Density Functional Theory and Transition Metals Reactions – Navigating the Alphabet Soup of Functionals

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There are countless reactions that involve the use of a transition-metal catalyst. Transition metals are key components of reactive systems that are of academic, industrial, pharmaceutical and ecological interest. With the aim of understanding the reactivity of transition metal complexes more completely, countless computational studies have been carried out, and density functional theory (DFT) is a leading computational method. However, with the alphabet soup of available exchange–correlation functionals, one big question remains: which functional should one use? Recently, Dohm et al. prepared a benchmark database of transition-metal reaction energies (which they denote as MOR41) and evaluated the performance of a range of modern and conventional exchange–correlation functionals.\textsuperscript{[1]} However, reaction energies are only half of the problem: the barrier heights need also to be determined. It is known that for main-group elements, functionals that perform well for reaction energies often fare poorly for reaction barrier heights.

Herein, we present a database of transition-metal reaction barriers. A set of thirty-nine transition-metal reactions was gleaned from the literature. These are reactions that have already been studied and involve a wide selection of transition metals, including early and late transition metals as well as 3d, 4d and 5d metals. For simplicity, all reactions involve only closed-shell singlet species. For consistency, all geometries were reoptimized at the TPSS\textsubscript{D3BJ}/def2-SVP/W06 level of theory and benchmark energies were calculated using a W1-like extrapolation of DLPNO-CCSD(T) energies. Finally, the performance of a wide selection of exchange–correlation functionals, including the latest from the Head-Gordon (\textit{i.e.}, \omega B97M-V,\textsuperscript{[2]} \omega B97X-V,\textsuperscript{[3]} B97M-V,\textsuperscript{[4]} and Truhlar (\textit{i.e.}, MN15,\textsuperscript{[5]} MN15-L,\textsuperscript{[6]} groups, is evaluated against these high-accuracy energies. In addition, the performance of these newer functionals – which were not considered in Dohn et al.’s initial study – against the MOR41 database are considered.