Dissociative chemisorption: A new paradigm for density functional design

NICK GERRITS

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, The Netherlands
n.gerrits@lic.leidenuniv.nl

ABSTRACT

Modeling of dissociative chemisorption requires dynamical simulations that explore the entire relevant potential energy surface (PES), because simplified transition state theory models often vastly overestimate the reactivity, even at catalytic temperatures. For example, several cases are known where two PESs obtained with different DFs, but with a similar minimum barrier height and geometry, yield considerably different reaction rates due to dynamical effects arising from other parts of the PES than the minimum energy path. Furthermore, the ubiquitous workhorse DFs are of the generalized gradient approximation (GGA) family, but they struggle to correctly describe both gas-phase molecules and metal surfaces, and especially often underestimate reaction barrier heights due to the self-interaction error. It has become clear that this class of reactions requires a DF that is robust across many different types of chemistry, making it an excellent case study for the development of next-generation robust workhorse DFs. I have recently shown that meta-GGA[1,2] and screened hybrid GGA DFs[3] can (partially) solve these problems, by employing (ring polymer) molecular dynamics[1,3,4], machine learned PESs[1,4], and beyond-GGA DFs[1-3]. I demonstrate with several examples that current of-the-shelf DFs are insufficient to provide (chemically) accurate PESs, since just going beyond the GGA is insufficient. The lessons learned here can be leveraged to develop accurate workhorse DFs that are suitable for a wide plethora of chemistry, and not just molecule-metal surface reactions.

References

[1] Gerrits, N.; et al. Highly Efficient Activation of HCl Dissociation on Au(111) via Rotational Preexcitation. J. Phys. Chem. Lett. **2021**, *12 (30)*, 7252–7260.

[2] Cai, Y.; et al. Improving Molecule-Metal Surface Reaction Networks Using the Meta-Generalized Gradient Approximation: CO_2 Hydrogenation. ChemRxiv **2023**

[3] Gerrits, N.; et al. Density Functional Theory for Molecule–Metal Surface Reactions: When Does the Generalized Gradient Approximation Get It Right, and What to Do If It Does Not. J. Phys. Chem. Lett. **2020**, *11 (24)*, 10552–10560.

[4] Gerrits, N.; et al. Accurate Reaction Probabilities for Translational Energies on Both Sides of the Barrier of Dissociative Chemisorption on Metal Surfaces. J. Phys. Chem. Lett. **2024**, *15 (9)*, 2566–2572.