# New advances in spin-states in biochemistry and inorganic chemistry

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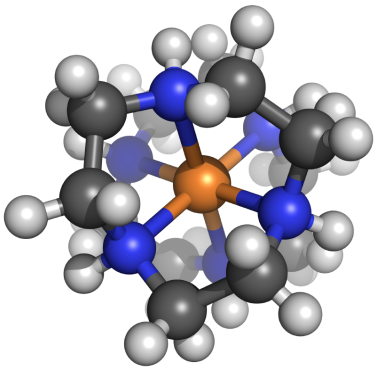
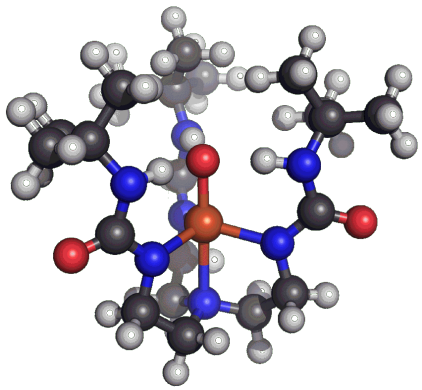


One of the most important challenges for Density Functional Theory is the proper description of spin states of transition-metal (TM) complexes.[1] At a recent ESF/CECAM workshop[2] (Sept. 2012, Zaragoza; highlighted in Nature Chemistry[3]), this was discussed and the need for a database with reliable examples of spin states of TM-complexes was put forward. The problem with these spin states arises because neither early pure DFT functionals (BP86, PBE), nor hybrid functionals (B3LYP, PBE0) can be trusted to give good results. In the case of hybrid functionals, this can be easily understood: they tend to overstabilize high spin states because of the inclusion of a portion of Hartree-Fock exchange.[4] A major breakthrough was the use of Handy-Cohen's OPTX functional (in OPBE[5]), leading ultimately to improved functionals (SSB-D,[6] S12g,[7] S12h[7]). Here I will discuss recent advances in spin-state studies (for example the exchange-enhanced reactivity model by Shaik and co-workers, or the spin distribution in heme proteins), and highlight recent studies in my group: competing pathways in polymerization mechanisms of α diimine iron catalysts,[8] spin states of biomimetic $Fe^{III/IV}$-oxo, $Fe^{III}$-hydroxo/hydroperoxo and $Fe^{III}$-peroxo complexes and the effect on a $Sc^{3+}$-capped iron-oxygen complex,[9] and those of bis-triazacyclononane complexes with some first-row transition-metal complexes.[10]



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