

## Mixed quantum-classical treatment of elementary electrochemical problems

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Most electrochemical systems are composed of a solid electrode to conduct electrons and a liquid electrolyte solution to conduct ions and molecules. Taken separately, the electrode and the electrolyte can be well described by modern solid- and liquid state theories, respectively. Brought into contact, they create an intriguing nanoscale zone, termed the electric double layer (EDL), where many new physicochemical phenomena occur.

In the first part, I will present a hybrid density-potential functional theory (DPFT) of EDL, combining quantum-mechanical density functional theory (DFT) for interacting electrons and classical DFT for charged particles in the electrolyte solution.[1] I will introduce the basic idea of the theory and important technique details involved in theoretical derivation and numerical implementation. This theory is then employed to unravel several interfacial properties of fundamental significance in electrochemistry.

In the second part, I will proceed further to touch upon electron transfer kinetics in the EDL. Specifically, I will present a mixed quantum-classical treatment for chemisorption, the elementary step in all electrocatalytic reactions.[2] Emphasis is placed on understanding multifaceted EDL effects on chemisorption. Apart from modifying the driving force and reactant concentration that have been considered in Frumkin corrections, EDL effects also modulate the interfacial solvent reorganization energy, thus adding a new term in the transfer coefficient. An additional level of intricacy comes into play when the reactant zone needs, upon approaching the interface, to replace solvent molecules originally adsorbed on the metal surface and a free energy penalty arises, accordingly. This free energy penalty shifts the transition state away from the metal surface, and thus modulates the activation barrier.

In the end, I will discuss possible connections between the theories and high-level spectroscopic studies.

Key references:

[1]. J. Huang, S. Chen, and M. Eikerling, *J. Chem. Theory Comput.* 2021, 17, 4, 2417–2430

[2]. J. Huang, *J. Chem. Phys.* 2020, 153, 164707