Theoretical Characterization of Electronic States of Iron Complexes

Ph.D. Thesis

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Statement

Before presenting my Ph.D. work, it is here clarified that all results of the thesis were obtained by myself, which were published in two first-author comprehensive papers $P_1, P_2$ also written by myself. Note that no other Ph.D. candidates were involved in these studies, therefore, the results are solely used in the present dissertation.
Abbreviations and Notations

1D = one-dimensional
2D = two-dimensional
ADF = Amsterdam Density Functional
ANO-RCC = relativistic correlation consistent atomic natural orbital
bipy = 2,2′-bipyridine
BSSE = basis set superposition error
CASPT2 = complete active space/multiconfigurational second-order perturbation theory
CASSCF = complete active space/multiconfigurational self-consistent field
CC = coupled cluster
CI = configuration interaction
COSMO = conductor-like screening model
CP(PPP) = core properties basis set
DFT = density functional theory
EFG = electric field gradient
EXAFS = extended X-ray absorption fine structure
GGA = generalized gradient approximation
GTO = Gauss-type orbital
HF = Hartree-Fock
HFx = Hartree-Fock exchange
HK = Hohenberg-Kohn
HOMO = highest occupied molecular orbital
IS = intermediate-spin
HS = high-spin
IR = infrared
JT = Jahn-Teller
KS = Kohn-Sham
LCAO-MO = linear combination of atomic orbitals-molecular orbitals
LDA = local density approximation
LIESST = light-induced excited spin-state trapping
LS = low-spin
LUMO = lowest occupied molecular orbital
MAE = mean absolute error
MC = metal-centered
MLCT = metal-to-ligand charge transfer
MO = molecular orbital
MRCI = multireference configuration interaction
MS = Mössbauer spectroscopy
N_{ax} = axial nitrogen atom
N_{eq} = equatorial nitrogen atom
OPTX = optimized exchange density functional
PES = potential energy surface
PT2 = second-order perturbation theory
RHF = restricted Hartree-Fock
RI = resolution of identity
RIJCOSX = resolution of identity chain of spheres exchange
RKS = restricted Kohn-Sham
RPA = random phase approximation
SA = state-averaged
SS = state-specific
SCC = single configurational coordinate
SCF = self-consistent field
SCO = spin crossover
STO = Slater-type orbital
TDA = Tamm-Dancoff approximation
TD-HF = time-dependent Hartree-Fock
TD-DFT = time-dependent density functional theory
terpy = 2,2′:6′,2″-terpyridine
TM = transition metal
TSCO = thermally induced spin crossover
tz = 1H-tetrazole
TZP = triple zeta polarized
TZVP = triple zeta valence polarized
UHF = unrestricted Hartree-Fock
UKS = unrestricted Kohn-Sham
WFT = wave function theory
XC = exchange-correlation
XAS = X-ray absorption spectroscopy
XES = X-ray emission spectroscopy
XRD = X-ray diffraction

The colouring of atoms in figures representing 3D molecular structures is the following:
Chapter 1

Introduction

1.1 Switchable Molecular Compounds of Iron

Among 3$d$ transition metals (TMs), iron and its compounds are of special interest due to their diverse chemistry, rich physics, and various important role in biological processes.\textsuperscript{1,2} Combined with the high natural abundance of Fe, their wide areas of utilization span from photocatalysis\textsuperscript{3,4} to magnetooptical applications.\textsuperscript{5-7} Molecular coordination compounds of Fe have many significant functions such as their rich bioactivity (oxygen transport and storage, electron transfer, etc.),\textsuperscript{1} use in organometallic chemistry,\textsuperscript{1} and recently magnetic bistability in molecules has became a very promising phenomenon to exploit. Switchable Fe complexes are well-known candidates for magnetic switches, data storage, data display, and optical devices.\textsuperscript{5-7} In these systems, the "OFF"$\leftrightarrow$"ON" switching ("0"$\leftrightarrow$"1" in binary coding) is most commonly realized by a transition between two states with different Fe-$3d$ electronic structures, a ground (low-spin, LS) and a (meta)stable or excited (high-spin, HS) state. For instance, in the case of a Fe(II) ($d^6$) complex in an octahedral ligand field, the LS$\leftrightarrow$HS transformation involves the $t_{2g}^6e_g^0$ (closed Fe-$3d$ subshell, $S = 0$, where $S$ is the total electron spin angular momentum of the iron) and $t_{2g}^4e_g^2$ (open Fe-$3d$ subshell, $S = 2$) electronic configurations, respectively (Figure 1.1). (The
Chapter 1. Introduction

t$_{2g}$ and e$_g$ symbols correspond to the symmetries of the Fe-3d orbitals in the $O_h$ point group, as also discussed in Section 3.1.) 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,\textsuperscript{8,9} 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 of the magnetically active molecules and the very fast photoswitching (on the ps timescale) between the two spin states. The information is easily read out, as most molecular properties (magnetic moment, molecular size, electronic and vibrational spectra) change dramatically at the spin-state transition. The current work is dedicated to the application of theoretical tools to the description of the different states of Fe-bearing molecules, providing aids to the experimental efforts.

Figure 1.1: Illustration of the functioning of an octahedral Fe(II) molecular switch with 3$d^6$ electron configuration. The transition between the "OFF" ("0") and "ON" ("1") positions is realized by a LS ($t_{2g}^6e_g^0$) $\leftrightarrow$ HS ($t_{2g}^4e_g^2$) transition.

1.2 Quantum Chemical Calculations

It has recently been confirmed that the mechanism of the photoinduced LS$\rightarrow$HS transition in Fe complexes involves several excited states possessing different spin multiplicities.\textsuperscript{10–16} For the complete understanding of the molecular switching mechanism, the characterization of the LS, HS, and other possible intermediate electronic states with their lifetimes...
is essential. Magnetization measurements or $^{57}$Fe Mössbauer spectroscopy (MS) are very effective methods for the identification of the LS and HS states. However, these slow techniques cannot capture the intermediate spin states due to the subpicosecond–femtosecond time scale of their lifetime. Presently, these are only accessible by the application of very involved ultrafast optical/X-ray spectroscopies or diffraction techniques, and quantum chemical calculations. Therefore, electronic structure methods are an invaluable tool for the identification of these states and the investigation of the details of the spin transition process. Moreover, the spectroscopic characterization of these states usually requires the theoretical prediction and interpretation of the measured spectra. Note that the very same also holds for all the static spectra obtained on stable or metastable states: theoretical support has a vital importance in the full assignment of the measured data. Density functional theory (DFT) is a very efficient, and at the same time, computationally affordable method for modeling the electronic structure of molecular Fe compounds. However, it has its limitations due to the application of approximate exchange-correlation functionals, as discussed in Section 2.3.4. Therefore, it is important to compare DFT results with those obtained with an approach of higher precision; for this, the method of multiconfigurational second-order perturbation theory (CASPT2) is presently one of the best choice, which is at the limit of being affordable for Fe compounds consisting of 40–60 atoms. Moreover, the computational results should also be carefully contrasted to experiments. Note that although these can never agree exactly —due to the fact that theoretical results are obtained from the minimum of the multidimensional potential energy surface (PES) determined at 0 K, which thus do not include thermal effects in contrast to experiments performed at a finite temperature— the comparison of calculated and measured values of molecular properties is widely applied for assessing the performances of different levels of theory. The accurate theoretical description of the ground- and excited states participating in the spin-state transition offers an ideal testing ground for the applicability of DFT and CASPT2.
1.3 Scope of the Present Study

Among Fe-based systems, photoswitchable molecular complexes could be the most promising candidates for 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.\textsuperscript{8,17} An extremely valuable step towards the design of the applicable materials can be achieved by unveiling all the fine details of the mechanism of molecular switching. We aim to contribute to the understanding of the fundamental mechanism by characterizing different states of molecular Fe compounds with the quantum chemical methods of DFT and CASPT2. This goal can be realized by accomplishing the following objectives:

1. In order to test the accuracy of CASPT2, and different DFT methods, we have selected a set of intensely investigated switchable Fe complexes, [Fe(tz)\textsubscript{6}]^{2+} (1) (tz = 1\textit{H}-tetrazole), [Fe(bipy)\textsubscript{3}]^{2+} (2) (bipy = 2,2\textsuperscript{′}-bipyridine), and [Fe(terpy)\textsubscript{2}]^{2+} (3) (terpy = 2,2\textsuperscript{′}:6\textsuperscript{′}:2\textsuperscript{″}-terpyridine), which contain respectively mono-, di-, and tridentate ligands. We intend to assess the performances of these computational techniques by the determination of the structural and energetic variations at the spin transition, which factors are decisive for the lifetime of the metastable HS state. Based on the comparison of DFT, CASPT2, and experimental LS and HS structures, as well as spin-state energetics, we seek the best performing density functional, which then can be chosen for the calculation of the potential energy surfaces discussed in the next paragraph.

2. We aim to calculate the potential energy surfaces of the lowest-lying singlet, triplet, and quintet 3\textit{d}\textsuperscript{6} states of the 1–3 complexes involved in the spin-state transition. These PESs are to be calculated along the configurational coordinate(s) relevant to the LS\ensuremath{\leftrightarrow}HS transition with DFT and time-dependent DFT (TD-DFT), and in the case of 3, also with CASPT2 (for 1 and 2, CASPT2 surfaces are available in the literature\textsuperscript{18,19}). The motivation of this part of the work is twofold: to compare the performances of TD-DFT and CASPT2 in the determination of \textit{d}-\textit{d} excitation energies as well as to contribute to the better understanding of the molecular switching by the analysis of the PESs and the
1.3. Scope of the Present Study

3. Finally, in the experimental identification of different states of longer-lived or stable Fe complexes, the application of Mössbauer spectroscopy is almost inevitable. This requires the development of a methodology for the accurate prediction of $^{57}$Fe Mössbauer parameters: the isomer shift and the quadrupole splitting. This task is to be collaterally expanded to provide a general recipe for iron complexes with any spin and valence state, in order to improve the reliability of the computational approach, and to offer a generalized tool to the Mössbauer community. These calculations are to be carried out within the framework of DFT, since the high number of computations and the relatively large size of compounds of interest do not allow the application of the CASPT2 method.

In the forthcoming chapters of the thesis the above 1–3 aims are realized. Chapter 2 introduces the theory of the applied computational methods (DFT, TD-DFT, and CASPT2), and describes also the utilization of atomic basis sets, and the possible treatment of molecular environment effects. In Chapter 3, a brief review is presented on the electronic structure of Fe complexes. The comparative DFT and CASPT2 study of the 1–3 molecular spin-transition systems (in correspondence with aims 1 and 2) is reported in Chapter 4. In Chapter 5, the DFT methodology to predict $^{57}$Fe Mössbauer spectral parameters is presented (in connection with aim 3). Finally, the summary and outlook of the entire thesis is described in Chapter 6. A series of supplementary tables is given in the Appendix.
Chapter 2

Theoretical Methods

In this chapter, the theory of the computational methods used in the thesis is summarized. After introducing the different approximations to the Schrödinger equation, the fundamentals of electron correlation and the applied methods—density functional theory (DFT), time-dependent DFT (TD-DFT), and complete active space self-consistent field/multiconfigurational second-order perturbation theory (CASSCF/CASPT2)—are described. Finally, some additional points including the applied atomic basis sets and the conductor-like screening model (COSMO) for environmental effects are presented. Note that the limited size of the thesis does not allow the detailed review of the applied methods of quantum chemistry; however, these techniques are well-established, and widely described in the literature. Also, the present chapter does not include the detailed description of the performed computations and the list of program packages applied in this work; these are given in the computational details part of Chapter 4 and 5.

2.1 Approximations to the Schrödinger Equation

Quantum chemical methods seek the solution of the Schrödinger equation, which describes the wave function of a quantum system with a Hamiltonian (i.e., the operator of the
2.1. Approximations to the Schrödinger Equation

In the absence of an external, time-dependent field, the time-independent Schrödinger equation is written as:

\[ \hat{H}\psi_i = E_i\psi_i \]  \hspace{1cm} (2.1)

where \( \hat{H} \) is the full Hamiltonian, whereas \( \psi_i \) and \( E_i \) are the full wave function and energy of the \( i \)-th quantum mechanical state, respectively. Note that both \( \hat{H} \) and \( \psi_i \) include electronic (\( \hat{H}_e, \psi_{i,e} \)) and nuclear (\( \hat{H}_N, \psi_{i,N} \)) terms. Unfortunately, the exact solution of the Schrödinger equation is only available in very simple cases, e.g., for the hydrogen atom. Therefore, for realistic molecular systems, approximations are needed, which are described below.

2.1.1 The Non-Relativistic Approximation

In order to provide a fully exact description of the electronic structure, one should solve the Dirac equation, which incorporates the special theory of relativity to the Schrödinger equation. However, for Fe complexes, these effects are of minor importance, since only electrons of elements with high atomic numbers (\( Z \geq 55 \)) reach relativistic speeds.\(^{29}\)

While relativistic effects were neglected in the presented DFT and TD-DFT calculations, in the case of CASSCF/CASPT2, they were taken into account by employing the Douglas-Kroll-Hess Hamiltonian.\(^{30,31}\) This is justified by the fact that in DFT, relativistic errors are of inferior importance, compared to those originating from the application of approximate density functionals. The same conclusion has been previously drawn when testing the need for the inclusion of relativistic effects in the calculation of Mössbauer parameters.\(^{32}\)

2.1.2 The Born-Oppenheimer Approximation

In general, the electronic and nuclear terms of \( \hat{H} \) and \( \psi_i \) cannot be decoupled. However, since the mass of the electron is ca. 1800 times smaller than the one of the smallest possible nucleus (and in a typical atom of a main group element or transition metal, such as Fe or
Co this ratio is much larger), the nuclei are practically fixed in space when compared to the very fast motion of the electrons. Therefore, the electronic and nuclear motion can be practically decoupled. In a simplified picture, the kinetic energy of the nuclei can be taken as zero, and the nucleus-nucleus repulsion interaction ($\hat{V}_{NN} = \sum_{A,B>A} z_A z_B / r_{AB}$) can be taken as a constant, in the sense that it is independent of the electronic motion. Consequently, the full Hamiltonian $\hat{H}$ can be approximated by $\hat{H}_e$, and it suffices to solve the electronic Schrödinger equation of the quantum mechanical system:

$$\hat{H}_e \psi_e = E_e \psi_e \quad (2.2)$$

with

$$\hat{H}_e = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN} \quad (2.3)$$

where $\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2$ is the kinetic energy operator of the electrons, and $\hat{V}_{Ne} = -\sum_{i,A} \frac{z_A}{r_{iA}}$ and $\hat{V}_{ee} = \sum_{i,j>i} \frac{1}{r_{ij}}$ are the nucleus-electron and electron-electron potentials, respectively (note that these terms, and also $\hat{V}_{NN}$ above are given in atomic units). An important consequence of the Born-Oppenheimer approximation is that the relevant potential energy surface (PES) for nuclear motion is defined by the $E_e$ eigenvalues of the electronic Schrödinger equation (Equation 2.2) at fixed nuclei positions. The Born-Oppenheimer method was applied in every computation presented in this work.

### 2.1.3 Using Slater Determinants: The Hartree-Fock Method

A simple, yet very useful approximation to solve a multielectronic problem of a molecule is the independent electron model. Assuming that the electrons of the system are fully independent from each other, the wave function is decomposed to the product of wave functions of the one-electron subsystems (i.e., molecular orbitals, MOs):
2.1. Approximations to the Schrödinger Equation

\[ \psi = \phi_1(1)\phi_2(2)\ldots\phi_n(N) \]  
\tag{2.4} \]

where \( n = N \) is the number of electrons, and the total electronic energy is obtained by summing up one-electron energies: \( E_{e,\text{tot}} = \sum_{i=1}^{N} \varepsilon_i \). The most important weakness of the wave function expressed in Equation 2.4 (which is called the Hartree product) is that within this model the electrons are not indistinguishable. Moreover, the Hartree product is not antisymmetric with respect to the exchange of two electron coordinates, therefore, it violates the Pauli principle. These failures can be amended by utilizing a Slater determinant (\( \psi_S \)) as wave function:

\[ \psi_S = \frac{1}{\sqrt{N!}} |\phi_1(1)\phi_2(2)\ldots\phi_n(N)| \]  
\tag{2.5} \]

Note that \( \psi_S \) is still an approximation to the exact wave function, \( \psi \). The Hartree-Fock (HF) method delivers the approximate solution of the Schrödinger equation by taking the wave function as a Slater determinant. The “best” \( \psi_S \) wave function is determined by the minimization of the electronic energy (according to the variational principle\(^{20,27}\)), in the procedure known as self-consistent field (SCF). This is realized by solving the HF equations iteratively for the effective one-electron Fock operator, \( \hat{f}_i = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} + \hat{V}_{\text{HF}}(i) \), as Hamiltonian:

\[ \hat{f}_i \phi_i = \varepsilon_i \phi_i \]  
\tag{2.6} \]

Here \( \hat{V}_{\text{HF}}(i) \) is the Hartree-Fock potential, the average interelectronic repulsive interaction between the \( i \)-th electron and all the others. Therefore, in the HF method, the electron-electron interaction is averaged over all electrons. \( \hat{V}_{\text{HF}} \) can be divided into a spin-independent and spin-dependent part, which are the Coulomb and exchange potentials, respectively. While the former is the quantum mechanical counterpart of the Coulomb interaction of charged particles known from electrostatics, the exchange interaction has no classical interpretation: it is a fully quantum mechanical phenomenon contributing to the
repulsion of electrons with like spin (α-α or β-β). Furthermore, the \( \phi_i \) MO components of \( \psi_S \) are expanded in a basis set of atomic orbitals \( \chi_\alpha \):

\[
\phi_i = \sum_a a_{i\alpha} \chi_\alpha
\]

(2.7)

This approach is named as the LCAO-MO method (linear combination of atomic orbitals-molecular orbitals). Depending on whether the same \( \phi_i \) is used for \( \alpha \) and \( \beta \) spins or not HF calculations can be carried out in a restricted (RHF) and unrestricted (UHF) manner. One of the most important drawbacks of using the HF method is that while electrons with parallel spin stay no more independent due to the antisymmetrized Slater determinant wave function (which obeys the Pauli principle), the correlation for electrons with opposite spin is completely neglected. Furthermore, the application of a single Slater determinant as wave function is frequently inadequate, e.g., when near-degeneracy effects are expected, which is often the case for Fe complexes. The inclusion of electron correlation can provide a more accurate theoretical description of the electronic structure, as discussed in Section 2.2 below.

2.2 Electron Correlation

Electron correlation (also known as Coulomb correlation) is the part of the electron-electron interaction not covered by HF theory. This is in the center of quantum chemistry, since possessing it directly leads to the exact solution of the electronic Schrödinger equation. It is characterized by the electron correlation energy, which is defined as \( E_{\text{correl}} = E_{e,\text{tot}} - E_{\text{HF}} \). It is important to recall that some interaction of electrons with parallel spin is already present in the HF method due to the application of a Slater determinant wave function, however, this is not included in the term electron correlation. This type of interelectronic repulsion is called ”exact” or Hartree-Fock exchange (HFx), and also Fermi correlation, which is built up by integrals defined in Equation 2.8.
2.2. Electron Correlation

\[
(\phi_i \phi_j | \phi_j \phi_i) = \int \int \frac{\phi_i(r_1) \phi_j^*(r_1) \phi_j(r_2) \phi_i^*(r_2)}{|r_1 - r_2|} dr_1 dr_2 \quad (2.8)
\]

HFx has a vital importance for the theoretical description of Fe complexes with different 3d electronic structure (see Section 4.4).

Electron correlation effects are often divided into dynamical and non-dynamical (static) parts. While the former one includes the instant correlation of electrons, determined by the \(1/r_{ij}\) electron-electron repulsion term—which is only treated in HF theory in an averaged manner—, the latter includes near-degeneracy effects, which are not covered in the case of using only a single Slater determinant. In principle, two conceptually different approaches are applied for the efficient treatment of electron correlation: the methods of wave function theory (WFT) and density functional theory (DFT). WFT aims to systematically improve the HF wave function by covering dynamical electron correlation with different methods, e.g., second-order perturbation theory (PT2), configuration interaction (CI), and coupled cluster (CC). Furthermore, static electron correlation effects are introduced by using a multiconfigurational reference, e.g., a complete active space self-consistent field (CASSSF) wave function. The combination of these two approaches leads to methods which can provide an accurate description of the electronic structure. Such methods include multireference configuration interaction (MRCI) or coupled cluster (MRCC), and multiconfigurational second-order perturbation theory (CASPT2). However, the applicability of WFT methods is limited by their high computational cost. DFT offers a solution to this problem by utilizing the more easily calculable electron density \(\rho(r) = \sum_i |\phi_i(r)|^2\) as basic quantity instead of \(\psi\), and covering a considerable part of electron correlation effects by using approximate exchange-correlation (XC) functionals. The main problem with DFT is that the expression of the exact XC functional is not known, and the theoretical description cannot be systematically improved by the application of more accurate density functionals. Nevertheless, for most problems, one can find functionals that provide correct results for a large set of molecules. In the following three Sections (2.3–2.5), the methods used for the calculation of ground- and excited electronic
states of Fe complexes; namely, DFT, TD-DFT, and CASSCF/CASPT2 are presented.

2.3 Density Functional Theory (DFT)

2.3.1 Electron Density Functionals

The basic idea behind DFT is to use the electronic density with the three cartesian variables \( x, y, \) and \( z \), instead of the electronic wave function with \( 4N \) variables (three spatial coordinates, and one spin coordinate for each electron). It can be justified by proving the first Hohenberg-Kohn (HK) theorem\(^{33} \) that the ground state electron density \( \rho_0 \) uniquely determines the Hamiltonian of the system via the \( \hat{V}_{N_e} \) potential, which further defines the ground state electronic wave function \( \psi_0 \) through the solution of the electronic Schrödinger equation. The second HK theorem is the variational principle derived for the energy functional of the electron density in analogy to the well-known Rayleigh-Ritz method.\(^{34} \) Then, the ground state electronic energy, \( E_0 \) can be written as the functional of \( \rho_0 \):

\[
E_0[\rho_0] = E_{N_e}[\rho_0] + T[\rho_0] + E_{ee}[\rho_0] = E_{N_e}[\rho_0] + F[\rho_0] \tag{2.9}
\]

where \( E_{N_e}[\rho_0] = \int \hat{V}_{N_e}\rho_0(r)dr \) is unique, while the \( F[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] \) functional is universal (\( E_{N_e}[\rho_0] \) and \( E_{ee}[\rho_0] \) denote the nucleus-electron attractive and electron-electron repulsive potential energy functionals, respectively, while \( T[\rho_0] \) stands for the kinetic energy functional). \( E_{ee}[\rho_0] \) can be partitioned into two terms as follows:

\[
E_{ee}[\rho_0] = J[\rho_0] + E_{\text{ncl}}[\rho_0] \tag{2.10}
\]

where \( J[\rho_0] = \frac{1}{2} \int \rho_1(r_1)\rho_2(r_2) |r_1 - r_2| \, dr_1 \, dr_2 \) and \( E_{\text{ncl}}[\rho_0] \) are the Coulomb and nonclassical electron-electron interaction functionals, respectively. The weakness of the second HK theorem is that the form of \( F[\rho_0] \), more explicitly, those of \( T[\rho_0] \) and \( E_{\text{ncl}}[\rho_0] \) are unknown. A solution to this issue was provided by Kohn and Sham,\(^{35} \) which is described below.
2.3.2 The Kohn-Sham Approach

The basis of the Kohn-Sham (KS) approach is the consideration of a fictitious system with non-interacting electrons. The Hamiltonian of this reference system can be written as:

$$\hat{H}_S = -\frac{1}{2} \sum_i^{N} \nabla_i^2 + \sum_i^{N} \hat{V}_S(r_i)$$  \hspace{1cm} (2.11)

where $\hat{V}_S(r)$ is an effective external potential. $\hat{V}_S(r)$ can be chosen in a way that the resulting electron density is identical to the one of the interacting system. The kinetic energy of the non-interacting reference ($T_S$) can be then exactly evaluated by approximating the wave function with a Slater determinant:

$$T_S = -\frac{1}{2} \sum_i^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle$$  \hspace{1cm} (2.12)

where $\phi_i$ is the $i$-th orbital component of $\psi_S$ (Equation 2.5). Of course, $T_C = T - T_S \neq 0$, where $T_C$ is the kinetic correlation energy, since in reality, electrons do interact. The density functional of the energy can be transformed to the following expression:

$$E_0[\rho_0] = E_{Ne}[\rho_0] + T_S[\rho_0] + J[\rho_0] + E_{XC}[\rho_0]$$  \hspace{1cm} (2.13)

where the exchange-correlation functional

$$E_{XC}[\rho_0] = T[\rho_0] - T_S[\rho_0] + E_{ee}[\rho_0] - J[\rho_0] = T_C[\rho_0] + E_X[\rho_0] + E_C[\rho_0]$$  \hspace{1cm} (2.14)

includes all unknown terms of $E_0[\rho_0]$. Here $E_X$ and $E_C$ are the exchange and correlation functionals, which respectively account for the correlation of electrons of like (Fermi correlation) and unlike (Coulomb correlation) spin. If the $E_{XC}[\rho_0]$ functional was known, the exact solution of the Schrödinger equation could be obtained by solving the Kohn-Sham equations:
\[ \hat{f}_{KS,i}\phi_{KS,i} = \varepsilon_i\phi_{KS,i} \quad (2.15) \]

where

\[ \hat{f}_{KS,i} = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} + \hat{V}_{Coul}(i) + \hat{V}_{XC}(i) \quad (2.16) \]

(\(\hat{V}_{Coul}(i) = \frac{\delta J[\rho_0]}{\delta \rho_0}\) and \(\hat{V}_{XC}(i) = \frac{\delta E_{XC}[\rho_0]}{\delta \rho_0}\) are the Coulomb and exchange-correlation potentials, respectively), and \(\phi_{KS,i}\) is the \(i\)-th Kohn-Sham orbital of the system. Note the resemblance between Eqs. 2.6 and 2.15: while the procedure of solving the HF and KS equations (and also their computational cost) is practically the same, KS-DFT incorporates electron correlation. Another similarity is that the \(\phi_{KS,i}\) orbitals are also expanded in an atomic basis set \(\chi_\alpha\), thus the LCAO-MO method is employed. Also, analogously to HF theory, a choice has to be made between a restricted and unrestricted formalism when performing KS-DFT calculations (these are known as the RKS and UKS methods, respectively). Unfortunately, \(E_{XC}[\rho_0]\) is unknown, thus the exact solution is not accessible. The ultimate goal of DFT is to provide an as accurate as possible expression for \(E_{XC}[\rho_0]\). This can be realized by introducing approximations at different levels, which are described below.

### 2.3.3 Jacob’s Ladder: The Hierarchy of Approximate Exchange-Correlation Functionals

The so-called Jacob’s ladder represents the hierarchy of approximate XC functionals in DFT (Figure 2.1). The analogy is taken from Jacob’s dream in the Bible, the book of Genesis, from a ladder ascending to heaven. The lowest level of theory is the local density approximation (LDA), in which the formulas for the exchange \(E_X[\rho]\) and correlation \(E_C[\rho]\) density functionals are taken from the model of the homogeneous electron gas. Both \(E_X[\rho]\) and \(E_C[\rho]\) depend on \(\rho\), but the electron density occur with different exponents, in these expressions. While LDA already performs well for solid metals,\(^{36,37}\)
2.3. Density Functional Theory (DFT)

it faces serious problems in the description of the electronic structure of molecular compounds.\textsuperscript{20,21} The main reason behind this is the fact that while in general, metals possess a rather homogeneous electron density, this is not the case for Fe complexes; in fact, $\rho$ is often very strongly varying, especially in the chemical bonding region. Therefore, LDA methods were not used in the present work.

Figure 2.1: Jacob’s ladder: the hierarchy of exchange-correlation functionals in DFT. In this figure, the most frequently used types of functionals are shown, and the DFT methods used in the thesis are written in red.

A logical way to improve LDA is to include the gradient of the electron density ($\nabla \rho$) in the expression of $E_{XC}[\rho]$. In the generalized gradient approximation (GGA), the gradient-corrected exchange-correlation functional, $E_{XC}[\rho, \nabla \rho]$ is forced to fulfill the requirements for the so-called true XC holes\textsuperscript{a} of taking negative values everywhere and containing only one (exchange hole) and zero (correlation hole) electron charges.\textsuperscript{20} XC holes not matching these conditions are set to zero. The resulting functionals, as is the one of Becke and Perdew, BP86,\textsuperscript{38,39} the revised one of Perdew, Burke, and Ernzerhof, RPBE,\textsuperscript{40} and those with optimized exchange, OPBE and OLYP,\textsuperscript{41–43} are typical GGAs, which methods

\textsuperscript{a}The XC hole $h_{XC}$ is defined as the conditional probability of finding any electron at a position in coordinate-spin space if there is another known to be at a different position subtracted by the uncorrelated probability.\textsuperscript{20} $h_{XC}$ can be formally decomposed into exchange (for parallel spins) and correlation (for both parallel and antiparallel spins) terms.
present a significant progress over LDA in electronic structure calculations.

