A QM/MM-NEGF approach to address electrified metallic/water interfaces

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Several macroscopic observations are intrinsically related to processes occurring at the nanoscale. In that regard, molecular modeling stands as a crucial tool in investigating many problems in nanotechnology. Most of those problems involve water in contact with metallic - often electrified - surfaces, especially when dealing with electrochemical processes. Nonetheless, traditional molecular modeling approaches, such as standard density functional theory, have limitations in realistically addressing the systems needed to simulate an electrochemical cell. Here we propose using a hybrid quantum mechanics/molecular mechanics (QM/MM) approach [1] combined with the non-equilibrium Green's functions (NEGF) formalism [2,3] implemented in the SIESTA code [4,5] to tackle electrified metallic/water interfaces. Using the NEGF allows us to mimic an electrochemical cell very closely to an experimental setup, where two metallic electrodes are kept under different chemical potentials, sandwiching a central cell containing liquid water, as sketched in Figure 1. To get a good cost-accuracy compromise, we describe the water molecules using a classical force field while the metallic electrodes are fully ab-initio. We demonstrate the effectiveness of the proposed method by applying it to a system containing liquid water in contact with gold electrodes. The approach is first validated by comparing the structural properties of water (layering and angle distribution) extracted from our QM/MM molecular dynamics (MD) against full ab-initio MD simulations. We then apply the method to perform QM/MM-NEGF MD simulations to these systems, where we demonstrate that our approach can correctly capture the changes in the structural properties of water and in the electronic structure of gold due to the voltage applied to the electrodes. Finally, we reveal that the performance reached by the proposed approach paves the way for applying it to way larger systems, containing as much as 7,500 atoms, where realistic electrolytes could be addressed.

References

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Figures

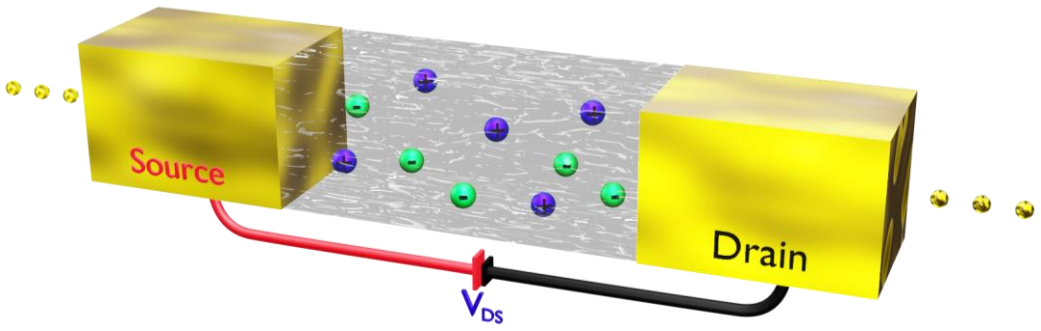

Figure 1: Sketch of the setup used to perform QM/MM-NEGF molecular dynamics.