

Definition of Electrode Potential from Density Functional + Implicit Solvation Theory

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Electrode potential is a general concept, in electrochemistry, which governs the charge transfer reactions such as ion insertion/extraction and reduction-oxidation at electrode/solution interfaces; the electrode potential should be appropriately included in the computational model.¹ In this study, we consider how the standard hydrogen electrode (SHE) potential, which is the equilibrium potential of the charge transfer reaction of H^+/H_2 , is theoretically evaluated.

We employed density functional theory (DFT) calculations combined with the effective screening medium (ESM) technique² + the reference interaction site method (RISM);³ ESM-RISM formulation⁴ makes it possible to simulate the electrode (+ reactive ions) and the solution based on quantum mechanics and implicit classical solvation model, respectively. Changing the chemical potential of electron, μ_e , referenced to the inner potential Φ_s at the bulk solution region, we compared the grand potentials Ω for the following reaction:



In the presentation, we will compare the potential profile of metal/solution/vacuum region obtained from ESM-RISM and the first-principles molecular dynamics calculation using ESM.⁵ We further discuss on the difference between $\mu_e@SHE$ and the absolute SHE obtained by Trasatti.⁶

References

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