A further direction in the suggested improvements of XC functionals, the one of meta-GGAs, is obtained by the inclusion of the second derivative of the electron density $\nabla^2 \rho$ and/or the kinetic energy density $\tau(\mathbf{r}) = \frac{1}{2} \sum_i^N |\nabla \phi_i(\mathbf{r})|^2$ to the GGA formula of $E_{XC}[\rho, \nabla \rho]$. One of the most popular meta-GGA method is the functional of Tao, Perdew, Staroverov, and Scuseria, TPSS.\textsuperscript{44,45}

A completely different approach to go beyond GGAs is to mix exact exchange (HFx) into the expression of $E_X[\rho]$. This concept is based on the fact that the local and semi-local functionals discussed above can be improved by the inclusion of nonlocality provided by a fraction of HFx (the nonlocality property is due to dependence of HFx on the molecular orbitals, see Equation 2.8). DFT methods constructed this way are called hybrid functionals, which are computationally more demanding than GGAs, due to the inclusion of HFx. Note that the consideration of 100\% HFx in the exchange expression is undesirable, since it would result in the combination of a fully nonlocal exchange with a completely local correlation functional. The most frequently used hybrid functional is B3LYP,\textsuperscript{41,46,47} which is the standard DFT method in many fields of computational chemistry, despite its known problems.\textsuperscript{48–52} The highest step of the ladder presented in Fig. 2.1 is obtained by mixing HFx to the meta-GGA expression $E_{XC}[\rho, \nabla \rho, \tau]$: these are the meta-hybrid methods. An often-used example is TPSSh,\textsuperscript{53} the hybrid version of TPSS. Note that claims for further rungs of Jacob’s ladder exist, however, these functionals (e.g., double hybrids,\textsuperscript{54} and also range-separated hybrid methods\textsuperscript{55,56}) were not proven to perform systematically better, nor were employed in the present study, due to their higher computational cost and/or the unavailability in the versions of the applied program packages. Therefore, the theoretical description of these methods is beyond the scope of this section.

2.3.4 Limitations of DFT

Although DFT is a powerful technique—with a very high accuracy/computational cost ratio—, it is not free from drawbacks. First of all, it is important to emphasize that no universal XC functional has yet been developed and it happens that a DFT method
located at a lower rung of the above hierarchy provides more accurate results for a certain property than higher level density functionals. This problem, i.e., that the description of electron correlation cannot be improved systematically is one of the central weaknesses of DFT. Further known issues are the self interaction error and the wrong asymptotic behavior of the XC potential, which are due to the approximate nature of the applied density functionals.\textsuperscript{20,21} Although all these deficiencies limit the applicability of DFT, presently it is the most effective computational technique for transition metal compounds, by treating electron correlation at a moderate computational cost, compared to WFT methods.

2.4 Time-Dependent Density Functional Theory

(TD-DFT)

Although in principle, DFT is a ground state theory, it can be extended to excited states: this method is known as time-dependent DFT (TD-DFT). Since TD-DFT can be considered as a modified version of the time-dependent Hartree-Fock (TD-HF) method, also known as the random phase approximation (RPA), first this method is briefly reviewed. The equations of RPA can be obtained within linear response theory, by the application of a formalism of either density matrices\textsuperscript{22,23} or the quantum mechanical equation of motion.\textsuperscript{57} The resulting equations are:\textsuperscript{23}

\[
\begin{pmatrix}
A & B \\
B^* & A^*
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix} = \omega
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
X \\
Y
\end{pmatrix}
\tag{2.17}
\]

where $\omega$ and $X, Y$ are the excitation energies and amplitudes, respectively, and the $A$ and $B$ matrices are defined as: $A_{ia,jb} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + (\phi_i \phi_a || \phi_j \phi_b)$ and $B_{ia,jb} = (\phi_i \phi_a || \phi_b \phi_j)$ ($i, j$ and $a, b$ correspond to the indices of occupied and virtual orbitals, respectively). The leading term of the $A$ matrix contains differences of orbital energies ($\varepsilon_a - \varepsilon_i$), while $(\phi_i \phi_a || \phi_j \phi_b) = (\phi_i \phi_a | \phi_j \phi_b) - (\phi_i \phi_j | \phi_a \phi_b)$ stands for the antisymmetrized two-electron integral. The basic foundations of TD-DFT are the Runge–Gross theorem\textsuperscript{58} (which is the
time-dependent version of the first HK theorem) and the time-dependent KS equations, which paved the way for the development of linear response TD-DFT. The derivation, and also the formula of the TD-DFT equations is analogous to those of the RPA (Equation 2.17), the only difference is in the definition of $A$ and $B$, which are modified to

$$ A_{ia,jb} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + (\phi_i \phi_a | \phi_j \phi_b) + (\phi_i \phi_a | f_{XC} | \phi_j \phi_b) $$

and

$$ B_{ia,jb} = (\phi_i \phi_a | \phi_b \phi_j) + (\phi_i \phi_a | f_{XC} | \phi_b \phi_j), $$

where

$$ f_{XC} = \frac{\delta^2 E_{XC}}{\delta \rho(r) \delta \rho(r')} $$

is the XC kernel. Therefore, similar to ground state DFT, electron correlation effects are accounted for by the application of a XC functional. Furthermore, Equation 2.17 can be simplified by neglecting the $B$ matrix; this approach is known as the Tamm-Dancoff approximation (TDA).\(^{57}\) While this transforms the non-Hermitian Equation 2.17 to the Hermitian eigenvalue problem

$$ AX = \omega X $$

it has only in general a negligible effect on the computed excitation energies.\(^{59}\) Therefore, TDA is a very efficient approximation to TD-DFT, and was applied in all excited state calculations in the thesis.

### 2.5 Multiconfigurational Second-Order Perturbation Theory (CASPT2)

Although DFT and TD-DFT are suitable techniques for the determination of the ground- and excited electronic states of Fe complexes, it is desirable to compare these results to those obtained with a method of WFT. CASSCF/CASPT2 is presently the most accurate WFT approach applicable to molecular Fe compounds at a barely affordable computational cost. In the CASSCF procedure, the reference wave function is constructed by the linear combination of Slater determinants:
2.5. Multiconfigurational Second-Order Perturbation Theory (CASPT2)

\[ \psi_{\text{CASSCF}} = \sum_m c_m \psi_{S,m} \]  

(2.20)

Similarly to the HF method, the MO components of \( \psi_{S,m} \) are expanded in atomic orbital bases \( \phi_i = \sum_a a_{i\alpha} \chi_{\alpha} \), and both \( c_m \) and \( a_{i\alpha} \) variation coefficients are optimized. In order to make this methodology affordable, a limited number of MOs are selected around the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), whose population can vary. Therefore, it is necessary to partition the molecular orbitals into active, inactive, and virtual spaces. In every CASSCF iteration, the eigenvalue problem of the Hamiltonian is solved in the basis of the Slater determinants generated by all possible occupations of the active MOs. As discussed before in Section 2.2, static electron correlation can be covered by this approach. CASSCF calculations can be carried out in a state-specific (SS) and state-averaged (SA) manner. In these methods, the MOs are optimized for a single electronic state and for an average of several states, respectively. The application of these approaches will be discussed in the description of the CASSCF/CASPT2 computations (Section 4.2).

In the CASPT2 method, dynamical electron correlation is treated by adding a correction term to the energy of the CASSCF reference provided by PT2 computed on the CASSCF wave function. The form of the resulting expression is the same as the one of PT2 performed on the HF reference wave function:

\[ E^{(2)} = \sum_{i<j}^{\text{occ}} \sum_{a<b}^{\text{virt}} \frac{[\langle \phi_i \phi_a | \phi_j \phi_b \rangle]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \]  

(2.21)

where the numerator and denominator of the above expression contain the two electron integrals of the molecular orbitals and the differences of orbital energies, respectively. Note that in the case of CASPT2, the latter term is replaced by a more complicated formula containing a sum weighted over all active orbitals.\(^{25}\) Although the appearance of intruder states (i.e., states not included in the active space) in the CASSCF reference wave function\(^{60,61}\) is a known weakness of CASPT2, this can be usually overcome by the level shift technique.\(^{61}\) In this approach, a small \( \epsilon \) constant is added to the denominator.
of the second order energy (Equation 2.21), which is followed by the approximate back transformation of the energy to the unshifted value. This latter procedure is necessary in order to decrease the $\epsilon$-dependence of the level shifted energy.

2.6 Miscellaneous

2.6.1 Atomic Basis Sets

As discussed in Sections 2.1.3, 2.3.2, and 2.5, all SCF-based procedures require the expansion of the molecular orbitals $\phi_m$ into atomic basis functions $\chi_\alpha$ (Equation 2.7), i.e., the application of the LCAO-MO method. It is important to point out that this approach is also an approximation, since all applied basis sets in practice are incomplete. Atomic basis orbitals for molecular electronic structure calculations can be divided into two main groups: exponential or Slater type orbitals (STOs), and Gaussian type orbitals (GTOs). STOs reproduce the nuclear cusp of the electron density by possessing an exponential radial decay, $\chi_{\text{STO}} \propto e^{-\zeta r}$. On the other hand, the computational cost of three- and four-center two electron integrals in these basis sets is high, because they cannot be evaluated analytically. Although the $\chi_{\text{GTO}} \propto e^{-\zeta r^2}$ form of GTOs indicate a less accurate description of the nuclear cusp and the asymptotic behavior of the wave function, their computational treatment is significantly more economic than those of STOs. An efficient approach is to produce linear combinations (contractions) of primitive Gaussians, which yields basis functions with similar accuracy to those of STOs. Additionally, auxiliary basis sets can be used for the resolution of identity (RI)\textsuperscript{62,63} and chain of spheres (RIJCOSX)\textsuperscript{64} approximations of Coulomb integrals for GGA and hybrid XC functionals, respectively (and for WFT-based methods as well). In principle, these methods transform the four-center two electrons integrals into three-center expressions, which leads to the significant reduction of the cost of electronic structure calculations. In this work, DFT calculations were carried out with both type of basis sets, while TD-DFT computations were performed only with GTOs, which have more favorable computational costs.
In addition to the higher computational scaling of WFT methods with the number of basis functions, for optimal performance these techniques require different (larger) basis sets compared to those used in DFT calculations. Relativistic correlation consistent atomic natural orbitals (ANO-RCCs, which are also GTOs)\textsuperscript{65–67} are highly accurate and contracted basis sets, which are convenient for WFT calculations. Although employing ANO-RCCs is computationally demanding, two-electron integrals can be also approximated, in this case with the Cholesky decomposition technique,\textsuperscript{68} which transforms the matrix of electron repulsion integrals into two triangular matrices. The CASSCF/CASPT2 computations were performed with this basis set methodology.

**2.6.2 The Conducting-Like Screening Model (COSMO)**

Discrepancies between experimental and computational results may often rise due to the fact that electronic structure calculations are typically carried out in vacuum, which is rarely the case for measurements for Fe compounds. In particular, Mössbauer experiments are performed in solid state, therefore, the inclusion of environmental effects might improve the theoretical results. The conducting-like screening model (COSMO)\textsuperscript{28} is an efficient method to carry out DFT calculations for molecules in a dielectric medium. COSMO, being a polarizable continuum model,\textsuperscript{69} approximates effects of the molecular environment (matrix, crystal, solvation) by considering the screening effect of a perfect conductor on the charge density of the molecule. This interaction is scaled with a factor dependent on the dielectric constant, $\varepsilon$:

$$f(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + x}$$  \hspace{1cm} (2.22)

Note that the above expression originates from basic electrostatics,\textsuperscript{70} and the $x = 1/2$ factor in the denominator was found to be the most effective.\textsuperscript{28} The molecule is then placed in a cavity, which is smoothly discretized into segments, each possessing constant charge density. COSMO focuses on the interaction between the molecular charge density and their compensating charges created on the surface embedding the molecule. These
charges and charge densities, as well as their interaction energies can be calculated in a self-consistent manner, which method can be conveniently implemented in the SCF procedure. The COSMO approach was used for investigating the effect of the environment on the calculated $^{57}$Fe Mössbauer parameters (Chapter 5).
Chapter 3

Electronic Structure of Fe Complexes

The presence and various occupation of $d$ orbitals in Fe complexes (and also in other TMs) results in a fundamentally different electronic structure from the one of molecules consisting of main group elements. Therefore, a brief review is presented here, focusing on the fundamental concepts used in the thesis.

3.1 The 3$d$ Electronic Structure of Octahedral Fe Complexes

In Fe ions, the valence shell is dominated by 3$d$ electrons, e.g., in the case of Fe$^{2+}$, it is characterized by the 3$d^6$ electron configuration. In a hypothetical Fe-centered system possessing a spherically symmetric charge distribution due to the surrounding negative point charges, the six electrons are distributed among the five degenerate $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$, and $d_{z^2}$ atomic orbitals. The very frequent octahedral coordination (O$h$ point group) of Fe complexes splits the five degenerate 3$d$ orbitals into a set of $d_{xy}$, $d_{xz}$, $d_{yz}$ of
$t_{2g}$ and $d_{x^2-y^2}, d_{z^2}$ of $e_g$ symmetry, which show three- and twofold degeneracy, respectively. This is illustrated for a general octahedral Fe compound in Figure 3.1.

![Diagram of energy levels and symmetries](image)

**Figure 3.1**: Energy levels of the 3d atomic orbitals in Fe-centered systems possessing spherical (left) and octahedral (right) symmetry. $\Delta_o$ stands for the octahedral ligand field splitting, which is determined by the charge and distance of the ligands.

In an octahedral Fe complex, an important feature of the 3d orbitals is their different orientation: while the $t_{2g}$ point between the ligands, the $e_g$ are aligned on the $x$, $y$, and $z$ axes in the direction of the $\sigma$-bonds between the Fe and the donor atoms of the ligands. As known from ligand field theory, in molecular iron compounds, $s$- and $p$-type orbitals of ligand donor atoms are mixed to the Fe-3d orbitals, which make up the corresponding molecular orbitals. In the case of the $t_{2g}$, no mixing occurs between the orbitals of the iron and the ligands along the three principle cartesian axes, therefore,
3.2 Electronic States of Fe Complexes

these are considered as $\sigma$-nonbonding orbitals. This can be indeed observed in Figure 3.2a, which shows the KS MOs for $[\text{Fe(CN)}_6]^{4-}$, a prototypical LS complex. The $e_g$-like MOs around the HOMO-LUMO are $\sigma$-antibonding. Their bonding counterparts, which are responsible for the coordinative bonds, and are centered on the ligands (they receive larger contribution from the ligand $p$ orbitals than those of the $d_{x^2-y^2}$ and $d_{z^2}$), are several $eV$s lower in energy. The antibonding character is denoted by using the $e_g^*$ notation for these orbitals. Note that the antibonding interaction energetically destabilizes the $e_g^*$-like MOs. Even though the $t_{2g}$ and $e_g^*$ levels are often split due to the distortion of the geometry from the perfect octahedral arrangement (e.g., for the splitting in the cases of $D_3$ and $D_{2d}$ point groups, see Figure 4.4), the $t_{2g}/e_g^*$ notation of the $d$-dominated MOs is often kept for simplicity. This convention is also applied in the forthcoming chapters of the thesis.

Although the description summarized below in Figure 3.2a provides an adequate treatment of the $\sigma$-bonding, it does not deal with possible $\pi$-bonding between the Fe and the ligands. For instance, in the case of the above discussed molecule, $[\text{Fe(CN)}_6]^{4-}$, the unoccupied $\pi^*$ orbitals of the CN$^-$ ions are close in energy to the $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals of the Fe, which, having the appropriate symmetry, result in a slight mixing, and consequently, in a weak Fe-CN $\pi$-backbonding (Figure 3.2b). Therefore, the $t_{2g}$-like MOs in Fe compounds constituting of ligands with a delocalized $\pi$ electronic structure might possess a simultaneous $\sigma$-nonbonding/$\pi$-bonding character.

3.2 Electronic States of Fe Complexes

The different filling of the above discussed Fe-$3d$ orbitals give rise to different electronic configurations. For instance, in the case of Fe(II) coordination compounds, these are the singlet ($S = 0$), triplet ($S = 1$), and quintet ($S = 2$) states. In the octahedral case, the lowest-lying singlet and quintet imply the $t_{2g}^6e_g^0$ and $t_{2g}^4e_g^2$ configurations, respectively, which were denoted as the LS and HS states in Section 1.1. We mention that ligand field theory considerations based on the Tanabe-Sugano diagram (which shows the correlation
between the energies of electronic states with respect to the ground state and the ligand field strength) of a $d^6$ ion indicates that for an octahedral Fe(II) complex, the lowest-lying triplet (IS = "intermediate-spin") can never become the ground state,\textsuperscript{72} therefore, only
the LS and HS states are discussed here.\textsuperscript{a} The stability of the LS and HS configurations in a complex are governed by two factors: the ligand field splitting (for an octahedral ligand field, $\Delta_o$) and the repulsive interelectronic interaction. $\Delta_o$ is the difference in the energies of the $t_{2g}$ and $e_g^*$ orbital sets, which defines the ligand field strength. A large $\Delta_o$, i.e., a strong ligand field, favors the LS state, since the promotion of electrons to the $e_g^*$ orbitals requires a considerable amount of energy. On the other hand, in the case of a small $\Delta_o$, i.e., a weak ligand field, the $e_g^*$ orbitals are accessible, and the HS configuration is realized due to the small energy gap. Moreover, in terms of Hund’s first rule, the larger repulsion between antiparallel electrons, compared to parallel ones, characterized by the exchange interaction, leads to the destabilization of the LS state. The determination of the ground electronic states of Fe coordination complexes relies on the correct description of the above discussed quantities, $\Delta_o$, and especially the exchange interaction, as also discussed in Section 4.4.

\textsuperscript{a}Note, however, that triplet excited states are known to be involved in the mechanism of molecular switching.\textsuperscript{13–16,73} Such excited states are explored in Sections 4.6 and 4.7.
Chapter 4

Theoretical Investigation of the Low-Spin↔High-Spin State Transition in Pseudo-Octahedral Fe(II) Complexes

4.1 Background: The Spin-State Transition

The electronic structure of transition metal compounds possessing 4–7 3d electrons and moderate field (i.e., a balance between strong and weak field) ligands can often be conveniently switched between the LS and HS electronic configurations by thermally induced spin-crossover (TSCO). This fascinating phenomenon was first observed for Fe(III) by Cambi et al. in the 1930s,74–76 and the effect was also found to occur in complexes of various TM ions, including Fe(II),77,78 Co(II),79 Co(III), Mn(II), Mn(III), and Cr(II).80 However, the focus of the research in this field is mainly on Fe(II) SCO materials due to their...
abrupt spin transition profile and thermal hysteresis behavior, which properties are advantageous for their application as molecular switches.\textsuperscript{5–7,9} Moreover, Fe compounds can be uniquely characterized with the measurement of the electron density and the electric field gradient at the $^{57}$Fe nucleus obtained from Mössbauer spectroscopy (MS, see Chapter 5), which method has been widely applied for the investigation of the LS$\leftrightarrow$HS transition.\textsuperscript{8,81–86} Besides MS, various experimental techniques were applied for the investigation of the spin transition including nuclear inelastic scattering (NIS),\textsuperscript{87–90} X-ray diffraction (XRD),\textsuperscript{91–95} magnetization measurements,\textsuperscript{93,96–99} infrared (IR), Raman,\textsuperscript{88,90,99–102} optical,\textsuperscript{10,11,103} X-ray absorption\textsuperscript{104,105} (XAS) and emission (XES)\textsuperscript{106} spectroscopies, neutron scattering\textsuperscript{107} and even more exotic techniques such as positron annihilation\textsuperscript{108–110} or muon spin rotation.\textsuperscript{111–113} During the TSCO in a quasi-octahedrally coordinated FeN$_6$ iron complex with 3$d^6$ electron configuration, a LS ground state of the system is converted to a HS excited state, which involves a $\Delta S = 2$ net change in the total electronic spin angular momentum of the iron(II) ion (Fig. 4.1). The LS$\leftrightarrow$HS transition can be typically described as taking place along a single configuration coordinate (SCC): a stretching mode which corresponds to the symmetric elongation of the six Fe-N bonds (the so-called breathing mode). This mode is characterized by the $\Delta r_{HL} = r_{HS} - r_{LS}$ parameter (where $r_{LS}$ and $r_{HS}$ are the equilibrium Fe-N bond lengths in the LS and HS states, respectively), which is typically ca. 0.2 Å for Fe(II) complexes. The elongation of Fe-N bond lengths is a consequence of the fact that two electrons are transferred from the non-bonding $t_{2g}$ to the $e_g^*$ type anti-bonding orbitals, which leads to the expansion of the system. Moreover, the spin-state transition is also characterized by the energy difference between the minima of the lowest singlet and quintet potential wells, $\Delta E_{HL} = E_{HS} - E_{LS}$, which is typically ca. 0–1000 cm$^{-1}$ for TSCO systems. The spin-state transition temperature $T_{1/2}$ is an experimentally observable quantity, which is known to be proportional to $\Delta E_{HL}$ ($\Delta E_{HL} \propto k_B T_{1/2}$).\textsuperscript{114,115} (In fact, $T_{1/2}$ is the temperature at which half of the complexes are converted to the HS state.)

The LS$\leftrightarrow$HS transition can be induced in a great number of Fe(II) complexes by varying the temperature or the pressure.\textsuperscript{8,10,11,81–113,116–120} Moreover, it was found for
Chapter 4. Theoretical Investigation of the LS↔HS State Transition in Fe(II) Complexes

Figure 4.1: Schematic illustration of the LS↔HS transition in Fe(II) complexes with 3d$^6$ electron configuration. The larger (red) circle represents the expansion of the system due to the occupation of two $e_g^*$-type anti-bonding orbitals. The potential energy curves corresponding to the LS and HS states, as well as $\Delta r_{HL}$ and $\Delta E_{HL}$ are also schematically represented.

several complexes that the LS↔HS state transition can also occur when irradiating the ground state of the system with light at low temperatures.\textsuperscript{121–123} Besides the spectroscopic evidence, it has also been shown that the structural changes at low temperature photoexcitation were identical to the ones observed for TSCO complexes.\textsuperscript{124} The mechanism of this kind of switching was investigated in great detail, the name, light-induced excited spin-state trapping (LIESST for the LS→HS transformation, and reverse LIESST for the HS→LS one)\textsuperscript{10,11,121,122} coined for the phenomenon describes the essence of it. Here we note that there is exciting potential in triggering spin conversion by light-induced transformations in the ligand sphere too, including ligand-driven light-induced spin change, LD-LISC,\textsuperscript{125} and light-driven coordination induced spin-state switching, LD-CISS.\textsuperscript{126,127} However, the investigation of these processes is beyond the scope of the present work.
Therefore we focus on the LIESST phenomenon, in which the system is excited with light from the LS ground state to metal-centered (MC) $d$-$d$ or metal-to-ligand charge-transfer (MLCT) excited states, which decay to the quintet HS state via intersystem crossings through the participation of triplet states.\textsuperscript{13-16,73} The lifetime of the excited HS state ($\tau_{\text{HS}}$) is mainly determined by $\Delta E_{\text{HL}}$ and $\Delta r_{\text{HL}}$.\textsuperscript{114,115,128} Namely, while $\tau_{\text{HS}}$ is inversely proportional to the LS-HS energy gap $\Delta E_{\text{HL}}$ (this relation is known as the inverse energy gap law), a large $\Delta r_{\text{HL}}$ implies smaller overlap of the LS and HS vibrational wave functions and an increased HS-LS barrier at low temperatures, which leads to a slower HS $\rightarrow$ LS relaxation, and thus to a higher HS lifetime. The mechanism of the switching can be investigated by pump-probe techniques: these are performed more conveniently on complexes with large $\Delta E_{\text{HL}}$ values (typically ca. 3500-6000 cm$^{-1}$ for Fe(II) complexes),\textsuperscript{114,115} which decay rapidly back to the ground state. The light-switching of Fe complexes have recently been investigated with time-resolved techniques that include optical,\textsuperscript{12,129,130} IR,\textsuperscript{131} Raman,\textsuperscript{12,129,130} XRD,\textsuperscript{132} X-ray absorption\textsuperscript{12,133-137} and emission spectroscopies.\textsuperscript{137-140}

One of the most studied spin-crossover Fe(II) complex is $[\text{Fe(ptz)}_6](\text{BF}_4)_2$ (ptz = 1-n-propyltetrazole),\textsuperscript{8,10,11,84,93,102,122} on which the LIESST effect was first observed. Recently, the bidentate iron complex $[\text{Fe(bipy)}_3]^{2+}$ also got into the focus of research, as the structure of its subnanosecond-lived HS state was determined by ultrafast X-ray absorption\textsuperscript{134,137} and emission spectroscopies.\textsuperscript{137,138} Furthermore, the mechanism of the photoswitching in this complex was very recently investigated with X-ray emission on the fs time scale.\textsuperscript{140} With $[\text{Fe(terpy)}_2]^{2+}$, a most striking result was obtained when doped into the matrix of the analogous Mn compound, $[\text{Mn(terpy)}_2](\text{ClO}_4)_2$: the lifetime of the light-induced excited HS state of this complex is more than 10 orders of magnitude larger than expected from the inverse energy gap law,\textsuperscript{115,128} which was found valid for all other Fe(II) spin-transition compounds.\textsuperscript{115,128} $[\text{Fe(terpy)}_2]^{2+}$ is in a LS state at room temperature, which implies a large $\Delta E_{\text{HL}}$, and hence a very fast decay of the light-induced HS state. The exact reason for this anomalous behavior is still to be revealed.\textsuperscript{115}

Modern quantum chemical methods have also been extensively applied to iron com-
plexes in order to investigate spin-state transitions. Such investigations address the accurate determination of structural changes, as well as the description of the electronic excited states involved in the LIEST process. Usually, the relatively large size of spin-crossover complexes (at least 40 atoms) and the presence of the central iron atom with open $d$ subshells limit the methods to DFT. The experimental values of the structural $\Delta r_{HL}$ parameter in octahedral Fe(II) complexes are usually well reproduced with DFT methods.\(^{114,115,141-143}\) However, extreme variations were observed for the DFT-calculated energy differences $\Delta E_{HL}$ for various density functionals.\(^{114,115,141-155}\) Although some functionals gave an acceptable estimate to these spin-state energies,\(^{114,115,141,143-159}\) none of them showed a good universal performance for all studied systems. It is important to note that several DFT,\(^{160-163}\) and ligand field molecular mechanics (LFMM)-based\(^{164-166}\) methods were found to provide accurate spin energetics, however, all these approaches employ additional factors obtained from experimental results. Such semi-empirical methods are not considered in the present chapter.

Beyond DFT, while MRCI is computationally too demanding, the CC approach may suffer from the possible multiconfigurational character of the system;\(^{167}\) moreover, the applicability of the latter method is also constrained to TM complexes of small size (up to ca. 20 atoms).\(^{167,168}\) Nevertheless, the CASSCF/CASPT2 method has been applied in a few cases for small,\(^{168-172}\) and also for medium-sized (ca. 40–60 atoms)\(^{15,18,19,172-176}\) Fe(II) complexes. In addition, the restricted active space self-consistent field (RASSCF)/RASPT2 method was also utilized for transition metal complexes, which allows a larger active space suitable for the simultaneous computation of different types of excitations\(^{177-180}\) (e.g., MC, MLCT and inter-ligand excitations). It has been shown that the CASPT2 method gives reliable estimates for both $\Delta r_{HL}$ and $\Delta E_{HL}$,\(^{15,18,19,169-173,175,176,181}\) albeit only a few Fe(II) complexes were considered so far. The overstabilization of the HS state by CASPT2 observed in a few works seems to contradict the previous statement,\(^{176,182-184}\) however, the combination of an appropriate active space and basis set can lead to an accurate estimate of spin-state splitting energies. In addition to $\Delta r_{HL}$ and $\Delta E_{HL}$, an accurate description of the excited states involved in the mechanism of the spin-state
transitions and in the HS→LS relaxation would also be of high importance. Currently, the TD-DFT and CASPT2 methods are available for the calculation of such excited states. CASPT2 was found to give reliable results for transition metal complexes in several cases,\textsuperscript{15,18,19,174,185–189} thus it can be used as a reference method for the estimation of excitation energies. On the other hand, an accurate CASPT2 method suffers from the fact that a very large active space is required for the simultaneous description of MC and MLCT states, which implies high computational cost. TD-DFT methods can be a solution for this problem, although it is well known that no universal functional exists with the accuracy of the CASPT2 method. Hence, the selection of an appropriate functional for the accurate description of excited states in several Fe(II) compounds would be desirable. Therefore, in the present chapter the systematic investigation of various DFT functionals, as well as the TD-DFT and the CASPT2 methods for the [Fe(tz)\textsubscript{6}]\textsuperscript{2+} (1), [Fe(bipy)\textsubscript{3}]\textsuperscript{2+} (2), and [Fe(terpy)\textsubscript{2}]\textsuperscript{2+} (3) (Fig. 4.2) Fe(II) complexes is presented. These compounds are reasonable model systems for the experimentally investigated switchable Fe(II) prototypes.

