

Report on the 3 day workshop on

AB INITIO ELECTROCHEMISTRY

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Scope of the workshop

Ab initio electrochemistry is an emerging field in computational materials science aiming at the development and application of electronic structure calculation methods for the modelling of electrochemical interfaces. The field is highly interdisciplinary merging electronic structure calculation methods from computational solid state physics and the physical chemistry of solution. Combination of methods from different backgrounds has the potential to lead to new synthetic approaches more powerful and versatile than its components. However, it also has a tendency to multiply technical problems, stretching methods by applications under new conditions, to the point that an all together fresh approach is required. The work on modelling of electrochemical interfaces to date has certainly lived up to this expectation creating a number of major challenges.

To define the scope we summarize the main issues discussed.

- a The modelling of solvent effects on electrode surfaces. The inclusion of solvent is absolutely crucial for charged electrodes providing the counter charge in the form of a layer with excess ionic charge (electrical double layers).
- b Computation of electrode potentials (equilibrium and non-equilibrium) at electrode electrolyte interfaces. This essentially amounts to the development of a computational normal hydrogen electrode
- c The development of a method for studying electrode processes under constant applied electrode potential. This is an critical issue for applications to electrocatalysis.

In the choice of program and invited speakers the organizers have tried to limit the scope of the workshop to these three issues. With these restrictions, they have excluded other key issues, such as the computation of currents (rate constants) and various difficulties encountered in the application of the Density Functional Theory (DFT) approximations used in condensed matter calculations to electrochemical interfaces. Of course these issues did come up during the discussion.

Main Outcome of key presentations

Conform the scope of the workshop most of the invited speakers focused on computational method development issues. There were of course also good number of more applied talks. The talks can be grouped around three main themes.

Electrode potential calculation and constant electrode potential methods

This is the central technical issue for this meeting. The first question is how to compute electrode potentials. The next question is how to change over from a simulation in which the surface charge is fixed and the interface potential varies depending on structural changes to conditions in which the electrode potential is imposed and the charge varies. The implementation of such a constant

electrode potential method is strongly dependent on the description of the solvent and ionic charge. The various approaches that have been developed were all represented at the workshop.

Filhol gave a review of the most commonly used method, the double reference method developed by him and Neurock (also present at the meeting). This approach uses a fully atomistic description of the solvent. Counter ions in the double are however represented by an homogeneous background (jellium). Electrode potentials are computed by referring the Fermi level of the metal to vacuum (work function method). The major advantage of this approach is that the surface charge can be fractional which is crucial to describe realistic surface charge densities in small DFT model systems. Rossmeisl presented a recent method developed by him and the Lyngby group in which both solvent and counterions are treated at an atomistic DFT level. A first implementation to hydrogen evolution catalyzed by a platinum electrode was discussed in some detail. The counterions are protons inserted on the surface (electrosorption). When inserted in the bulk solvent the free energy can be directly converted to an electrode potential versus the normal hydrogen electrode (NHE) without the detour of a vacuum reference for the electrostatic potential. This method is however still a constant charge approach. The charge is moreover limited to integer values because the charge of the counter ions is necessarily integer. The state point at given potential is obtained by inverting the potential charge relation using the computed capacitance of the double layer. Cheng presented a related method for a “first principle” computational hydrogen electrode. Rather than the enthalpy this method uses the solvation free energy of the proton as energy reference. The solvation free energy is computed using a combination of DFT based molecular dynamics and free energy perturbation methods.

The alternative to atomistic description of the electrolyte is a continuum model (with a varying layer of water treated at the DFT level). Morikawa reviewed the ESM method in which a DFT model of a charged solid slab and a zone of water is separated from a plane of counter charge by a continuum representing pure solvent. Dabo reported on an advanced continuum model in which the counter charge is residing in a diffuse double layer modelled by solving a generalized Poisson Boltzmann equation (i.e including ion size effects). Santos reviewed a theoretical approach using a Valence Bond type Hamiltonian (the Santos-Schmickler-Koper model) parametrized by DFT calculation of chemisorption energies. Based on Marcus theory this approach can be used to calculate reorganization energies and electron transfer rates, going way beyond what is feasible using current DFT based direct simulation of atomic models,

Solvent effects on surface phase diagrams and electro-catalysis

Approximately one day of talks was devoted to applications to interface structure and electro-catalysis. Model systems included metals as well as metal oxides. Some of these investigations used the double reference or a continuum solvent method. There were however also applications using the thermodynamic electrode model by Rossmeisl and Norskov. This is an elegant and most efficient alternative to explicit or continuum modelling of solvent. The conditions in an electrochemical cells at finite cell potential and non-neutral pH are simulated by biasing the chemical potential of electrons. The limitation is that species adsorbing or leaving the surface cannot carry charge. While this method has shown to provide an extremely useful tool for the study of electro catalytic mechanism, it falls somewhat outside the scope of the meeting which was meant to go beyond this model explicitly introducing solvent and electrical double layers.

