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Accurate Modeling of Spin-State Energetics in Spin-Crossover Systems with Modern Density Functional Theory

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The energies of different spin multiplicities of a range of iron complexes are computed using modern density functional theory (DFT) methods of the generalized gradient approximation (GGA; BP86 and OPBE), meta-GGA (TPSS), hybrid meta-GGA (TPSSh), hybrid (B3LYP), and double-hybrid (B2PLYP) types. It is shown that so far only the double-hybrid density functional B2PLYP, in conjunction with large and flexible basis sets (def2-QZVPP), is able to provide qualitatively correct results of spin-state energetics for the investigated non-spin-crossover complexes. An energy difference of −6 to 0 kcal/mol is proposed to be indicative of spin-crossover behavior.

The interest in "molecular material" science has been fueled by the increasing demands for smaller size communication devices. The goal is the design and utilization of molecule-based materials that fulfill the functions of conventionally employed silicon-based devices. Spin-crossover (SCO) complexes exhibit a change of the spin ground state as a function of external perturbations such as temperature, pressure, light irradiation [light-induced excited-spin-state trapping (LIESST)], and pulsed magnetic fields.[1] Such properties define this class of compounds as especially promising materials for future applications in the fields of molecular electronics, data storage, nonlinear optics, and photomagnetism.[2]

While experimentalists have made significant advances in understanding SCO phenomena, quantum-chemical studies on such molecules have met with mixed success.[3] The most critical question from a theoretical point of view is whether it is possible to predict the correct spin multiplicity of the electronic ground state. If this were possible with high confidence prior to the actual synthesis of the complex, it would open the door to the rational design of molecules and materials with tailored properties. However, given the size of typical SCO complexes, presently the only practical choice for theoretical investigations is density functional theory (DFT). The alternative Hartree−Fock (HF) method is strongly biased in favor of high-spin (HS) states and hence has no predictive power in the SCO field. Yet, even DFT methods, while being much superior to HF, also have difficulties in correctly predicting spin-state energetics in transition-metal complexes.[4] In general, local and gradient density functionals (DFs; for example, BP86[5]) systematically favor low-spin (LS) over HS states.[6] An admixture of exact HF exchange into hybrid DFs (for example, B3LYP[7]) results in a stabilization of the HS state that is proportional to the fraction of exact exchange.[3a,8]

More recently, the new class of double-hybrid DFs (DHDFs) with corrections from second-order many-body perturbation theory (the first and prototypical member being termed B2PLYP) has been proposed.[9] The introduction was triggered by the idea that not only nonlocal exchange (53% HF exchange) but also nonlocal correlation is required in order to improve on existing Kohn−Sham DFT. With only two empirical parameters, very good results for the thermodynamic and kinetic properties of a wide range of chemical systems were achieved.[9,10] Excellent results have also been obtained for geometries[11] and excited states.[12] Motivated by this success, we investigate here the ability of the B2PLYP functional to model spin-state energetics for a variety of iron complexes with different ground-state spin multiplicities and

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apply the method to a problem of current interest. In addition to the archetypal SCO complex, Fe(1,10-phenanthroline)$_2$(NCS)$_2$[13] (**1**), other complexes chosen for this study are difficult cases in terms of spin-state energetics. Experimentally, it was demonstrated that the change of the axial ligand L [L = NO^+ (**2**), CO (**3**), PMe_3 (**4**), PH_3 (**5**), N_2H_4 (**6**), NH_3 (**7**)] in the series of $[Fe(L)(N_HS_4)]^{0/+}$ [$N_HS_4^{2-}$ = 2,2′-bis(2-mercaptophenylthio)diethylamine dianion] complexes leads to different spin ground states.[14] Theoretical investigations by Reiher and co-workers revealed that the purpose-specific B3LYP*[3a] DF is able to correctly reproduce the experimentally observed ground states of this series. Later studies have shown that B3LYP* performs as well as the original B3LYP functional in chemical applications.[15] The generalized gradient approximation (GGA) exchange functional OPTX[16] (as used in OPBE and OLYP) was also reported to give correct predictions of the lowest-energy spin multiplicities of this series.[17] More recently, Pierloot and co-worker reported that high-level ab initio calculations using second-order perturbation-theory-corrected complete active space self-consistent-field theory (CASSCF/CASPT2)[18] predict the correct spin ground states of this series.[19] For $Fe^{III}PCl$ (P = porphyrinate) (**8**), the PW91 calculations predict an $S = {}^3/_2$ ground state. This is inconsistent with experiment, which indicates a sextet ground state. The B3LYP method yields nearly identical energies for the lowest quartet and sextet states in this case.[20] In addition, several smaller-size iron complexes ($[Fe(H_2O)_6]^{2+}$ (**9**), $[Fe(NH_3)_6]^{2+}$ (**10**), and $[Fe^{IV}O(NH_3)_5]^{2+}$ (**11**)) that had been studied previously by high-quality ab initio techniques are also included in the present study.[21]