![Figure 4.2: 3D representation of the studied iron complexes: [Fe(tz)\textsubscript{6}]\textsuperscript{2+} (1), [Fe(bipy)\textsubscript{3}]\textsuperscript{2+} (2), and [Fe(terpy)\textsubscript{2}]\textsuperscript{2+} (3). In the case of 2, the notation for N and N* is shown on two neighbouring bipy units, whereas for 3, the axial and equatorial N positions of a ligand is denoted.](image)

Theoretical studies have already been made for systems 1–3. Potential energy curves of 1 and 2 corresponding to the lower energy states were calculated at the CASPT2 level,\textsuperscript{15,18,19} and for the latter compound $\Delta E_{\text{HL}}$ was computed with various DFT meth-
Chapter 4. Theoretical Investigation of the LS↔HS State Transition in Fe(II) Complexes

ods,\textsuperscript{114,172} and also with CASPT2.\textsuperscript{172} Additionally, the breakdown of the single configuration mode of the LS↔HS transition in [Fe(terpy)\textsubscript{2}]\textsuperscript{2+} has been suggested by a DFT study.\textsuperscript{115} This means that the symmetric Fe-N\textsubscript{ax} stretching mode alone is insufficient for the adequate description of the spin-transition in the system: a second coordinate corresponding to a bending mode of the terpyridine rings is also required. Although all these computational results are of high relevance, a systematic, density functional and multiconfigurational study on the same systems is necessary to gain new insights into the electronic structure, as well as to better understand the performance of the available computational methods. Therefore, in this chapter a comparative theoretical study on the applicability of DFT, TD-DFT and CASPT2 methods to investigate the ground and excited electronic states relevant to spin-crossover is presented. In addition, in the case of 3, the importance of the departure from the single configuration coordinate model is discussed.

4.2 Computational Details

4.2.1 DFT and TD-DFT Computations

DFT calculations were carried out with the ORCA2.8\textsuperscript{190,191} and ADF2010.02\textsuperscript{192,193} program packages. In the case of ORCA calculations, geometries of the LS and HS states of the studied iron complexes were fully optimized with the gradient-corrected (GGA) exchange-correlation functionals RPBE,\textsuperscript{40} OPBE,\textsuperscript{42,43} BP86\textsuperscript{38,39} and OLYP,\textsuperscript{41,43} the hybrid functionals B3LYP\textsuperscript{41,46,47} and B3LYP*\textsuperscript{144} (B3LYP* is a hybrid functional with 15% exact exchange contribution, while the standard B3LYP functional contains 20% of HFx), the meta-GGA functional TPSS\textsuperscript{44,45} and the meta-hybrid density functional TPSSh\textsuperscript{53} in combination with the GTO-TZVP basis set.\textsuperscript{194} These functionals are representatives of different rungs of Jacob’s ladder (Figure 2.1), and have extensively been applied before to switchable Fe(II) complexes for the calculation of structural parameters and spin-state energy splittings.\textsuperscript{114,115,141–156,160,162} In the case of closed-shell systems —such as the LS
states of the 1–3 complexes—, the RKS method was applied. On the other hand, the
lowest-lying open-shell electronic states (e.g., the HS and first triplet states investigated
in this chapter) were calculated with the UKS formalism using the maximal value for
the total electronic spin quantum number ($M_S$) defined by the multiplicity of the state
(triplet or quintet). Although UKS introduces spin contamination, deviations up to
only 0.1 were found between the expectation value of the square of the electronic spin
momentum operator and the exact value of $S(S + 1)$. This RKS/UKS approach for
closed/open-shell molecules is also followed in Chapter 5. In all cases, vibrational fre-
quencies were calculated as second derivatives of the electronic energy, in order to verify
whether the stationary points correspond to the true minima of the potential energy sur-
face. $\Delta E_{HL}$ spin-state energy splittings were calculated as $E_{HS} - E_{LS}$, where $E_{HS}$ and $E_{LS}$
are the electronic energies of the DFT-optimized structures. Since the computation of
vibrational terms at the CASPT2 level of theory is too demanding, and one of the main
scopes of this chapter is to compare the performances of DFT and CASPT2, zero-point
vibrational energies were not considered. Two-electron integrals were approximated by
the RI for GGA, and by the RIJCOSX method for hybrid exchange-correlation function-
als.\textsuperscript{63,64} Calculations with the ADF program package have also been carried out, for this
code allows the application of several interesting constraints. For ADF computations, the
BP86, RPBE, and OPBE GGA functionals were used in combination with the STO-TZP
basis set.\textsuperscript{a} In case of 2 and 3, fractional occupation numbers were applied with ADF
for the calculation of the $^5E$ quintet state. In contrast to ORCA calculations, in which
case no molecular symmetry was applied, in ADF calculations, the molecular symmetry
groups $C_1$, $D_3$ and $D_{2d}$ were respectively applied for the investigated complexes 1, 2 and
3. Moreover, the $C_2$ symmetry group was also applied for 2 and 3, in order to investigate
the Jahn-Teller effect in the $^5E$ HS state.

TD-DFT calculations were performed with the ORCA code. During the computa-
tional procedure, the approach of the TDA was followed.\textsuperscript{23,57} Thirty excited states were
\textsuperscript{a}The computationally very demanding evaluation of the gradient of the electronic energy with the
current version of ADF did not allow the application of hybrid functionals with this program package.
calculated with the TD-B3LYP* functional in combination with the TZVP basis set. This functional provided reliable results for $\Delta E_{HL}$ for the studied complexes, as reported in Section 4.4. In all cases, the lowest-lying MC excited states were selected by careful examination of the corresponding Kohn-Sham molecular orbitals and configurations extracted from the converged wave function. For the calculation of the triplet states, two different methods were applied: (a) the TD-DFT procedure was invoked on a triplet reference or (b) on the singlet ground state. For 1 and 2, unrelaxed potential energy curves were evaluated by performing TD-DFT calculations at geometries generated from DFT-optimized structures by varying the Fe-N bond lengths, while for 3, curves were calculated along a combined coordinate of the axial Fe-N distance ($r_{Fe-Nax}$) and the NNN angle ($\varphi_{NNN}$), which connects the $^1A_1$ and $^5E$ minima.

In order to evaluate the two-dimensional (2D) PESs of complex 3, geometries were generated from the DFT-optimized structure of the $^5E$ state reflecting the $D_{2d}$ point group symmetry by simultaneously varying the $r_{Fe-Nax}$ bond length and the $\varphi_{NNN}$ bond angle, while the rest of the internal coordinates within the terpyridine ligands were kept frozen. Then, constrained geometry optimizations were performed at the generated geometries for singlet, triplet, and quintet electronic states in order to include geometry relaxation. In these computations, all internal coordinates were optimized with the exception of $r_{Fe-Nax}$ and $\varphi_{NNN}$, and the B3LYP*/TZVP method was applied. The handling of point group symmetry in ORCA did not allow the separate computation of the nearly degenerate quintet surfaces. Therefore, both symmetry components of the quintet state were computed on the same relaxed surface.

### 4.2.2 CASPT2 Computations

In addition to the (TD-)DFT investigation of the 1–3 complexes, [Fe(terpy)$_2$]$^{2+}$ was also studied with the CASPT2 method (CASPT2 results for 1 and 2 are available in the literature$^{18,19}$) using a reference wave function obtained by the state-specific (SS) and state-averaged (SA) CASSCF methods as implemented in the MOLCAS7.6 program package.$^{24,26,195}$ In these computations, the $C_2$ symmetry constraint was used with the
Fe-N<sub>ax</sub> bond being the symmetry axis, and the Douglas-Kroll-Hess Hamiltonian was applied to account for scalar relativistic effects. The ANO-RCC basis sets<sup>65-67</sup> were used with the following contractions: (7s6p5d4f3g2h) for the Fe, (4s3p1d) for N, (3s2p) for C, and (2s) for H atoms. During the CASPT2 procedure, the deep core electrons (Fe [1s<sup>2</sup>...2p<sup>6</sup>]; C,N [1s<sup>2</sup>]) were not included in the treatment of electron correlation. Additionally, in the CASSCF calculation, the Fe-3p orbital along the Fe-N<sub>ax</sub> bond had to be kept frozen in order to maintain the character of the active orbitals in the whole Fe-N<sub>ax</sub> investigated range. In the CASPT2 calculations, the standard IPEA shift of 0.25 a.u. in the zeroth-order Hamiltonian, was applied.<sup>196</sup> In order to exclude possible intruder states, the level shift technique<sup>61,197</sup> was applied with 0.2 a.u. level shift in each CASPT2 computation. Test computations with lower level shifts have shown that excitation energies were stabilized with respect to the level shift at this value.

The active space for all the computations consisted of 10 electrons correlated in 12 orbitals. We followed Pierloot’s strategy<sup>172</sup> by selecting the following active orbitals: the two e<sub>g</sub> orbitals with bonding Fe-N character, the three 3d(t<sub>2g</sub>) orbitals of Fe, the two e<sub>g</sub>* orbitals with anti-bonding Fe-N character, and an additional set of five 4d orbitals on the Fe (see Fig. 4.3). These additional orbitals are required to properly describe the dynamical correlation of the 3d electrons.<sup>198</sup> The applied basis set and active space was previously found to give accurate energetics for 1 and 2.<sup>18,19</sup>

For [Fe(terpy)<sub>2</sub>]<sup>2+</sup>, 2D potential energy surfaces were computed for the lowest singlet, triplet, and quintet states along the Fe-N<sub>ax</sub> bond length and ϕ<sub>NNN</sub> bond angle also with CASPT2. Since geometry optimization for this system at the CASPT2 level is far too demanding, a nonrelaxed potential scan was performed using the structural parameters optimized for the 5E state by DFT. The value of ΔE<sub>HL</sub> was determined by the calculation of CASPT2 energies at the minima of the lowest-lying singlet and quintet states. 1D potential energy curves were calculated along a combined coordinate of r<sub>Fe-Nax</sub> and ϕ<sub>NNN</sub>, similar to the one previously described for the DFT calculations.

Energies obtained from separate CASSCF/CASPT2 calculations can only be compared when the active orbitals are identical in the two separate calculations. The char-
Figure 4.3: 3D representation of the (a) Fe $3d-e_g^*$ antibonding, (b) Fe $3d-t_{2g}$ non-bonding and (c) Fe-N $2p-e_g$ bonding active orbitals applied in the multiconfigurational treatment of $[\text{Fe(terpy)}_2]^{2+}$. For simplicity, the additional set of $4d$ active orbitals (3 $t_{2g}$ and 2 $e_g$) is not shown.

acter of the orbitals as outlined above could perfectly be maintained in a SS-CASSCF treatment of the quintet states of each irreducible representation at all considered geometries. Unfortunately, this was not the case for the singlet and triplet states. For example, in case of the singlet ground state, the Fe-$3d$ orbitals of $e_g^*$ character were unoccupied in the dominant electronic configuration of the wave function (a small non-zero occupation number arises by a small admixture of excited determinants to the main $t_{2g}^6 e_g^0$ determinant). Hence, the correlating orbitals for these $e_g^*$ orbitals did not always stay in the active space. To solve this issue, a SA-CASSCF approach was applied, in which the orbitals were optimized for an average of the four lowest roots, in the case of singlet states, and for an average of the two lowest roots, in the case of triplet states when computing 2D surfaces. The electronic configurations of the excited singlet roots include
occupied $t_{2g}^2$, $e_g^1$ orbitals, and therefore, the correlating Fe-$3d$ orbitals of $e_g^*$ character were then easily kept in the active space for the SA computation. To ensure that the calculated singlet-quintet energy difference is not affected by the slight imbalance of the SS treatment of the quintet and the SA treatment of the other two spin states, a quasi-SS energy was generated at one geometry for the singlet. This was done by gradually increasing the weight of the ground state with respect to the excited states in a three-state average computation. 10:1:1 turned out to be the largest ratio of weights for the ground and the two excited states, respectively for which the active orbitals still had the desired character. We took the resulting CASPT2 energy as anchor point for the standard singlet SA calculations to relate these to the quintet and triplet states. This was justified by performing test computations on the $[\text{Fe}(\text{NCH})_6]^{2+}$ model system, whose results indicate that SA- and quasi-SS energies evolve in a nearly parallel manner when the geometry of the complex changes.

For the calculation of excitation energies along the before mentioned combined coordinate, different number of roots were applied, corresponding to the states of interest. According to this principle, 3, 2, 2, 4, 3, and 2 roots were applied for the singlet A, singlet B, triplet A, triplet B, quintet A and quintet B states, respectively. Note that although here the A and B symmetries of the $C_2$ point group are used for the nomination of individual states of 3, the following sections will apply the notations of the $D_{2d}$ point group. On the other hand, for $[\text{Fe}(\text{tz})_6]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$, we apply the octahedral labels for the electronic states. This is justified by the fact that the molecular symmetry of 1 and 2 is far closer to octahedral, than the the one of 3, in which complex a significant axial distortion occurs, as is discussed in Sections 4.3 and 4.6. The correspondence between the notations for the different point groups used in the thesis is shown in the Appendix (Table A1).\(^b\) Care had also to be taken of choosing the appropriate threshold for the

\(^b\)Note that in the identification of the symmetries of electronic states the principal $x$, $y$, and $z$ axes were chosen to be oriented in the direction of the ligands. Therefore, in the (pseudo-)octahedral case, the $e_g^*$-like MOs always possess $d_{x^2-y^2}$ or $d_{z^2}$ character. Although this results in the exchange of $d_{x^2-y^2}$ and $d_{xy}$ orbitals, compared to the notation of character tables, using this orientation of axes systematically in the entire thesis leads to symmetries consistent with those utilized in the literature of transition metal chemistry.
Cholesky decomposition of the two-electron integrals.\textsuperscript{68} Using a threshold value of $10^{-4}$ \(E_h\) (this was the default of the program) resulted in small irregularities of 1-10 meV in the potentials which disappeared when the threshold was reduced to $10^{-6} \ E_h$. While these irregularities are rather small, they make it difficult to exactly locate the minimum of the potentials.

In the forthcoming parts of this chapter, computational results and their interpretation are described for the investigated 1-3 complexes. After reporting the results for the structural (Section 4.3) and energetic (Section 4.4) variations at spin-state transitions, as well as for the Jahn-Teller effect in \([\text{Fe(bipy)}_3]^{2+}\) and \([\text{Fe(terpy)}_2]^{2+}\) (Section 4.5), the 1D PESs corresponding to the lowest-lying MC states are presented (Section 4.6). Finally, the DFT and CASPT2 2D PESs and the $5B_2$ and $5E$ HS states of \([\text{Fe(terpy)}_2]^{2+}\) are discussed (Section 4.7). Note that the CASPT2 results of de Graaf \textit{et al.} for \([\text{Fe(tz)}_6]^{2+}\)\textsuperscript{18} and \([\text{Fe(bipy)}_3]^{2+}\)\textsuperscript{19} are only used to provide a full comparison of the performances of the (TD-)DFT and CASPT2 methods for all studied compounds.

4.3 Molecular Structures of the LS and HS States of the Investigated Complexes

1. \([\text{Fe(tz)}_6]^{2+}\) is the model compound of the \([\text{Fe(Rtz)}_6]^{2+}\) family, \(R\) being methyl (mtz), ethyl (etz), or propyl (ptz) group, which compounds exhibit thermal spin crossover. Therefore, they can be characterized both in the LS and HS states by experimental techniques conveniently. We selected the \([\text{Fe(ptz)}_6](\text{BF}_4)_2\) system to compare the experimental results with the calculations, because in contrast to the cases of the other two members of the family, the spin transition is independent of the crystallographic phase change. The crystal structure of this complex is known from XRD studies,\textsuperscript{93,95} which suggest that the spin transition in tetrazole derivatives can be fully described along the \(r_{HL}\) configuration coordinate.\textsuperscript{94} This is clearly reflected in the DFT-optimized LS and HS structures of 1: practically no structural differences are observed apart from the
4.3. Molecular Structures of the LS and HS States of the Investigated Complexes

Elongation of the Fe-N bonds. Most of DFT-optimized values of $r_{\text{LS}}$ are in good agreement with experimental results, although the RPBE, B3LYP and B3LYP* functionals overestimate the experimentally reported value by 0.04–0.05 Å (Table 4.1). Note that although most of the structural experimental data for the 1, and also for the LS states of 2 and 3 complexes were taken from solid state measurements, these values should be still comparable to the results obtained from calculations in gas phase. This is supported by the fact that only slight variations (up to 0.02 Å) are observed in the XRD and extended X-ray absorption fine structure (EXAFS) Fe-N bond lengths of the LS and HS states of Fe(II) spin-crossover complexes measured in solid state and solution, respectively.\textsuperscript{199,200} Additionally, Daku et al. also found only slight variations in the structures of 2 optimized in the gas phase and obtained from \textit{ab initio} molecular dynamics (AIMD) study of its aqueous solution.\textsuperscript{201}

RPBE and OPBE overestimate $r_{\text{HS}}$ with respect to the experimental value by ca. 0.09 Å. For B3LYP and B3LYP*, this deviation is 0.05–0.06 Å, while all of the other investigated density functionals yield more accurate results. The $\Delta r_{\text{HL}}$ parameter is better reproduced with the hybrid B3LYP, B3LYP*, and the BP86 density functionals than by the other GGA methods, as the latter overestimate $\Delta r_{\text{HL}}$ with respect to the experimental value by 0.04–0.07 Å. In addition, TPSS and TPSSH also reproduce this structural parameter up to 0.03 and 0.02 Å, respectively. In contrast to DFT, CASPT2 slightly underestimates $r_{\text{LS}}$ and $r_{\text{HS}}$, while it predicts accurately $\Delta r_{\text{HL}}$.\textsuperscript{18} Finally, it is noted that in the previous CASPT2 study of Ordejón et al.,\textsuperscript{18} the plane of the tetrazole rings are in the orthogonal $xy$, $xz$ and $yz$ planes (where $x$, $y$ and $z$ axes are defined along the $\sigma$ Fe-N bonds), whereas in the presented DFT-optimized structures the planes of the ligands are twisted by ca. 45 degrees with respect to each other around the Fe-N axes. Although this is clearly a relevant difference between the two structures, we will show in Section 4.4 that the potentials of 1 are not sensitive to these sort of different orientations of the ligands in the isolated molecule.

2. $[\text{Fe(bipy)}_3]^{2+}$ stays in the LS state at all temperatures, thus XRD data is only available for the LS state.\textsuperscript{202} However, the Fe-N bond length of the subnanosecond-lived
Chapter 4. Theoretical Investigation of the LS↔HS State Transition in Fe(II) Complexes

Table 4.1: DFT-optimized and CASPT2 values of $r_{\text{Fe-N}}$ for $[\text{Fe(tz)}_6]^{2+}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{\text{LS}}$/Å</th>
<th>$r_{\text{HS}}$/Å</th>
<th>$\Delta r_{\text{HL}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.$^a$</td>
<td>1.991±0.002</td>
<td>2.176±0.004</td>
<td>0.185±0.002</td>
</tr>
<tr>
<td><strong>ORCA (GTO basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZVP</td>
<td>1.990</td>
<td>2.214</td>
<td>0.224</td>
</tr>
<tr>
<td>RPBE/TZVP</td>
<td>2.031</td>
<td>2.266</td>
<td>0.235</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
<td>1.995</td>
<td>2.270</td>
<td>0.275</td>
</tr>
<tr>
<td>OLYP/TZVP</td>
<td>2.037</td>
<td>2.291</td>
<td>0.254</td>
</tr>
<tr>
<td>B3LYP/TZVP</td>
<td>2.048</td>
<td>2.242</td>
<td>0.194</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
<td>2.033</td>
<td>2.233</td>
<td>0.200</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
<td>1.990</td>
<td>2.209</td>
<td>0.219</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
<td>2.002</td>
<td>2.211</td>
<td>0.209</td>
</tr>
<tr>
<td><strong>ADF (STO basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZP</td>
<td>1.994</td>
<td>2.216</td>
<td>0.222</td>
</tr>
<tr>
<td>RPBE/TZP</td>
<td>2.034</td>
<td>2.268</td>
<td>0.234</td>
</tr>
<tr>
<td>OPBE/TZP</td>
<td>1.994</td>
<td>2.266</td>
<td>0.272</td>
</tr>
<tr>
<td><strong>MOLCAS (ANO-RCC basis)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CASPT2$^b$</td>
<td>1.95</td>
<td>2.15</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^a$ experimental values for $[\text{Fe(ptz)}_6](\text{BF}_4)_2$ were taken from refs. 93 and 95.

$^b$ from ref. 18.

The HS state of 2 has been determined by time-resolved EXAFS spectroscopy. The trigonal distortion splits the $^5T_{2g}$ ($O_h$) state into the $^5A_1$ and $^5E$ states in the $D_3$ point group symmetry, thus two excited HS states can be present in 2 (Figure 4.4a and b).

Although the spin transition in 2 involves slight bendings of the bidentate ligands, these are negligible variations compared to the elongation of the Fe-N bond length. Consequently, the single Fe-N stretching mode is again a good approximation for the configuration coordinate of the LS↔HS transition, similar to the case of 1. Therefore, we do not consider additional structural parameters describing the spatial arrangement of
Tables 4.2 and 4.3 reveal that CASPT2 underestimates the $r_{LS}$ bond length, while the RPBE and hybrid density functionals overestimate it. Yet, BP86, OPBE, TPSS and TPSSh give very accurate results compared to the experimental value of 1.967 Å. $r_{HS}$ is well reproduced by almost all methods with the exception of OPBE, which overestimates it, and the CASPT2 method, which
Chapter 4. Theoretical Investigation of the LS↔HS State Transition in Fe(II) Complexes

Table 4.2: DFT-optimized values of $r_{\text{Fe-N}}$ for $[\text{Fe(bipy)}_3]^{2+}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{\text{LS}}$/Å</th>
<th>$r_{\text{HS}}$/Å</th>
<th>$\Delta r_{\text{HL}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. – XRD$^a$</td>
<td>1.967±0.002</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Exp. – EXAFS$^b$</td>
<td>1.99±0.02</td>
<td>2.19±0.04</td>
<td>0.20±0.02</td>
</tr>
</tbody>
</table>

ORCA (GTO basis)

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{\text{LS}}$/Å</th>
<th>$r_{\text{HS}}$/Å</th>
<th>$\Delta r_{\text{HL}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP86/TZVP</td>
<td>1.977</td>
<td>2.185</td>
<td>0.208</td>
</tr>
<tr>
<td>RPBE/TZVP</td>
<td>2.004</td>
<td>2.223</td>
<td>0.219</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
<td>1.963</td>
<td>2.201</td>
<td>0.238</td>
</tr>
<tr>
<td>OLYP/TZVP</td>
<td>2.000</td>
<td>2.230</td>
<td>0.230</td>
</tr>
<tr>
<td>B3LYP/TZVP</td>
<td>2.029</td>
<td>2.224</td>
<td>0.195</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
<td>2.015</td>
<td>2.214</td>
<td>0.199</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
<td>1.978</td>
<td>2.182</td>
<td>0.204</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
<td>1.987</td>
<td>2.190</td>
<td>0.203</td>
</tr>
</tbody>
</table>

$^a$ from ref. 202.
$^b$ from ref. 134.

In case of these ORCA calculations, only one HS state could be computed, as the very small difference between the two HS structures could not be reproduced without the application of point group symmetry.

underestimates the experimentally observed Fe-N bond length in the HS state. OPBE slightly overestimates $\Delta r_{\text{HL}}$ by ca. 0.04 Å, while all other methods give a result within the ±0.02 Å uncertainty interval of the absorption measurement. Finally, there are only very minor geometrical differences (up to ca. 0.02 Å) between the $^5\text{A}_1$ and $^5\text{E}$ HS structures of $[\text{Fe(bipy)}_3]^{2+}$, which are not likely to be resolved experimentally.

3. $[\text{Fe(terpy)}_2]^{2+}$ is the Fe(II) complex of the strong-field tridentate terpy ligand, which, similarly to 2, cannot be converted to the HS state by varying the temperature. While the XRD structure of the LS state is known for decades, the bond lengths referring to the first coordination sphere of the Fe(II) cation have only been determined very recently, with the application of picosecond EXAFS spectroscopy. It is very likely that the SCC model is insufficient to describe the variations for 3: besides bond elongations,
the spin transition must involve also a bending mode of the terpyridine rings.\footnote{115} This mode implies the in-plane rotation of the two side pyridine rings with respect to the middle one, which can be described by the apparent bending of the three N atoms of the ligand. The breakdown of the single mode model is supported by the DFT-calculated values of the variation of the NNN angle ($\varphi_{\text{NNN}} = 5–6^\circ$, see Table 4.6), which describes the bending of the ligands during the LS$\leftrightarrow$HS transition. Further complexity arises in the HS state. Similar to the case of \textit{2}, two different HS states can be present, $^5\text{B}_2$ and $^5\text{E}$, due to the removal of the threefold degeneracy of the $t_{2g}$ electron orbitals by the axial distortion (Fig. 4.4c). The experimental values of $r_{\text{LS}}$ for both $N_{\text{ax}}$ and $N_{\text{eq}}$ (for the applied notations, see Fig. 4.2) are well reproduced by DFT, while the CASPT2 method gives slightly larger deviations from experiments (Tables 4.4 and 4.5). All applied methods also give very accurate estimates to $\varphi_{\text{NNN}}$ with the exception of the RPBE, B3LYP and B3LYP* methods, which slightly overestimate it compared to the experimental value. Additionally, while only very small differences (0.00–0.02 Å) are observed in the DFT-calculated $r_{\text{HS}}$(Fe-N$_{\text{eq}}$) and $\Delta r_{\text{HL}}$(Fe-N$_{\text{eq}}$) values for the $^5\text{B}_2$ and $^5\text{E}$ states, slightly larger differences (0.04–0.06 Å) are seen in the corresponding $r_{\text{HS}}$(Fe-N$_{\text{ax}}$) and $\Delta r_{\text{HL}}$(Fe-N$_{\text{ax}}$) values between the two quintets. The comparison of EXAFS-measured values of $r_{\text{HS}}$ and $\Delta r_{\text{HL}}$ with those optimized by the best-performing density functionals (e.g., BP86) for the axial case suggests that $^5\text{E}$ is the experimentally detected HS state (see Table 4.4). Although the CASPT2 structure is in better correspondence with the $^5\text{B}_2$, this apparent

### Table 4.3: DFT-optimized and CASPT2 values of $r_{\text{Fe-N}}$ for [Fe(bipy)$_3$]$^{2+}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{\text{LS}}$/Å</th>
<th>$r_{\text{HS}}$–$\gamma_{\text{A}_1}$/Å</th>
<th>$\Delta r_{\text{HL}}$–$\gamma_{\text{A}_1}$/Å</th>
<th>$r_{\text{HS}}$–$\gamma_{\text{E}}$/Å</th>
<th>$\Delta r_{\text{HL}}$–$\gamma_{\text{E}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ADF (STO basis)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZP</td>
<td>1.976</td>
<td>2.201</td>
<td>0.225</td>
<td>2.179</td>
<td>0.203</td>
</tr>
<tr>
<td>RPBE/TZP</td>
<td>2.004</td>
<td>2.242</td>
<td>0.238</td>
<td>2.220</td>
<td>0.216</td>
</tr>
<tr>
<td>OPBE/TZP</td>
<td>1.956</td>
<td>2.226</td>
<td>0.270</td>
<td>2.201</td>
<td>0.245</td>
</tr>
<tr>
<td><strong>MOLCAS (ANO-RCC basis)</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CASPT2$^a$</td>
<td>1.93</td>
<td>2.14</td>
<td>0.21</td>
<td>2.13</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^a$ from ref. 19. For the experimental Fe-N bond lengths of \textit{2}, see Table 4.2.
contradiction is due to the tendency of this method to overestimate the strength of Fe-N coordinative bonds, as also observed for 1 and 2 above. This effect is further addressed in the next paragraph.

### Table 4.4: DFT and CASPT2-calculated values of $r_{\text{Fe-N}_{\text{ax}}}$ for [Fe(terpy)$_2$]$^{2+}$.

<table>
<thead>
<tr>
<th></th>
<th>$r_{\text{LS}}$/Å</th>
<th>$r_{\text{HS}}-\gamma_{\text{Bz}}$/Å</th>
<th>$\Delta r_{\text{HL}}-\gamma_{\text{Bz}}$/Å</th>
<th>$r_{\text{HS}}-\gamma_{\text{E}}$/Å</th>
<th>$\Delta r_{\text{HL}}-\gamma_{\text{E}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. – XRD\textsuperscript{a}</td>
<td>1.892±0.005</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Exp. – EXAFS\textsuperscript{b}</td>
<td>1.873±0.006</td>
<td>–</td>
<td>–</td>
<td>2.079±0.013</td>
<td>0.206±0.007</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>ORCA (GTO basis)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BP86/TZVP</td>
<td>1.889</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RPBE/TZVP</td>
<td>1.904</td>
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<tr>
<td></td>
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<td>OPBE/TZVP</td>
<td>1.867</td>
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<td></td>
<td></td>
<td>OLYP/TZVP</td>
<td>1.893</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B3LYP/TZVP</td>
<td>1.926</td>
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<td></td>
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<td>B3LYP*/TZVP</td>
<td>1.915</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPSS/TZVP</td>
<td>1.891</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TPSSh/TZVP</td>
<td>1.897</td>
</tr>
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<td>ADF (STO basis)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>BP86/TZP</td>
<td>1.886</td>
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<td></td>
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<td>RPBE/TZP</td>
<td>1.905</td>
</tr>
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<td></td>
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<td>OPBE/TZP</td>
<td>1.868</td>
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<td></td>
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<td>MOLCAS (ANO-RCC basis)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CASPT2\textsuperscript{c}</td>
<td>1.850</td>
</tr>
</tbody>
</table>

\textsuperscript{a} from ref. 203.
\textsuperscript{b} from ref. 204.
\textsuperscript{c} CASPT2 values were determined from the minima of the corresponding 2D PES (for details see section 4.7).

