

# Theoretical Characterization of Electronic States of Iron Complexes

Ph.D. thesis booklet

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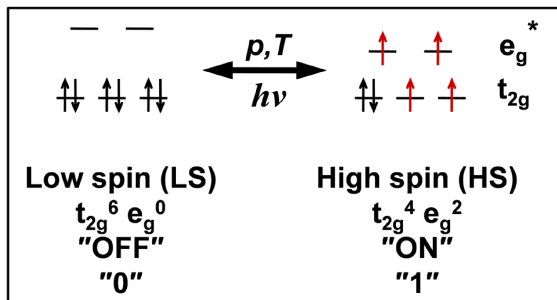
Budapest

**2014**



# 1 Introduction

Magnetic bistability in molecules is one of the most intriguing and most actively studied phenomenon in iron complexes. Switchable molecular Fe compounds are well-known candidates for magnetic switches, data storage, data display, and optical devices. The most common realization of the "OFF"  $\leftrightarrow$  "ON" switching in these complexes is the low-spin (LS)  $\leftrightarrow$  high-spin (HS) transition. The LS and HS states imply two different Fe-3d electronic structures, e.g., for an octahedral Fe(II) ( $d^6$ ) complex, the  $t_{2g}^6 e_g^0$  (closed Fe-3d subshell,  $S = 0$ , where  $S$  is the electron spin angular momentum of the Fe(II) ion) and  $t_{2g}^4 e_g^2$  (open Fe-3d subshell,  $S = 2$ ) configurations, respectively (Figure 1).



**Figure 1:** Illustration of the functioning of an octahedral Fe(II) molecular switch with  $3d^6$  electron configuration. The switching between the "OFF" ("0") and "ON" ("1") positions is realized by a LS ( $t_{2g}^6 e_g^0$ )  $\leftrightarrow$  HS ( $t_{2g}^4 e_g^2$ ) transition.

For compounds with intermediate ligand field strength, the LS  $\leftrightarrow$  HS transition can be induced by several effects, e.g., the variation of temperature or pressure, or by the irradiation with light, and is often referred to as the spin-crossover (SCO) phenomenon. The application of molecular compounds exhibiting spin-state transitions as switchable magnetic devices is very appealing, due to the small size ( $d < 1$  nm) of the magnetically active molecules and the very fast photoswitching (on the ps time scale) between the two spin states.

It has recently been confirmed that the mechanism of the spin-state transition in Fe complexes involves several excited states possessing different spin multiplicities. For the complete understanding of the molecular switching mechanism, the characterization of the LS, HS, and other possible intermediate electronic states is essential. In addition to experimental techniques, such as magnetization measurements,  $^{57}\text{Fe}$  Mössbauer and very

involved ultrafast optical/X-ray spectroscopies, quantum chemical calculations are a very valuable tool for the identification of these states and the investigation of the SCO process. Moreover, the spectroscopic characterization of the electronic states usually requires the theoretical prediction and interpretation of the measured spectra. This is especially the case for Mössbauer spectroscopy, which is almost inevitable in the investigation of Fe compounds, and for which theoretical support has a vital importance in the full interpretation of the measured spectra. Furthermore, the accurate theoretical identification of the ground and excited states participating in the spin-state transition offers an ideal testing ground for the applicability of computational methods.

## 2 Scope of the Present Study

Among Fe-based systems, photoswitchable complexes could be the most promising candidates for magnetic molecular switches and memory devices. Although no such compound working at room temperature has yet been discovered, low temperature analogues (functioning below 50 K) exist. A very valuable step towards the design of the applicable materials can be achieved by unveiling all the details of the mechanism of molecular switching. The aim of the present work is to contribute to the understanding of the fundamental mechanism by characterizing different states of Fe complexes with state-of-the-art quantum chemical methods, namely density functional theory (DFT) and multiconfigurational second-order perturbation theory (CASPT2). This goal can be realized by accomplishing the following objectives:

- the assessment of different density functionals in the determination of the structural and energetic variations at the LS $\leftrightarrow$ HS state transformation, which factors are decisive on the lifetime of the metastable HS state. For this, three intensely investigated switchable Fe complexes, which contain respectively mono-, di-, and tridentate ligands, were chosen:  $[\text{Fe}(\text{tz})_6]^{2+}$  (**1**) (tz = 1*H*-tetrazole),  $[\text{Fe}(\text{bipy})_3]^{2+}$  (**2**) (bipy = 2,2'-bipyridine), and  $[\text{Fe}(\text{terpy})_2]^{2+}$  (**3**) (terpy = 2,2':6',2''-terpyridine).
- the calculation of the potential energy surfaces (PESs) of the lowest-lying singlet, triplet, and quintet  $3d^6$  states of the **1–3** complexes involved in the spin-state transition. These PESs were calculated along the configurational coordinate(s) relevant to the LS $\leftrightarrow$ HS transition with DFT and time-dependent DFT (TD-DFT) by the application of a well-performing exchange-correlation functional selected

on the basis of the above discussed assessment. For **3**, these PESs were also calculated with CASPT2; for **1** and **2**, the CASPT2 surfaces were available in the literature [L1] [L2].

- the support of the experimental identification of LS and HS states by the development of a DFT methodology for the accurate prediction of  $^{57}\text{Fe}$  Mössbauer parameters: the isomer shift and the quadrupole splitting. This was collaterally expanded to provide a general recipe for iron complexes with any spin, oxidation state, and coordination number in order to improve the reliability of the computational approach, and to offer a generalized tool to the Mössbauer community.

### 3 Applied Computational Methods

The computational methods applied in the present work include DFT, TD-DFT, and CASPT2. In the case of DFT, calculations were performed with the gradient-corrected (GGA) exchange-correlation functionals RPBE, BP86, OLYP, and OPBE, the hybrid functionals B3LYP and B3LYP\*, the meta-GGA functional TPSS, and the meta-hybrid density functional TPSSh in combination with Gauss- and Slater-type atomic basis sets of triple zeta quality (GTO-TZVP and STO-TZP). For the determination of  $^{57}\text{Fe}$  Mössbauer parameters, the GTO-TZVP was modified by using the core-polarized CP(PPP) atomic orbitals basis set (which contain 17  $s$  functions) for the Fe atom, in order to obtain a more accurate theoretical description at the nucleus. TD-DFT computations were performed with the B3LYP\* method (in combination with the TZVP basis set), which functional provided accurate results for the structural and energetic variations at the spin-state transition in the **1–3** systems, as discussed in the T1 thesis statement below. In the case of the CASPT2 investigation of complex **3**, the active space consisted of 10 electrons correlated in 12 orbitals, which was set by selecting the following active orbitals: the two  $e_g$  orbitals with bonding Fe-N character, the three  $3d(t_{2g})$  orbitals of the Fe, the two  $e_g^*$  orbitals with anti-bonding Fe-N character, and an additional set of five (three  $t_{2g}$  and two  $e_g^*$ )  $4d$  orbitals on the Fe atom. The inclusion of these latter orbitals into the active space is necessary to better describe the dynamical correlation of the Fe- $3d$  electrons. For these computations, the ANO-RCC basis sets were used with the following contractions: ( $7s6p5d4f3g2h$ ) for the Fe, ( $4s3p1d$ ) for N, ( $3s2p$ ) for C, and ( $2s$ ) for H atoms.

## 4 Results, Thesis Statements

**I.** Results on the LS $\leftrightarrow$ HS state transition in the **1–3** Fe(II) complexes [P1].

**T1.** I have determined which exchange-correlation functional provides accurate values for the structural and energetic variations associated with the spin-state transition, focusing on the  $\Delta r_{\text{HL}} = r_{\text{HS}} - r_{\text{LS}}$  parameter describing the difference between the HS and LS Fe-N bond lengths and the  $\Delta E_{\text{HL}} = E_{\text{HS}} - E_{\text{LS}}$  energy difference, where  $E_{\text{HS}}$  and  $E_{\text{LS}}$  denote the energy minima of the HS and LS states, respectively. The hybrid B3LYP\* method is found to reproduce correctly the typical value of  $\Delta r_{\text{HL}} \cong 0.2$  Å for the LS $\leftrightarrow$ HS transition in Fe(II) compounds, and also gives rather reliable estimates for the spin-state splitting energy,  $\Delta E_{\text{HL}}$ , agreeing with the corresponding CASPT2 values, which can be used as reference. Based on these results, this functional was selected for the calculation of the (TD)-DFT PESs corresponding to the lowest-lying  $3d^6$  states of the **1–3** complexes.