A highlight directly addressing the topic of the meeting was the talk by Gross, who showed that thermally induced disorder and reorganization of water in contact with metal electrodes can have a significant effect on the work function and therefore on the electrode potential (potential of zero charge). He also discussed the implication for surface phase diagrams computed under constant potential conditions. Another presentation with results directly relevant to the theme of the meeting was the talk by Spohr. Using an empirical valence model for the interactions

between water, protons and a platinum electrode he was able to extend the duration of molecular dynamics trajectories to the nanoseconds. In an application to the hydrogen evolution reaction he showed that this time scale can reveal events that are qualitatively different from what can be observed in the time window (10 ps) accessible the density functional based molecular dynamics. A further notable talk was by VandeVondele showcasing the progress that has been achieved in extending the size of DFT molecular dynamics models (“Car-Parrinello”) of solid-liquid interfaces. He also reported on the spectacular reduction in computational costs for the application of hybrid functionals in periodic condensed phase models systems that he and Hutter have achieved by implementing new methods in the CP2K code.

Solid solid interfaces and defects

The study interfaces between semiconductor and other semiconductors (heterojunctions) or a metals (Schottky barriers) and of electrically active defects in semiconductors has already a long track record in computational solid state physics and materials science. Some of the methods that were developed, in particular methods for alignment of electronic energy levels at interfaces (called the band-offset problem in the field) and methods for the computation of charge transition of defects could be of interest for computational electrochemistry. There were three invited talks by “delegates” of this community (Pacchioni, Stengel and Pasquarello). Stengel gave an introduction on his work on the dielectric constant and capacitance of nano-capacitors (layers of conducting and insulating perovskites) using Maximally localized Wannier function methods. Of particular interest was the implementation of constant potential conditions using electrostatic enthalpy Hamiltonian. Pacchioni presented his latest results on engineering of charged defects in thin wide gap semiconducting films on metals.

Report on selected discussions

In the time for questions following the presentations technical as well a more chemical issues were discussed. As the focus of the workshop was on computational method we mention in this report only some of the important technical issues. One such issue concerns the popular double reference method. This method applies a correction for interactions with the homogeneous back ground compensating for the charge on the electrode. While this background is a poor representation of the ionic component of a double layer the objection was raised in response to the presentation by Filhol that in a consistent electrostatic calculation all interactions should be taken into account, realistic or not. There was no consensus on this rather fundamental issue. An equally basic question was raised about the reference potential in continuum models of the electrolytic solution. Some work reported during talks abandoned the vacuum reference and used instead the average electrostatic (Poisson) potential of the model solvent (electrolytic solution). In explicit solvent models this is generally avoided because the average Poisson potential is strongly model dependent. The question is why this should be appropriate in continuum models. Some of the participants felt that this is not correct because the average Poisson potential is not an observable and plays no role in the thermodynamic determination of the absolute NHE potential. The conclusion of this discussion was that there may indeed be a problem with this practice.

In the general discussion during the final afternoon session, there was a general but “qualified” (see below) confidence that electronic structure has a role to play. Electrochemical experiments measure current versus potential, this can only provide very indirect information of surface structures and reaction mechanisms. Electronic structure simulations offer a link between electrochemical measurements and the atomic scale properties of the electrochemical interface. The success of the thermodynamical electrode model of Rossmeisl and Norskov in explaining the mechanism of electrocatalytic reactions is clear evidence justifying this optimism. This approach is however

limited to neutral species (reactants, intermediates products) and the inclusion of solvent was considered by everybody present to be an integral part of the extension to ionic species. In the same context the development of a computational hydrogen electrode and methods for imposing constant potential conditions were also considered crucial. There was agreement that progress has been made but that it is yet too early for a proper comparison of the various methods that have been developed.

Most of the participants also agreed that at present there is a very wide gap between experimental observations such as voltammetry and what calculations can say about this. Detailed explicit representation of the solvent will be required to narrow this gap. This will be crucial for the computation of reorganization energies and ultimately electron transfer rates. However a number of experts (among them Schmickler) expressed doubts that a more quantitative prediction of electrode currents is achievable by electronic structure based simulations or whether this should be a goal of at all. In Wieckowski's experience as theory friendly experimentalist the two fields: theoretical, including quantum, and practical electrochemistry will need to go separate ways, at least for a while. In his view there is no consensus how to combine it, and it is probably not worthwhile to do it.

Strong and weak points

The workshop was meant to bring together representatives of different communities working on various aspects of computational electrochemistry from often different perspectives. The majority of the speakers were members of the surface science community. Their entrance to the subject is extension of DFT techniques for treating solid surfaces to solid-liquid interfaces. There were also a number of talks by representatives of the Car-Parrinello community who coming from a background in the simulation of liquids and solutions have begun to insert slabs of solid in their liquid MD cells. These two groups were joined by solid state physicists studying solid solid interfaces and defects in semiconductors. In addition to presentations on computational work there were also more theory oriented presentations and two talks by experimentalists. To get these people from rather diverse background to listen to talk to each other and share ideas and doubts can be regarded as a strong point.

The subject is new. A number of problems remain unresolved, both computational and even fundamental. This was clear from the presentations and discussion. Some of concepts were new for non-experts and even for experts difficult to grasp or agree on. This created a stimulating but at times somewhat uncertain atmosphere. With longer and more tutorial talks followed by longer discussions the interaction between the participants could perhaps have been more productive.

Suggestions for new workshops on the topic

There was agreement that there would be a strong interest in a follow-up workshop possibly with a somewhat altered format (see strong and weak points). Rossmeis and others are considering to submit a proposal for a Cecam workshop on this topic for 2011 to be held in Bremen.