The above results indicate that the LS geometries of the studied iron complexes are well described by density functional methods, as expected for the $d^6$ closed subshell ($t_{2g}^6$) electronic structure. While for all studied complexes the BP86, OPBE, TPSS and TPSSh predicted values of $r_{\text{LS}}$ are in excellent agreement with experiments, RPBE and hybrid B3LYP and B3LYP* functionals slightly overestimate this bond length. The overestimation of Fe-N bond lengths by hybrid density functionals is due to the fact that the inclusion of Hartree-Fock exchange slightly weakens the Fe-N bond, similarly to the HF method itself,\textsuperscript{20,114} which effect can be attributed to inbalanced treatment of Coulomb and Fermi correlation in the HF method (while the latter is included, the former is not).
4.3. Molecular Structures of the LS and HS States of the Investigated Complexes

<table>
<thead>
<tr>
<th>Table 4.5: DFT-calculated values of $r_{\text{Fe-N}_{eq}}$ for $[\text{Fe(terpy)}_2]^{2+}$.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Exp. – XRD$^a$</td>
</tr>
<tr>
<td>Exp. – EXAFS$^b$</td>
</tr>
<tr>
<td><strong>ORCA (GTO basis)</strong></td>
</tr>
<tr>
<td>BP86/TZVP</td>
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<tr>
<td>RPBE/TZVP</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
</tr>
<tr>
<td>OLYP/TZVP</td>
</tr>
<tr>
<td>B3LYP/TZVP</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
</tr>
<tr>
<td><strong>ADF (STO basis)</strong></td>
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<tr>
<td>BP86/TZP</td>
</tr>
<tr>
<td>RPBE/TZP</td>
</tr>
<tr>
<td>OPBE/TZP</td>
</tr>
</tbody>
</table>

$^a$ from ref. 203.

$^b$ from ref. 204.

Moreover, test PBE calculations with the same correlation functional as in RPBE yield significantly lower bond lengths, in good agreement with the experimental values, which indicates that the related behavior of RPBE to those of the hybrid functionals discussed above also stems from the exchange part. This effect is explained by the increased gradient correction to the LDA exchange in RPBE, compared to the one in PBE.$^{114}$ On the other hand, CASPT2 slightly underestimates the Fe-N bond length in the LS states of all studied complexes. A possible reason for this is the application of an unbalanced basis set and/or the presence of the basis set superposition error (BSSE). This latter effect has already been observed before in the multiconfigurational treatment of related transition metal complexes.$^{174,205}$

The predicted HS structures of the investigated Fe(II) complexes show a slightly larger deviation from experimental geometries than the LS structures. Still, BP86, and
### Table 4.6: DFT and CASPT2-calculated values of \( \varphi_{\text{NNN}} \) for [Fe(terpy)_2]^{2+}.

<table>
<thead>
<tr>
<th></th>
<th>( \varphi_{\text{LS}} )</th>
<th>( \varphi_{\text{HS} \rightarrow \text{Bz}} )</th>
<th>( \Delta \varphi_{\text{HL} \rightarrow \text{Bz}} )</th>
<th>( \varphi_{\text{HS} \rightarrow \text{E}} )</th>
<th>( \Delta \varphi_{\text{HL} \rightarrow \text{E}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp.(^a)</td>
<td>102.4</td>
<td>–</td>
<td>–</td>
<td>105.6</td>
<td>3.3</td>
</tr>
<tr>
<td>ORCA (GTO basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZVP</td>
<td>102.3</td>
<td>107.3</td>
<td>5.0</td>
<td>108.3</td>
<td>6.0</td>
</tr>
<tr>
<td>RPBE/TZVP</td>
<td>103.0</td>
<td>108.0</td>
<td>5.0</td>
<td>109.0</td>
<td>6.0</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
<td>102.4</td>
<td>107.6</td>
<td>5.2</td>
<td>109.0</td>
<td>6.6</td>
</tr>
<tr>
<td>OLYP/TZVP</td>
<td>103.2</td>
<td>108.3</td>
<td>5.1</td>
<td>109.5</td>
<td>6.3</td>
</tr>
<tr>
<td>B3LYP/TZVP</td>
<td>103.6</td>
<td>108.8</td>
<td>5.2</td>
<td>109.0</td>
<td>5.4</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
<td>103.2</td>
<td>108.5</td>
<td>5.3</td>
<td>108.8</td>
<td>5.6</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
<td>102.4</td>
<td>107.5</td>
<td>5.1</td>
<td>108.3</td>
<td>5.9</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
<td>102.6</td>
<td>108.0</td>
<td>5.4</td>
<td>108.4</td>
<td>5.8</td>
</tr>
<tr>
<td>ADF (STO basis)</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>BP86/TZP</td>
<td>102.6</td>
<td>107.2</td>
<td>4.6</td>
<td>108.4</td>
<td>5.8</td>
</tr>
<tr>
<td>RPBE/TZP</td>
<td>103.2</td>
<td>107.9</td>
<td>5.7</td>
<td>108.8</td>
<td>5.6</td>
</tr>
<tr>
<td>OPBE/TZP</td>
<td>102.8</td>
<td>107.5</td>
<td>4.7</td>
<td>108.8</td>
<td>5.0</td>
</tr>
<tr>
<td>MOLCAS (ANO-RCC basis)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CASPT2(^b)</td>
<td>102.3</td>
<td>105.4</td>
<td>3.3</td>
<td>105.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

\(^a\) from ref. 203.
\(^b\) CASPT2 values were determined from the minima of the corresponding 2D PES (for details see Section 4.7).

Also TPSS and TPSSh give a reliable estimate for the structural parameters of the 1–3 compounds. In contrast, RPBE, B3LYP, B3LYP*, and especially OPBE overestimate \( r_{\text{HS}} \) for 1. This behavior of the former three functionals for the LS state was attributed to erroneous treatment of the exchange interaction, which is even more pronounced in the HS state. The overestimation of the Fe-N distance in the HS state with 0.09 Å for 1 by OPBE is unexpected, as it is not observed for the LS state. On the other hand, the OPBE-optimized values of \( r_{\text{HS}} \) for 2 and 3 agree with the experimental values. The CASPT2 method again underestimates the corresponding bond lengths in the HS state in all studied complexes, similarly to the LS state.

The calculation of the LS and HS structures of Fe(II) complexes is essential for the
characterization of the spin transition. In this section, it has been shown that the overall performance of BP86, TPSS and TPSSh is the most satisfactory in predicting structural parameters of the LS and HS states of Fe(II) complexes, which agrees with previously reported observations.\textsuperscript{142,152,206–208} Moreover, the B3LYP and B3LYP* functionals seem to be also suitable for the accurate estimation of the $\Delta r_{\text{HL}}$ parameter, although they tend to systematically overestimate the relevant Fe-N bonds. The performance of RPBE is inferior compared to those of the above discussed functionals, since it overestimates also $\Delta r_{\text{HL}}$, not only the LS and HS bond lengths. The largest deviations from experimental geometrical parameters are observed for the OPBE functional. Despite the fact that this functional was praised for giving very reliable results for the structures of some other transition metal compounds in a previous study,\textsuperscript{150} our results raise questions about the suitability of this method for the estimation of structural parameters. It can also be concluded from the presented tables that the type of basis set (STO or GTO) does not affect the optimized geometries, which agrees well with previous results.\textsuperscript{114} Furthermore, the computed structures for 2 and 3 are in good agreement with previously reported DFT results.\textsuperscript{114,115} Finally, the accuracy of the applied CASPT2 method did not reach those of the best DFT functionals in the prediction of structural parameters. This effect can be due to BSSE in the case of CASPT2, and the lack of geometry relaxation, which would have been computationally far too demanding at this level of theory.

4.4 The LS-HS Splitting Energy $\Delta E_{\text{HL}}$ in Fe(II) Complexes

The spin-state splitting energy $\Delta E_{\text{HL}}$ determines the relative stability of the different spin-states in transition metal compounds. $\Delta E_{\text{HL}}$, besides $\Delta r_{\text{HL}}$, is the most decisive parameter that determines the lifetime of the HS states at low temperatures, where the HS→LS relaxation can only proceed through tunneling.\textsuperscript{114,115} It is evident that the reliable prediction of this parameter could be extensively applied in the understanding and
the design of switchable transition metal compounds. However, the accurate estimation of $\Delta E_{HL}$ is a very challenging task. Namely, it was shown for various Fe(II) compounds that DFT-calculated $\Delta E_{HL}$ values are highly dependent on the applied density functional.\textsuperscript{114,115,141,143–155,160,169,170,172,175,176,209} No universal DFT method was found to reliably reproduce $\Delta E_{HL}$, albeit the RPBE, OPBE and B3LYP* and TPSSh functionals gave acceptable results for several iron complexes.\textsuperscript{114,115,141,143–155,157} CASPT2 provided high quality results in several cases, although its computational cost is immensely higher and relatively few cases have been considered so far.\textsuperscript{18,19,171–175,181,189} However, to assess the performance of DFT, there is no better option than to compare DFT to the CASPT2 results, as exact experimental values of this parameter are not available. Also, from the relation $\Delta E_{HL} \propto k_B T^{1/2}$, for $\Delta E_{HL}$ a few hundred cm\(^{-1}\) ($0\text{–}1000 \text{ cm}^{-1}$) are expected for compounds exhibiting thermal spin-crossover, and several thousand cm\(^{-1}\) ($3500\text{–}6000 \text{ cm}^{-1}$) for the low-spin ones.\textsuperscript{114,115}

DFT and CASPT2 $\Delta E_{HL}$ values for 1–3 calculated in this work are given in Table 4.7 (for 1 and 2, the corresponding CASPT2 values were taken from refs. 18 and 19). The 220 cm\(^{-1}\) for $[\text{Fe(tz)}_6]^{2+}$,\textsuperscript{18} 4617 cm\(^{-1}\) for $[\text{Fe(bipy)}_3]^{2+}$,\textsuperscript{19} and 5888 cm\(^{-1}\) for $[\text{Fe(terpy)}_2]^{2+}$ CASPT2-calculated values of $\Delta E_{HL}$ are in excellent agreement with the experimental observations that while derivatives of 1 undergo thermal spin-crossover at around 100–200 K,\textsuperscript{84} 2 and 3 remain in the LS state at all temperatures and thus can only be converted to the HS state by excitation with light.\textsuperscript{115} These results suggest that in principle, this multiconfigurational methodology could be widely applied to spin-crossover complexes, although it has also limitations as discussed above. These difficulties might be overcome by the application of an appropriate DFT method; therefore, the assessment of exchange-correlation functionals belonging to different rungs of the Jacob’s ladder has been carried out and is presented below.

The pure GGA-BP86 and meta-GGA TPSS functionals strongly overestimate $\Delta E_{HL}$ for all three Fe(II) complexes, thus they overstabilize the LS state. On the other hand, an opposite behavior is observed for the hybrid B3LYP method: it erroneously favors the HS state in all cases, compared to the spin energetics predicted by the CASPT2
4.4. The LS-HS Splitting Energy $\Delta E_{\text{HL}}$ in Fe(II) Complexes

Table 4.7: DFT and CASPT2-calculated values of $\Delta E_{\text{HL}}$ for $1-3$ (values are given in cm$^{-1}$).

<table>
<thead>
<tr>
<th></th>
<th>[Fe(tz)$_6$]$^{2+}$ (1)</th>
<th>[Fe(bipy)$_3$]$^{2+}$ (2)</th>
<th>[Fe(terpy)$_2$]$^{2+}$ (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ORCA (GTO basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZVP</td>
<td>6675</td>
<td>10364</td>
<td>11335</td>
</tr>
<tr>
<td>RPBE/TZVP</td>
<td>1285</td>
<td>6259</td>
<td>7701</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
<td>$-2775$</td>
<td>4196</td>
<td>6422</td>
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<tr>
<td>OLYP/TZVP</td>
<td>$-3626$</td>
<td>2683</td>
<td>4637</td>
</tr>
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<td>B3LYP/TZVP</td>
<td>$-2160$</td>
<td>445</td>
<td>755</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
<td>189</td>
<td>3076</td>
<td>3447</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
<td>6957</td>
<td>10636</td>
<td>11503</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
<td>2529</td>
<td>5768</td>
<td>6297</td>
</tr>
<tr>
<td><strong>ADF (STO basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP86/TZP</td>
<td>6511</td>
<td>10374</td>
<td>11385</td>
</tr>
<tr>
<td>RPBE/TZP</td>
<td>485</td>
<td>6156</td>
<td>7594</td>
</tr>
<tr>
<td>OPBE/TZP</td>
<td>$-3763$</td>
<td>3890</td>
<td>6140</td>
</tr>
<tr>
<td><strong>MOLCAS (ANO-RCC basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CASPT2</td>
<td>$220^a$</td>
<td>$4617^b$</td>
<td>$5888^c$</td>
</tr>
</tbody>
</table>

$^a$ from ref. 18.
$^b$ from ref. 19.
$^c$ For 3, the CASPT2 value was determined from the minima of the corresponding 2D PES (for details see section 4.7).

For $2$ and $3$, the lower-lying component of the HS state was considered and the Jahn-Teller effect was taken into account at the DFT level of theory.

Method. This failure can be amended by the reduction of the Hartree-Fock exchange from 20% to 15%: the modified B3LYP* functional provides $\Delta E_{\text{HL}}$ values $-189$, $3076$, and $3447$ cm$^{-1}$ for the $1-3$ complexes, respectively—in reasonable agreement with the corresponding CASPT2 results. The performance of this functional and the role of HF exchange is further discussed in the next paragraph. Besides B3LYP*, RPBE and TPSSh also provides reliable results, by delivering rather accurate $\Delta E_{\text{HL}}$ values for all the $1-$
3 systems. Moreover, while OPBE gives the best agreement with CASPT2 results for $[\text{Fe(bipy)}_3]^{2+}$ and $[\text{Fe(terpy)}_2]^{2+}$, it fails to predict the correct LS state for $[\text{Fe(tz)}_6]^{2+}$. Although the accuracy of this DFT method is clearly remarkable for 2 and 3, as also reported by Swart et al.,\textsuperscript{148–150} in this case it provides inferior overall results, compared to those of the best-performing hybrid functionals, e.g., the one of B3LYP*. Finally, we note that $\Delta E_{\text{HL}}$ is practically independent of the type of the applied basis set: GTO and STO spin-state splittings are in agreement.

The above results clearly demonstrate that the correct treatment of the exchange interaction in DFT is essential for the accurate determination of $\Delta E_{\text{HL}}$. In the case of standard GGAs such as BP86, the overstabilization of the LS state is due to the fact that the gradient corrected exchange is still LDA-dominated, which is too low, compared to the exact one.\textsuperscript{169} As discussed in Section 4.3, the RPBE exchange functional includes increased gradient correction, which leads to the stabilization of the HS state, and thus to improved results for spin-state energetics. Therefore, it can be stated that the performance of RPBE is better for energetics, than for geometries, which is in agreement with previous findings.\textsuperscript{156,210,211} Finally, the ambiguous performance of the OPBE method is attributed to the lack of transition metals in the optimization set of the OPTX exchange functional (i.e., this functional has been optimized to the Hartree-Fock energies of 18 first and second row atoms).\textsuperscript{43}

The incorrect preference of the LS configuration can be compensated by mixing Hartree-Fock exchange (HFx) in the expression of the density functional, which stabilizes the HS state with four parallel $d$-electrons according to Hund’s first rule. It is important to point out that this correction is also due to the fact that the self interaction error is reduced in hybrid functionals, compared to those in pure GGA methods.\textsuperscript{154,155} However, the standard 20% HFx introduced in the B3LYP functional is too high for 1–3, and also for several other complexes,\textsuperscript{114,115,141,144,151–153} since the error in $\Delta E_{\text{HL}}$ induced by the GGA exchange is overcompensated. This behavior can be amended by the reduction of HFx to 15%: the modified B3LYP* method of Reiher et al.\textsuperscript{144} provides fairly accurate spin energetics in many cases\textsuperscript{114,115,141,143–147,154,155,157,159,212} including the present ones. Additionally, it was found that B3LYP* performs for thermochemistry of the standard G2
test set\textsuperscript{213,214} and various TM complexes as well as the B3LYP method itself.\textsuperscript{215} However, it is very likely that this is not the functional of choice in all cases, since it performs significantly weaker for the small model Fe(II) compounds [Fe(H\textsubscript{2}O)\textsubscript{6}]\textsuperscript{2+}, [Fe(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+}, and [Fe(NCH)\textsubscript{6}]\textsuperscript{2+}.\textsuperscript{168–170} It is remarkable that all Fe-ligand bonds in these systems are rather ionic, i.e., with relatively low ligand-to-metal $\sigma$-donation.\textsuperscript{175} For these "ionic" complexes, a larger 20–25\% HFx is the optimal choice.\textsuperscript{168–170} However, the 15\% HFx of B3LYP* is quite adequate for covalently bonded Fe compounds, such as 1–3, hence, this functional was selected for testing the TD-DFT approach in calculating the excited state spectra of these compounds and the 2D PESs of [Fe(terpy)\textsubscript{2}]\textsuperscript{2+}.

\section*{4.5 Jahn-Teller Effect in [Fe(bipy)\textsubscript{3}]\textsuperscript{2+} and [Fe(terpy)\textsubscript{2}]\textsuperscript{2+}}

It is well known that degenerate electronic states of nonlinear molecules are subject to the Jahn-Teller (JT) effect. Since this is the case for the HS states of 2 and 3, the DFT-computed structures are indeed slightly distorted from the full D\textsubscript{3} and D\textsubscript{2d} point group symmetries, respectively. These distortions imply changes of 0.01–0.02 \textdegree\! in the Fe-N bond lengths and ca. 4$^\circ$ in the N-Fe-N* bending angle for complex 2 (where N and N* are the N atoms of two neighboring bipy units, see Figure 4.2), and $\beta = 4^\circ$ twisting of the planes of the terpyridine ligands for complex 3. Moreover, these structural changes are accompanied by 0.08–0.11 eV (600–900 cm$^{-1}$) energy lowering of the 5$^E$ state\textsuperscript{c} calculated at the DFT level of theory (Table 4.8). In the case of 2, this lowering has a considerable effect on $\Delta E_{HL}$. On the other hand, for 3, the energy lowering of the 5$^E$ state does not imply a relevant reduction of the spin-splitting energy, since the JT effect shifts the 5$^E$ barely below the 5$^2B_2$; thus $\Delta E_{HL}$ remains almost the same, as also discussed in Section 4.7. Note that the B3LYP* potentials and PESs presented in the following sections were calculated without constraints on the symmetry (with the ORCA code); therefore, the JT effect was taken into account. The JT lowering of the 5$^E$ energy was also estimated by

\footnote{Strictly speaking, after the consideration of the JT effect, one should not keep the same notation for the split electronic states. Yet for simplicity and easier readability, we retain the 5$^E$ nomination, used often in the literature.}
Table 4.8: DFT and CASPT2-calculated values of the Jahn-Teller lowering of the $^5E$ state for $[\text{Fe}(\text{bipy})_3]^{2+}$ and $[\text{Fe}(\text{terpy})_2]^{2+}$ (values are given in cm$^{-1}$).

<table>
<thead>
<tr>
<th>Method</th>
<th>$[\text{Fe}(\text{bipy})_3]^{2+}$ (2)</th>
<th>$[\text{Fe}(\text{terpy})_2]^{2+}$ (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP86/TZP$^a$</td>
<td>639</td>
<td>769</td>
</tr>
<tr>
<td>RPBE/TZP$^a$</td>
<td>763</td>
<td>909</td>
</tr>
<tr>
<td>OPBE/TZP$^a$</td>
<td>713</td>
<td>767</td>
</tr>
<tr>
<td>CASPT2$^b$</td>
<td>846</td>
<td>$-72; 11$</td>
</tr>
</tbody>
</table>

$^a$ calculated with the ADF code (STO basis) by optimizing the corresponding structures with the full $D_{2d}/D_3$ and $C_2$ symmetry.

$^b$ calculated with the MOLCAS program package (ANO-RCC basis) at DFT-optimized $D_{2d}/D_3$ and $C_2$ structures. The second value for 3 (given after the semicolon) was obtained at $\beta = 0.4^\circ$; for details see Section 4.7 and Fig. 4.13.

CASPT2, based on geometries optimized by DFT with higher ($D_3$ or $D_{2d}$) and lower ($C_2$) symmetries. For 2, in agreement with the DFT results, ca. 0.1 eV (800 cm$^{-1}$) lowering was obtained, while for 3, negligible energy differences were observed (Table 4.8). In fact, for the $C_2$-optimized geometry, the energy was elevated by 72 cm$^{-1}$, compared to the undistorted case, while a CASPT2 energy scan along the $\beta$ mode revealed that the minimum of the $^5E$ PES was found at $\beta = 0.4^\circ$, for which a JT lowering of 11 cm$^{-1}$ was obtained (see Section 4.7 and Fig. 4.13). The above results are in agreement with the fact that the FeN$_6$ core in the corresponding DFT-optimized $^5E$ structures is more distorted from the higher symmetries for 2, than for 3. Note that in the computations no JT effect is observed for $[\text{Fe}(\text{tz})_6]^{2+}$, which is due to the lack of degenerate irreducible representation(s) in the $C_1$ point group.

Finally, it is important to discuss the vibrational frequency analysis of the studied complexes. While no imaginary frequency was found for all LS and HS structures of 1 and 2, and also for those of the LS and $^5E$ of 3, the $^5B_2$ structure of the latter compound corresponds to a transition state, since two (degenerate) imaginary frequencies
4.6 Potential Energy Curves of the Metal-Centered Excited States of the Studied Fe Complexes

were observed (−74 cm⁻¹ was obtained at the B3LYP*/TZVP level), which correspond to mixed Fe-N stretching/interligand bending modes. However, test single point B3LYP* computations along these modes yield negligible lowering (below 10 cm⁻¹), compared to the energy of the equilibrium 5B₂ geometry, therefore, this structure can be practically considered as the minimum of the PES.

4.6 Potential Energy Curves of the Metal-Centered Excited States of the Studied Fe Complexes

The detailed knowledge of MC excited states is essential for the understanding of spin-state transitions. At equilibrium positions, some of the d-d transitions can be measured by optical absorption spectroscopy, although in general they are suppressed by selection rules. Therefore, it is necessary to obtain accurate estimations for the d-d excitation energies, as the excited state potentials are supposed to play an important role in the mechanism of spin transitions. The spin transition process was recently investigated for a few Fe(II) complexes (including 1 and 2) by the calculation of potential energy curves connecting the different excited states at the CASPT2 level, which proved to be a suitable method for the description of MC excited states, despite its high computational cost. The performance of the readily available TD-DFT method in the prediction of PESs has not yet been reported (the TD-DFT PESs of Ru(II) complexes have been reported in parallel to the present results published in our paper P1), only vertical excitation energies were computed for [Fe(ptz)₆]²⁺, [Fe(bipy)₃]²⁺ and [Fe(terpy)₂]²⁺, and also for [Fe(2-picolyamine)₃]²⁺ and [Fe(phen)₃]²⁺ (phen = 1,10-phenanthroline). In this section, the excited states of the studied complexes, above the coordinate(s) relevant to the spin transition are explored with TD-DFT. For this, the B3LYP* functional is selected, which gave reliable results for the energetics of 1–3, as discussed in Section 4.4. Below, the performances of the TD-B3LYP* and CASPT2 methods are compared for the studied Fe(II) complexes.
First, the TD-B3LYP* potential energy curves for 1 and 2 are presented, where the spin transition can be described along a SCC. These energy curves calculated along the Fe-N breathing mode are in good agreement with the previously published CASPT2 PESs\(^{18,19}\) (Figures 4.5 and 4.6). Moreover, in the case of 1, the TD-B3LYP* calculated vertical excitation energies at equilibrium positions match the CASPT2-calculated values,\(^ {18}\) and only show ca. 0.1–0.2 eV deviations from the experimental results\(^ {10}\) (Table 4.9). The maximum deviations in the relative positions of crossing points and in the minimum energies from the corresponding CASPT2 values are 0.05 Å and 0.14 eV, respectively, which are small compared to the relevant bond length and energy scales. Although in the case of complex 2, slightly larger variations are observed in the TD-DFT and CASPT2 potentials (the CASPT2 relative crossing points are reproduced up to 0.08 Å, while the energy values corresponding to the minima of the individual states are underestimated by ca. 0.15–0.30 eV), the performance of TD-B3LYP* is still acceptable, since it reproduces all crossing points and minimum energies of the individual states with reasonable accuracy. Note that all TD-DFT curves are shifted by 0.08 Å towards larger Fe-N bond lengths, compared to the CASPT2 results, which is due to the tendency of CASPT2 to systematically underestimate the Fe-N bond lengths, as discussed previously in Section 4.3.

The good agreements above also suggest that the potentials and the \(\Delta E_{H_{\text{L}}L}\) value of 1 do not depend on the different orientations of the tetrazole ligands, as mentioned in Section 4.3. This is confirmed in Figure 4.7, where the comparison between TD-DFT curves obtained on orthogonal and DFT-optimized geometries (in which the ligand planes are twisted by ca. 45 degrees) is shown.

Despite the rather good description of most of the excited states, complications arose for the calculation of the triplet states with TD-DFT. The lowest-lying triplet states of 1 and 2 presented in Figs. 4.5, 4.6, and 4.7 were computed using a triplet reference state (for details see the computational section). These TD-B3LYP* calculated curves are in good agreement with the reported CASPT2 results for 1.\(^ {18}\) Note that in TD-DFT calculations of optical spectra of transition metal compounds, triplet states are not
4.6. Potential Energy Curves of the Metal-Centered Excited States of the Studied Fe Complexes

Figure 4.5: (a) TD-B3LYP*/TZVP and (b) CASPT2-calculated potential energy curves for \([\text{Fe(tz)}_6]^{2+}\). Note that the points corresponding to CASPT2 energies calculated at geometries with different \(r_{\text{Fe-N}}\) values are not available in ref. 18, therefore, only the energy curves are shown. The zero value of the energy scale is set to the minimum of the \(^1\text{A}_1\) potential. In the case of the TD-DFT calculation, the \(^3\text{T}_1\) state was computed by a triplet SCF calculation, while the \(^3\text{T}_2\) state was calculated with the TD-DFT method, using the \(^3\text{T}_1\) reference state, as described in the text.

Figure 4.6: (a) TD-B3LYP*/TZVP and (b) CASPT2-calculated potential energy curves for \([\text{Fe(bipy)}_3]^{2+}\). Note that the points corresponding to CASPT2 energies calculated at geometries with different \(r_{\text{Fe-N}}\) values are not available in ref. 19, therefore, only the energy curves are shown. The zero value of the energy scale is set to the minimum of the \(^1\text{A}_1\) potential. In the case of the TD-DFT calculation, the \(^3\text{T}_1\) state was computed by a triplet SCF calculation, while the \(^3\text{T}_2\) state was calculated with the TD-DFT method, using the \(^3\text{T}_1\) reference state, as described in the text.

The results obtained by these two TD-DFT methods applying a singlet or triplet reference computed from a triplet reference state, but from a singlet reference determinant.\(^{221,222}\)
Table 4.9: Comparison of experimental, CASPT2, and TD-B3LYP* calculated values of vertical excitation energies at equilibrium positions for [Fe(tz)₆]²⁺ (values are given in eV).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Exp.ᵃ</th>
<th>CASPT2ᵇ</th>
<th>TD-B3LYP*ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹A₁ → ¹T₁</td>
<td>2.26</td>
<td>2.17</td>
<td>2.15</td>
</tr>
<tr>
<td>¹A₁ → ¹T₂</td>
<td>3.27</td>
<td>3.38</td>
<td>3.19</td>
</tr>
<tr>
<td>⁵T₂ → ⁵E</td>
<td>1.51</td>
<td>1.57</td>
<td>1.45</td>
</tr>
<tr>
<td>¹A₁ → ³T₁</td>
<td>1.28</td>
<td>1.19</td>
<td>1.05 (1.39)ᵈ</td>
</tr>
<tr>
<td>¹A₁ → ³T₂</td>
<td>1.77</td>
<td>1.77</td>
<td>1.65 (1.65)ᵈ</td>
</tr>
</tbody>
</table>

ᵃ from ref. 10.
ᵇ from ref. 18.
ᶜ this work.
ᵈ for the triplet transitions, the first TD-B3LYP* value was obtained with a triplet reference, while values given in parentheses were calculated applying a singlet reference state.