Table 1. Relative Energies[a] (kcal/mol) of the HS[b] and LS (Intermediate-Spin)[c] States for **1**—**11** As Predicted by Different DFs Employing a def2-QZVPP Basis Set

	BP86	OPBE	TPSS	TPSSh	B3LYP	B2PLYP	exp.
1	11.2	−3.6	13.7	3.5	−9.0	−5.8	$S = 0$
2	34.2	30.2	33.6	24.4	9.7	48.6	$S = 0$
3	38.9	34.7	37.5	24.5	8.7	26.7	$S = 0$
4	29.4	21.9	28.4	15.1	−1.8	12.9	$S = 0$
5	26.8	21.7	27.5	12.7	−3.7	9.7	$S = 0$
6	13.0	3.3	13.6	1.3	−14.0	−6.2	$S = 2$
7	−1.5	−12.2	−0.5	−12.7	−27.4	−21.1	$S = 2$
8	7.7	−3.3	8.0	2.6	−1.9	−2.4	$S = 5/2$
9	−25.4	−49.1	−21.4	−27.2	−31.2	−34.4	$S = 2$
10	0.3	−20.0	2.8	−5.8	−13.7	−20.8	$S = 2$
11	9.5	−0.6	11.5	6.8	0.5	3.8	$S = 1$

[a] The energy of the LS (intermediate-spin) state is taken as the zero-energy reference level. Energy differences include the zero-point energy correction. [b] The HS states for **1**—**7** and **9**—**11** are quintet states, and that for **8** is a sextet state. [c] The LS states for **1**—**7** and **9**—**11** are singlet states; the intermediate-spin state for **8** is a quartet state, and that for **10** is a triplet state.

As shown in Table 1, all DFT methods employed predict the correct ground-state spin multiplicity for complexes containing strong-field ligands such as NO^+ and CO. In the case of weak-field complexes with smaller energy differences between different spin multiplicities, a significant overstabilization of the LS state is observed for GGA DFs (BP86 predicts LS and intermediate-spin ground states for **6** and **8**, respectively, which contradicts the experimental findings). The same trend is also observed for the TPSS[22] and TPSSh[23] functionals. On the other hand, the hybrid B3LYP DF gives erroneous predictions of the ground-state multiplicity (HS) for the phosphine complexes (**4** and **5**).[3a] The behavior of the OPBE functional is somewhat ambiguous. Quite surprisingly, OPBE favors the HS state for **11**, which is inconsistent with the closely related experimental analogue $[Fe^{IV}(O)(TMC)(CH_3CN)]^{2+}$ (TMC = tetramethylcyclam).[24] Conversely, OPBE suggests the LS state to be the ground state for **6**, which is in contrast to earlier calculations that used small basis sets.[17] As can be clearly seen from Table 1, the only DF that is able to yield qualitatively correct predictions for all investigated non-SCO complexes is B2PLYP. In the case of the SCO complex **1** with vanishing energy separation between different spin multiplicities, B2PLYP incorrectly predicts a HS ground state. We noted that the metal−ligand distances are excellently predicted for the LS state (mean error of < 0.04 Å) and are too long by ~0.1 Å for the HS state in the BP86-optimized structure (Table S2 in the Supporting Information). A similar trend was also observed for the B3LYP*-optimized structure.[25] Test calculations on $[Fe(NH_3)_6]^{2+}$, which has the same first coordination sphere as **1**, showed that this structural bias stabilizes the HS state by ~6 kcal/mol. In order to obtain more accurate geometries for the different spin states of **1**, geometry optimizations were carried out using the scalar relativistic zeroth-order regular approximation (ZORA).[26] The BP86/ZORA-optimized structures for the two spin states are in excellent agreement with the X-ray structures with a mean deviation of the Fe−N bond lengths of less than 0.03 Å (Table S2 in the Supporting Information). However, the B2PLYP calculations on the improved geometries still predict that the singlet state is destabilized by 6.0 kcal/mol compared to the quintet state. The same energy gap (5.7 kcal/mol) was also obtained by the B2PLYP calculations based on the crystal structures of the two spin-state isomers of **1**. Thus, we tentatively propose that the HS−LS energy differences calculated by the B2PLYP functional in a range of −6 to 0 kcal/mol should be taken as being indicative of SCO complexes.

