# Consequences of Gas-Phase Errors in Computational Electrocatalysis

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Free energies obtained from density functional theory (DFT) are the main input for computational models to rationally screen and design improved electrocatalysts for numerous environmental and industrial reactions, such as the (co)reduction of nitrogen and carbon oxides into valuable chemical compounds [1]. However, DFT has important limitations to describe the free energies of molecules. This is a major shortcoming, as customary tools to design/assess suitable catalysts, such as free-energy diagrams and volcano plots, rely on accurate equilibrium potentials, adsorption energies and reaction energies [2].

In this presentation, I will provide examples on how to calculate such errors for several compounds using different exchange-correlation functionals. [2-5] Subsequently, I will illustrate how these errors affect widespread tools such as adsorption-energy scaling relations and volcano plots [4].
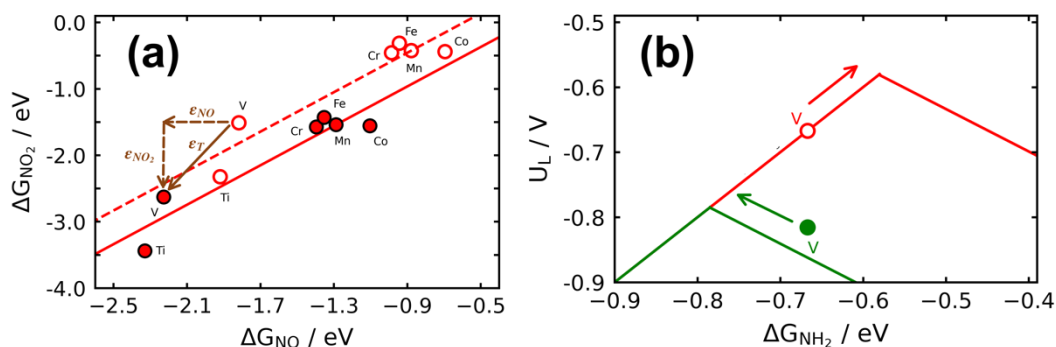


**Figure 1.** Impact of gas-phase errors on a) scaling relations between *NO$_2$ and *NO, and b) volcano plots for electrochemical ammonia synthesis using a vanadium metalloporphyrin.

Our main conclusion is that even at the highest levels of theory, gas-phase errors are large and harm the predictive capabilities of computational models of massive use in electrocatalysis. This is exemplified in Figure 1a, which shows the effect of gas-phase errors on the adsorption-energy scaling relation between *NO$_2$ and *NO. The uncorrected trend (dashed lines and open circles) is shifted with respect to the corrected trend (solid lines and filled circles) by a combination of the $NO_{(g)}$ and $NO_{2(g)}$ errors. Moreover, Figure 1b shows the effect of gas-phase errors on the volcano plot for the ammonia synthesis reaction (ASR) on a porphyrin with a V center. The uncorrected (red) volcano prescribes the weakening of the

adsorption energy of $*NH_2$ to reach the top, while the corrected (green) volcano suggests the opposite.

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