Figure 4.7: TD-B3LYP*/TZVP potential energy curves for [Fe(tz)₆]²⁺ calculated on DFT-optimized (empty symbols) and orthogonal (filled symbols) geometries. The zero value of the energy scale is set to the minimum of the ¹A₁ potential.

for the calculation of triplet states for 1 are compared in Fig. 4.8. Computing the triplet states from a singlet reference, the excitation energies at the ¹A₁ minimum are well
reproduced (Table 4.9), but the positions of the $^1\text{A}_1/^3\text{T}_1$ and $^1\text{A}_1/^3\text{T}_2$ crossing points relative to the LS equilibrium position do not agree with the CASPT2 results (see Table A2 in the Appendix). On the other hand, in the case of the TD-DFT calculation with a triplet reference state, the correct number of states is not reproduced (Figure 4.8). While both CASPT2-calculated triplet states, $^3\text{T}_1$ and $^3\text{T}_2$ show the approximate threefold degeneracy,\textsuperscript{18} provided that at least 6 roots are included in the calculation, the TD-DFT procedure applying a triplet reference state describes the $^3\text{T}_1$ state only with a single determinant, thus not more than 4 of the 6 states are accessible. This is obviously not the case for the triplet TD-DFT calculation invoked on the singlet reference state, for which all the 6 triplet states are obtained. The above difficulties do not concern the singlet and quintet states. While all calculated singlet and quintet states can be generated with a single excitation from the corresponding ground states, this is not the case for the triplet states: certain triplet states could have only been derived by a double excitation from the lowest-lying triplet state (note the two missing configurations in Figure 4.8b). These electronic states with double excitation character are not treated appropriately within the applied linear response TD-DFT approach.\textsuperscript{23}

Figure 4.8: TD-B3LYP*/TZVP calculated triplet states for 1 when invoking the corresponding excitations on a (a) singlet and (b) triplet reference state. The electron configurations corresponding to the individual triplet states are schematically represented in an octahedral ligand field (note that for the sake of simplicity in case of (b) we do not show spin-polarized energy levels). For a better contrast, the $^1\text{A}_1$ ground state potential is also shown. The zero value of the energy scale is set to the minimum of the $^1\text{A}_1$ potential.
Finally, the results obtained for the MC excited states of \([\text{Fe(terpy)}_2]^{2+}\) is discussed. As previously shown, the structural variations at the spin transition in this iron complex cannot be described using a SCC alone, which is most often the breathing mode: the inclusion of a bending mode of the terpyridine ligands — described by the change in the \(\varphi_{NNN}\) angle — is also necessary. In consequence, PESs for 3 should be calculated above the plane spanned by the \(r_{\text{Fe-Nax}}\) and \(\varphi_{NNN}\) coordinates. Such surfaces for the lowest singlet, triplet, and quintet states will be presented in the next section. However, the numerous set of MC excited states are best compared along one dimension that connects the LS and HS minima. Therefore, the potential energies for 3 along this line have been evaluated, in order to get comparable results to those of 1 and 2. TD-DFT and CASPT2-calculated curves are presented in Fig. 4.9.

![Figure 4.9: (a) TD-B3LYP* and (b) CASPT2-calculated PESs for \([\text{Fe(terpy)}_2]^{2+}\) along a combined coordinate, which connects the LS and HS minima (in the case of (a), the triplet states were computed using a triplet reference ground state). The notation for each calculated state refers to the \(D_{2d}\) point group symmetry. The zero value of the energy scale is set to the minimum of the \(1\text{A}_1\) potential.](image)

A reasonably good agreement is observed between TD-B3LYP* and CASPT2-computed curves, even if — similarly to the case of 2 — larger differences were found in the TD-DFT computed relative energies of the individual states, compared to CASPT2 values, than for 1. On the other hand, it is clear from Fig. 4.9 that the calculated number of MC triplet states differs for the two applied methods. This has been already observed
in the calculation of triplet states for 1, as discussed above. However, this effect is more apparent for 3 due to the strong axial distortion of the FeN$_6$ core. This distortion results in a larger splitting of the triplet states, which could not be properly described by the applied TD-DFT approach using a triplet reference. Nevertheless, the singlet and quintet states and the remaining triplets are qualitatively well reproduced by the TD-B3LYP* method for 3. Therefore, the conclusion drawn here is that while the TD-B3LYP* method is a very economic alternative to multiconfigurational approaches for the calculation of singlet and quintet MC excited states for the studied complexes, it requires more care for the computation of triplet states.

4.7 Detailed Investigation of The Electronic Structure of [Fe(terpy)$_2$]$^{2+}$ at the Spin-State Transition

As noted previously, the spin transition in 3 cannot be described along a single Fe-N coordinate: the inclusion of the bending of the terpy ligands is also required, which can be characterized by the NNN angle of the three pyridine rings ($\varphi_{\text{NNN}}$). Therefore, the PESs were computed above the plane spanned by $r_{\text{Fe-Nax}}$ and $\varphi_{\text{NNN}}$ for the lowest singlet, triplet, and quintet electronic states with the CASPT2 and B3LYP* methods, which are shown in Fig. 4.10. For DFT, a relaxed surface, whereas for CASPT2 a non-relaxed PES was computed, because geometry optimizations are computationally too demanding for this latter method. For CASPT2, this potential scan was also used to determine the $r_{\text{Fe-Nax}}$ and $\varphi_{\text{NNN}}$ parameters for the LS and HS minima and the $\Delta E_{\text{HL}}$ value, which were discussed in Sections 4.3 and 4.4. As seen in the figure, the description of the LS$\leftrightarrow$HS state transition indeed requires both the $r_{\text{Fe-Nax}}$ and $\varphi_{\text{NNN}}$. It is interesting to note that reaching the triplet $^3\text{A}_2$ state takes place to a good approximation along only one of these modes: via opening the NNN angle when arriving from the singlet state, or via the bond length shortening from the quintet state. It holds for both the DFT and CASPT2 PESs.
that while the calculated values of the NNN angle for the triplet and quintet states are fairly similar, the axial Fe-N distances of the triplet state show resemblance to that of the singlet state.

**Figure 4.10:** (a) B3LYP* and (b) CASPT2-calculated PESs for the lowest-lying singlet, triplet and quintet states. The zero value of the energy scale is set to the minimum of the $^1A_1$ surface. The blue lines represent the combined coordinates for the calculation of 1D potentials. CASPT2 and DFT-calculated energies were splined with a 2D cubic interpolation routine. Contour lines were drawn at the 2, 5, 10, 20 and 50 meV energy values from the minimum of the corresponding PES.

The interpretation of the above results requires the analysis of the Kohn-Sham orbitals of $[\text{Fe(terpy)}_2]^2+$. The Fe-3d electronic structure of the $^1A_1$, $^5B_2$, and $^5E$ states is shown in Figure 4.11. An important feature of complex 3 is that the strong axial distortion not only splits the molecular orbitals with dominant $d_{xz}$, $d_{yz}$, and $d_{xy}$ character, but also the Fe-N antibonding, $e_g^*$-like orbitals. As can be seen in Fig. 4.11, these latter MOs with main $d_{x^2-y^2}$ and $d_{z^2}$ atomic contribution possess strong Fe-N$_{eq}$ and Fe-N$_{ax}$ antibonding character, respectively. Therefore, it is clear that while the $r_{\text{Fe-Nax}}$ mode is connected to the occupation of the $d_{z^2}$-like orbital, $\varphi_{\text{NNN}}$ is associated with the filling of the $d_{x^2-y^2}$-type MO. These split, antibonding orbitals are both occupied with an electron in the $^5B_2$ and $^5E$ HS states, which leads to an increase in $r_{\text{Fe-Nax}}$ and $\varphi_{\text{NNN}}$, compared to the values corresponding to the LS state. Therefore, the departure from the SCC model is attributed to the occupation of these split, $e_g^*$-like MOs. These results also provide a
4.7. Detailed Investigation of The Electronic Structure of [Fe(terpy)$_2$]$^{2+}$ at the Spin-State Transition

clear explanation for the structural variations observed above for the $^3A_2$ state: while the occupation of the lower-lying MO with $d_{x^2-y^2}$ character leads to the opening of the NNN angle, the Fe-N$_{ax}$ distance practically remains unchanged, compared to the LS one, since the higher-lying orbital with $d_{z^2}$ main contribution is still unoccupied in the triplet $^3A_2$ state.

Figure 4.11: Schematic representation of the electronic configuration and 3D illustration of the Kohn-Sham $e_g^*$ orbitals of the $^1A_1$ state of the [Fe(terpy)$_2$]$^{2+}$ complex. The electronic configuration of the $^5B_2$ and $^5E$ states is also shown. The yellow arrows represent the $r_{Fe-N_{ax}}$ and $\varphi_{NNN}$ modes. The B3LYP*/TZVP orbital energies of the MOs with Fe-3$d$ character are given.

Finally, the lowest-lying quintet states of [Fe(terpy)$_2$]$^{2+}$ are highlighted, since their properties are decisive for the most relevant characteristics of the molecular switching. As discussed before in Section 4.3, lowering the symmetry to $D_{2d}$ splits the $^5T_{2g}$ ($O_h$) state into the $^5B_2$ and $^5E$ quintet states in 3. We have investigated the structural and energy
Theoretical Investigation of the LS$\leftrightarrow$HS State Transition in Fe(II) Complexes

differences of these two states, and found quite small differences in the $r_{\text{Fe-Nax}}$ and $\varphi_{\text{NNN}}$ values between the minima of the two quintet states provided by the DFT and CASPT2 methods. This can be quantified as 0.04–0.05 Å and 0.02 Å difference in the axial Fe-N bond length for the B3LYP* and CASPT2 method, respectively. Moreover, while 0.5 degrees of difference is seen in the B3LYP*-calculated $\varphi_{\text{NNN}}$ value between the two quintet minima, only 0.2 degrees of variation is predicted by the CASPT2 method. It is important to point out that the main structural variations between the two quintet states show itself in the slightly lower $r_{\text{Fe-Nax}}$ values for the $^5E$, than for the $^5B_2$. This is attributed to the weak $\pi$-backbonding connected to the Fe-N$_{\text{ax}}$ mode, which is operative in the $^5E$ state due to the occupation of the weakly $\pi$-bonding Fe-3$d$ molecular orbitals with $z$ component ($d_{xz}$ and $d_{yz}$, see Fig. 4.12) with a beta electron. This $\pi$-bonding interaction slightly enhances the Fe-N$_{\text{ax}}$ bond strength, and therefore leads to the shortening of this bond. This effect is absent in the $^5B_2$, since instead the orbitals with $d_{xz}$ or $d_{yz}$ contribution, the one with nonbonding $d_{xy}$ character is doubly occupied, which leads to slightly larger $r_{\text{Fe-Nax}}$ values, compared to those of the $^5E$. The adequacy of this interpretation is confirmed by the 0.387 and 0.329 DFT-calculated values of the Mayer bond order (a powerful parameter quantifying the strength of chemical bonds) corresponding to the Fe-N$_{\text{ax}}$ bonds of the $^5E$ and $^5B_2$ states, respectively. The difference in the $\pi$-bonding character of the t$_{2g}$-like $d_{xz}$, $d_{yz}$ and $d_{xy}$ orbitals in 3 is explained by the departure from octahedral symmetry in this axially distorted complex.

Furthermore, the relative stability of the $^5E$ and $^5B_2$ states has been evaluated by optimizing the corresponding HS structures with various density functionals and compared their corresponding energy to the CASPT2 value in Table 4.10. As shown, all methods suggest that these states are energetically quasi-degenerate, although the sign of the relative energies varies. While pure functionals and CASPT2 favors the $^5E$ state, the hybrids stabilize the $^5B_2$ HS state. Moreover, GGA functionals combined with the STO-TZP basis set using the D$_{2d}$ point group symmetry predict a higher energy difference, clearly overstabilizing the $^5B_2$ state compared to the CASPT2 result. Although this large stability of the $^5B_2$ state over the $^5E$ one at D$_{2d}$ symmetry has also been reported
4.7. Detailed Investigation of The Electronic Structure of [Fe(terpy)$_2$]$^{2+}$ at the Spin-State Transition

**Figure 4.12:** Electronic configuration of the split $t_{2g}$ subshell for the $^5B_2$ and $^5E$ states of [Fe(terpy)$_2$]$^{2+}$. The 3D representations of the Kohn-Sham orbitals with nonbonding $d_{xy}$ (left) and $\pi$-antibonding $d_{xz}$ (right) character are shown for the $^5B_2$ and $^5E$ states, respectively. Note that for the sake of simplicity, only one component of the degenerate pair of the MOs with $d_{xz}$, $d_{yz}$ characters is shown.

in a previous DFT study,$^{115}$ note that in this case the Jahn-Teller effect is disregarded. This is confirmed by the fact that GGA methods with $C_2$ symmetry constraint lower the energy of the $^5E$ state resulting in energy differences similar to those obtained with the GTO-TZVP basis set without using any symmetry constraint (see Table 4.10). It is important to note that this ca. 0.1 eV energy lowering is accompanied by a slight twisting (ca. $\beta = 4^\circ$) of the planes of the terpyridine rings, which is due to the Jahn-Teller effect, as discussed in Section 4.5. On the other hand, the minimum of the CASPT2 $^5E$ PES is found when the ligand planes are twisted by only $\beta = 0.4^\circ$, which lowers the CASPT2 energy by 11 cm$^{-1}$, compared to the undistorted case (Figure 4.13). (Larger distortions elevate the energy of the $^5E$ state; e.g., ca. 6 and 550 cm$^{-1}$ energy differences are observed for 1 and 4 degrees of twisting, respectively.)

The CASPT2 energetics thus indicate the relative stability of the $^5E$ state over the $^5B_2$ state for 3, in good agreement with previous$^{223}$ and present (Section 4.3) findings.
obtained for the structure of the HS state. The lifetime of the quintet state is mainly determined by the $\Delta r_{HL}$ and $\Delta E_{HL}$ values in most spin-transition complexes. In the case of the $^5E$ state of 3, the DFT-calculated $\Delta r_{HL}(\text{Fe-N}_\text{ax})$ value is 0.21–0.23 Å, which is close to 0.20 Å, the typical value for Fe(II) SCO compounds. On the other hand, the variation of this bond length for the $^5B_2$ state is 0.25–0.29 Å, thus showing a larger deviation from 0.20 Å. As discussed in Section 4.1, larger structural variations can slow down the relaxation at low temperatures by increasing the barrier between the LS and HS states.\textsuperscript{115} However, this alone is unlikely to account for the extremely high lifetime of the HS state for $[\text{Fe(terpy)}_2]^{2+}$ observed in loose matrices;\textsuperscript{115,128} moreover, $^5E$ has been identified as the lower-lying component of the HS state by CASPT2. In terms of the SCC model, the energetics would indicate a shorter lifetime for 3 through the inverse energy gap law,\textsuperscript{115} as all density functionals predict slightly larger values for the LS-HS state splitting energies for 3 than for 2. Furthermore, the comparison of the 4617 cm$^{-1}$ CASPT2 $\Delta E_{HL}$ value for 2, with the 5888 cm$^{-1}$ value for 3, also supports this statement.
Table 4.10: DFT and CASPT2-calculated $\Delta E = E(^5B_2) - E(^3E)$ energy differences for the HS states of [Fe(terpy)$_2$]$^{2+}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta E$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORCA (GTO basis)</td>
<td></td>
</tr>
<tr>
<td>BP86/TZVP</td>
<td>205</td>
</tr>
<tr>
<td>RPBE/TZVP</td>
<td>47</td>
</tr>
<tr>
<td>OPBE/TZVP</td>
<td>140</td>
</tr>
<tr>
<td>OLYP/TZVP</td>
<td>14</td>
</tr>
<tr>
<td>B3LYP/TZVP</td>
<td>$-198$</td>
</tr>
<tr>
<td>B3LYP*/TZVP</td>
<td>$-110$</td>
</tr>
<tr>
<td>TPSS/TZVP</td>
<td>61</td>
</tr>
<tr>
<td>TPSSh/TZVP</td>
<td>$-80$</td>
</tr>
<tr>
<td>ADF$^a$ (STO basis) with symmetry $D_{2d}$; $C_2$</td>
<td></td>
</tr>
<tr>
<td>BP86/TZP</td>
<td>$-677; 92$</td>
</tr>
<tr>
<td>RPBE/TZP</td>
<td>$-964; -55$</td>
</tr>
<tr>
<td>OPBE/TZP</td>
<td>$-708; 59$</td>
</tr>
<tr>
<td>MOLCAS (ANO-RCC basis)</td>
<td></td>
</tr>
<tr>
<td>CASPT2$^b$</td>
<td>329; 340</td>
</tr>
</tbody>
</table>

$^a$ In case of ADF results, the two presented values were obtained using the $D_{2d}$ and $C_2$ point group symmetries, respectively.

$^b$ The CASPT2 values were calculated on a symmetric, $D_{2d}$ geometry and on a slightly distorted structure, (where the ligand planes were twisted by ca. 0.4 degrees), respectively.

DFT values were computed by optimizing the quintet structures of 3, while CASPT2 values were determined from the corresponding PESs.

Therefore, this straightforward approach is not applicable for 3, as was also proposed by Hauser et al.$^{115}$ A more appropriate configuration coordinate for 3 is made up by the combination of the Fe-N$_{ax}$ stretching mode and the bending mode of the ligands. This two-mode model can account for the longer lifetime of the light-excited quintet states for 3 (2.5 ns), when compared to the one of 2 (665 ps), measured in solution under ambient conditions.
conditions.\textsuperscript{134,204,224} It can be thus concluded that the light-induced spin-state transitions in 2 and 3 in solutions are relatively well understood, but the reason for the extremely high lifetimes of the HS state of [Fe(terpy)$_2$]$^{2+}$ observed in solid state measurements still remains unknown.

4.8 Conclusion

In this chapter, DFT, TD-DFT, and CASPT2 calculations were carried out to investigate the electronic structure of Fe(II) coordination compounds at LS$\leftrightarrow$HS state transitions. The conclusions drawn from the present results can be grouped in the following four points:

1. DFT is better suited for the determination of the LS and HS molecular structures of the studied complexes, than CASPT2; however, both techniques provide equally good estimates for the variation of the Fe-N coordinate bond lengths ($\Delta r_{HL}$) at the spin-state transition process. The weaker performance of CASPT2 is seen in its tendency to underestimate the Fe-N bond lengths, which effect can be either due to the basis set superposition error or the lack of geometrical relaxation. The BP86, TPSS and TPSSh functionals were found to give geometries in the best agreement with the experimental ones. Based on the structures delivered by these DFT methods, the experimentally detected HS state of [Fe(terpy)$_2$]$^{2+}$ is assigned to the $^5E$ component.

2. The $\Delta E_{HL}$ spin-state splitting energy for all studied complexes was also computed with various density functionals, and for [Fe(terpy)$_2$]$^{2+}$, also with the CASPT2 method. The RPBE, B3LYP*, and TPSSh functionals provided reasonable results, even if the quantitative precision of the CASPT2 method could not be reached. Nevertheless, the B3LYP* functional gave rather reliable estimates for the spin-state splitting energies of all Fe(II) complexes investigated in this study. This result suggests that the 15% Hartee-Fock exchange included in B3LYP* is adequate for the covalently bonded Fe compounds, such as 1–3. It was found that the JT effect has to be taken into account for the $^5E$ states of 2 and 3, since it lowers their energy by ca. 0.1 eV, as calculated at the DFT level of theory. A similar JT lowering value was obtained with the CASPT2 method for
2; however, for 3, only a very small effect was observed.

3. The CASPT2-calculated 1D potential energy surfaces corresponding to metal-centered electronic states of 1–3 were reproduced by the TD-B3LYP* method. In the case of 1, the agreement of TD-DFT and CASPT2 relative energies was particularly excellent. However, the TD-DFT procedure using the triplet reference state did not provide the correct number of triplet states. We reported that this problem can be avoided by starting the triplet TD-DFT calculation from a singlet reference determinant; however, the calculation for certain triplet states is less accurate, in such cases. The results suggest that the TD-B3LYP* method can be an acceptable and economic alternative to multi-configurational approaches for the calculation of MC excited states in Fe(II) complexes, although care should be taken to verify the results for all spin states.

4. Finally, the two-dimensional PESs for the lowest-lying singlet, triplet, and quintet states of [Fe(terpy)$_2$]$^{2+}$ were evaluated along the $r_{Fe-Nax}$ and $\varphi_{NNN}$ configuration coordinates with both DFT and CASPT2 methods to contribute to the better understanding of the spin-state transition and relaxation processes. DFT and CASPT2-calculated energy surfaces of 3 revealed that the minimum of the $^3A_2$ state lies far out from the line connecting the LS and HS states: only $\varphi_{NNN}$ shows significant changes when going from the lowest-lying singlet to the triplet state. In contrast, a transition between the triplet and quintet states does not change this angle, but it requires a large variation of $r_{Fe-Nax}$. The analysis of the corresponding Kohn-Sham orbitals with Fe-3$d$ character revealed that these observations are due to the occupation of the split, antibonding MOs with Fe-N$_{ax}$ and Fe-N$_{eq}$ antibonding character. Furthermore, the CASPT2 results indicate that the $^5E$ HS state is energetically more favorable than the $^5B_2$ one by 340 cm$^{-1}$. Both experimental and computational results suggest that while the longer lifetime of the HS state of 3, compared to that of 2 under ambient conditions, can be attributed to the breakdown of the single configuration mode model, its anomalous behavior at low temperatures requires a more elaborate explanation.
Chapter 5

Density Functional Theory

Prediction of Mössbauer Parameters
of Iron-Containing Molecules

5.1 Background

Mössbauer spectroscopy\textsuperscript{81,225–227} (MS, and its synchrotron radiation based
derivatives\textsuperscript{228–234}) is a very powerful experimental tool in different fields of chemistry,
materials science and physics, as this technique can obtain invaluable information on
the local electronic structure, symmetry and magnetic properties. Although it can be
applied to more than 40 kinds of nuclides, the properties of $^{57}$Fe are by far the best
suited for MS. Therefore, most experiments focus on the measurement of iron. Since
the demonstration of the Mössbauer-effect,\textsuperscript{225} thousands of iron-bearing systems have
been investigated including simple inorganic salts,\textsuperscript{226,235,236} complexes with chelating lig-
ands,\textsuperscript{81,226,227,235,237} organoiron\textsuperscript{226,227,235} and intermetallic compounds,\textsuperscript{226,235} alloys,\textsuperscript{226,235}
magnetic thin films,\textsuperscript{238–240} multilayers,\textsuperscript{241–243} biologically important heme- and ferropro-
5.1. Background

teins$^{226,235,237}$ and so on. As mentioned in Section 4.1, Mössbauer spectroscopy is a well-suited and frequently applied technique for the investigation of Fe(II) spin crossover, therefore, it has a special importance in the characterization of the LS and HS electronic states of switchable Fe complexes.

The interpretation of Mössbauer spectra is not straightforward, and the support of theory is essential for extracting all the relevant physical/chemical information from the measured data. Furthermore, a suitable method providing a good agreement between experiment and theory can lead to thorough understanding and even reliable prediction of spectroscopic properties. Among state-of-the-art quantum chemical methods, presently DFT is the most frequently used technique for the calculation of spectroscopic parameters of Fe complexes, due to its relatively high accuracy at a moderate computational cost. However, as discussed in Section 2.3.3, this technique utilizes approximate exchange-correlation functionals which can lead to contradictory results. A careful exploration of the application of the functionals to the studied problem is, therefore, crucial to the successful application of DFT. Nevertheless, this approach has been successfully used for the calculation of $^{57}$Fe Mössbauer parameters by several research groups.

The literature of these calculations is substantial; in what follows a few relevant works are listed from the last 15 years. First of all, band structure DFT calculations have been successful to compute the $^{57}$Fe Mössbauer parameters in solids; $^{244,245}$ however, the main scope of the thesis is to describe molecular systems. E. Oldfield et al. calculated the isomer shifts ($\delta$) and quadrupole splittings ($\Delta E_Q$) of numerous iron-containing compounds including organometallic molecules, $^{246}$ protein model systems, $^{246-251}$ two- and three-coordinated $^{252}$ Fe(II) and spin-crossover complexes. $^{253}$ Several researchers including L. Noodleman and co-workers applied DFT to compute the Mössbauer properties of the active and intermediate sites of biologically important proteins. $^{254-267}$ The Mössbauer spectral properties of high-valent Fe complexes were also computed with DFT. $^{268-272}$ In all these previous efforts a good overall performance of DFT methods was achieved in the estimation of the Mössbauer parameters, even when different selected classes of iron complexes were considered. $^{32,258,273-279}$ In particular, important achievements were reported
Chapter 5. DFT Prediction of Mössbauer Parameters of Iron-Containing Molecules

by R. Friesner et al., who investigated the influence of the applied density functionals and geometries on the computed Mössbauer parameters for a large set of Fe complexes. However, in this and also in several other works, DFT failed for certain systems, leading to large deviations from the experimental values, particularly for the quadrupole splitting parameter. Furthermore, it is not yet clear which computational method (i.e., density functional, basis set, inclusion of solvent effects, etc.) is to be applied in case of an arbitrarily selected Fe complex. The present chapter aims to address these issues by investigating the applicability of various density functional techniques to a very extended and diverse set of iron complexes. The performance of the DFT approach is also tested in some chemically relevant issues (isomerism, transformations, etc.). The motivation of this chapter is to provide benchmarks, as well as a recipe for predictive calculations, and show how problematic cases can be recognized and treated.

5.2 Computational Details

The ORCA2.8 program package is a suitable software for the geometry optimizations and the calculation of isomer shifts and quadrupole splittings of the investigated iron compounds. The program uses GTOs for the construction of molecular orbitals. In order to study the influence of the type of the primitive basis set (GTOs or STOs) on the computed Mössbauer parameters as well as to treat the electronically degenerate states of certain special Fe(II) complexes, we also utilized the ADF2012.01 code.

5.2.1 ORCA Calculations

The geometries of all investigated Fe complexes were fully optimized at the BP86/TZVP level of theory. This method provided accurate structures for previously studied transition metal compounds. The electron density and the electric field gradient (EFG) tensor at the $^{57}$Fe nucleus were computed with the RPBE, OLYP, B3LYP, B3LYP*, TPSS, and TPSSH XC functionals at the BP86-optimized geometries. These functionals have been frequently used before to calculate Mössbauer
5.2. Computational Details

parameters\textsuperscript{32,246–281} and/or other important properties (e.g., spin-state energy splittings,\textsuperscript{114,115,141,143,223} as also applied in Section 4.4) of iron complexes. Note that DFT-optimized geometries, which are good approximations to the experimental structure, have been successfully applied previously in the accurate computation of Mössbauer parameters using different density functionals.\textsuperscript{32,246,275,277,278} The computed electron densities and EFGs were used to evaluate the isomer shifts and quadrupole splittings, as described in Sections 5.6 and 5.7, respectively. It is also mentioned that counterions and solvent molecules were not included in the calculations, as previous results suggest that they have only a minor effect on these quantities.\textsuperscript{252,278} Since calculations utilizing regular GTO basis functions for Fe would surely fail,\textsuperscript{277} for the accurate description of the electron density and the EFG at the $^{57}$Fe nucleus we used the core-polarized CP(PPP)\textsuperscript{32,276,277} set of basis functions for the iron atom. For the other atoms the TZVP basis set was used; nevertheless for the sake of simplicity, this combined basis will be referred to as CP(PPP). Relativistic effects were not included in the computations, since it was shown that they do not improve the quality of the computed Mössbauer parameters.\textsuperscript{32} The integral accuracy parameter was increased to 7.0 at the Fe centre in order to provide more accurate core properties. Similarly to the calculations presented in Chapter 4, two-electron integrals were approximated by the RI/RIJCOSX method\textsuperscript{63,64} for GGA/hybrid exchange-correlation functionals. Since the calculation of Mössbauer properties in gas phase might be far from realistic, the geometry optimizations and the calculation of Mössbauer parameters were repeated by approximating the solid-state effects of the molecular environment with the COSMO\textsuperscript{28} with a dielectric constant for methanol ($\varepsilon = 32.7$). This is of course arbitrary, but —probably due to the intermediate dielectric constant of methanol— it is a frequent choice for modeling the effect of the molecular environment in the condensed phase.\textsuperscript{258,273,274}

5.2.2 ADF Calculations

The electron densities and EFGs were also computed with the functionals introduced above in combination with the STO-TZP all-electron basis set at the BP86-optimized
geometries. The calculations were also repeated with the application of the COSMO method. We note that while ORCA computes the electron density directly at the $^{57}\text{Fe}$ nucleus, ADF evaluates this property on a small sphere; however, this barely affects the calculated isomer shifts, as was shown in ref. 274. For the case studies described in Section 5.8, we retain the best-performing functionals only: the COSMO-TPSSh method for the investigation of low-spin octahedral Fe(II) cis-trans isomers and the B3LYP functional for the study of electronically degenerate triplet/quintet states, spin-crossover complexes and orbital singlet and doublet states of Fe(II) compounds. In the case of these B3LYP computations, the triplet states of Fe(TPP) and the quintet states of $[\text{Fe(DTSQ)}_2]^{2+}$, $[\text{Fe(H}_2\text{O)}_6]^{2+}$ and $[\text{Fe(DCTU)}_6]^{2+}$ (for the abbreviations, see Table 5.1) were assessed by imposing the corresponding occupations of the orbitals with Fe-3$d$ character within the $D_{2h}$, $D_{2d}$ and $D_{3d}$ point group symmetries, respectively. Additionally, for $[\text{Fe(DCTU)}_6]^{2+}$, we substituted the large cyclohexyl groups with methyls, in order to reduce computational cost. For the evaluation of the sign of the EFG, the COSMO-TPSSh method was selected, which was identified as one of the best-performing methods for the calculation of quadrupole splittings over the whole investigated data set. All these computations were also carried out at the BP86-optimized geometries, with the application of the STO-TZP basis set.

