

CPP 59: Solid-liquid interfaces: Reactions and electrochemistry IV (joint session O/CPP)

Time: Wednesday 16:45–18:00

Location: MA 144

CPP 59.1 Wed 16:45 MA 144

Implicit solvation functionality for surface supercell calculations with the full-potential DFT code FHI-aims — ●JAKOB TIMMERMANN, MARVIN LECHNER, STEFAN RINGE, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München

The necessity to account for solvation effects in electrochemical simulations is by now well established. Notwithstanding, explicitly resolving the solvation environment in first-principles based simulations leads to system sizes and sampling requirements that are still often computationally intractable. For this reason, implicit solvation methods, first pioneered over 80 years ago, are currently undergoing a renaissance. One such example is the modified Poisson-Boltzmann implicit solvation functionality that was recently implemented in the numeric atomic orbital based full-potential density-functional theory code FHI-aims [1]. Here, we extend this functionality to periodic boundary conditions, which allows to compute extended solid/liquid interfaces in supercell geometries. The performance and numerical efficiency of the approach is illustrated by computing the potential of zero charge for a range of reference close-packed metal surfaces.

[1] S. Ringe *et al.*, *J. Chem. Theory Comput.* 12, 4052 (2016).

CPP 59.2 Wed 17:00 MA 144

First-Principles Calculation of Solvent-Mediated Proton Transfer at the TiO₂(110) Surface: Kinetic Barriers and the Effect of Functionals — ●AHMAD AGUNG, THOMAS STECHER, KARSTEN REUTER, and HARALD OBERHOFER — Technische Universität München

To date, a majority of theoretical studies of (photo-)electrochemical surface reactions focuses on their thermodynamic feasibility. Only recently an *ab initio* molecular dynamics (AIMD) approach utilizing QM-MM embedding, explicit solvation and the HSE06 hybrid functional was applied to determine the kinetic barrier of H₂O dissociation on a rutile TiO₂(110) surface [1]. Despite advanced sampling techniques and a comparatively small QM region, the use of the hybrid functional rendered these simulations computationally extremely expensive. To this end, we assess in how much generalized-gradient approximation (GGA) functionals can be employed to reduce the computational cost. Not too surprisingly, we find the inferior GGA energetics to yield a significantly different reaction barrier, when directly evaluating GGA-based AIMD trajectories. We therefore assess in how much these GGA trajectories yield at least an appropriate sampling of phase space, thereby offering computational savings by restricting the expensive hybrid level calculations to snapshots along these trajectories.

[1] T. Stecher, K. Reuter and H. Oberhofer, *Phys. Rev. Lett.* 117, 276001 (2016).

CPP 59.3 Wed 17:15 MA 144

Beyond Catalyst Screening for Electrocatalytic Materials – Importance of Active Site Structure, Mechanism, and Kinetics for the OER on Transition Metal Oxides — ●CRAIG PLAISANCE, SIMEON BEINLICH, and KARSTEN REUTER — Technische Universität München, Germany

Over the past decade or so, the computational design of catalysts for electrochemical reactions has been dominated by an approach in which the catalytic performance of a material is quickly estimated by calculating the values of one or two atomic-level descriptors, typically binding energies of key intermediates on a low index surface of the material. While this approach allows for rapid screening of a vast number of catalyst materials and has indeed identified improved catalysts in several cases, it is based on rather drastic assumptions and can thus only give a rough estimate of catalytic performance. This talk examines the suitability of the descriptor-based screening approach for

the OER on doped 3d transition metal oxides, a promising class of earth-abundant materials for catalyzing this reaction. Specifically, we examine whether or not the scaling and Bronsted-Evans-Polanyi relations on which the screening approach is based are robust with respect to changes in the geometry of the active site and the mechanism. We also address whether or not it is necessary to consider the kinetics of certain reaction steps in addition to the thermodynamics. In the end, we conclude that perhaps a more detailed understanding of the quantum chemical properties controlling electrocatalytic performance is needed in order to rationally design an optimal active site.

CPP 59.4 Wed 17:30 MA 144

Band alignment at semiconductor/water interfaces using explicit and implicit descriptions for liquid water — ●NICOLAS HÖRMANN¹, ZHENDONG GUO², FRANCESCO AMBROSIO², OLIVIERO ANDREUSSI¹, ALFREDO PASQUARELLO², and NICOLA MARZARI¹ — ¹Theory and Simulation of Materials (THEOS) and MARVEL, EPFL, Lausanne, Switzerland — ²Chair of Atomic Scale Simulations (CSEA) and MARVEL, EPFL, Lausanne, Switzerland

We compare the band alignment of several semiconductor/water interfaces for GaAs, GaP, CdS and TiO₂ as determined from explicit water *ab-initio* molecular dynamics simulations based on density functional theory (DFT) to results obtained within a DFT + implicit solvation model (SCCS) [1] as implemented in ENVIRON. It has been demonstrated that solvation effects are an important ingredient to describe the interface energetics in electrochemical systems adequately [2,3], however, it is still unclear how the choice of the explicit water molecules included affects the computational results. This work will allow us to estimate the expected errors of using implicit solvation models, with and without thermodynamic sampling and can serve as a guideline for the amount of interfacial water that should be treated quantum mechanically. [1] O. Andreussi, *et al.*, *J. Chem. Phys.* 136, 064102 (2012); [2] L. Sementa, *et al.*, *Catal. Sci. Technol.*, 6, 6901-6909 (2016); [3] J. Huang, N. Hörmann, *et al.* submitted to *Nature Materials* (2017), under review

CPP 59.5 Wed 17:45 MA 144

On the enhanced self-dissociation of water by bidimensional nanoconfinement — ●DANIEL MUÑOZ-SANTIBURCIO^{1,2} and DOMINIK MARX² — ¹CIC nanoGUNE, Tolosa Hiribidea 76, 20018 San Sebastián, Spain — ²Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Nanoconfined liquids present strikingly different properties compared to the bulk regime. Water in particular is the subject of intense investigation, and in previous works we described how nanoconfinement affects the mechanisms and energetics of chemical reactions therein [1] and also the peculiar differences between the structural diffusion mechanism of H⁺(aq) and OH⁻(aq) compared to the bulk [2,3]. Now, we present interesting results of advanced *ab initio* simulations which show how bidimensional nanoconfinement enhances one of the most important reactions in water, namely the self-dissociation of H₂O(aq) into H⁺(aq) and OH⁻(aq) [4]. This surprising feature goes hand in hand with the enhancement of the parallel component of the dielectric constant tensor of the nanoconfined water layer.

[1] D. Muñoz-Santiburcio and D. Marx, *Chem. Sci.* 8 (5), 3444-3452 (2017).

[2] D. Muñoz-Santiburcio and D. Marx, *Nat. Commun.* 7, 12625 (2016)

[3] D. Muñoz-Santiburcio, C. Wittekindt and D. Marx, *Nat. Commun.* 4, 2349 (2013)

[4] D. Muñoz-Santiburcio and D. Marx, *Phys. Rev. Lett.* 119, 056002 (2017).