Electrochemistry at electrode/electrolyte interfaces from first principles

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Electrochemical energy storage and conversion are of significant technological importance for our future energy supply. Still, in spite of its relevance, our knowledge about the microscopic structure of electrochemical electrode-electrolyte interfaces and the processes occurring at these interfaces is still rather limited. The theoretical description of these interfaces is hampered by several facts.

i) In electrochemistry, structures and properties of the electrode-electrolyte interfaces are governed by the electrode potential which adds considerable complexity to the theoretical treatment since charged surfaces have to be considered.

ii) The theoretical treatment of processes at solid-liquid interfaces includes a proper description of the liquid (see Fig. 1) which requires to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed.

iii) Since electrochemistry is intimately linked to electron transfer processes, a quantum chemical approach is necessary for a proper atomistic description of electrochemical electrode/electrolyte interfaces. Electronic structure methods based on density functional theory (DFT) combine numerical efficiency with a satisfactory accuracy. However, still some shortcomings of the DFT implementations need to be overcome.

In this tutorial talk, I will address how electrochemical electrode/electrolyte interfaces such as the one illustrated in the figure can be described using first-principles methods. I will show recent advances, but I will also sketch challenges that still lie ahead of us for a reliable and more complete theoretical description of electrochemical systems.

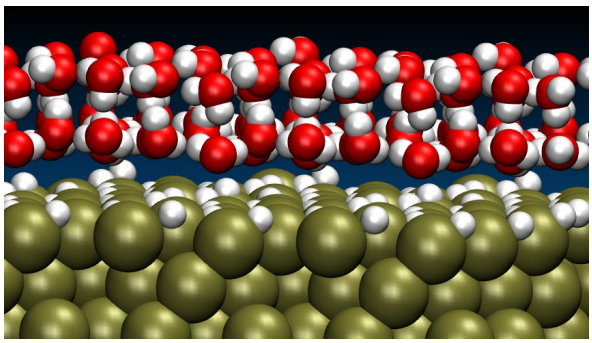

Fig1. Illustration of the structure of the electrochemical interface between an aqueous electrolyte and a Pt(111) electrode at low electrode potentials.