5.3 The Studied Iron Complexes

The data set describing the studied Fe complexes and their experimental Mössbauer parameters is given in detail in Table 5.1. Although many of the investigated compounds have been studied in previous computations focusing on the Mössbauer properties, several complexes included in our data set are new in this respect. The diversity of the studied systems was set by choosing from inorganic salts, covalent compounds and complexes with chelating ligands various systems with different local symmetries, oxidation and spin states of the Fe center. The selected set provides wide, $(-0.82) – (+1.38)$ and $(-4.01) – (+4.25)$ mms$^{-1}$ ranges for the isomer shift and quadrupole splitting parame-
ters, respectively. To the best of our knowledge, this is the largest and the most diverse data set investigated in Mössbauer spectral studies. Note that the conception for constructing this set for such a study is rather complementary to the one applied in the recent work of R. Friesner et al. While the authors of that work restricted their investigation to compounds with available crystallography and low-temperature Mössbauer data (measured at 4.2 K), present chapter wishes to address a chemically very diverse set of Fe complexes, and for many systems only higher temperature experimental data is available. To overcome this drawback, for the isomer shifts all measured values were corrected to 4.2 K by an approximation of the shift due to the second-order Doppler effect. The correction was approximated by a shift of 0.12 mms\(^{-1}\) for \(\delta_{4.2K} - \delta_{300K}\), which was reported to be linear with the temperature. For the quadrupole splittings, the temperature dependence cannot be expressed in an explicit general form; therefore, it can be only kept in mind that the calculated value corresponds to the low-temperature measurement. Also, the approach of only choosing systems with known X-ray structures was not followed, partly because the applicability of using these geometries for the predictive calculation of Mössbauer parameters is limited, and more importantly, because a combined spectroscopy-theory approach should be sufficient and successful in itself, and is also more easily available for a larger community. Finally, antiferromagnetically coupled systems (such as nitrosyls and polynuclear Fe complexes) were not considered, since the calculation of their Mössbauer properties with a broken-symmetry approach has already been discussed in several previous works. On the other hand, three Fe(II) and two Fe(III) spin-crossover systems were included, in connection with the study of the 1–3 complexes presented in Chapter 4.
Table 5.1: The Mössbauer data set of iron complexes investigated in the present chapter ($\delta$ and $\Delta E_Q$ values are given in mms$^{-1}$).

<table>
<thead>
<tr>
<th>Entry</th>
<th>System</th>
<th>Symm.$^a$</th>
<th>Fe ox.$^b$</th>
<th>$S^c$</th>
<th>$T/K$</th>
<th>$\delta^d$</th>
<th>$\delta_{2K}^d$</th>
<th>$\Delta E_Q^e$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Fe(phen)$_2$(NCS)$_2$ LS</td>
<td>C$_2$</td>
<td>2</td>
<td>0</td>
<td>77</td>
<td>0.34</td>
<td>0.37</td>
<td>0.34</td>
<td>82, 284</td>
</tr>
<tr>
<td>5</td>
<td>Fe(LN)$_4$(NCS)$_2$ LS</td>
<td>C$_1$</td>
<td>2</td>
<td>2</td>
<td>80</td>
<td>0.44</td>
<td>0.47</td>
<td>0.77</td>
<td>285</td>
</tr>
<tr>
<td>6</td>
<td>Fe[HC(3,5-Me$_2$py)$_3$]$_2$(I)$_2$ LS</td>
<td>C$_1$</td>
<td>2</td>
<td>0</td>
<td>4.2</td>
<td>0.46</td>
<td>0.46</td>
<td>0.21</td>
<td>286</td>
</tr>
<tr>
<td>7</td>
<td>Fe[OEP]$_3$(CO)</td>
<td>C$_4v$</td>
<td>2</td>
<td>0</td>
<td>4.2</td>
<td>0.27</td>
<td>0.27</td>
<td>1.84</td>
<td>287</td>
</tr>
<tr>
<td>8</td>
<td>Na$_2$[Fe(CN)$_5$(NO)]</td>
<td>C$_4v$</td>
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<td>0</td>
<td>77</td>
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<td>0.15</td>
<td>+1.72</td>
<td>288</td>
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<tr>
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<td>77</td>
<td>0.03</td>
<td>0.03</td>
<td>2.75</td>
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<td>Cp$_2$Fe</td>
<td>D$_{2d}$</td>
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<td>0.53</td>
<td>0.56</td>
<td>+2.38</td>
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<tr>
<td>12</td>
<td>[CpFe(CO)$_3$]PF$_6$</td>
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<td>0.05</td>
<td>0.08</td>
<td>1.88</td>
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<td>13</td>
<td>CpFeCO$_2$Cl</td>
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<td>4.2</td>
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<td>0.27</td>
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<td>1.87</td>
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<td>0</td>
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<td>0</td>
<td>77</td>
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<td>−1.46</td>
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<td>C$_1$</td>
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### 5.3. The Studied Iron Complexes

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<th>Tetrahedral Splitting</th>
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</table>

*a* approximate point group symmetry of the molecular structure.

*b* Fe oxidation state.

*c* Fe spin state.

*d* referred to α-iron at room temperature.

*e* if available, the experimental sign of ΔE_Q (+ or −) is given; in all other cases, the absolute value of quadrupole splitting is shown.

*f* in the computation, the large TP pivP ligand was substituted with porphin.

*The following abbreviations are used in the table: phen = 1,10-phenanthroline, LN4 = N-[(1-H-imidazo-4-yl)methylene]-N’-[(1-pyrindin-2-yl-ethylidene)-2,2-dimethyl-propane-1,3-diamine, pz = pyrazolyl ring, OEP = dianion of octaethylporphyrin, DTSQ = bis(dithiosquarato-S,S’) dianion, TPyPivP = “pivalamidopicket-fence” porphyrin, DBC = dibenzo-18-crown-6, TPP = tetraphenyolphyrinate, TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline, LN4 = N,N-bis[(1H-imidazo-4-yl)methylene]-2,2-dimethyl-propane-1,3-diamine, cyclam = 1,4,8,11-tetraazacyclo-tetradecane, thp = dianion of pyruvic acid thiosemicarbazone, acpa = anion of N-(1-acetyl-2-propyldiene)(2-piridylnylmethyl)amine, MBTHs = bis(N-methylbenzothio-hydroxamato) anion, EDTA = tetra-anion of ethylenediaminetetraacetic acid, acac = acetylacetonate, tfa = trifluoroacetylacetonate, dtc-Et2 = diethylthiocarbamate, MAC* = tetra-anion of 1,4,8,11-tetraaza-13,13-diyethyl-2,2,5,5,7,7,10,10-octamethyl-3,6,9,12,14-pentaoxocyclotetradecane, mnt = cis-1,2-dicyano-1,2-ethylenedithiolato, idzm = 2-[(p-pyridyl)-4,4,5,5-tetramethylimidazolium, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, "S2" = 1,2-benzenedithiolato-S,S’ dianion, B* = tetra-anion of 3,3,6,6,9,9-hexamethyl-3,4,8,9-tetrahydro-1H-1,4,8,11-benzotetraazacyclotridecine*
Chapter 5. DFT Prediction of Mössbauer Parameters of Iron-Containing Molecules

2,5,7,10(6H,11H)-tetroine.
Note that counterions were not included in the computations.

5.4 The Origin of the Isomer Shift and the Quadrupole Splitting

Before introducing and discussing the computational results, a theoretical review on electric hyperfine interactions — in fact the origin of the isomer shift and the quadrupole splitting—, followed by the separation of the electric field gradient into electronic and ligand parts are presented. Note that magnetic interactions are not considered here, as are beyond the scope of the current work.

The isomer shift and quadrupole splitting parameters are a result of the electric hyperfine interaction between the nuclear charge density $\rho_n(r)$ and the electric potential $\Phi(r)$ of the surrounding charges:

$$E_{\text{int}} = \int \rho_n(r)\Phi(r)d^3(r) \quad (5.1)$$

$\Phi(r)$ can be expanded in a Taylor series around the $^{57}\text{Fe}$ nucleus at $r = 0$:

$$\Phi(r) = \Phi(0) + \sum_{\alpha=1}^{3} \frac{\partial \Phi}{\partial x_\alpha} \bigg|_{r=0} x_\alpha + \frac{1}{2} \sum_{\alpha,\beta=1}^{3} \frac{\partial^2 \Phi}{\partial x_\alpha \partial x_\beta} \bigg|_{r=0} x_\alpha x_\beta + \ldots \quad (5.2)$$

and substituting it to Equation 5.1 yields:\textsuperscript{237,328}

$$E_{\text{int}} = \int \rho_n(r)\Phi(r)d^3(r) = \Phi(0)\int \rho_n(r)d^3(r) + \sum_{\alpha=1}^{3} \frac{\partial \Phi}{\partial x_\alpha} \bigg|_{r=0} \int \rho_n(r)x_\alpha d^3(r)$$

$$+ \frac{1}{2} \sum_{\alpha,\beta=1}^{3} \frac{\partial^2 \Phi}{\partial x_\alpha \partial x_\beta} \bigg|_{r=0} \int \rho_n(r)x_\alpha x_\beta d^3(r) + \ldots \quad (5.3)$$

\textsuperscript{a}It is important to note that the nucleus is not point-like, but has a finite size, which can vary for different nuclear states. Also, it may deviate from spherical symmetry, which is determined by its quadrupole and possible higher even multiple moments. This is all included in $\rho_n(r)$. 

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5.4. The Origin of the Isomer Shift and the Quadrupole Splitting

Since \( \int \rho_n(r) d^3(r) = Ze \), the nuclear charge, the interaction described by the first term of the right-hand side of Equation 5.3 shifts all nuclear levels by an equal amount, therefore, it does not affect the nuclear transitions. Furthermore, the second term vanishes, as the dipole moment of the nucleus is zero (\( \int \rho_n(r)x_\alpha d^3(r) = 0 \)). Thus, only the third term is relevant for the Mössbauer transition, which contains the second derivatives of the potential. The first derivative of the electric potential is the electric field \( E = -\nabla \Phi \); therefore, the negative second derivatives make up the electric field gradient (EFG). Introducing the traceless EFG tensor:

\[
V_{\alpha\beta}(r) = -\left[ \frac{\partial^2 \Phi}{\partial x_\alpha \partial x_\beta} - \frac{1}{3} \Delta \Phi(r) \delta_{\alpha\beta} \right]
\]

(5.4)

(where \( \Delta = \nabla^2 \) is the Laplace operator and \( \delta_{\alpha\beta} \) is the symbol for Kronecker’s delta). The third term of Equation 5.3 can be further transformed as:

\[
\frac{1}{2} \sum_{\alpha,\beta=1}^{3} \frac{\partial^2 \Phi}{\partial x_\alpha \partial x_\beta} \bigg|_{r=0} \int \rho_n(r)x_\alpha x_\beta d^3(r) = \frac{1}{2} \sum_{\alpha,\beta=1}^{3} \left[ -V_{\alpha\beta}(0) + \frac{1}{3} \Delta \Phi(0) \delta_{\alpha\beta} \right] 
\]

\[
\left[ \int \rho_n(r) \left( x_\alpha x_\beta - \frac{r^2}{3} \delta_{\alpha\beta} \right) d^3(r) + \int \rho_n(r) \frac{r^2}{3} \delta_{\alpha\beta} d^3(r) \right] \]

(5.5)

Since

\[
\sum_{\alpha,\beta=1}^{3} \Delta \Phi(0) \delta_{\alpha\beta} \int \rho_n(r) \left( x_\alpha x_\beta - \frac{r^2}{3} \delta_{\alpha\beta} \right) d^3 r = \sum_{\alpha=1}^{3} \Delta \Phi(0) \int \rho_n(r) \left( x_\alpha^2 - \frac{r^2}{3} \right) d^3 r = 
\]

\[
\int \Delta \Phi(0) \rho_n(x_1^2 - \frac{r^2}{3} + x_2^2 - \frac{r^2}{3}x_3^2 - \frac{r^2}{3}) d^3 r = 0
\]

(5.6)

where \( x_1^2 + x_2^2 + x_3^2 = r^2 \) and
\[ \sum_{\alpha,\beta=1}^{3} V_{\alpha\beta}(0) \int \rho_n(r) \frac{r^2}{3} \delta_{\alpha\beta} d^3r = \sum_{\alpha=1}^{3} V_{\alpha\alpha} \int \rho_n(r) \frac{r^2}{3} d^3r = 0 \quad (\sum_{\alpha} V_{\alpha\alpha} = 0) \] (5.7)

these two terms of Equation 5.5 vanish. Thus, it is clear from the above derivation that for nuclear transitions the relevant electric interactions stem from the second derivative of the potential:

\[ E_{\text{int}}(2) = \frac{1}{6} \Delta \Phi(0) \int \rho_n(r) r^2 d^3r - \frac{1}{2} \sum_{\alpha,\beta=1}^{3} V_{\alpha\beta}(0) \int \rho_n(r) \left( x_{\alpha} x_{\beta} - \frac{r^2}{3} \delta_{\alpha\beta} \right) d^3r \] (5.8)

The first, electric monopole term of Equation 5.8 can be written as:

\[ E_M = \frac{1}{6} \Delta \Phi(0) \int \rho_n(r) r^2 d^3r = \frac{1}{6} \Delta \Phi(0) Z e \langle r^2 \rangle = -\frac{1}{6 \varepsilon_0} \rho_e(0) Z e \langle r^2 \rangle = -\frac{Ze}{10 \varepsilon_0} \rho_e(0) R^2 \] (5.9)

Here, \( R = \sqrt{\frac{5}{3} \langle r^2 \rangle} \) is the classical radius of the nucleus, regarded as a sphere with homogeneous charge density, and \( \varepsilon_0 \) is the permittivity of the vacuum. Also, note that the first Maxwell equation was applied:

\[ \text{div} E(r) = \text{div}( - \text{grad} \Phi(r)) = -\Delta \Phi(r) = \frac{\rho_e(r)}{\varepsilon_0} \] (5.10)

thus, second derivatives of the \( \Phi(r) \) potential are replaced by the more easily calculable electron density. It can be realized that this is the term where the trace of the original EFG tensor, \( \Delta \Phi \), is utilized. The isomer shift is a consequence of the fact that the nucleus has a finite size (which changes during the Mössbauer-transition) and is determined by the difference of two \( E_M \) terms, evaluated for the absorber (A) and the source (S):

\[ \delta = E_M(A) - E_M(S) = -\frac{Ze}{10 \varepsilon_0} (\rho_e(0)_A - \rho_e(0)_S) \Delta R^2 \] (5.11)
5.4. The Origin of the Isomer Shift and the Quadrupole Splitting

The second term shown in Equation 5.8 describes the electric quadrupole interaction \((E_Q)\) between the non-spherical nucleus (i.e., a nucleus with a quadrupole moment) and the asymmetry of the electron distribution represented by the EFG at the \(^{57}\text{Fe}\) nucleus, and can be expressed as:

\[
E_Q = -\frac{1}{2} \sum_{\alpha,\beta=1}^{3} V_{\alpha\beta}(0) \int \rho_n(r) \left( x_\alpha x_\beta - \frac{r^2}{3} \delta_{\alpha\beta} \right) d^3r = -\frac{1}{2} \sum_{\alpha,\beta=1}^{3} V_{\alpha\beta}(0) Q_{\alpha\beta} \tag{5.12}
\]

where \(Q_{\alpha\beta}\) is the quadrupole moment tensor of the nucleus. With the diagonalization of the \(V_{\alpha\beta}\) and \(Q_{\alpha\beta}\) tensors (which can be achieved by the transformation to a principal axis system with \(z\) on the axis of the largest distortion of the electron distribution), the following expression is obtained for the electric quadrupole interaction:

\[
E_Q = -\frac{e}{6} \sum_{\alpha=1}^{3} V_{\alpha\alpha} Q_{\alpha\alpha} \tag{5.13}
\]

Since the diagonalized EFG tensor

\[
V_{\alpha\alpha} = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} \tag{5.14}
\]

is traceless (see Eq. 5.4), it can be characterized by two independent parameters: the main tensor component \(V_{zz}\), and the asymmetry parameter \(\eta = (V_{xx} - V_{yy})/V_{zz}\) (with \(|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|\)). The correct negative sign in the definition of \(V_{\alpha\alpha}\) is usually omitted in the M"ossbauer literature, therefore, from this point on we shall adapt to this convention, and thus do not consider it for \(V_{zz}\) (and also for \(V_{xx}\), and \(V_{yy}\)). Note that the quantities defined this way have letters of the Latin alphabet for indices \((V_{xx}, V_{yy}, V_{zz})\) in contrast to the physically correct ones indicated by Greek letters in the indices. We also mention that in many cases it suffices to take into account the \(V_{zz}\) term only, since the contribution of \(\eta\) is small and thus can be neglected. The quadrupole interaction splits
the $I = 3/2$ excited state of $^{57}$Fe into two sublevels, with $m_I = \pm 3/2$ and $\pm 1/2$, while the $I = 1/2$ ground state remains unsplit. The quadrupole splitting ($\Delta E_Q$) is defined as the energy separation of the two $I = 3/2$ substates.

5.5 The Ligand and Electronic Contributions to the Electric Field Gradient in Iron Complexes

A nonzero EFG in iron complexes can either stem from the non-octahedral arrangement of the ligands, i.e., the ligand contribution or the asymmetric filling of the Fe valence $(3d)$ subshell, i.e., the electronic contribution. One can obtain the ligand contributions within a simple model by considering a potential $\Phi = q/r$ generated by a point charge $q$. In this case, the components of the diagonalized and traceless EFG can be expressed as:

$$V_{xx} = \frac{\partial^2 \Phi}{\partial x^2} = q(3x^2 - r^2)r^{-5} = q(3\sin^2 \vartheta \cos^2 \varphi - 1)r^{-3}$$  \hspace{1cm} (5.15)

$$V_{yy} = \frac{\partial^2 \Phi}{\partial y^2} = q(3y^2 - r^2)r^{-5} = q(3\sin^2 \vartheta \sin^2 \varphi - 1)r^{-3}$$  \hspace{1cm} (5.16)

$$V_{zz} = \frac{\partial^2 \Phi}{\partial z^2} = q(3z^2 - r^2)r^{-5} = q(3\cos^2 \vartheta - 1)r^{-3}$$  \hspace{1cm} (5.17)

Here the $x$, $y$, and $z$ coordinates were transformed to polar coordinates ($\vartheta$ is the angle between the $z$ axis and the position vector of the $q$ charge, $\varphi$ is the angle in the $xy$ plane.). Selecting the proper orientation for $x$, $y$, and $z$, and if the charge distribution is similar in the $x$ and $y$ directions, it is sufficient to deal with the $V_{zz}$.

In addition to the ligand contributions, a non-zero $V_{zz}$ can also arise due to the asymmetric occupation of the valence Fe-$3d$ orbitals. The contribution of an arbitrary valence electron can be evaluated by calculating the
\[
(V_{zz})_{\text{val},i} = -e \left\langle \psi_i(r, \vartheta, \varphi) | (3\cos^2 \vartheta - 1) r_i^{-3} | \psi_i(r, \vartheta, \varphi) \right\rangle = \\
- e \sum_i \left\langle \psi_i(\vartheta) | 3\cos^2 \vartheta - 1 | \psi_i(\vartheta) \right\rangle \left\langle r_i^{-3} \right\rangle
\] (5.18)

expectation value (\(\psi_i\) is the molecular orbital occupied by the valence electron and \(\langle r^{-3} \rangle = \int \psi(\mathbf{r}) r^{-3} \psi(\mathbf{r}) r^2 d\mathbf{r}\)). Substituting \(\psi_i\) with the five Fe-3d orbitals, the following values are obtained for the electron-only contributions to the \(V_{zz}\):

<table>
<thead>
<tr>
<th>Orbital</th>
<th>((V_{zz})_{\text{val},i} / e \langle r^{-3} \rangle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{xy})</td>
<td>+ 4/7</td>
</tr>
<tr>
<td>(d_{xz})</td>
<td>- 2/7</td>
</tr>
<tr>
<td>(d_{yz})</td>
<td>- 2/7</td>
</tr>
<tr>
<td>(d_{x^2-y^2})</td>
<td>+ 4/7</td>
</tr>
<tr>
<td>(d_{z^2})</td>
<td>- 4/7</td>
</tr>
</tbody>
</table>

As discussed in Section 3.1, in the frequent octahedral (and also in tetrahedral) coordination the symmetry splits the five Fe-3d orbitals into a threefold degenerate \(t_{2g}\), and a twofold degenerate \(e_g\) subshells, which include the \(d_{xy}\), \(d_{xz}\), and \(d_{yz}\), and the \(d_{x^2-y^2}\), \(d_{z^2}\) orbitals, respectively. Using the above table an important observation can be made: the evenly filled \(t_{2g}\) and \(e_g\) subshells do not contribute to the EFG. This includes all the following configurations and their possible combinations: \(t_{2g}^0\), \(t_{2g}^3\), \(t_{2g}^6\), \(e_g^0\), \(e_g^2\), \(e_g^4\).

### 5.6 Calculated Isomer Shift Results: Correlation with Experiment

In a typical Mössbauer experiment, the spectrum is recorded by moving a single-line (i.e., unsplit) source with respect to a \(^{57}\)Fe-containing absorber with different velocities, and recording the transmitted intensity. When the differences in the nuclear transition
energies in the source and the absorber are compensated by the Doppler-effect, the transmission decreases (this is why in the Mössbauer literature the nuclear energy is measured in the mm$s^{-1}$ unit of Doppler velocity). The detected resonance absorption is characterized by the isomer shift ($\delta$), which arises due to the different electron densities at the $^{57}$Fe nuclei in the absorber and the source (Eq. 5.11). Since $\rho_e(0)_S$ can be taken as a constant (as the same source can be used for taking all Mössbauer spectra), the isomer shift can be expressed as:

$$\delta = \alpha \rho(0) + \beta$$  \hspace{1cm} (5.19)

where $\rho(0)$ is the electron density at the absorbing Fe nucleus and $\alpha$, $\beta$ are calibration constants. As $\rho(0)$ is readily available with DFT calculations, $\alpha$ and $\beta$ can be evaluated by the linear fit to the experimental isomer shifts versus the computed electron densities. This technique has been widely applied for the calculation of isomer shifts of various iron compounds. An alternative approach was suggested by R. Kurian and M. Filatov, who calculated $^{57}$Fe isomer shifts by the differentiation of electronic energy with respect to the nuclear radius; however, in several cases the results showed large deviations from the experimental values.

We have fit the above Equation 5.19 to the electron density determined with the different DFT theories using 6 functionals and 2 type of basis sets for all the 66 investigated molecules. The large set of $\rho(0)$ and $\delta$ values are presented in Table A8 in the Appendix and Tables S4–S7, Figs. S2–S5 in the Supporting Information (SI) of paper P2, whereas the fits are described in Table 5.3.

All results were obtained by fitting the full data set with a single line; therefore, in contrast to certain previous fits, present parametrization does not depend on the Fe oxidation state or other parameters. The linear fits obtained for the RPBE and B3LYP density functionals are presented in Figures 5.1 and 5.2 (these two functionals are representatives of the pure (GGA) and hybrid DFT methods, respectively). The results presented in these figures and Table 5.3 indicate that the hybrids (B3LYP, B3LYP*
5.6. Calculated Isomer Shift Results: Correlation with Experiment

Table 5.3: \( R^2 \), MAE and maximum deviation parameters obtained for the calculation of isomer shifts (values given after the semicolon correspond to results obtained with the COSMO).

<table>
<thead>
<tr>
<th>method</th>
<th>( R^2 )</th>
<th>MAE ( ^b ) (mms(^{−1} ))</th>
<th>max. dev. ( ^c ) (mms(^{−1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GTO-CP(PPP) basis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>0.919; 0.944</td>
<td>0.10; 0.08</td>
<td>0.30; 0.21</td>
</tr>
<tr>
<td>OLYP</td>
<td>0.900; 0.940</td>
<td>0.11; 0.09</td>
<td>0.28; 0.22</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.975; 0.983</td>
<td>0.06; 0.05</td>
<td>0.15; 0.14</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>0.964; 0.979</td>
<td>0.07; 0.05</td>
<td>0.20; 0.15</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.937; 0.958</td>
<td>0.09; 0.07</td>
<td>0.25; 0.19</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0.965; 0.979</td>
<td>0.06; 0.05</td>
<td>0.21; 0.15</td>
</tr>
<tr>
<td><strong>STO-TZP basis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>0.910; 0.940</td>
<td>0.10; 0.08</td>
<td>0.33; 0.24</td>
</tr>
<tr>
<td>OLYP</td>
<td>0.840; 0.881</td>
<td>0.14; 0.13</td>
<td>0.37; 0.28</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.976; 0.984</td>
<td>0.05; 0.05</td>
<td>0.17; 0.12</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>0.967; 0.979</td>
<td>0.06; 0.05</td>
<td>0.21; 0.15</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.932; 0.945</td>
<td>0.09; 0.08</td>
<td>0.30; 0.25</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0.954; 0.966</td>
<td>0.07; 0.06</td>
<td>0.25; 0.17</td>
</tr>
</tbody>
</table>

\(^a\) square of the correlation coefficient obtained for the linear fits.  
\(^b\) mean absolute error.  
\(^c\) maximum deviation from the corrected experimental values.

and TPSSh) provide better linear fits than the GGA functionals, in agreement with previous studies.\(^b\),\(^32,277,278\) This is due to the fact that while the potential generated by GGA functionals is in most cases unsatisfactory in the vicinity of the \(^{57}\)Fe nucleus, the inclusion of the nonlocal corrections in global hybrid functionals results in a more accurate potential and electron density.\(^330\) Although the very popular B3LYP functional is often inadequate for many properties of transition metal complexes (e.g., for the calculation of

\(^b\)Although the weak performance of B3LYP and B3LYP* in the prediction of isomer shifts has been reported in ref. \(^274\); this was due to the makeup of the data set and the fact that poor geometries were obtained for polynuclear Fe complexes.
spin-state splitting energies, see Section 4.4 and refs. 114, 115, 141, 143, and 151), in this case it gives excellent results, somewhat outperforming B3LYP* and TPSSh. Comparing the results obtained with the three GGA functionals, only small differences were found in their performance indicating that the HFx included in hybrid density functionals has a vital role for the correct description of the electron density around the Fe nucleus.

Figure 5.1: Linear correlations between the (a) RPBE, (b) B3LYP, (c) COSMO-RPBE, (d) COSMO-B3LYP (in combination with the GTO-CP(PPP) basis set) calculated electron density ($\rho_0$) at the $^{57}$Fe nucleus and the corrected experimental isomer shift ($\delta_{4.2K}$). The fitting parameters are indicated for the B3LYP method, for all other applied DFT methods the results are shown in the Tables A6 and A7 in the Appendix.
5.6. Calculated Isomer Shift Results: Correlation with Experiment

Figure 5.2: Linear correlations between the (a) RPBE, (b) B3LYP, (c) COSMO-RPBE, (d) COSMO-B3LYP (in combination with the STO-TZP basis set) calculated electron density ($\rho_0$) at the $^{57}$Fe nucleus and the corrected experimental isomer shift ($\delta_{4.2K}$). The fitting parameters are indicated for the B3LYP method, for all other applied DFT methods the results are shown in Tables A6 and A7 in the Appendix.

We have also tested whether the results can be improved by employing an approximation for the effects of the host solid matrix. The application of the COSMO improves the mean absolute errors (MAE) obtained for the isomer shifts by 0.01–0.02 mms$^{-1}$ for all density functionals; it also reduces the maximum deviation values in several cases by up to 0.09 mms$^{-1}$. In particular, the COSMO-B3LYP method gives a value of $R^2 = 0.984$, similar to the one reported by F. Neese et al.;\textsuperscript{277} however, present results were obtained on a much larger and more diverse test set. Note that previous results\textsuperscript{277,279} suggest that similarly accurate isomer shifts can be obtained with the double hybrid B2PLYP\textsuperscript{54}
method, yet, the computational cost of this functional is higher than the one of B3LYP due to the included correction of second-order perturbation theory.

