DS 17: Frontiers of Electronic-Structure Theory: Focus on the Interface Challenge V (joint session O/CPP/DS/TT)

Time: Wednesday 10:30–13:15   Location: H9

Topical Talk   DS 17.1   Wed 10:30   H9
Theoretical Investigations of Electrochemical CO2 Reduction
— •Karen Chan — Department of Physics, Technical University of Denmark

The electroreduction of CO_2 has the potential to store energy from intermittent renewable sources and to produce carbon-neutral fuels and chemicals; In this talk, I will discuss new developments in modeling the electrochemical interface. I will then present the application of these models of the interface to CO_2 reduction: the determination of reaction pathways and kinetics on transition metals, field and solvation effects, pH effects on C_2 product selectivity, and implications for catalyst design.

Topical Talk   DS 17.2   Wed 11:00   H9
First-principles approach to model electrochemical reactions at the solid-liquid interface — •Mira Todorova, Sudarsan Surendralal, and Jörg Neugebauer — MPI für Eisenforschung, Düsseldorf

Processes at solid-liquid interfaces are at the heart of many present day technological challenges related to the improvement of battery materials, electro-catalysis, fuel cells, corrosion and others. Describing and quantifying the underlying fundamental mechanisms is equally challenging for experimental and theoretical techniques.

Utilizing concepts from semiconductor physics, we have developed a novel potentiostat design, which enables us to perform ab initio calculations under controlled bias conditions. Easily applied in standard density functional theory codes, it controls the electrode potential of the system by tuning the excess charge of the working electrode and allows us to obtain direct insight into key mechanisms of electrocatalysis and corrosion. As a prototype example, we consider one of the most corrosive systems under wet conditions - Mg. Using the new approach we solve a 150-year-old problem, which links H-evolution under anodic conditions to Mg dissolution [1].

[1] S. Surendralal, M. Todorova, M.W. Finnis and J. Neugebauer, Phys. Rev. Lett. 120, 246801 (2018).

DS 17.3   Wed 11:30   H9
Towards out of the box implicit solvation at liquid-liquid interfaces — •Jakob Filser[1], Markus Sinstein[1], Christoph Scheurer[1], Sebastian Matera[2], Karsten Reuter[1], and Harald Oberhofer[1] — [1]Technische Universität München — [2]Freie Universität Berlin

Implicit solvation models are widely used to incorporate solvent effects in electronic structure theory. Treating the solvent as a structureless dielectric continuum, they lift the necessity to explictly sample solvent degrees of freedom. However, even state of the art models currently cannot treat solvation at technically highly important dielectric interfaces, e.g. between two immiscible liquids.

As a remedy, we modify the multipole expansion (MPE) model to also account for liquid-liquid interfaces, specifically focusing on the electrostatics of mutually interacting dielectric regions. Non-electrostatic free energy contributions thereby are treated with a simple linear model, fitted to experimental free energies of solvation in the two liquids. We demonstrate the efficacy of this approach for small molecules at a water–1-octanol interface, which show the correct qualitative behaviour with respect to orientation and position at the interface.

Future, quantitative applications of our new implicit solvation interface methods are clearly possible but will necessitate both improvements to the non-electrostatic free energy terms and a more exhaustive parameterization effort for a wide range of solvents.

DS 17.4   Wed 11:45   H9
Continuum models of the electrochemical diffuse layer in electronic-structure calculations — •Francesco Nattino[1], Oliviero Andreussi[2], and Nicola Marzari[1] — [1]Theory and Simulations of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland — [2]Department of Physics, University of North Texas, Denton, TX 76207, USA

The electrical diffuse layer is a structure that spontaneously forms at essentially any solvated interface, such that its presence in electrochemistry is ubiquitous. While first-principles methods are desirable to describe any process occurring at the surface, fully-atomistic models of electrolyte solutions suffer from computational limitations. In this context, continuum models represent a practical tool to bypass these difficulties and to account for the presence of the diffuse layer at electrified interfaces. However, despite the increasing popularity of continuum models in the field of materials science, even relatively simple observables such as the differential capacitance (DC) of single-crystal electrode surfaces remain challenging to model quantitatively. I will present and discuss the performance of a hierarchy of continuum diffuse-layer models that we have implemented and coupled to an atomistic first-principles description of a charged metal surface. In particular, I will compare computed DC values for the prototypical Ag(100) surface in an aqueous solution to experimental data, and validate in this way the accuracy of the models considered.

DS 17.5   Wed 12:00   H9
***Ab initio* molecular dynamics of Pt(111)/H_2O interfaces in an electrolytic cell setup** — •Sudarsan Surendralal, Mira Todorova, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany.

Recently, we developed a novel scheme to perform density functional theory (DFT) simulations of electrochemical interfaces under conditions of constant applied voltage utilizing charge transfer from a semiconductor counter electrode [1]. We use a fractionally doped Ne counter electrode because of its inertness, wide band gap, and low deformation potential. Our DFT based molecular dynamics calculations of the Pt(111)/H_2O interface in this setup reveals that we are able to accurately reproduce macroscopic observables like the potential of zero charge (PZC). We discuss the work function drop at the interface at the PZC, due to the charge polarization by the non-dissociative chemisorption of water molecules at the Pt surface. Possible pitfalls due to the choice of the DFT exchange-correlation functional, non-converged computational parameters and confinement effects due to the presence of the counter electrode will also be discussed.

