

Accurate Spin State Energies for 1st Row Transition Metal Compounds

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Summary

An overview is given of spin-state splittings for a number of compounds containing iron and other first-row transition metals, which were obtained by DFT calculations using the OPBE functional with Slater-Type Orbitals. This functional was recently shown to give accurate spin-state splittings for iron compounds, and is here reported to work excellently also for other transition metals.

Introduction

Determining spin ground-states of transition metal compounds remains a challenging task for both theory and experiment.¹⁻² On the experimental side, the situation may be complicated by ligand-exchange reactions, dimerization processes, oxidation/reduction, impurities, or temperature-dependences of the spin ground-states. The latter is for instance observed in spin-crossover compounds, where low-spin compounds upon heating change to high-spin, or high-spin compounds upon cooling change to low-spin.

In principle, theory should be able to help with the interpretation of the experimental data, predict the spin ground-state and help to determine reaction mechanisms. However, theory is not without its own problems. The most accurate ab initio theoretical methods (CCSD(T), MR-CI) are too demanding for everyday use, and in some cases (such as CASPT2) need expert knowledge of the methodology. More efficient are calculations based on density functional theory (DFT), but the results are shown to depend largely on the choice of DFT functional that is being used.

This is in particular true for the calculation of relative spin-state energies, where the choice of the DFT functional¹ and the basis set³ used both play a major role. Standard pure functionals (like LDA or BLYP) systematically over-stabilize low-spin states,^{1,2} while hybrid functionals (e.g. B3LYP) over-stabilize high-spin states due to the inclusion of a portion of Hartree-Fock (HF) exchange.^{2,4} Reiher and co-workers therefore reduced the amount HF exchange to 15% (instead of 20% in B3LYP), dubbed B3LYP*,⁵ which indeed improves the B3LYP results for many systems. However, it was not successful for all iron compounds, as for instance is the case for the $\text{Fe}(\text{phen})_2(\text{NCS})_2$ spin-crossover compound,⁶ for which a further reduction to 12% of HF exchange seems necessary. Therefore, with B3LYP and B3LYP*, it is *a priori* unknown if the amount of HF exchange is appropriate for the transition metal compound under study, which is an undesirable situation.

The influence of the basis set was found to be substantial.³ In principle, with an infinitely large basis set, both Slater-type orbital (STO) and Gaussian-type orbital (GTO) series should converge to the same final answer, which is indeed what we observed for both *vertical* and *relaxed* spin-state splittings. However, we found that the STO basis sets give consistent and rapidly converging results, while the convergence with respect to the basis set size is much slower for the GTO basis sets (see Figure 1). The use of basis sets containing effective core potentials (ECPBs) resulted in spin-state splittings that are systematically different from the converged STO-GTO results.

