Applications of Many Body Perturbation Theory: From Vacuum to Electrochemical Systems

By Ziyang Wei
Prof. Sautet Group

ABSTRACT: Electrocatalysis plays a key role in sustainable energy conversion and storage. Although tremendous efforts from the experimental side have been devoted to elucidating the reaction mechanism, the detailed reaction pathways are still controversial due to intrinsic difficulty of in situ spectroscopy under electrochemical conditions. Therefore, computational studies based on density functional theory (DFT) energetics serve as an important tool to clarify the reaction mechanism. However, current DFT exchange correlation functionals present qualitative and quantitative errors. This is the case for example for the CO adsorption site and energy on transition metal catalysts, which is key for several catalytic processes. The random phase approximation (RPA), a post Hartree-Fock method based on the many-body perturbation theory, is a promising approach to address these issues and provide more accurate understanding of the electrochemical interfaces. However, the cost of RPA for surface systems is often unaffordable, and the combination of RPA with implicit solvation and further the grand canonical treatment of electrons to describe the electrochemical potential, is generally not established. Here, to pave the way to further electrochemical applications using RPA, we exploit a k-space extrapolation scheme to reduce the cost for surface calculations and then combine the RPA framework for electrified interfaces, including implicit solvation described using the linearized Poisson-Boltzmann equation and the grand canonical treatment of electrons. We show that the RPA results are qualitatively and quantitatively different from commonly used functionals and match better with the experimental results.

For questions, please contact: stephanie.roman@chem.ucla.edu

Tuesday, May 31st, 2022
10:00 a.m. | Young Hall 2033
& via Zoom