

Ab Initio Calculations for Spin-Gaps of Non-Heme Iron Complexes

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Heme and nonheme mononuclear iron oxygenases and their synthetic analogues are known to perform a wide range of catalytic oxidative transformations in chemistry and biochemistry.^[1] The most typical Fe reaction is the C-H hydroxylation which has been proposed to be performed by an iron-oxo Fe^{IV}=O active intermediate. The rate limiting step in these reactions was found to be the hydrogen atom abstraction process. These systems are also known for their multi-state reactivity. We have seen that many methods have problems with accurately calculating this reaction.^[2]

Therefore, we have performed an extensive computational study of the quintet-triplet gap ΔE_{TQ} of a series of non-heme Fe^{IV}=O species.^[3] We employed our recently proposed multireference approach CASPT2/CC^[4] to calculate the gaps and subsequently used these results to benchmark two variants of local coupled cluster approaches (DLPNO-CCSD(T) and LUCCSD(T0)). We have showed that current implementations of the local coupled cluster method are not sufficiently accurate. DLPNO-CCSD(T) systematically overstabilizes the quintet state by about 8 kcal/mol, whereas LUCCSD(T0) gives the too stable triplet ground state. Interestingly, we observed a good linear correlation between the ΔE_{TQ} values predicted by CASPT2/CC and DLPNO-CCSD(T). Therefore, a simple correction scheme, which significantly improves the accuracy of the latter method was proposed and validated. We have tested this correction on the calculation of the triplet-quintet gaps and on the example of the C-H activation reaction.

References

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