor, but their interpretation has remained elusive. Here, we develop a quantum-mechanical theory of the intertwined fluid and electronic flows, taking advantage of the non-equilibrium Keldysh framework. We predict that a globally neutral liquid can generate an electronic current in the solid wall along which it flows. This hydrodynamic Coulomb drag originates from both direct Coulomb interactions and interactions mediated by the solid's phonons. We derive explicitly the Coulomb drag current in terms of the solid's electronic and phononic properties, as well as the liquid's dielectric response, a result which quantitatively agrees with recent experiments at the liquid-graphene interface. Furthermore, we show that the current generation counteracts momentum transfer from the liquid to the solid, leading to a reduction of the hydrodynamic friction coefficient through a quantum feedback mechanism. Our results provide a roadmap for controlling nanoscale liquid flows at the quantum level, and suggest strategies for designing materials with low hydrodynamic friction.

O 46.3 Wed 15:30 H6

A fully periodic treatment of the chemisorption function for the analysis of adsorbate-substrate interactions — ●SIMIAM GHAN¹, KARSTEN REUTER¹, and HARALD OBERHOFER² — ¹Fritz-Haber-Institut der MPG, Berlin, Germany. — ²University of Bayreuth, Bayreuth, Germany

We discuss the extension of our improved Projection-Operator Diabatization scheme POD2GS[1] to the study of electronic coupling on surfaces within periodic density-functional theory (DFT) simulations. Using POD2GS, we calculate diabatic electronic couplings H_{ab} between adsorbate and surface bands throughout k -space. It becomes thus possible to directly calculate the chemisorption function of Newns and Anderson[2], a weighted density of states which appears often in the theoretical description of surface interactions.

Interpreting the chemisorption function within the Fermi Golden Rule yields ultrafast (spin)electron transfer lifetimes directly comparable to experiment, as we demonstrate for the case of core-excited Argon monolayers on ferromagnetic substrates Fe(110), Co(0001) and

Ni(111)[3]. Our scheme reveals the importance of sampling the Brillouin zone to gain accurate and convergent electron transfer rates, and offers an array of further applications.

[1] J. Chem. Theory Comput. 2020, 16, 12, 7431-7443.

[2] Phys. Rev. 1969, 178, 1123.

[3] Phys. Rev. Lett. 2014, 112, 086801.

O 46.4 Wed 15:45 H6

A Revised Fourth-Generation Neural Network Potential for the Accurate Representation of Multiple Charge States — ●ALEXANDER KNOLL, TSZ WAI KO, and JÖRG BEHLER — Georg-August-Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Göttingen, Germany

Machine learning potentials (MLPs) have become a mature tool for large-scale atomistic simulations in chemistry and materials science. Recently, a fourth-generation high-dimensional neural network potential (4G-HDNNP) has been introduced, in which the atomic charges are determined in a charge equilibration step enabling the description of long-range charge transfer. The quality of the charge prediction depends on environment-dependent electronegativities expressed by atomic neural networks, which poses a challenge for structures with differing total charges but nearly-identical nuclear positions. Here, we propose a generalized method applicable to these situations, and for a series of model systems we demonstrate that this extension leads to additional flexibility of the atomic electronegativities, ultimately resulting in more accurate atomic charges, energies, and forces.

O 46.5 Wed 16:00 H6

Machine learning potentials for complex aqueous systems made simple — ●CHRISTOPH SCHRAN¹, FABIAN L. THIEMANN^{1,2}, PATRICK ROWE¹, ERICH A. MÜLLER², ONDREJ MARSALEK³, and ANGELOS MICHAELIDES¹ — ¹University of Cambridge, UK — ²Imperial College London, UK — ³Charles University, Czech Republic

Simulation techniques based on accurate and efficient representations of potential energy surfaces are urgently needed for the understanding of complex systems such as solid-liquid interfaces. Here we present a machine learning framework that enables the efficient development and validation of models for complex aqueous systems. Instead of trying to deliver a globally optimal machine learning potential, we propose to develop models applicable to specific thermodynamic state points in a simple and user-friendly process. After an initial ab initio simulation, a machine learning potential is constructed with minimum human effort through a data-driven active learning protocol. Such models can afterward be applied in exhaustive simulations to provide reliable answers for the scientific question at hand or to systematically explore the thermal performance of ab initio methods. We showcase this methodology on a diverse set of aqueous systems. Highlighting the accuracy of our approach with respect to the underlying ab initio reference, the resulting models are evaluated in detail with an automated validation protocol that includes structural and dynamical properties and the precision of the force prediction of the models. Finally, we demonstrate the capabilities of our approach for providing insight into the solid-liquid interface for various systems.

