IWCE2018

International Workshop on Computational Electrochemistry

9th to 12th of July 2018 at Aalto University

http://iwce2018.computational-electrochemistry.org/

State of the art

Much work has been done on atomistic calculations of surfaces, interfaces and molecular adsorption. DFT usually grants a reasonable description of those. Even local and semilocal exchange-correlation density functionals can yield quantitatively accurate adsorption energies for a number of systems. However, this good description does not extend to surfaces with a net charge or where the position of the Fermi level is a tunable parameter. Obviously this imposes a serious drawback to modeling electrochemical interfaces where the effect of the potential is explicitly taken into account. In practice, one needs to resort to workarounds.

Seminal work was done in the 2000s, most notably by the Nørskov group in Denmark, and since then several approximations have been proposed. The simplest solution is to include potential differences only implicitly as an energy shift. Another way is through the inclusion of a constant external electric field within the electrode-water interface. One can also introduce an explicit excess charge (positive or negative) by changing the number of electrons in the calculation, which spontaneously accumulate on the metal surface. A different approach is to charge the electrode indirectly by introducing hydrogen atoms adsorbed on the surface metal sites.

On top of the issue of electrode potential, a crucial point in electrochemistry is how solvation, electrical double layer structure, counter-ions and pH effects are all taken into

account. Implicit and explicit solvation models can be used, depending on available CPU resources. pH is usually only included implicitly because of system size limitations.

These combined issues make accurate computational electrochemistry modeling extremely challenging and all of these approaches have their own advantages and inconsistencies. In this workshop we looked at the latest developments and approaches to dealing with these effects.

Major outcomes

* The consensus is that, while the field is advancing, there is still much improvement to be done methodologically before the role of simulations in computational electrochemistry can shift from "rationalizing" experimental results to "doing a computational experiment". This was summarized by Axel Gross as "this has been and still is a field *towards*".

* In connection to the point above, in one of the "rump" sessions the participants identified the need for a "standardized test" that allows to establish and compare the performance of the very many approaches currently available. There was no consensus as to what this test should be.

* A major development with respect to early literature in the field seems to be the generalized adoption of dynamical solvent effects as a necessary ingredient in computational electrochemistry. That is, while early work often used static (i.e., ice-like) water and only few monolayers of solvent, current work uses molecular dynamics and many solvent "monolayers" to correctly include dynamical or entropic effects. There was for instance a special "rump" session on how to incorporate entropic effects into simulations.

* Another promising strategy to introduce electrode potential in simulations was presented by Mira Todorova, where a very wide gap insulator (neon in the example) is chosen as counter electrode. Because the gap is so large, the Fermi level is straddled by the conduction band mimimum and valence band maxima of the counter electrode for a wide range of applied potentials. This is in contrast to a typical two-metal electrode configuration, where the necessary presence of a global Fermi level in regular DFT calculations would mean the suppression of an applied electric field.

* A personal disappointment for one of the organizers (MAC), following up on the point above, was that the community has not explored the possibility of truly applying different Fermi levels on the different electrodes via non-equilibrium Green's functions. Somewhat related were some presented developments from Pasquarello's group at EPFL of "constant Fermi level" molecular dynamics, where fractional occupancies are changed throughout the MD so that the global Fermi level evolves towards a chosen value.

* Another identified trend is "doing more with less" with regards to solvation effects. In particular, implicit solvation models and joint density functional theory are being adopted in combination with explicit solvation to deal with extended solvent regions. Jarvist Frost from KCL, introduced the idea of using tight-binding to deal with extended systems and a new

"hairy probe" formalism to deal with different electrochemical potentials at different electrodes.

* On the more applied side, people are striving to find CO2 reduction catalysts for fuel production, and also other molecules, such as NH3. We had several talks on calatyst search and characterization, including carbon nanotubes and novel oxides and perovskite materials and even an iron-based molecular catalyst. This area remains very active due to the obvious indutry applications.

* In the area of charge transfer we had contributions focusing on DFT-based parametrization of Marcus theory (e.g., constrained DFT), coupling the proton degrees of freedom to electron transfer phenomena (i.e., proton coupled electron transfer) and a new approach, "molecular" DFT. MDFT is conceptually related to joint DFT, where the molecular details of the solvent are kept but in a continuum level of description. It remains to be seen if these approaches will become generally adopted by the community.

Community needs

We feel that the community's need for HPC resources is well covered. It seems that getting CPU time for problems in electrocatalysis is not an issue because of the need for clean energy sources, offsetting carbon emissions, more efficient industrial processes and so on. These needs are usually well perceived by funding agencies and non-specialist committees (e.g., sitting at HPC infrastructure centers), as opposed to some more niche areas in electronic structure like development of highly accurate schemes (e.g., many-body or wave-function-based approaches).

It is possible that cross-talk with experimentalists is somewhat missing, and the community could benefit from it. In particular, with experimentalists doing fundamental work with well defined systems. We had an invited experimentalist, Víctor Climent, whose very fundamental work on well-controled Pt electrochemistry was very well received by the audience. However, we also feel, from Víctor's feedback, that the computational work may have taken a path towards highly technical and theoretical approaches (e.g., fundamental developments in electronic structure theory) which makes cross-talk somewhat difficult. It would be useful to have some instrument (possibly in the form of a targetted workshop) available to bridge this communication gap.

We asked for anonymous feedback on the IWCE2018 workshop. The consensus was that the participants very much enjoyed this workshop and would welcome a similar event being held biannually in Europe. It would be good to have some level of CECAM commitment which allowed us to create a wider organizing committee involving people in several universities so that this event can rotate throughout Europe. The detailed feedback on the workshop can be obtained from Miguel Caro upon request.

Funding

Most participants seemed to be receiving funding majoritarily from their national research or science foundations and basic funding at their local institutions. Some participants also

had European funding available to them, i.e., from the European Research Council. One or two speakers showed industry involvement in their work (for applied electrocatalysis). Joint funding opportunities were not openly discussed during the meeting, at least that we are aware of. Topics in electrocalatylis are always well suited for targeted calls related to clean and efficient energy production. Topics in analytical electrochemistry are also well received for targeted calls related to medical diagnostics and environment.

Societal benefits

On the one hand, as we have mentioned before, some aspects of the computational side of the electrochemistry field are still far away from making a large direct impact on society, and many efforts are directed towards developing theory and methodologies towards accurate and affordable simulation of electrochemical systems. The potential impact on society once these methods are better established and more accurate is huge. We highlight the possibility to optimize biomolecule detection systems for in vivo health monitoring and diagnostics, but there are many others. On the other hand, the extensive work carried out on electrocatalysis for fuel production has the potential of impacting the development of new catalytical processes and materials. It is possible that cheap alternatives to Pt for water splitting may emerge from the myriad of different material systems which are currently being surveyed by the community. The community is also hard at work on finding semiconductors, mostly oxide based, for solar-energy-mediated water splitting. We feel that this direction may also have an impact on society in the near future, as new promising materials are being characterized via simulations.

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