# 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

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While density functional theory (DFT) is perhaps the most used electronic structure theory in chemistry, many of its practical aspects remain poorly understood. For instance, DFT at the generalized gradient approximation (GGA) tends to fail miserably at describing gas-phase reaction barriers, while it performs surprisingly well for many molecule–metal surface reactions relevant to heterogeneous catalysis. GGA-DFT also fails for many systems in the latter category, and up to now it has not been clear when one may expect it to work. Here, I show that GGA-DFT tends to work if the difference between the work function of the metal and the molecule's electron affinity is greater than ~7 eV and to fail if this difference is smaller, with sticking of O_2 on Al(111) being a spectacular example. Using dynamics calculations I show that, for this system, the DFT problem may be solved as done for gas-phase reactions, i.e., by resorting to hybrid density functionals (DFs), but using screening at long-range to obtain a correct description of the metal. The results suggest that the GGA error in the O_2 + Al(111) barrier height to be functional driven. The results also suggest the possibility to compute potential energy surfaces for the difficult-to-treat systems with computationally cheap non-self-consistent calculations in which a hybrid functional is applied to a GGA density.
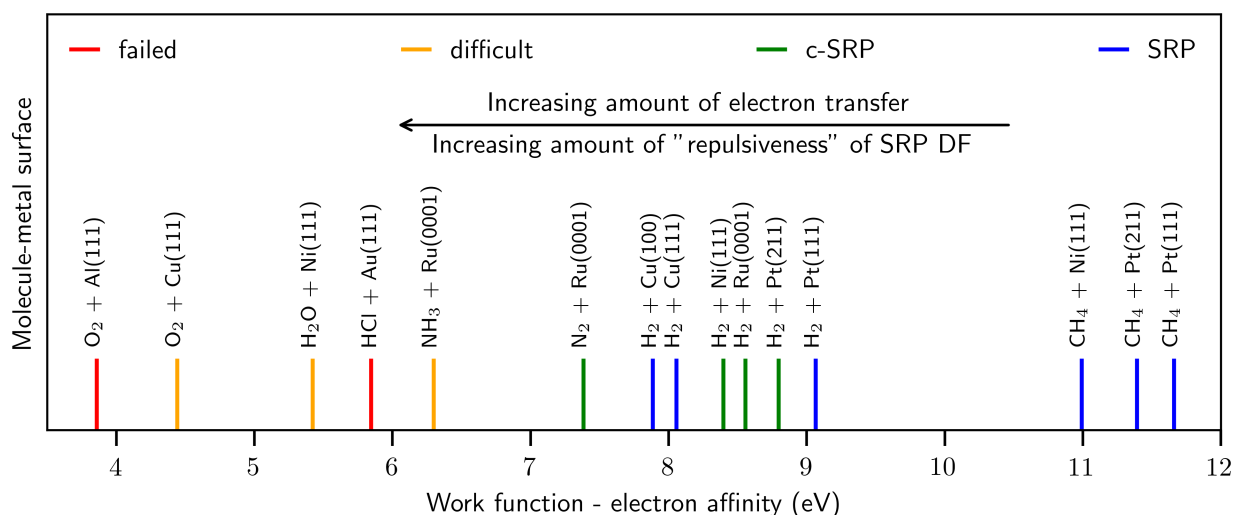
Correlation between the difference of the work function of the metal surface and the electron affinity of the molecule with the ability of GGA exchange-based DFs to accurately describe barrier heights to dissociative chemisorption in the systems shown. The color indicates whether efforts to develop a specific reaction parameter (SRP) density functional (DF) based on GGA exchange for a molecule–metal surface reaction have failed or yielded an SRP DF, where an SRP DF gives a chemically accurate description of a molecule-metal surface reaction.

[1] Nick Gerrits, Egidius W. F. Smeets, Stefan Vuckovic, Andrew D. Powell, Katharina Doblhoff-Dier, Geert-Jan Kroes. (**2020**). *J. Phys. Chem. Lett.*, *24*, 10552. DOI: 10.1021/acs.jpclett.0c02452