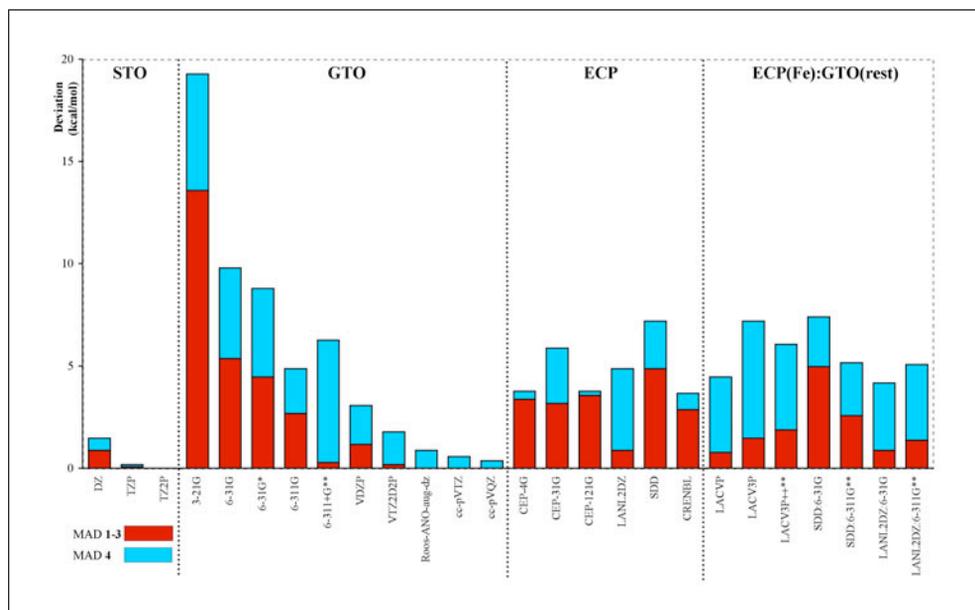


Figure 1. Mean absolute deviations (MAD) for different basis sets (from ref. 3).

From these and related studies, it became clear that recent and improved functionals provide more accurate results. This is in particular true for the OPBE functional, that combines Handy and Cohen's optimized exchange (OPTX)⁷ functional with the PBE⁸ correlation functional, which provided the correct spin ground-state for a number of Fe(II)/Fe(III) compounds.¹ This good performance of OPBE concurs with recent benchmark studies on the energy profiles of nucleophilic substitution reactions,⁹ and on the NMR chemical shifts of organic molecules.¹⁰ Han and Noodleman recently obtained the Mössbauer isomer shift parameters for OPBE,¹¹ and used these to study hydroxylase intermediates of soluble methane monooxygenase (MMOH).¹² It was shown that OPBE does not overestimate Fe-ligand covalency and correctly predicted high-spin anti-ferromagnetically (AF) coupled Fe⁴⁺ sites.

Here we give an overview of previous OPBE results for iron compounds, and some preliminary results for first-row transition metal compounds. In all cases does OPBE give excellent results.

Methods

All DFT calculations were performed with the Amsterdam Density Functional (ADF) suite of program.¹³ MOs were expanded in an uncontracted set of Slater type orbitals (STOs) of triple- ζ quality containing diffuse functions and one (TZP) or two (TZ2P) sets of polarization functions. Energies and gradients were calculated using the local density approximation (LDA; Slater exchange and VWN correlation) with gradient-corrections (GGA) for exchange (OPTX)⁷ and correlation (PBE)⁸ included self-consistently, i.e. the OPBE functional.¹⁴ Geometries were optimized with the QUILD program¹⁵ using adapted delocalized coordinates¹⁶ until the maximum gradient component was less than 1.0e-4 atomic units. The solvent environment was in some cases included through a dielectric continuum (COSMO) model.¹⁷

Results

The OPBE functional has recently¹⁻² been used to obtain the spin-state splittings for a number of iron compounds, which consist of three benchmark systems (Figure 2) and difficult compounds (Figure 3), among others.

The benchmark systems had previously¹⁸ been studied with high-level CASPT2 calculations and, for comparison, with Hartree-Fock and some DFT functionals. Hartree-Fock always predicted a high-spin ground-state, wrongly also for the low-spin bipyridyl compound, and showed spin-state splittings with large deviations from the reference CASPT2 data. Somewhat better results were obtained in the CASPT2 paper¹⁸ with DFT functionals, which showed deviations between 9-15 kcal·mol⁻¹; however, the hybrid functionals (B3LYP, PBE0) also failed to predict the low-spin ground-state for the bipyridyl compound. These results are improved upon² by OPBE, whose deviation from the reference CASPT2 data is an order of magnitude smaller (1-2 kcal·mol⁻¹). In fact, the difference between CASPT2 and OPBE falls well within the estimated accuracy of the reference CASPT2 data.

