Towards Ab-initio Calculate Adsorption Energy on a Ultra-large System: Solving 11,000 Orbitals System at CCSD(T) Level

(Session 2, poster)

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Adsorption energy is fundamental in the study of issues like catalysis, yet it often proves difficult to obtain directly from experiments. Employing quantum chemical methods or started from the first-principle to calculate adsorption energy is more feasible. The use of what is considered the gold standard of ab-initio quantum chemistry methods, CCSD(T), is deemed highly reliable. However, due to the daunting complexity of CCSD(T), scaling up models for very delocalized adsorption systems is challenging, and the results suffer from significant finite size error. Graphene + water monomer system maybe the worest case who has the interacting range span 21 Å in certain adsorption configuration. The Systematically Improvable Ab-initio Quantum Embedding (SIE)[1] presents a solution that allows for the calculation of larger systems while ensuring accuracy, aiming to address a gerenal memthod to obtain adsorption energy at CCSD(T) level. In this study, we first benchmarked the accuracy of SIE+CCSD(T) using MgO(001) + CO, graphene + small organic molecules, and the metal-organic framework CPO-27-Mg + CO/CO_2. The results show that the adsorption energies calculated by SIE+CCSD(T) align within chemical accuracy with experimental values, achieving sub-chemical accuracy in the cases of MgO(001) + CO and CPO-27-Mg + CO/CO_2. Subsequently, we attempted to calculate graphene + water monomer by expanding the substrate under both PBC and OBC to eliminate finite size errors. We scaled up to graphene model consisting of 600 carbon atoms. The final results indicate no significant preference in the orientation of the water monomer adsorbed on graphene, with the adsorption energy under both OBC and PBC conditions closely matching around 120 meV at the bulk limit, confirming the accuracy of our calculations. By rotating the water monomer, we also discovered that the interaction between water monomer and graphene can be modulated between delocalized and localized ranges, thereby identifying the polarity of the water molecule as a critical factor influencing the interaction range. We hope our findings provide insights for subsequent experiments and molecular dynamics calculations, thus aiding the development of the field.

[1] Nusspickel M, Booth G H. Systematic improvability in quantum embedding for real materials[J]. *Physical Review X*, 2022, 12(1): 011046.