**T2.** The one-dimensional (1D) potential energy surfaces (PESs) connecting the LS and HS states, and corresponding to the lowest-lying singlet, triplet, and quintet metal-centered (MC) electronic states involved in the mechanism of the spin-state transition of the investigated Fe complexes were computed. These calculations were performed with TD-DFT (using the B3LYP\* functional), and for **3**, also with the CASPT2 method. The TD-DFT curves show a good overall agreement with those calculated with CASPT2. Therefore, the TD-DFT method can be considered as an economic alternative to the computationally more demanding CASPT2 approach for the calculation of  $d-d$  excitation energies of the **1–3** molecular Fe compounds.

**T3.** The B3LYP\* and CASPT2 two-dimensional (2D) PESs of the  $[\text{Fe}(\text{terpy})_2]^{2+}$  complex both give evidence that in contrast to the case of the other two investigated Fe compounds,  $[\text{Fe}(\text{tz})_6]^{2+}$  and  $[\text{Fe}(\text{bipy})_3]^{2+}$  (and most other Fe(II) SCO compounds), the transitions from the lowest-lying triplet-to-quintet ( ${}^3\text{A}_2 \rightarrow {}^5\text{E}$ ) and singlet-to-triplet ( ${}^1\text{A}_1 \rightarrow {}^3\text{A}_2$ ) electronic states in  $[\text{Fe}(\text{terpy})_2]^{2+}$  take place along different vibrational modes. These are the symmetric Fe- $\text{N}_{\text{ax}}$  stretching ( $\text{N}_{\text{ax}}$  is the middle N atom of the terpy ligand) ( $r_{\text{Fe-N}_{\text{ax}}}$ ) and the bending mode of the terpyridine rings ( $\varphi_{\text{NNN}}$ ). The reason for this behavior is attributed to the occupation of the split molecular orbitals with Fe-N antibonding  $e_g^*$

character. Therefore, the single configuration coordinate (SCC) model, which is generally applicable for the description of the LS $\leftrightarrow$ HS transition, should be replaced by the two-mode model, in which two configuration coordinates are used:  $r_{\text{Fe-Nax}}$  and  $\varphi_{\text{NNN}}$ . The two-mode model can account for the longer lifetime of the HS state of  $[\text{Fe}(\text{terpy})_2]^{2+}$  ( $\tau_{\text{HS}} = 2.5$  ns), compared to the one of  $[\text{Fe}(\text{bipy})_3]^{2+}$  ( $\tau_{\text{HS}} = 665$  ps) measured in aqueous solutions under ambient conditions, which is not expected from the inverse relation between  $\tau_{\text{HS}}$  and  $\Delta E_{\text{HL}}$  (i.e., the inverse energy gap law) in terms of the SCC model.

**II.** The second part of the current work reports results on the accurate DFT prediction of  $^{57}\text{Fe}$  isomer shifts ( $\delta$ ) and quadrupole splittings ( $\Delta E_{\text{Q}}$ ) [P2], which are summarized in the thesis statements below.

**T4.**  $^{57}\text{Fe}$  isomer shifts and quadrupole splittings were calculated with various density functionals for the largest and chemically most diverse set of Fe compounds (66 complexes were considered) investigated in computational Mössbauer spectral studies. In the case of the isomer shifts, all experimental  $\delta$  values are correctly reproduced with a mean absolute error (MAE) of  $0.05 \text{ mms}^{-1}$  and a maximum deviation of  $0.12 \text{ mms}^{-1}$ , using a single exchange-correlation functional, B3LYP in combination with the conducting-like screening model (COSMO) for environmental effects.

**T5.** For the quadrupole splittings, although a good general agreement is obtained with a MAE of  $0.20\text{--}0.35 \text{ mms}^{-1}$ , for all applied DFT methods, several complexes are identified as outliers, for which large deviations from the experimental values (up to  $0.73\text{--}1.94 \text{ mms}^{-1}$ ) are observed. The largest discrepancies between experiment and theory are attributed to the fact that in problematic cases, the treatment of the electronic structure by DFT is inadequate. I have overcome these difficulties by developing a chemical classification, and utilizing different types of density functionals for different chemical classes of Fe complexes. In most cases, the COSMO-TPSSh method (i.e., the TPSSh functional combined with the COSMO) yields accurate results. However, for the  $S = 2$  Fe(II) and  $S = 3/2$  Fe(III) complexes, the B3LYP is the optimal exchange-correlation functional (in the latter case, without the application of the COSMO). In the case of certain special molecular systems, including  $\pi$ -bonded or planar  $S = 1$  Fe(II) compounds as well as open-shell highly-distorted hexacoordinate complexes, the COSMO-RPBE method is the best choice. This carefully selected DFT approach provides accurate  $\Delta E_{\text{Q}}$  values with a

MAE of  $0.12 \text{ mms}^{-1}$  (7% error), and a maximum deviation of  $0.55 \text{ mms}^{-1}$  (17% error) over the variety of all 66 investigated Fe compounds.

