

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

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Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. Unfortunately, currently no first principles methods can be relied upon to deliver the required accuracy. As a first step to solving 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 (H_2 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). Also, thanks to a collaboration with Jörg Behler (University of Göttingen) we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons, for polyatomic molecules interacting with metals. Furthermore, 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) or meta-GGA level would seem to be insufficiently accurate. Examples that will be discussed include $\text{HCl} + \text{Au}(111)$ (in a collaboration with Alec Wodtke and Jan Geweke from the MPI Göttingen) and $\text{O}_2 + \text{Al}(111)$. From the latter two systems, we have evidence to suggest that the accuracy for systems that are characterized by low values of $(F - EA)$ (the work function of the metal surface minus the electron affinity of the molecule) can be described more accurately with screened hybrid density functionals 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. Finally, I will discuss quantum Monte-Carlo results for $\text{H}_2 + \text{Al}(110)$, that were obtained in a collaboration with Katharina Doblhoff-Dier. These results suggest that GGA-DFT correctly describes the energetic corrugation of the barrier heights (how they vary with impact site), although their absolute number may be wrong.