O 46.6 Wed 16:15 H6

Quantifying the breakdown of electronic friction theory during molecular scattering of NO from Au(111) — ●CONNOR L. BOX¹, YAOLONG ZHANG², RONGRONG YIN², BIN JIANG², and REINHARD J. MAURER¹ — ¹Department of Chemistry, University of Warwick, United Kingdom — ²Department of Chemical Physics, University of Science and Technology of China, Hefei, China

The Born-Oppenheimer approximation fails to capture the extent of multiquantum vibrational energy loss recorded during molecular scattering from metallic surfaces.[1] NO scattering on Au(111) has been one of the most studied examples in this regard, providing a testing ground for developing various nonadiabatic theories. The exact failings compared to experiment and their origin from theory are not established for any system, particularly since dynamic properties are affected by many compounding simulation errors, of which the quality of nonadiabatic treatment is just one. We use a high-dimensional machine learning representation of the energy and the electronic friction tensor to minimize errors that arise from quantum chemistry.[1,2]

This allows us to perform a comprehensive quantitative analysis of the performance of molecular dynamics with electronic friction in describing state-to-state scattering. We find that electronic friction theory accurately predicts elastic and single-quantum energy loss, but underestimates multi-quantum energy loss and overestimates molecular trapping at high vibrational excitation. Our analysis reveals potential remedies to these issues. [1] C. L. Box & Y. Zhang et al, JACS Au, 2020 [2] R. Yin et al, J. Phys. Chem. Lett, 2019

O 46.7 Wed 16:30 H6

Accurate computation of chemical contrast in field ion microscopy — ●SHALINI BHATT — Max Planck Institut für Eisenforschung GmbH Düsseldorf Germany

Field ion microscopy (FIM) was the first microscopy technique to image individual atoms on a metal surface with near atomic spatial resolution. In short an imaging gas (e.g. He, Ne) is ionized above a surface subject of a few field 10^{10} V/m. The imaging contrast is dominated by the ionization probability at 5-10 Å above the surface. To simulate this within density-functional theory (DFT), we adapt the Tersoff-Hamann theory known from scanning tunneling microscopy (STM).

The gigantic electric field leads to very fast decay of wavefunctions into the vacuum. At the ionization height, they run into a regime that is dominated by numerical noise. To address this noise challenge inherent to any global-scale Kohn-Sham solver employed in DFT codes, wavefunction tails must be recomputed. To solve 3D Schrödinger equation at local scale we develop the extrapolated tail via reverse algorithm (EXTRA). The decaying tails are obtained by reverse integration (from outside in) using a Numerov-like algorithm. The starting conditions are then iteratively adapted to match the values of planewave DFT

wavefunctions close to the surface. We demonstrate chemical contrast for Ta and W at Ni surface using this new technique.

O 46.8 Wed 16:45 H6

Designing Covalent Organic Frameworks Through Active Machine Learning — ●YUXUAN YAO^{1,2}, CHRISTIAN KUNKEL³, KARSTEN REUTER³, and HARALD OBERHOFER² — ¹Chair for Theoretical Chemistry and Catalysis Research Center, Technical University Munich — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft — ³Chair for Theoretical Physics VII, University of Bayreuth

Covalent organic frameworks(COFs) are a class of materials with potential applications in many fields such as catalysis, sensing, or optoelectronics. It is well known that their design space is far too large to sample one by one. Focusing on their electronic properties, we modify an earlier active machine learning(AML) approach that explores the molecular design through the use of surrogate models for charge injection and transport descriptors. In this method, the Gaussian Process Regression(GPR) and AML are combined to train the molecular space. This way we ensure that only promising molecules or candidates that are very different from already explored ones have their descriptors evaluated on a comparatively expensive quantum mechanical level. Specifically, we modify molecular generation rules in order to produce three-fold rotational symmetric candidates molecules for use in COFs. In the future this approach can be generalized for any other symmetries, to potentially even allow for 3-dimensional network generation. The generation of a candidate space with well defined symmetries together with AML ensures a high efficiency in the detection of promising COFs with superior charge conduction properties and demonstrates the utility of this approach.