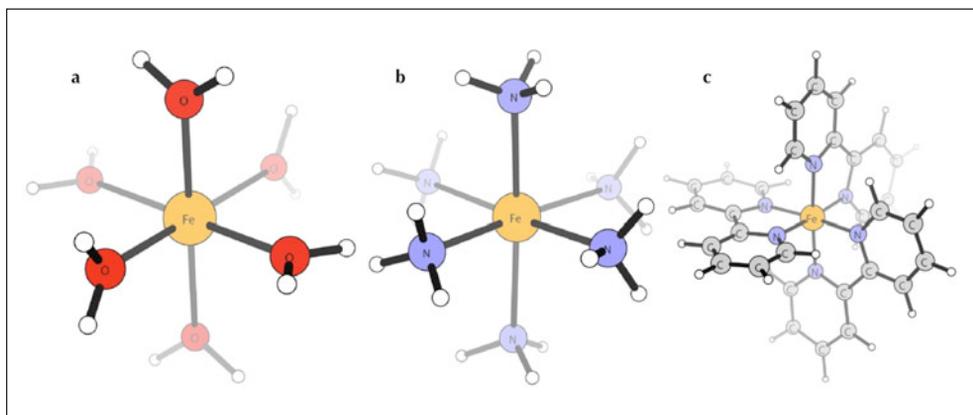


Figure 2. Benchmark iron compounds: $Fe(II)(H_2O)_6^{2+}$ (a), $Fe(II)(NH_3)_6^{2+}$ (b), $Fe(II)(bpy)_3^{2+}$ (c).

The pyridylmethylamine (pma) compounds (Figure 3b-c) had been studied because they are structurally similar with approximately an octahedral arrangement of ligands around the iron, yet they show a different spin ground-state. The combination of these two molecules therefore is a very stringent check on the performance of computational methods. The mono-pma compound is high-spin and the di-pma compound low-spin, both in experiment and by OPBE.² In contrast, standard pure DFT functionals fail to predict the high-spin ground-state of mono-pma, while hybrid functionals fail to predict the low-spin ground-state of di-pma.²

The spin-crossover compound $Fe(phen)_2(NCS)_2$ (Figure 3a) was previously studied by Reiher, who showed that both B3LYP and B3LYP* were unable

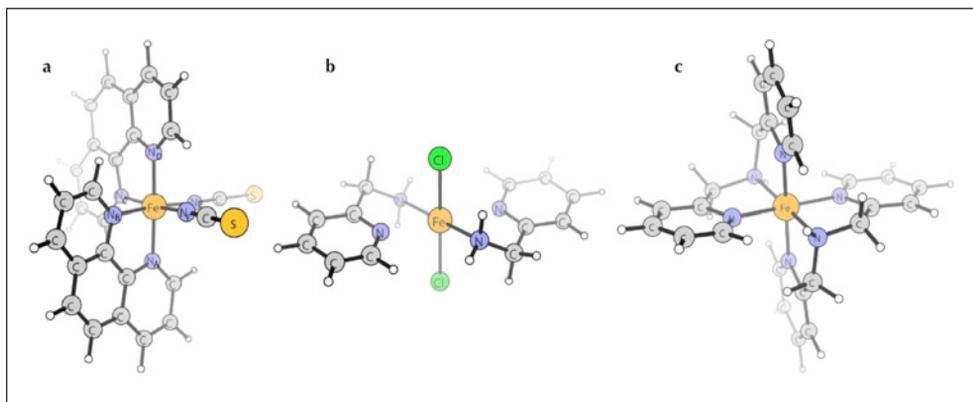


Figure 3. Difficult iron compounds: spin-crossover compound $Fe(II)(phen)_2(NCS)_2$ (a), mono-pyridylmethylamine $Fe(II)(amp)_2Cl_2$ (b), di-pyridylmethylamine $Fe(II)(dpa)_2^{2+}$ (c)

