Atomic Details of Electrical Double Layer: Mean-field QM/MM Study

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Electrochemistry is based on the physicochemical phenomena for the solid-liquid interface with applied voltage. To get insights from the atomic level, many researchers try to collaborate experiments with atomic-scale simulation. To make a robust understanding of electrochemical interface theoretically, mean-field coupling of DFT and MD can be used. It can enlarge both scales of time and length, simultaneously.

Here, the mean-field QM/MM method is further developed for studying the interface with excess charges, and principles of EDL are deeply studied. One of the unsolved issues for EDL is so-called camel-shaped differential capacitance, which theoretical models cannot explain. Here, this phenomenon is reproduced, and its origin is unveiled. It originates from the combined dynamics of water and ions and their contributions for cathode and anode are different. In the cathode, the water molecules' rotation coupled with the cations' accumulation makes two states at the same potential. Otherwise, ion's specific adsorption compensates for the excess charges. Finally, the effect of EDL on CO2 reduction is discussed revealing the cation is essential for the reaction.