

## COMPUTATIONAL TOOLS FOR DESIGNING NEW CATALYSTS: OPPORTUNITIES AND CHALLENGES

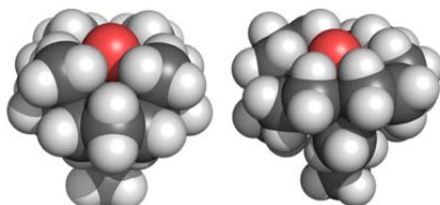
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Bioinspired homogeneous catalysis is an active area of research for both theoretical, computational and experimental chemists, leading to new insights of transition-metal chemistry that help understand metalloenzymes. Recently, big steps forward have been made by joint computational/experimental studies, focusing on spectroscopy of different kinds (IR, rRaman, UV-vis, EPR, Mössbauer, X-ray Absorption, NMR, etc.) that can be studied both experimentally and computationally. Validation of the computational results to prove or disprove assumptions about electronic/geometric structures relies mostly on the spectroscopic data, and hence the presence or absence of these remains a challenge and opportunity at the same time.



Here I will present the results of such a joint experimental/computational study, with a new twist to an old story. This is based on adaptations of the TMC (tetramethylcyclam) ligand in combination with the Fe(IV)=O complex for Hydrogen Atom Transfer (HAT) and Oxygen Atom Transfer (OAT) mechanisms. At the same time, the spin-resolved charge displacement function analysis is highlighted, which allows a clear distinction between Hydrogen Atom Transfer and concerted Proton Coupled Electron Transfer and leads to deeper understanding of the differences in reactivity arising from differences in spin states.

Over the past 20+ years spin-state splittings have evolved from being a challenge for theoretical chemistry towards providing exciting opportunities. Early GGAs and LDA show a systematic overestimation of the stability of low-spin states, while the inclusion of Hartree-Fock exchange in hybrid functionals goes towards a shifting scale with a preference for high-spin states. Indeed, a recent study by Pinter and co-workers showed the “optimal” amount of HF exchange to range from -12% to +179% (Chem. Eur. J. 2018, 24, 5281).

In the outlook to the future, I will present new density functionals based on the most-cited functional (PBE) and show that its failure in assessing spin states can be remedied by increasing its flexibility. This more flexible PBE functional for the first time shows an exchange functional that satisfies the LDA limit at  $s=0$  **and** can now accurately predict spin states.

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[1] B. Pinter, A. Chankisijjev, P. Geerlings, J.N. Harvey, F. De Proft, Chem. Eur. J. 2018, 24, 5281