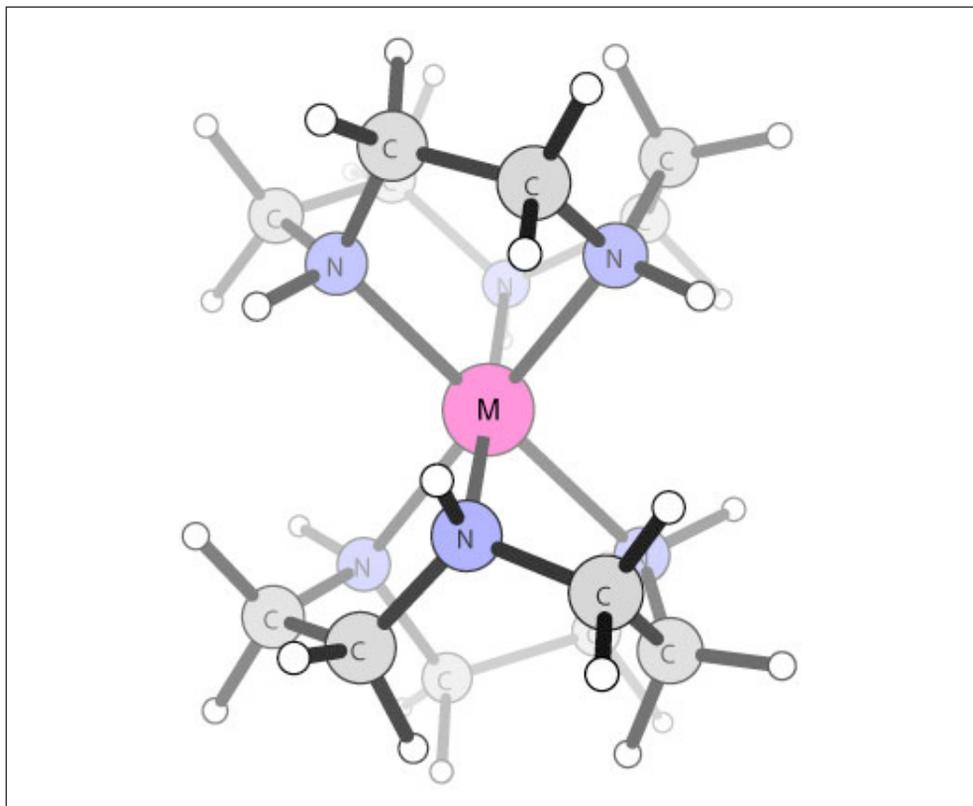


Figure 4. Bis complex of transition-metal (TM) with 1,4,7-triazacyclononane ligands $TM([9]aneN_3)_2^{n+}$.

to classify this molecule as a spin-crossover compound.⁶ Instead, both these methods predicted it to have a high-spin ground-state at all temperatures. Only by lowering the amount of Hartree-Fock exchange to 12% did Reiher obtain a reasonable energy splitting of ca. 3 kT, and a low-spin ground-state. In contrast, OPBE directly predicts a low-spin ground state and an (ΔE_{HL}) energy splitting of 2.1 kcal·mol⁻¹ (3.5 kT), in excellent agreement with experiment. Similar to the pma-compounds, other DFT functionals are unable to classify this molecule as spin-crossover, e.g. they either predict a too large energy splitting, or one with the wrong sign.

With this good performance¹⁻² of OPBE for these iron compounds in mind, we were interested if it would also work as well for other transition metals.¹⁹ Therefore, we took a complex for which experimental data are available for a series of transition metals (Cr, Mn, Fe, Co, Ni, Cu, Zn; some of which in different oxidation states), which are based on the triazacyclononane ligand (Figure 4). It was already shown that OPBE correctly predicts the spin ground-

state for the Fe(III) compound, and also for the other transition metals, for those which more than one spin-state is available, does OPBE predict the correct ground-state.

Similar good performance is observed for a set of spin-crossover compounds, for which B3LYP was shown to fail. In contrast, our studies with OPBE¹⁹ show that it correctly predicts a low-spin ground-state with a small ΔE_{HL} energy splitting between high and low-spin.

Conclusions

We have presented an overview of recent studies on spin ground-states of first-row transition-metal compounds, as obtained with the OPBE functional. The mean absolute deviation from benchmark high-level CASPT2 data is ca. 1 kcal·mol⁻¹, i.e. an order of magnitude smaller than other DFT functionals. Moreover, it correctly predicts the splittings for spin-crossover compounds, pyridylmethylamine compounds, and for a series of cyc[9]ane compounds.

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