**T6.** I have investigated the applicability of the DFT methodology by utilizing it in chemically relevant special cases, as well as in those for which the calculations described in the thesis statements T4 and T5 gave inaccurate results. These include: (a) the identification of the true ground state of  $[\text{Fe}(\text{DTSQ})_2]^{2-}$  (DTSQ = bis(dithiosquarato-*S,S'*) dianion),  $^5\text{A}_2$ , from among the electronically quasi-degenerate ones by constraining the occupation of the orbitals with Fe-3*d* character by the application of point group symmetry, (b) the reproduction of the relative ligand contributions to the electric field gradient (EFG) derived by a point charge model and the experimental quadrupole splittings of *cis/trans*- $\text{Fe}^{\text{II}}\text{A}_2\text{B}_4$  and  $\text{Fe}^{\text{II}}\text{AB}_5$  complexes (A,B = monodentate ligands), (c) the accurate determination of  $\Delta E_{\text{Q}}$  at phase transitions, such as SCO and the inversion of the orbital ground state, and (d) the reproduction of experimental signs of the quadrupole splitting for all those Fe complexes for which it has been determined experimentally. These results suggest the wide applicability and predictive power of the proposed DFT methodology in Mössbauer spectroscopy.

## 5 Summary and Outlook

In the present study, the electronic structure of molecular Fe compounds was investigated with various theoretical methods by focusing on the electronic states involved in the LS $\leftrightarrow$ HS transition as well as on the prediction of Mössbauer parameters. First, a carefully selected DFT methodology based on the accurate theoretical description of the spin transition in the **1–3** complexes was successfully applied for the determination of the potential energy surfaces of the  $d^6$  states relevant to molecular switching. The good agreement between (TD-)DFT and literature (**1** and **2**)/own (**3**) CASPT2 results suggests the wide applicability of the computationally less demanding TD-DFT method in the determination of  $d-d$  excitation energies, and thus in the identification of various spin states. Moreover, the 2D PESs of  $[\text{Fe}(\text{terpy})_2]^{2+}$  were computed above the plane spanned by the  $r_{\text{Fe-Nax}}$  and  $\varphi_{\text{NNN}}$  configuration coordinates at both DFT and CASPT2 levels. These surfaces as well as the analysis of the relevant Kohn-Sham orbitals indicate that the difference in the HS lifetimes of **2** and **3**, detected in aqueous solution, can be attributed to the breakdown of the SCC model.

The experimental identification of the electronic states was supported



by the DFT investigation of Mössbauer isomer shifts and quadrupole splittings for a very diverse and extended set of 66 Fe-containing systems. A clear recipe was provided for obtaining accurate  $\delta$  and  $\Delta E_Q$  values. While for the isomer shifts, this can be realized by using a single DFT method (COSMO-B3LYP), for the quadrupole splittings, it is based on a chemical classification approach, where the method to be used is selected from a set of three exchange-correlation functionals, depending on the spin and oxidation state of the Fe complex. In addition, the investigation was extended by chemically relevant case studies of the quadrupole splitting for electronically degenerate states, *cis-trans* isomers, phase transitions, as well as with the accurate determination of the sign of  $\Delta E_Q$ .

A further contribution to the theoretical research on molecular switching is here proposed by the extension of the current study to singlet and triplet MLCT states. The mapping of the MLCTs would directly lead to the knowledge of all PESs relevant to the LS $\leftrightarrow$ HS transformation. This could provide a strong basis for quantum dynamic simulations yielding branching ratios of the relaxation processes, as well as lifetimes of the intermediate and metastable electronic states. The accomplishment of these perspectives may pave the way for the design of transition metal-based molecular switches working near room temperature.

## 6 References

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## 7 Publications Forming the Basis of the Thesis

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- [P2] Pápai, M.; Vankó, G. On Predicting Mössbauer Parameters of Iron Containing Molecules with Density-Functional Theory. *J. Chem. Theory Comput.* **2013**, *9*, 5004–5020. Highlighted by the Mössbauer Effect Data Center ([http://www.medc.dicp.ac.cn/news/201403/20140320\\_10000020.php?id=10000020](http://www.medc.dicp.ac.cn/news/201403/20140320_10000020.php?id=10000020)).

## 8 Other Publications

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