Furthermore, the performances of the STO and the GTO basis sets have been also compared. As discussed in Section 2.6.1, the electron density shows a cusp at the nucleus, which is better reproduced by STO basis functions, than GTOs.\textsuperscript{331} This drawback can be overcome by using a core-polarized basis set for Fe, (e.g., Partridge\textsuperscript{332} or Watchers\textsuperscript{333} basis functions, or the CP(PPP) basis developed by F. Neese,\textsuperscript{32,276,277} which was used in our calculations); without this, GTO-based computations could not compete with those using STOs. The results show that the application of the STO-TZP basis set barely improves the quality of the computed isomer shifts for the B3LYP and B3LYP* methods. For the other four functionals, the performance of the GTO-CP(PPP) basis set is even superior when compared to the one of the STO-TZP basis (Table 5.3). To conclude this section, it is stated that the COSMO-B3LYP is a very reliable method for the calculation of Mössbauer isomer shifts for the different types of Fe compounds covered in the present chapter. This method provides accurate results (with a MAE of 0.05 mms\textsuperscript{-1} and a maximum deviation of 0.12 mms\textsuperscript{-1}), therefore, it can become a first choice for predictions.

### 5.7 Calculated Quadrupole Splitting Results: Correlation with Experiment

As was discussed in Section 5.4, the quadrupole splitting ($\Delta E_Q$) observed in the Mössbauer experiment originates from the electric quadrupole interaction between the nuclear quadrupole moment and the electric field gradient. Rewriting Equation 5.13 for the $I = 3/2$, $m_I = \pm 3/2$ and $I = 3/2$, $m_I = \pm 1/2$ nuclear states of $^{57}$Fe, the expression that describes the energy splitting for the case of the $^{57}$Fe nucleus is:
\[ \Delta E_Q = E_Q(I = 3/2, m_I = \pm 3/2) - E_Q(I = 3/2, m_I = \pm 1/2) = \frac{1}{2} eQV_{zz} \sqrt{1 + \frac{1}{3} \eta^2} \] (5.20)

Since \( Q \), the nuclear quadrupole moment can be taken as a constant (0.16 barn for \(^{57}\)Fe),\(^{32} \) the EFG uniquely determines \( \Delta E_Q \). The EFG describes the asymmetry of the charge distribution around the Fe center, which is influenced by both the local electronic structure and the coordination of the ligands (i.e., the electronic and ligand contributions, respectively; see Section 5.5). The values of \( V_{xx}, V_{yy} \) and \( V_{zz} \) are obtained by the diagonalization of the traceless EFG matrix (see Section 5.4). The EFG is determined as a second derivative of the potential arising from the charge distribution around the nucleus in a full \textit{ab initio} manner using:

\[ \Phi(0) = \frac{1}{4\pi\varepsilon_0} \left( - \int \frac{\rho(r) d^3r}{r} + \sum_{i} \frac{z_i e_i r_i}{r_i} \right) \] (5.21)

The task of the DFT calculations is thus to provide a rather accurate charge distribution around the nucleus.

We have performed the \( \Delta E_Q \) calculation for the same set of Fe compounds with the same conditions as before. (Note that in this section only the magnitude of \( \Delta E_Q \) is considered, since experimentally its sign has only been determined for a limited number of Fe compounds. The results obtained for those cases with a known sign is presented in Section 5.8.5.) The calculated \( \Delta E_Q \) and \( \eta \) values are presented in Table A8 in the Appendix and Tables S8–S14 in the SI of paper P2, the comparison between calculations and experiments for a GGA (RPBE) and a hybrid (B3LYP) method is shown in Figures 5.3 and 5.4. The results exhibit a good overall agreement with the experiment. However, the deviations from the experimental values are larger than those of the isomer shifts: the observed MAE values are between 0.20 and 0.35 mms\(^{-1} \) for the different functionals (Table 5.4), which correspond to 10–18% absolute error. This has several contributing factors, which include the experimental error in the determination of \( \Delta E_Q \), its possible
dependence on the temperature and the molecular structure, and the fact that it is a second derivative and its calculated value is determined fully ab initio, while experimental δ values are used for the calibration of isomer shifts. Furthermore, while with the isomer shifts the best-performing methods provide accurate δ values over the whole investigated data set, this is not the case for Δ\(E_Q\). In fact, even the best-performing functionals produce maximum deviations up to 0.7–1.1 mms\(^{-1}\) (corresponding to 48–66% absolute error) between the experimental and calculated values of Δ\(E_Q\) (Table 5.4).

**Table 5.4:** \(R^2\), MAE and maximum deviation parameters obtained for the calculation of quadrupole splittings (values given after the semicolon correspond to results obtained with the COSMO).

<table>
<thead>
<tr>
<th>method</th>
<th>(R^2) (^a)</th>
<th>MAE(^b) (mms(^{-1}))</th>
<th>max. dev.(^c) (mms(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GTO-CP(PPP) basis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>0.875; 0.926</td>
<td>0.31; 0.24</td>
<td>1.69; 1.19</td>
</tr>
<tr>
<td>OLYP</td>
<td>0.852; 0.918</td>
<td>0.32; 0.24</td>
<td>1.89; 1.40</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.926; 0.947</td>
<td>0.24; 0.25</td>
<td>1.29; 1.20</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>0.925; 0.948</td>
<td>0.24; 0.22</td>
<td>1.20; 1.11</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.906; 0.936</td>
<td>0.28; 0.23</td>
<td>1.42; 0.87</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0.942; 0.942</td>
<td>0.21; 0.19</td>
<td>0.82; 1.05</td>
</tr>
<tr>
<td><strong>STO-TZP basis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>0.887; 0.919</td>
<td>0.30; 0.23</td>
<td>1.73; 1.48</td>
</tr>
<tr>
<td>OLYP</td>
<td>0.870; 0.906</td>
<td>0.31; 0.24</td>
<td>1.94; 1.54</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.949; 0.958</td>
<td>0.21; 0.25</td>
<td>1.01; 1.11</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>0.949; 0.960</td>
<td>0.21; 0.21</td>
<td>0.80; 1.09</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.914; 0.923</td>
<td>0.27; 0.22</td>
<td>1.49; 1.66</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0.948; 0.955</td>
<td>0.21; 0.18</td>
<td>0.73; 1.12</td>
</tr>
</tbody>
</table>

\(^a\) square of the correlation coefficient of the linear fit obtained for experimental and calculated values of quadrupole splittings.  
\(^b\) mean absolute error.  
\(^c\) maximum deviation from the experimental values.
5.7. Calculated Quadrupole Splitting Results: Correlation with Experiment

Concerning the effect of the type of the basis set, we recall that the application of the CP(PPP) basis set on the Fe atom is essential for the reproduction of the cusp at the nucleus; without this, the performance of the GTOs would be inferior, compared to those of the STO basis functions. For the prediction of quadrupole splittings, the general performance of the STO-TZP basis set is slightly better than that of the GTO-CP(PPP) basis (Table 5.4), but in several cases, CP(PPP) provides more accurate results (e.g., for complexes 59 and 60, see Figures 5.3a,c and 5.4a,c). Therefore, in agreement with previous computational Mössbauer spectral results, the clear preference for the use of the STO basis over the core-polarized GTO basis set is not observed.
Chapter 5. DFT Prediction of Mössbauer Parameters of Iron-Containing Molecules

Figure 5.4: Comparison of experimental and (a) RPBE, (b) B3LYP, (c) COSMO-RPBE, (d) COSMO-B3LYP (in combination with the STO-TZP basis set) calculated quadrupole splittings ($\Delta E_Q$). The red line was drawn at $\Delta E_Q$ (exp.) = $\Delta E_Q$ (calc.). The largest outliers can be identified by the numbers defined in Table 5.1. Correlations for all the other applied DFT methods are shown in Figures S7 and S9 in the SI of paper P2.

In order to assess the applicability of different exchange-correlation functionals, their influence on the calculated quadrupole splittings is investigated. In general, the application of hybrid functionals results in more accurate $\Delta E_Q$ values, thus the inclusion of the HFx improves the theoretical description. Moreover, systematic variations are found in the comparison of results obtained with GGA- and hybrid-type functionals. For instance, B3LYP provides significantly larger $\Delta E_Q$ values (up to 1.7 mms$^{-1}$) than RPBE, for the HS ($S = 2$) Fe(II) and IS ($S = 3/2$) Fe(III) complexes, and also slightly larger $\Delta E_Q$ values than the other two hybrid functionals, B3LYP* and TPSSh. On the other hand, for LS ($S = 0$) Fe(II) compounds, only small differences are seen between the $\Delta E_Q$ values.
calculated with GGA and hybrid functionals. As is well known, the exchange interaction increases with the value of the spin angular momentum.\textsuperscript{114} Hence, the above effect is obviously due to the fact that the influence of the HFx on the EFG is more dominant for intermediate- and high-spin complexes than for the low-spin ones.

Present results give evidence that GGA functionals substantially underestimate $\Delta E_Q$ for the $S = 2$ Fe(II) and $S = 3/2$ Fe(III) complexes (see Figures 5.3 and 5.4), which likely stems from the inadequate description of the exchange interaction. These cases are better described with the hybrid methods due to the inclusion of HFx. Furthermore, it is pointed out that the 20\% amount of HFx included in the B3LYP functional is required to better reproduce the quadrupole splittings of the HS Fe(II) and intermediate-spin Fe(III) compounds: the corresponding experimental $\Delta E_Q$ values are underestimated with the other two hybrids, B3LYP* and TPSSh, by 0.3–0.6 mm\,s\textsuperscript{-1}. On the other hand, the TPSSh method reproduces better the experimental $\Delta E_Q$ values of the $S = 0$ Fe(II), $S = 1/2$ Fe(III), Fe(IV), Fe(V) and Fe(VI) compounds. All applied density functionals yield accurate quadrupole splittings for the $S = 0$ Fe(II), and $S = 5/2$ Fe(III) complexes (except for complex 11, see below), which is explained by the reliable description of the symmetrically occupied Fe-3\textit{d} subshell by DFT.

In order to test the role of the environment of the molecule, the effect of the COSMO on the calculated quadrupole splittings was also investigated. The inclusion of the molecular environment was found to improve the general performance of most methods (except for B3LYP, where $R^2$ increases, but also MAE increases, see Table 5.4), which is in agreement with a previous study.\textsuperscript{258} However, the results indicate that in the case of hybrid functionals, it results in the dramatic increase of $\Delta E_Q$ for the HS ($S = 2$) Fe(II) complexes. Since the effect is only pronounced for these systems, it must be related to the enhanced exchange interaction. While COSMO partially corrects the mentioned deficiencies of the GGA methods for several $S = 2$ Fe(II), and $S = 3/2$ Fe(III) complexes, it induces the overestimation of quadrupole splittings provided by the hybrid functionals up to 1.12 mm\,s\textsuperscript{-1} (52\% error). On the other hand, COSMO turned out to be beneficial for all other Fe complexes with various oxidation and spin states. In particular, in the case

93
of complex 68, while the gas phase DFT computations underestimate the experimental $\Delta E_Q$ value by ca. 0.8 mms$^{-1}$, COSMO reduces this error by 0.3–0.4 mms$^{-1}$.

The largest differences observed between the measured and DFT-calculated values of $\Delta E_Q$ are worth a careful examination. In principle, several possible sources of errors can contribute to the mismatch observed between the experimental and calculated quadrupole splittings, which include the effect of temperature, the poor approximation of solid-state effects, unsatisfactory molecular geometry used in the calculations; these issues are briefly addressed here, focusing on the outliers (11, 24, 29, 33, 37 and 43) of one of the best-performing exchange-correlation functional, COSMO-TPSSh. It is unlikely that the largest discrepancies stem from temperature effects, since the corresponding experimental $\Delta E_Q$ values were taken from Mössbauer measurements carried out at liquid He (4.2 K) or liquid N$_2$ (77 K) temperatures, and relevant thermal variations of the quadrupole splitting typically take place at higher temperatures. Furthermore, calculations made on X-ray structures do not produce better overall performance, and results also in numerous outliers, as has been seen in ref. 278; these suggest that solid-state effects do not alter the EFG of the complexes significantly. Finally, in order to investigate the possibility of inadequacy of the structures obtained in the molecular optimization with the pure BP86 functional, further test computations were carried for the problematic complexes. Both geometry optimizations and the calculation of the quadrupole splitting were performed with at the COSMO-TPSSh level, and the large errors of the outliers were not found to be amended this way (Table 5.5).

As the consideration of the possible sources of errors has not provided a satisfying explanation of the outliers, it shall be considered whether the treatment of the electronic structure is appropriate in all cases. For GGAs, the discrepancies in most cases can be assigned to the incorrect treatment of the exchange interaction, as stated above. Although hybrid functionals give more accurate results, even for these methods large deviations from the corresponding experimental values are observed in a few cases. For instance, in the case of ferrocene (Cp$_2$Fe, complex 11), the experimental quadrupole splitting is systematically overestimated by all hybrid functionals, while GGAs provide results
5.7. Calculated Quadrupole Splitting Results: Correlation with Experiment

Table 5.5: Comparison of experimental and COSMO-TPSSh $|\Delta E_Q|$ values for selected Fe complexes computed with the GTO-CP(PPP) basis set at different geometries (values are given in mms$^{-1}$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Exp.</th>
<th>BP86 geometry</th>
<th>COSMO-TPSSh geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>2.38</td>
<td>2.85</td>
<td>2.86</td>
</tr>
<tr>
<td>24</td>
<td>2.51</td>
<td>3.56</td>
<td>3.62</td>
</tr>
<tr>
<td>29</td>
<td>3.14</td>
<td>3.68</td>
<td>3.73</td>
</tr>
<tr>
<td>33</td>
<td>2.14</td>
<td>3.04</td>
<td>3.23</td>
</tr>
<tr>
<td>37</td>
<td>1.60</td>
<td>0.55</td>
<td>0.59</td>
</tr>
<tr>
<td>43</td>
<td>3.43</td>
<td>3.96</td>
<td>3.96</td>
</tr>
</tbody>
</table>

in good agreement with this value, as also reported in ref. 275. This effect originates from the fact that GGA functionals reproduce better the energetics of $\pi$-type charge-transfer (Cp-$\pi$$\rightarrow$Fe-$3d^*$ donation and Fe-$3d$$\rightarrow$Cp-$\pi^*$ backdonation) and the experimental HOMO-LUMO energy gap than hybrid methods,275,334 which quantities are decisive for the bonding and the increased EFG in Cp$_2$Fe. Large deviations are also observed between the experimental and hybrid DFT $\Delta E_Q$ values for the square planar $S = 1$ Fe$^{111}$(OEP) (37) and Fe$^{111}$(TPP) (38) complexes. On the other hand, the GGA-type RPBE method yields accurate results for these systems. As will be addressed in Section 5.8.1, the key to this effect stems from the treatment of electronically degenerate states by DFT. Furthermore, for the hybrids, we also identified two main outliers: [Fe(terpy)$_2$]$^{3+}$ (43) and Fe(PPh$_3$)$_2$ ("S2") (64). In contrast to our results presented above, in these distorted open-shell hexacoordinate complexes, the inclusion of the exact exchange was found to result in the overestimation of $\Delta E_Q$. This effect is surprising, since hybrid methods provide reliable results for other quasi-octahedral systems possessing the same $S = 1/2$ $3d^5$, and $S = 1$ $3d^1$, electron configurations. Also, the results indicate that the hybrid methods give accurate estimates to the ligand-only contributions of quadrupole splittings for hexacoordinate complexes (e.g., deviations up to only 0.1 mms$^{-1}$ were observed for 22, which is the $S = 0$ Fe(II) analogue of 43). Therefore, these discrepancies for 43 and
most likely stem from the incorrect description of the partially occupied, and split \( t_{2g} \)-like orbitals. For systems with such electronic structure (including a relevant distortion), the application of GGA functionals is proposed, which provides accurate \( \Delta E_Q \) values.

It is concluded from the above results that the hybrid TPSSh functional combined with COSMO gives satisfactory results for most cases. However, for the \( S = 2 \) Fe(II) and \( S = 3/2 \) Fe(III) complexes, the B3LYP (for the latter compounds in combination with the COSMO model) method provides more accurate \( \Delta E_Q \) values. Furthermore, in the special cases of \( \pi \)-bonded compounds, square-planar arrangements with \( S = 1 \) and largely distorted open-shell hexacoordinate systems the usage of the GGA-type COSMO-RPBE method is suggested. Therefore, although none of the applied density functionals show a good universal performance over the whole investigated data set, a very promising approach for the accurate prediction of quadrupole splittings is here proposed, in which an appropriate DFT method from a set of three XC functionals (TPSSh, B3LYP, and RPBE) for different classes of Fe compounds is selected. The application of the carefully selected DFT methodology described above in this paragraph yields a MAE value of 0.12 mms\(^{-1}\) (7% error) and a maximum deviation of 0.55 mms\(^{-1}\) (17% error) on the investigated set of 66 complexes. These results are shown in Figure 5.5a. Therefore, the conclusion is that the suggested approach provides accurate \( \Delta E_Q \) values over the variety of the investigated complexes, which enables the reliable prediction of \(^{57}\)Fe quadrupole splittings.

It is apparent from Figure 5.5a that the classes of compounds treated separately in the above recipe fall into different regions. This interesting observation hints that a strategy can also be proposed, where the selection of the applied density functional is solely guided by the experimentally observed \( \Delta E_Q \) values. A good correlation with the experiment over the whole investigated \( \Delta E_Q \) range may provide a basis for the development of stronger model-independent techniques for the accurate prediction of quadrupole splittings. Encouraged by this, the applicability of an alternative approach utilizing the above idea—with the use of three arbitrarily selected regions: \( \Delta E_Q \leq 1.5 \), \( 1.5 < \Delta E_Q \leq 2.0 \), \( \Delta E_Q > 2.0 \)—is tested. These results are shown in Figure 5.5b. The obtained MAE value of
5.8. Case Studies for the Quadrupole Splitting in Mössbauer Spectroscopy

In this section the reliability of the DFT approach is checked by testing its performance in the prediction of quadrupole splittings in a few chemically relevant applications of Mössbauer Spectroscopy.
MS. Also, the apparent difficulties introduced by the electronically degenerate states of open-shell Fe(II) complexes is examined, and a method is proposed to overcome these problems.

5.8.1 Electronically Degenerate States of \( S = 1 \) Fe(II) Complexes

An intriguing class of compounds possesses open-shell electronically degenerate states in solids. As noted previously in Section 5.7, the incorrect treatment of these states induces large variations in the experimental and calculated \( \Delta E_Q \) values. For instance, the experimental quadrupole splittings of the planar \( S = 1 \) Fe(OEP) (37) and Fe(TPP) (38) porphyrin-derivative complexes are underestimated with the B3LYP/CP(PPP) method by 1.2–1.3 mms\(^{-1}\). On the other hand, the serious overestimation of \( \Delta E_Q \) (by 1.4–2.3 mms\(^{-1}\)) for these complexes was also experienced in earlier works, when hybrid exchange-correlation functionals were applied with no symmetry constraints, or when the EFG was computed with the GGA-type BPW91 functional on a \( D_{4h} \) structure of complex 38. However, a quite acceptable \( \Delta E_Q \) value of 1.75 mms\(^{-1}\) was obtained with the same functional, when the \( D_{2d} \) symmetry of the system (obtained from its crystal structure) was employed. We made efforts to understand the reasons behind these discrepancies by a detailed investigation.

The lowest-lying electronic states of Fe(TPP), applying the \( D_{4h} \) point group symmetry are the triplet \( ^3A_{2g} \) and \( ^3E_g \) states. The DFT calculations deliver quadrupole splitting values of \( \Delta E_Q(^3A_{2g}) = 0.40 \) mms\(^{-1}\) and \( \Delta E_Q(^3E_g) = 3.08 \) mms\(^{-1}\). This large difference suggests that the origin of the above mentioned discrepancy between theory and experiment requires a close and careful inspection of the electronic structure. As discussed in Section 5.5, the five Fe-3\( d \) orbitals make different contributions to the EFG (Equation 5.18, Table 5.2); therefore, their occupation has a major influence on the quadrupole splitting. In Figure 5.6, it is shown that the small \( \Delta E_Q \) obtained for the \( ^3A_{2g} \) state is due to the symmetric occupation of the degenerate orbitals with \( d_{xz}, d_{yz} \) characters and
the double occupation of the MO with \( d_{z^2} \) main atomic contribution, whereas the large quadrupole splitting in \( 3E_g \) can be attributed to the asymmetric occupation of these orbitals. Since the energy separation of these states is small (ca. 0.12 eV), DFT calculations can converge to either of these states. Lowering the symmetry removes the degeneracy. \( D_{2h} \) was found to be the highest symmetry for which a mixing of the \( d_{xy} \) and \( d_{z^2} \) orbitals in the ground state (mediated by the ligands) was observed, which resulted in the accurate quadrupole splitting value of 1.25 mms\(^{-1}\). It is mentioned that the mixing was also observed when utilizing the RPBE/CP(PPP) method, without the application of any symmetry constraints, which also provided accurate results. This is justified by the fact that the correct handling of near-degeneracy effects require the inclusion of substantial static (non-dynamical) electron correlation, which is treated better with GGA methods, than hybrid density functionals.\(^{155}\)

5.8.2 Electronically Degenerate States of a \( S = 2 \) Fe(II) Complex

The DFT-calculated \( \Delta E_Q \) values of a \( S = 2 \) Fe(II) quasi-tetrahedral complex, [Fe(DTSQ)]\(^{2-}\) (26) reported in previous studies\(^{273,278}\) also showed very large deviations (0.71–1.65 mms\(^{-1}\)) from the experimental value of 4.01 mms\(^{-1}\). When investigating the electronic structure of this complex in the \( D_{2d} \) symmetry, its two lowest-lying states, \( ^5A_2 \) and \( ^5B_2 \) were found to be degenerate. The calculated quadrupole splittings for these states show a large difference due to the different occupation of the orbitals with \( d_{z^2} \) and \( d_{x^2-y^2} \) characters. While the \( \Delta E_Q(^5A_2) = 4.30 \) mms\(^{-1}\) value is in good agreement with the experiment, the 2.92 mms\(^{-1}\) value obtained for the \( ^5B_2 \) state is as far from the experimental one as those reported in refs. 273 and 278 (Figure 5.7). Therefore, the comparison between the calculation and the experiment permits the identification of the true ground state, and the problematic \( ^5B_2 \) electronic configuration can be avoided by the application of symmetry. Note that 26 does not appear as an outlier in Figs. 5.3 and 5.4, since in every case for the calculations it could be converged to the \( ^5A_2 \) state, which yielded
Figure 5.6: Schematic representation of the electronic configurations and the 3D illustration of the KS orbitals with main Fe-3d contribution corresponding to the triplet $^3A_{2g}$ and $^3E_g$ ($D_{4h}$) states of Fe(TPP) (35). Note that for the sake of simplicity spin-polarized energy levels are not shown and only one component of the degenerate orbitals with $d_{xz}, d_{yz}$ characters and of the $^3E_g$ states is shown. The given $\Delta E_Q$ values were computed at the B3LYP/STO-TZP level of theory and are to be compared with the experimental value of 1.51 mms$^{-1}$.

quadrupole splittings in agreement with the magnitude of the experimental $\Delta E_Q$. Furthermore, the sign of the experimental $\Delta E_Q$ has also been determined for this compound: it is negative. This is in very good agreement with our calculations, where $\Delta E_Q(^5A_2) < 0$ and $\Delta E_Q(^5B_2) > 0$, which allows the unambiguous identification of the true ground state for this system: it is the $^5A_2$. Without imposing the Fe-3d electronic configuration corresponding to this state, DFT calculations (with both GGA and hybrid functionals) can converge either to the $^5A_2$ or to the $^5B_2$ state depending on the starting geometry and the applied exchange-correlation functional. The above results suggest that the largest
differences observed between the experimental and DFT-calculated $\Delta E_Q$ values in previous studies\textsuperscript{273,278,280,281} can also be attributed to the selection of the inappropriate ground state from the electronic quasi-degenerate states.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.7.png}
\caption{Schematic representation of the electronic configurations and the 3D illustration of the DFT orbitals with main Fe-3$d$ contribution corresponding to the quintet $^5A_2$ and $^5B_2$ states of [Fe(DTSQ)$_2$]$^{2-}$ (26). Note that for the sake of simplicity spin-polarized energy levels are not shown and that one component of the degenerate orbitals with $d_{xz}$, $d_{yz}$ characters is shown. The given $\Delta E_Q$ values were computed at the B3LYP/STO-TZP level of theory and are to be compared with the experimental value of $-4.01 \text{ mms}^{-1}$.}
\end{figure}

5.8.3 Geometric Isomerism of Octahedral Low-Spin Fe(II) Complexes

In addition to the valence electrons, the ligands also contribute to the electric potential and the $V_{zz}$ at the $^{57}$Fe nucleus, and this can also be a rich source of chemical information. Compounds where the $V_{zz}$ induced by the electrons cancels (e.g., in the case of LS Fe(II)
complexes) provide an ideal testing ground to study how DFT reproduces the ligand contribution. In this section, we investigate how geometric isomerism can affect the $V_{zz}$.

In octahedral geometry, complexes with a composition of FeA$_2$B$_4$ can have two different isomers with the two A ligands in trans or cis positions (Figure 5.8a and b). Applying the point charge model introduced in Section 5.5 by representing the A and B ligands by the $q_A$ and $q_B$ point charges, and using Equation 5.17, the following expression is obtained for the $V_{zz}$ corresponding to the $q_A$ charges, in the trans case ($\vartheta = 0^\circ$):

$$V_{zz} = \frac{\partial^2 \Phi}{\partial z^2} = q_A (3 \cos^2 \vartheta - 1) r^{-3} = 2q_A (3 \cos^2(0) - 1) r^{-3} = 4q_A r^{-3}$$  \hspace{1cm} (5.22)

and for the four $q_B$ charges ($\vartheta = 90^\circ$):

$$V_{zz} = \frac{\partial^2 \Phi}{\partial z^2} = q_B (3 \cos^2 \vartheta - 1) r^{-3} = 2q_B (3 \cos^2(\pi) - 1) r^{-3} = -4q_B r^{-3}$$  \hspace{1cm} (5.23)

Figure 5.8: 3D representation of the structures of the octahedral (a) trans-FeA$_2$B$_4$, (b) cis-FeA$_2$B$_4$ and (c) FeAB$_5$ complexes. Parametric $V_{zz}$ values expected from the point charge model are also shown. The orientation of the $z$ axis was chosen to be the principal axis.

Therefore, the total $V_{zz}$ equals $4(q_A - q_B)$ (note that here the constant $r^{-3}$ term is
omitted and \( \eta = 0 \), due to the axial symmetry). Similarly, the \(-2(q_A - q_B)\) and \(2(q_A - q_B)\) values are derived for the \(\text{cis-Fe}^{\text{II}}A_2B_4\) and \(\text{Fe}^{\text{II}}AB_5\) complexes, respectively (Figure 5.8). In the case of the \(S = 0\) \(\text{Fe(II)}\) electronic configuration, no unpaired electron contributes to the EFG, thus the ligand contribution determines the EFG and \(\Delta E_Q\), and the above point charge approximation should give acceptable results. Therefore, a \(-1 : 2\) ratio is expected for the quadrupole splittings of \textit{cis} and \textit{trans} isomers of \(\text{LS Fe}A_2B_4\) complexes.

Also, for the \(\text{FeAB}_5\) system a \(V_{zz}\) of \(2(q_A - q_B)\), thus a \(1 : 2\) ratio to the \textit{trans} case is expected. One of the best-performing DFT methods, the COSMO-TPSSH functional was found to reproduce the above derived \(-1 : 2 : 1\) ratio of the corresponding quadrupole splittings reasonably well, in the case of octahedral \(\text{Fe(II)}\) model compounds (Table 5.6). For the \textit{cis-trans} isomers of \(\text{FeX}_2(\text{RNC})_4\), and \(\text{FeX}(\text{RNC})_5^+\) (\(X=\text{CN}, R=\text{Et or X = Cl, R = Ph}\)), experimental data is also available, and the DFT-predicted \(\Delta E_Q\) values not only show the approximate \(-1 : 2 : 1\) ratio, but are also in a fair agreement with the measured values, as seen in Table 5.7.

