

Reliable modeling of homogenous transition metal-based electrocatalysis

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Homogeneous electrocatalysis provides a promising approach to produce fuels, for example, by H₂ generation or CO₂ reduction with earth-abundant metals. Here, computational chemistry can help to develop novel catalysts. Elucidating the underlying mechanisms, tuning ligand structures to archive lower over-potentials, higher turnover frequencies, and better substrate selectivity are typical applications. However, the choice of reliable quantum chemical (QC) methods applicable to the target system size (20-150 atoms) and the often quite complicated electronic structures of typical electrocatalysts is difficult.

To figure out, which QC methods are suited for that purpose, we compiled a set of vertical ionization potentials (IPs) and electron affinities (EAs) comprising 28 medium-sized, diverse 3d TM complexes with practical importance as electrocatalysts, termed 3dTMV. For this set, we analyzed different diagnostics for static correlation, such as the FOD, A₁₀₀[TPSS], T₁, spin splitting energies, spin contamination, and r_{nd}. We performed a principal component analysis and evaluated the benefit of different diagnostics to identify different degrees of static correlation. Specifically, the charged systems with diverse multiplicities render the 3dTMV benchmark set useful for investigating static correlation problems in electrocatalysts. To generate reference data for the assessment of common Kohn-Sham DFT methods and special multi-reference DFT based approaches, we employed the "gold-standard" CCSD(T) method and carefully analyze for which degree of static correlation single reference coupled-cluster theory can still reliably predict vertical IPs and EAs for transition metal complexes.