The most reliable estimates of LS−HS energy differences have thus far been obtained by CASPT2 and by the

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spectroscopy-oriented configuration interaction (SORCI)[27] method. The LS−HS gaps calculated with B2PLYP are in quantitative agreement with those predicted by CASPT2 for **2**−**4**, **6**, and **10**.[19,28] Likewise, the B2PLYP results agree quantitatively with SORCI for **9**[29] and **10**,[30] thus lending credence to the results of these calculations. CASPT2 calculations with a rather small basis set on FePCl provided a sextet−quartet gap of −19.6 kcal/mol (sextet at lower energy).[20] B2PLYP also favors the sextet but by a much smaller margin (Table 1). In contrast to our previous SORCI calculations on **11** with a fairly small basis set,[31] B2PLYP predicts that the triplet state has lower energy, which is in line with experimental results on analogous systems.[24]

In comparison with DHDFs, the basis set dependence for hybrid DFs such as B3LYP has been found to be negligible. This is in contrast to the findings reported by Swart et al.[32] Our test calculations show that the B3LYP HS−LS energy splittings for **4** and **5** using systematically enlarged basis sets are in the range of 2−7 kcal/mol, while the corresponding energy gaps calculated with the B2PLYP functional span the range −8 to +12 kcal/mol (Table S1 in the Supporting Information). Moreover, the B2PLYP calculations with small basis sets [SV(P), TZV(P), and even TZV(2D,P)] yield qualitatively incorrect spin-state energetics for **4** and **5**. (Solvation effects are also documented in the Supporting Information.) Thus, in order to obtain reliable results from B2PLYP calculations, it is imperative to apply very large and flexible basis sets such as def2-QZVPP.

In general, such calculations are very demanding. In order to accelerate the B2PLYP calculations with extended basis sets, the density fitting and "chain of spheres" approximations (RIJCOSX)[33] for the SCF part and the density fitting (RI) approximation[34] for the PT2 correction were employed in the present work. This leads to dramatically reduced computation times without loss of accuracy.[33] For example, it only takes 36 h to complete the single-point calculation of the HS state for **1** by the B2PLYP/def2-QZVPP method (2537 basis functions, 1935 RI-J auxiliary functions, and 6051 RI-MP2 auxiliary functions) using four processors; the corresponding LS calculation only needs ~16 h, and the analogous B3LYP calculation finishes in ~10 h. Thus, for at least medium-sized transition-metal complexes, B2PLYP calculations with extended basis sets are still feasible.

In order to test the predictive power of this new method, we apply it to a recently studied SCO system. The LIESST complex $\mathrm{Fe(L)(CN)_2}$[35] (**12**; L = 2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentene) displays a short optical addressing time (picosecond scale), which renders it suitable for data storage. The B2PLYP calculations predict the HS state of **12** to be 5.5 kcal/mol lower in energy than the LS state. The computed energy gap falls into the proposed range, thus demonstrating the capabilities of the B2PLYP functional.

In conclusion, it is still very challenging for DFT methods to reliably predict the correct ground-state spin multiplicities of transition-metal complexes. Our results show that the newly developed double-hybrid class of DFs is able to provide qualitatively correct results for the spin-state energetics of non-SCO complexes. In the case of SCO complexes, B2PLYP appears to be slightly biased in favor of HS states. Thus, predicted energy differences in the range of −6 to 0 kcal/mol may be regarded as being indicative of SCO behavior. A case study confirmed the applicability of the suggested method. This has important consequences for the theoretical modeling of SCO phenomena and further adds to the credibility of the new methods. Thus, the B2PLYP double-hybrid functional is an important theoretical tool for experimentalists in their design and prescreening of new molecule-based materials with tailored properties. We anticipate widespread applications of this method in the field of molecular materials.

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Supporting Information Available: Computation details, basis set dependence, solvation effects, a table of the key structural parameters, coordinates of all compounds, and a table of the calculated energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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