

Density Functional Theory and Transition Metals Reactions – Part II: Open-Shell First-Row Transition Metal Complexes

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There are a countless number of reactions that involve the use of a transition-metal catalyst. Transition metals are key components of reactive systems in academic, industrial, pharmaceutical and ecological interest but often how they react remains uncertain. To this end, there are countless computational studies into reaction mechanisms of transition-metal complexes, and density functional theory (DFT) is a leading computational method. However, with the alphabet soup of available exchange–correlation functionals, how should one select which functional to use?

Recently, Dohm *et al.* prepared a benchmark database of transition-metal reaction energies (which they denoted as MOR41) and evaluated the performance of a range of modern and conventional exchange–correlation functionals.¹ However, reaction energies is only half of the problem, and it is known, at least for main-group elements, that functionals that perform well for reaction energies often fare poorly for reaction barrier heights.

At last year’s Sanibel symposium,² I presented MOBH35 – our dataset of closed-shell transition-metal complex reaction energies and barrier heights, and how well various DFT functional fare against it.³⁻⁴ Benchmark energies were calculated using a W1-like extrapolation to the basis-set limit

of DLPNO-CCSD(T) energies with a iterative-triples correction – $\Delta(T)$. One major question remaining is whether the results obtained for closed-shell complexes are transferable to open-shell systems, and especially systems that may involve multiple spin-states.

This year, I will present our dataset of open-shell transition metal reaction energies and barrier heights, and how well the plethora of DFT functionals perform compared to these benchmark values, with special emphasis on double-hybrid functionals that have proven so effective.⁵

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3. Iron, M. A.; Janes, T. Evaluating Transition Metal Barrier Heights with the Latest DFT Exchange–Correlation Functionals – the MOBH35 Benchmark Dataset. *Journal of Physical Chemistry A* **2019**, *123*, 3761-3781.
4. Iron, M. A.; Janes, T. Correction to “Evaluating Transition Metal Barrier Heights with the Latest Density Functional Theory Exchange–Correlation Functionals: The MOBH35 Benchmark Database”. *Journal of Physical Chemistry A* **2019**, *123*, 6379-6380.
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