

Towards a Chemically Accurate Description of Reactions of Molecules with Transition Metal Surfaces

Content

Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. However, currently no first principles methods can be relied upon to deliver the required accuracy. Aiming to solve this problem, in 2009 we came up with a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). While the original procedure was restricted to cases where the Born-Oppenheimer static surface (BOSS) model could be used (H₂ with surfaces), we can now also use it for heavier molecules interacting with metals. For this, we can combine SRP-DFT with Density Functional Molecular Dynamics (DFMD). Additionally, we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons using a machine learning approach, for polyatomic molecules interacting with metals. The effects of electron-hole pair excitation can be modeled with the local density friction approximation (LDFA) and with orbital dependent friction (ODF). We are increasingly turning to systems for which DFT at the generalized gradient approximation (GGA) and even the meta-GGA level is insufficiently accurate. The example that will be discussed is O₂ + Al(111), which is infamous for how difficult it is to model with DFT. For systems like O₂ + Al(111), we have evidence to suggest that the accuracy for systems characterized by low values of (the work function of the metal surface minus the electron affinity of the molecule) can be described more accurately with screened hybrid than with GGA functionals. Also, for such systems (which are treated inaccurately with GGA-DFT) meta-GGA functionals already give results that are improved over GGA results. I will also discuss quantum Monte-Carlo results for H₂ + Al(110), that were obtained in a collaboration with Katharina Doblhoff-Dier. These results suggest that even GGA-DFT correctly describes the energetic corrugation of the barrier heights (how they vary with impact site and orientation of the molecule), although their absolute number may be wrong. They also suggest a way to obtain chemically accurate results for systems with (WF-EA) < 7 eV. Finally, I will briefly touch on efforts to develop an extended benchmark-database that may be used to test density functionals for their performance on dissociative chemisorption barriers on metal surfaces.

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