[1] S. Surendralal, M. Todorova, M. W. Finnis, and J. Neugebauer, Phys. Rev. Lett. 120, 246801 (2018).

DS 17.6   Wed 12:15   H9
Swipe left for water molecules? - Implicit vs explicit descriptions of liquid water at interfaces. — •Nicolas Hörmann[1], Oliviero Andreussi[2], and Nicola Marzari[1] — [1]Theory and Simulation of Materials (THEOS), and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), EPFL, CH-1015 Lausanne, Switzerland — [2]Department of Physics, University of North Texas, Denton, TX 76207, USA

We present a study of relevant electrochemical interfaces, such as semiconductor-water and metal-water interfaces based on periodic density functional theory (DFT) calculations with the interface modelled with different degrees of complexity. Water at metallic surfaces is modelled within the self-consistent continuum solvation scheme (SCCS) [1] with explicit application of a potential which allows the comparison of pH dependent properties with experimental results [2,3]. In the case of semiconductors, different amounts of interfacial water are substituted with implicit solvent and observables such as the measured band alignment are obtained from thermal averaging over molecular dynamics snapshots. We find that it is necessary and sufficient to include strongly bound interfacial water molecules (dissociated or not) explicitly and replace the rest with an implicit model, in order to obtain consistent results with all-explicit simulations [4]. Based on these result we simulate the surface Pourbaix diagrams of the most stable surfaces of GaAs, GaN, GaP, CdS and anatase and rutile TiO_2.

[1] *J. Chem. Phys.* **136**, 064102 (2012); [2] *Nat Commun.* **9**, 3117 (2018). [2,3] NH (2018) submitted

DS 17.7   Wed 12:30   H9
Transition metal oxide nanoparticles as efficient catalysts for proton exchange membrane electrolyzers: morphology, activity and stability — •Daniel Opalka, Yonghyuk Lee, Jakob Tim-

mermann, Christoph Scheurer, and Karsten Reuter — Technische Universität München

Transition metal oxides such as RuO_2 and IrO_2 are currently the best known electrocatalysts for the oxygen evolution reaction from liquid water in proton exchange membrane (PEM) electrolyzers. However, dynamic load operation of PEM cells induces transformations of the catalyst morphology leading to metal dissolution and catalyst degradation. We present a computational model to predict the morphology, activity and stability from *ab initio* electronic structure theory and fundamental thermodynamic principles. Based on this model, we have explored novel strategies to reduce material expenses and improve catalyst stability while preserving high catalytic activity via nanoparticles with a core-shell design. From an analysis of different surface coverages with oxygen, hydroxyl and hydroxo species, voltage-dependent phase diagrams for catalyst surfaces are presented which correlate with characteristic features observed in cyclovoltammetric measurements. Results from atomistic models of selected nanoparticles on the basis of Wulff's Theorem show negligible size effects, but a strong influence of the facet terminations on the surface relaxation.

DS 17.8   Wed 12:45   H9

Modelling the fingerprint of chemical reactions on catalytic surfaces in core-electron binding energies — ●Johannes Lischner and Juhan Matthias Kahk — Imperial College London

Core-electron X-ray photoemission spectroscopy is a powerful experimental technique to gain information about chemical reactions on catalytic surfaces. Interpreting experimental spectra, however, is often challenging and theoretical modelling of core-electron binding energies is required to meaningfully assign peaks to adsorbate species. In this talk, I will present a novel first-principles modelling strategy to calculate core-electron binding energies of molecules on metallic surfaces. Specifically, we combine plane-wave/pseudoptential DFT calculations

of surface slab models for geometry optimizations with all-electron Delta-SCF calculations on cluster models for determining accurate core-electron binding energies. This approach is computationally efficient and yields good agreement with experimental measurements for a wide range of adsorbates on copper(111) surfaces.

DS 17.9   Wed 13:00   H9

What Makes a Successful Photoanode?   - The Role of the Semiconductor–Catalyst Interface — ●Franziska Simone Hegner[1], Benjamin Moss[2], James Durrant[2], Sixto Gimenez[3], José-Ramón Galán-Mascarós[1], and Núria López[1] — [1]Institute of Chemical Research of Catalonia (ICIQ) — [2]Imperial College London — [3]Institute of Advanced Materials, Castellón

A large scale implementations of artificial photosynthesis is still limited by the low efficiencies of the employed photoelectrochemical systems. A common strategy to improve performance is to deposit a co-catalyst on the light-harvesting photoanode. However, the role of the catalyst is controversial; is it acting as a true catalyst, i.e. transferring charges, or is it merely influencing the electronic structure of the semiconductor?[1]

The semiconductor-catalyst interface is key to catalytic performance, but its accurate description is limited since linear scaling relationships no longer apply. Herein the function of the co-catalyst (cobalt hexacyanoferrate) is discussed on two photoanode interfaces, Fe2O3 and BiVO4. Density Functional Theory and time-resolved spectroscopy were used to shed light on the underlying charge-transfer processes. Taking into account the advantages and disadvantages of all applied techniques, a relationship between electronic structure alignment, interface morphology, and photocatalytic efficiency is proposed.[2]

[1] D. R. Gamelin, Nat. Chem., 4 (2012), 965-967. [2] F. S. Hegner, D. Cardena-Moscoros, S. Gimenez, N. López, J. R. Galán-Mascarós. ChemSusChem, 10 (2017) 4552-4560.