<table>
<thead>
<tr>
<th>Complex</th>
<th>\textit{trans-FeA}_2B_2</th>
<th>\textit{cis-FeA}_2B_2</th>
<th>FeAB_5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Fe(CN)}_2(\text{CO})_4)</td>
<td>-1.08</td>
<td>+0.48</td>
<td>-0.65</td>
</tr>
<tr>
<td>(\text{Fe(CN)}_4(\text{CO})_2)</td>
<td>+0.71</td>
<td>-0.33</td>
<td>+0.37</td>
</tr>
<tr>
<td>(\text{Fe(CN)}_2(\text{NCS})_4)</td>
<td>-1.38</td>
<td>+0.69</td>
<td>-0.63</td>
</tr>
<tr>
<td>(\text{Fe(CN)}_4(\text{NCS})_2)</td>
<td>+1.52</td>
<td>-0.81</td>
<td>+0.81</td>
</tr>
<tr>
<td>(\text{Fe(CN)}_2(\text{PMe}_3)_4)</td>
<td>-1.23</td>
<td>+0.74</td>
<td>-0.69</td>
</tr>
<tr>
<td>(\text{Fe(CN)}_4(\text{PMe}_3)_2)</td>
<td>+0.81</td>
<td>-0.53</td>
<td>+0.40</td>
</tr>
<tr>
<td>(\text{Fe(CO)}_2(\text{CH}_3\text{CN})_4)</td>
<td>-0.51</td>
<td>+0.23</td>
<td>-0.25</td>
</tr>
<tr>
<td>(\text{Fe(CO)}_4(\text{CH}_3\text{CN})_2)</td>
<td>+0.50</td>
<td>-0.26</td>
<td>+0.20</td>
</tr>
</tbody>
</table>
Table 5.7: Comparison of experimental and DFT-calculated $\Delta E_Q$ values of octahedral Fe(II) complexes (values are given in mms$^{-1}$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp./K</th>
<th>Exp.$^a$</th>
<th>COSMO-TPSSh.$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trans-Fe(CN)$_2$(EtNC)$_4$</td>
<td>300</td>
<td>0.59</td>
<td>−0.43</td>
</tr>
<tr>
<td>cis-Fe(CN)$_2$(EtNC)$_4$</td>
<td>300</td>
<td>0.29</td>
<td>+0.18</td>
</tr>
<tr>
<td>Fe(CN)(EtNC)$_5^+$</td>
<td>300</td>
<td>0.17</td>
<td>−0.24</td>
</tr>
<tr>
<td>trans-FeCl$_2$(PhNC)$_4$</td>
<td>295</td>
<td>1.55</td>
<td>+1.70</td>
</tr>
<tr>
<td>cis-FeCl$_2$(PhNC)$_4$</td>
<td>295</td>
<td>0.78</td>
<td>−0.88</td>
</tr>
<tr>
<td>FeCl(PhNC)$_5^+$</td>
<td>295</td>
<td>0.73</td>
<td>+0.77</td>
</tr>
</tbody>
</table>

$^a$ experimental $\Delta E_Q$ values were taken from ref. 237.

$^b$ in combination with the STO-TZP basis set.

5.8.4 Phase Transitions

MS is also a powerful tool to study phase transitions.$^{227,237,336-338}$ Here we focus on those where the microscopic origin is either spin crossover or a change in the orbital degeneracy$^{339-341}$ in Fe complexes. The $\Delta E_Q$ is very sensitive to the variations in the electronic structure induced by both processes. The quadrupole splitting is typically small for octahedral LS ($S = 0$) Fe(II) and HS ($S = 5/2$) Fe(III) complexes, where the distribution of the 3$d$ electrons is symmetric: $t_{2g}^6e_{g}^0$ or $t_{2g}^3e_{g}^2$, therefore the electronic contribution to the $V_{zz}$ is zero. On the other hand, it is large in their counter-pairs in the spin crossover process, the HS ($S = 2$) Fe(II) and LS ($S = 1/2$) Fe(III) compounds. With their respective configurations, $t_{2g}^4e_{g}^2$ and $t_{2g}^5e_{g}^0$, the filling of the 3$d$ (in fact, the $t_{2g}$) subshell is uneven, thus the $d$-electron contribution to the $V_{zz}$ is large, according to its population dependence discussed in Section 5.5 (see Table 5.2, and also Figure 5.9a and b below). Consequently, these values reflect the variations in the occupation of the corresponding Fe-3$d$ orbitals. As can be seen in Table 5.8, DFT provides reliable $\Delta E_Q$ results for Fe(II) and Fe (III) SCO compounds, thus it gives a strong support for the prediction and interpretation of the Mössbauer spectra at spin-state transitions.

A different type of phase transition triggered by the redistribution of the 3$d$ electrons
is the inversion of the orbital ground state. This phenomenon was intensively studied in the HS ($S = 2$) $[\text{Fe(H}_2\text{O)}_6]^{2+}$ and $[\text{Fe(DCTU)}_6]^{2+}$ (DCTU = $N,N'$-dicyclohexylthiourea) complexes, frequently with MS.\textsuperscript{339,340} The symmetry of the system is $D_{3d}$, which corresponds to a trigonally distorted octahedron. Being a HS complex, five of the six $d$ electrons are equally distributed on the five $3d$ orbitals, hence it is the sixth one which
Table 5.8: Comparison of experimental and DFT-calculated $\Delta E_Q$ values of Fe(II) and Fe(III) spin-crossover complexes (values are given in mms$^{-1}$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Temp./K</th>
<th>Exp.$^a$</th>
<th>B3LYP$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(phen)$_2$(NCS)$_2$ (LS) (4)</td>
<td>77</td>
<td>0.34</td>
<td>0.40</td>
</tr>
<tr>
<td>Fe(phen)$_2$(NCS)$_2$ (HS) (23)</td>
<td>77</td>
<td>2.82</td>
<td>2.94</td>
</tr>
<tr>
<td>Fe(LN)$_4$(NCS)$_2$ (LS) (5)</td>
<td>80</td>
<td>0.77</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe(LN)$_4$(NCS)$_2$ (HS) (24)</td>
<td>80</td>
<td>2.51</td>
<td>2.50</td>
</tr>
<tr>
<td>Fe[HC(3,5-Me$_2$pz)$_3$I]$_2$(I)$_2$ (LS) (6)</td>
<td>4.2</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Fe[HC(3,5-Me$_2$pz)$_3$I]$_2$(I)$_2$ (HS) (25)</td>
<td>180</td>
<td>3.86</td>
<td>4.00</td>
</tr>
<tr>
<td>Fe(thpu)(Hthpu) (LS) (39)</td>
<td>80</td>
<td>3.09</td>
<td>3.45</td>
</tr>
<tr>
<td>Fe(thpu)(Hthpu) (HS) (46)</td>
<td>241</td>
<td>0.81</td>
<td>1.17</td>
</tr>
<tr>
<td>[Fe(acpa)$_2$][PF$_6$] (LS) (40)</td>
<td>78</td>
<td>2.24</td>
<td>2.24</td>
</tr>
<tr>
<td>[Fe(acpa)$_2$][PF$_6$] (HS) (47)</td>
<td>320</td>
<td>0.53</td>
<td>0.67</td>
</tr>
</tbody>
</table>

$^a$ experimental values were taken from refs. given in Table 5.1.
$^b$ in combination with the STO-TZP basis set.

For the abbreviations, also see Table 5.1.

will contribute to the $V_{zz}$ (see Figure 5.9c). The lowest-lying orbitals are a twofold-degenerate $e_g$ (with $d_{xz}$, $d_{yz}$ characters) and $a_{1g}$ (with $d_{xy}$ character). Depending on the distortion, either of them can be lowest, and thus populated by the sixth electron, giving rise to the orbitally degenerate doublet (D) or singlet (S) state (Figure 5.9c) (in solids, the crystal symmetry may stabilize the D state). The corresponding term is $5E_g$ for the D, and $5A_{1g}$ for the S state. Note that the electron-only contribution to the $V_{zz}$ for the S and D states is 2 : 1, according to Table 5.2. The experiments revealed that at low temperatures the system is in the orbital singlet ground state, which undergoes a phase transition around 200 K, and at higher temperature the doublet becomes the ground state.$^{339,340}$ Mössbauer measurements yield smaller $\Delta E_Q$ values for the D ($5E_g$) state than for the S ($5A_{1g}$) one, by ca. 2 mms$^{-1}$, which is attributed to the population variations associated with the singlet-doublet transition. As shown in Table 5.9, this
5.8. Case Studies for the Quadrupole Splitting in Mössbauer Spectroscopy

Table 5.9: Comparison of experimental and DFT-calculated $\Delta E_Q$ values of orbital singlet (S) and doublet (D) states of Fe(II) complexes (values are given in mms$^{-1}$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>State</th>
<th>Temp./K</th>
<th>Exp.$^a$</th>
<th>B3LYP$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(H}_2\text{O)}_6]^{2+}$</td>
<td>S</td>
<td>107</td>
<td>−3.36</td>
<td>−3.66</td>
</tr>
<tr>
<td>$[\text{Fe(H}_2\text{O)}_6]^{2+}$</td>
<td>D</td>
<td>295</td>
<td>+1.40</td>
<td>+1.25</td>
</tr>
<tr>
<td>$[\text{Fe(DCTU)}_6]^{2+}$</td>
<td>S</td>
<td>77</td>
<td>−3.31</td>
<td>−3.27</td>
</tr>
<tr>
<td>$[\text{Fe(DCTU)}_6]^{2+}$</td>
<td>D</td>
<td>300</td>
<td>+1.32</td>
<td>+0.94</td>
</tr>
</tbody>
</table>

$^a$ experimental values were taken from refs. 339 and 340.
$^b$ in combination with the STO-TZP basis set.

Note that for $[\text{Fe(DCTU)}_6]^{2+}$, the calculations were performed on the $[\text{Fe(DMTU)}_6]^{2+}$ (DMTU = $N,N'$-dimethylthiourea) model compound in order to reduce computational cost.

phenomenon is also reflected well by the DFT results, for which a good agreement was observed with the experimental quadrupole splittings.

5.8.5 Determination of the Sign of the Quadrupole Splitting

In most of the foregoing, the sign of $\Delta E_Q$ was not considered, only its magnitude, because the sign is usually not reported in the experimental literature. However, the sign of the quadrupole splitting gives information on the charge distribution that is very relevant to structural or coordination chemistry, as became obvious in the previous case studies too. It is determined by the sign of the $V_{zz}$, the largest component of the diagonalized traceless EFG tensor. For instance, in case of an axially distorted octahedral complex with six identical ligands, the sign of the $V_{zz}$ reveals whether the system is compressed or stretched along the principal $z$ axis (Figure 5.10). Different ligands can also change the sign of the EFG, according to the electron density on their donor atoms. The effect of a negative $V_{zz}$ is that it inverts the energy ordering of the quadrupole-split $m_I = \pm 3/2$ and $\pm 1/2$ nuclear energy levels for the $I = 3/2$ excited state, thus, it flips the lines of the quadrupole doublet. The detection of this flipping, in fact the detection of the
sign of the $V_{zz}$ is therefore very difficult experimentally because it requires either the application of an external magnetic field or the orientation-dependent measurement of the line intensities on a single crystal.

![Figure 5.10: Illustration of the sign of the EFG for a distorted spherical charge distribution (top), and for Fe complexes with O$_h$ symmetry (bottom). In case of a negative (resp. positive) $V_{zz}$, the charge distribution around the Fe nucleus is represented as an oblate (resp. prolate) spheroid, while the complex undergoes a tetragonal distortion by being compressed (resp. stretched) along the principal $z$ axis. Note that a zero $V_{zz}$ corresponds to a fully symmetric system with an undistorted charge distribution, represented by a sphere, or equal bond lengths for the O$_h$ case.](image)

We evaluated and compared the DFT-calculated and measured signs of $\Delta E_Q$ and found an excellent agreement in correctly reproducing the sign for all compounds for which it has been determined experimentally (see Table A8 in the Appendix). In particular, the calculations predict the correct negative sign for the $^5A_2$ state of complex 26, while the opposite sign is predicted for $^5B_2$; which also supports the results presented in Section 5.8.2. Also, the correct relative signs were obtained for the cis/trans-FeA$_2$B$_4$ and FeAB$_5$ complexes. Furthermore, the computations provide the correct signs for the or-
bital singlet and doublet states of the \([\text{Fe(H}_2\text{O)}_6]^{2+}\) and \([\text{Fe(DCTU)}_6]^{2+}\) complexes (Table 5.9), which signs were also obtained from the interpretation of an axial, trigonal crystal field.\(^{340}\) These results suggest that the computational approach is highly effective for the determination of the sign of quadrupole splittings, which should be considered as a very powerful tool in the investigation of the electronic structure and local symmetry.

The data obtained with combination of the four different techniques using a chemical classification (presented previously in Figure 5.5a) has also been reevaluated, this time using the sign of \(\Delta E_Q\), when available from the experiment, and assuming the calculated one, when it is not. The plot and the fitted line along with the parameters describing the fit and its goodness is shown in Figure 5.11. The agreement is very good, and the parameters indicate that exploiting the sign of the quadrupole splitting can make MS a more powerful technique in structural research.

\[ R^2 = 0.986 \]
\[ \text{MAE} = 0.12 \text{ mms}^{-1} (7\%) \]
\[ \text{max. dev.} = 0.55 \text{ mms}^{-1} (17\%) \]

\[ \text{COSMO-TPSSh} \]
\[ \text{COSMO-RPBE} \]
\[ \text{\pi-bonded; } S = 1 \text{ Fe(II); open-shell highly-distorted hexacoordinate complexes} \]
\[ \text{COSMO-B3LYP} \]
\[ S = 3/2 \text{ Fe(III)} \]
\[ \text{B3LYP} \]
\[ S = 2 \text{ Fe(II)} \]

Figure 5.11: Comparison of experimental and DFT-calculated quadrupole splittings (\(\Delta E_Q\)), applying exchange-correlation functionals for different chemical classes of Fe complexes and using the sign of \(\Delta E_Q\) as described in the text above.
5.9 Conclusion

In this chapter, DFT calculations on a large and diverse data set of Fe complexes were presented, to investigate the applicability of various density functional methods in the prediction of Mössbauer parameters. For the isomer shifts, the performance of hybrid functionals was found to be superior, compared to those of the pure DFT methods, due to the inclusion of nonlocal corrections. Moreover, the approximation of the environment of the molecule by the application of the COSMO made the calculations more reliable in predicting isomer shifts. The results do not indicate the clear preference for STOs, as the enhanced core-polarized Gaussian basis set showed a similar performance. The best agreement between experiment and theory was obtained for the COSMO-B3LYP method, which provided accurate $^{57}$Fe isomer shifts for all the 66 investigated compounds.

The results for the prediction of quadrupole splittings also indicate an improved general performance of the hybrid methods over those of the GGAs. While in general TPSSh provided the most accurate results, the also well-performing B3LYP method turned out to be the optimal for HS ($S = 2$) Fe(II) and IS ($S = 3/2$) Fe(III) complexes. However, large deviations from experiment were observed for the $\Delta E_Q$ values obtained with hybrid density functionals for molecules with $\pi$-type charge-transfer, for square planar $S = 1$ compounds, or highly-distorted hexacoordinate open-shell Fe complexes (including the systems 11, 43, 37, 38 and 64). For these systems, GGA functionals were found to give a correct description of the EFG. On the other hand, while hybrid functionals gave reliable results for IS and HS complexes, GGA methods seriously underestimated the corresponding, relatively large quadrupole splittings of these systems, most probably due to the inappropriate description of the exchange interaction in GGAs, which is better handled in hybrid functionals by the inclusion of Hartree-Fock exchange. The application of the COSMO method to approximate the role of the molecular environment improved the DFT-calculated quadrupole splittings for the majority of the studied Fe complexes. However, COSMO led to the serious overestimation of the quadrupole splittings of high-spin Fe(II) complexes when used in combination with hybrid functionals. Similar to the
5.9. Conclusion

isomer shift results, the clear preference of the Slater-type basis set over the core-polarized Gaussian one was also not observed for the prediction of quadrupole splittings.

Although no single universal method can be proposed for the calculation of $^{57}$Fe quadrupole splittings, in most cases hybrid exchange-correlation functionals in combination with the COSMO model yield sufficiently accurate results. However, in the special cases mentioned above, the omission of COSMO and/or the application of a suitable GGA functional are essential to avoid the failures described in Section 5.7. A recipe has been provided for choosing the proper DFT technique based on a chemical classification of the compounds. This combined DFT approach delivers an excellent agreement between experimental and calculated quadrupole splittings for all investigated Fe complexes. An alternative method is also tested, where the density functional is chosen according to the magnitude of the experimental $\Delta E_Q$, which could pave the way to a model-independent approach in assigning the Mössbauer spectra. However, the performance of this approach is barely better to that of the best hybrid, because it cannot remedy the problem of outliers.

The reliability of the DFT approach was also investigated by verifying its performance for a few case studies related to problems of high chemical relevance. It was found that the largest differences between the experimental and DFT-calculated quadrupole splittings in the present work and the literature can be mainly attributed to the difficulties introduced by the description of the proper ground state. This effect was observed for the 26 and 38 complexes, and by the investigation of their electronic structure it was concluded that these failures can be avoided by the careful treatment of the symmetry of these molecules to select the appropriate one from among their (quasi-) degenerate states. The results indicate that the DFT-calculated quadrupole splittings of LS cis/trans-Fe$^{II}$A$_2$B$_4$ and Fe$^{II}$AB$_5$ compounds follow the ratio $−1 : 2 : 1$ estimated in a point charge model, and agree with the experimental values. The computational method was also tested for the prediction of quadrupole splittings at phase transitions, such as spin crossover and the inversion of the orbital ground state. DFT provided results in agreement with experiment, confirming that a combined theory and MS approach is a powerful tool to
study such transitions. Finally, a perfect agreement was found for the experimental and DFT-determined signs of quadrupole splittings, which suggests the wide applicability of DFT calculations in the prediction and interpretation of this property, which is invaluable for the description of the electronic structure and local symmetry.
Chapter 6

Summary and Outlook

In the present work, the electronic structure of molecular Fe compounds was investigated with various theoretical methods by focusing on the electronic states involved in the LS↔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 [Fe(terpy)$_2$]$^{3+}$ 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 relevant Kohn-Sham orbitals indicate that the difference in the HS lifetimes of 1 and 2, detected in aqueous solution, can be attributed to the breakdown of the SCC model. Furthermore, based on the structural and energetic investigation of complex 3, its HS state was assigned to the $^5E$.

In the second part of the work, 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 valence 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, and phase transitions. Also, the benefit of utilizing the sign of $\Delta E_Q$ in characterizing distortions or identifying the appropriate electronic state at the assignment of the spectral lines was discussed.

An extension of the present work could be achieved by improving spin-state energetics with the application of DFT methods with dispersion corrections and the inclusion of zero-point vibrational energies. Moreover, a further contribution to the theoretical research on molecular switching is here proposed by aiming the investigation of singlet and triplet MLCT excited 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.
Publications Forming the Basis of the Thesis


Other Publications


Bibliography


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Abstract

The accurate description of Fe complexes with their numerous electrons and open sub-shells impose a great challenge to theory. Yet there is a large demand for the detailed understanding of the electronic structure in these complexes, as many of them are involved in processes important for different disciplines ranging from biology through chemistry to physics. The current work deals with the characterization of the electronic structure of Fe compounds, which are of high interest as functional molecules.

The electronic structures of the $[\text{Fe(tz)}_6]^{2+}$ (1) ($\text{tz} = \text{1H-tetrazole}$), $[\text{Fe(bipy)}_3]^{2+}$ (2) ($\text{bipy} = 2,2'$-bipyridine), and $[\text{Fe(terpy)}_2]^{2+}$ (3) ($\text{terpy} = 2,2':6',2''$-terpyridine) Fe(II) complexes relevant to the low-spin (LS)↔high-spin (HS) transition are investigated with (time-dependent) density functional theory (DFT) and multiconfigurational second-order perturbation theory (CASPT2). The application of the selected B3LYP* method, based on the assessment of various DFT methods in the determination of the structural and energetic variations at the spin transition, leads to the correct reproduction of the CASPT2 potential energy surfaces corresponding to the lowest-lying 3$d^6$ states of the 1–3 complexes. Furthermore, the higher HS lifetime of 3, compared to the one of 2, detected in aqueous solution, is attributed to the breakdown of the single configuration coordinate model, by the analysis of its 2D DFT and CASPT2 energy surfaces and relevant Kohn-Sham orbitals.

The second main topic of the thesis supports the experimental identification of the electronic states by the prediction of Mössbauer parameters, the isomer shift ($\delta$) and the quadrupole splitting ($\Delta E_Q$), for a comprehensive set of 66 Fe-containing systems. The Mössbauer spectrum provides invaluable information on the local electronic structure of Fe: $\delta$ reflects the variation of the electron density at the Fe nucleus, whereas $\Delta E_Q$ is a measure of the asymmetry of the charge distribution determined by its electric field gradient at the nucleus. Besides providing a clear recipe for obtaining accurate $\delta$ and $\Delta E_Q$ values, the detailed theoretical modeling of the quadrupole splitting is presented. This latter investigation includes chemically relevant case studies as well as the utilization of the sign of $\Delta E_Q$ in the assignment of the spectral lines.
Kivonat

A vaskomplexek elektronszerkezetének pontos leírása nagyszámú elektronjaik és nyúlt alhéjaik miatt, nagy kihívást jelent az elméleti vizsgálatok számára; ezek részletes ismeretére azonban mégis nagy az igény, mivel fontos biológiai, kémiai, és fizikai folyamatban meghatározó szerepük van. Munkám során olyan vasvegyűletek elektronszerkezetét tanulmányoztam, melyek funkcionális molekulákként nagy érdeklődésre tartanak számot.

A kisspinű és nagyspinű állapot közötti átmenetet mutató \([\text{Fe(tz)}_6]^{2+}\) (1) \((\text{tz} = 1H\text{-tetrazol})\), \([\text{Fe(bipy)}_3]^{2+}\) (2) \((\text{bipy} = 2,2'\text{-bipiridin})\), és \([\text{Fe(terpy)}_2]^{2+}\) (3) \((\text{terpy} = 2,2':6',2''\text{-terpiridin})\) Fe(II) kompleksek elektronszerkezetét (konvencionalis és időfüggő) sürűség-funkcionál-elmélettel (DFT = density functional theory) és multikonfigurációs másodrendű perturbációsázmátiással (CASPT2 = multiconfigurational second-order perturbation theory) vizsgáltam. A B3LYP*-ot alkalmazva, melyet számos funkcionál közül az alapján választottam ki, hogy az alkalmazott módszerük milyen pontosan határozzák meg a spinátknem arab szelekt és energetikai változásokat, kiszámítottam az 1–3 kompleksek legalacsonyabban elhelyezkedő 3d⁶ állapotainak potenciálisenergiagörbét. Ezek az energiagörbék jó egyezést mutattak a referencia CASPT2 eredményekkel.

A \([\text{Fe(terpy)}_2]^{2+}\) komplek kétdimenziós DFT és CASPT2 energiafelületeinek és jellemző Kohn-Sham pályáinak vizsgálatával megállapítottam, hogy az egykonfigurációs koordináta modell korlátozott alkalmazhatósága magyarázatul szolgálhat a 3 molekula nagyspinű állapotának 2-hez képesti vizes oldatban mért hosszabb élettartamára.

Disszertációim második fő témája az elektronállapotok kísérleti azonosításához kapcsolódóan a ^{57}Fe Mössbauer-paraméterek, az izoméretilolódás (δ) és a kvadrupólusfelhasadás (ΔE_Q) pontos számítása. A Mössbauer-spektrum értékes ismerettel szolgál a Fe lokális elektronszerkezetéről: δ a Fe-mag körüli elektronsőrűséggel arányos, ΔE_Q pedig a magnál lévő elektronsos térgradiens által meghatározott töltésseloszlás asszimetríáját méri. Doktori munkám során egy eljárást fejlesztettem ki, mellyel 66 Fe komplex Mössbauer-paramétereit pontosan meghatározhatóak voltak. Továbbá kémiaiag releváns speciális eseteket vizsgálva, és a ΔE_Q előjelét a spektrumvonalak asszignálásában használva sikerült kiaknázom a ΔE_Q számításának alkalmazási lehetőségeit.
### Appendix

**Table A1:** Correspondance between the notation of the electronic states for the point group symmetry used in the thesis.

<table>
<thead>
<tr>
<th>O point group</th>
<th>D$_{2d}$ point group</th>
<th>C$_2$ point group</th>
<th>D$_{4h}$ point group</th>
<th>D$_{3d}$ point group</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>$^1A_1$</td>
<td>$^1A(1)$</td>
<td>$^1A_{1g}$</td>
<td>$^1A_{1g}$</td>
</tr>
<tr>
<td>$^1T_1$</td>
<td>$^1A_2$</td>
<td>$^1A(2)$</td>
<td>$^1B_{1g}$</td>
<td>$^1A_{2g}(1)$</td>
</tr>
<tr>
<td>$^1T_2$</td>
<td>$^1E$</td>
<td>$^1B(1)$</td>
<td>$^1E_g$</td>
<td>$^1E_g(2)$</td>
</tr>
<tr>
<td>$^1T_1$</td>
<td>$^1E$</td>
<td>$^1B(2)$</td>
<td>$^1E_g$</td>
<td>$^1E_g(2)$</td>
</tr>
<tr>
<td>$^3T_1$</td>
<td>$^3A_2$</td>
<td>$^3A(1)$</td>
<td>$^3A_{2g}$</td>
<td>$^3A_{2g}$</td>
</tr>
<tr>
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<td>$^3E(1)$</td>
<td>$^3B(1)$</td>
<td>$^3E_g(1)$</td>
<td>$^3E_g(1)$</td>
</tr>
<tr>
<td>$^3T_1$</td>
<td>$^3E(1)$</td>
<td>$^3B(2)$</td>
<td>$^3E_g(1)$</td>
<td>$^3E_g(1)$</td>
</tr>
<tr>
<td>$^3T_2$</td>
<td>$^3B_1$</td>
<td>$^3A(2)$</td>
<td>$^3B_{2g}$</td>
<td>$^3A_{1g}$</td>
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<td>$^3T_2$</td>
<td>$^3E(2)$</td>
<td>$^3B(3)$</td>
<td>$^3E_g(2)$</td>
<td>$^3E_g(2)$</td>
</tr>
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<td>$^3E(2)$</td>
<td>$^3B(4)$</td>
<td>$^3E_g(2)$</td>
<td>$^3E_g(2)$</td>
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<tr>
<td>$^5T_2$</td>
<td>$^5B_2$</td>
<td>$^5A(1)$</td>
<td>$^5B_{2g}$</td>
<td>$^5A_{1g}$</td>
</tr>
<tr>
<td>$^5T_2$</td>
<td>$^5E$</td>
<td>$^5B(1)$</td>
<td>$^5E_g$</td>
<td>$^5E_g(1)$</td>
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<td>$^5B(2)$</td>
<td>$^5E_g$</td>
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<td>$^5B_1$</td>
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Table A2: Comparison of TD-B3LYP* and CASPT2-calculated values of crossing points of potentials corresponding to d-d transitions of [Fe(tz)$_6$]$^{2+}$. Values are given in atomic units relative to the minimum of the B3LYP* or CASPT2 $^1$A$_1$ potential.

<table>
<thead>
<tr>
<th>Crossing point</th>
<th>TD-B3LYP*</th>
<th>CASPT2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$A$_1$/$^3$T$_1$</td>
<td>0.20 (0.35)</td>
<td>0.19</td>
</tr>
<tr>
<td>$^1$A$_1$/$^3$T$_2$</td>
<td>0.33 (−$^b$)</td>
<td>0.30</td>
</tr>
<tr>
<td>$^1$A$_1$/$^5$T$_2$</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>$^1$A$_1$/$^5$E</td>
<td>0.26</td>
<td>0.23</td>
</tr>
<tr>
<td>$^1$T$_1$/$^5$T$_2$</td>
<td>−0.11</td>
<td>−0.06</td>
</tr>
<tr>
<td>$^1$T$_1$/$^5$E</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>$^3$T$_1$/$^5$T$_2$</td>
<td>0.02 (−0.03)</td>
<td>0.03</td>
</tr>
<tr>
<td>$^3$T$_1$/$^5$E</td>
<td>0.31 (0.23)</td>
<td>0.26</td>
</tr>
<tr>
<td>$^3$T$_2$/$^5$T$_2$</td>
<td>−0.06 (−0.06)</td>
<td>−0.03</td>
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<tr>
<td>$^3$T$_2$/$^5$E</td>
<td>0.19 (0.19)</td>
<td>0.20</td>
</tr>
</tbody>
</table>

$^a$ from ref. 18.

For crossing points involving triplet states, the first TD-B3LYP* value was obtained with a triplet reference, while values given in parenthesis were calculated applying a singlet reference state.

$^b$ no crossing point was observed in the investigated range.
Table A3: Comparison of the TD-B3LYP* and CASPT2-calculated values of minimum energies corresponding to the potentials of the metal-centered electronic states of [Fe(tz)$_6$]$^{2+}$. Values are given in eV relative to the minimum of the B3LYP* or CASPT2 $^{1}A_1$ potential (from ref. 18).

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>TD-B3LYP*</th>
<th>CASPT2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$^1T_1$</td>
<td>1.91</td>
<td>1.89</td>
</tr>
<tr>
<td>$^3T_1$</td>
<td>0.72 (1.09)</td>
<td>0.86</td>
</tr>
<tr>
<td>$^1T_2$</td>
<td>1.33 (1.37)</td>
<td>1.42</td>
</tr>
<tr>
<td>$^5T_2$</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>$^5E$</td>
<td>1.39</td>
<td>1.46</td>
</tr>
</tbody>
</table>

$^a$ from ref. 18.

For triplet states, the first TD-B3LYP* value was obtained with a triplet reference, while values given in parenthesis were calculated applying a singlet reference state.
**Table A4:** Comparison of TD-B3LYP* and CASPT2-calculated values of crossing points of potentials corresponding to $d$-$d$ transitions of [Fe(bipy)$_3$]$^{2+}$. Values are given in atomic units relative to the minimum of the B3LYP* or CASPT2 $^1A_1$ potential.

<table>
<thead>
<tr>
<th>Crossing point</th>
<th>TD-B3LYP*</th>
<th>CASPT2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1/^3T_1$</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>$^1A_1/^3T_2$</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>$^1A_1/^5T_2$</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>$^1A_1/^5E$</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>$^1T_1/^5T_2$</td>
<td>−0.10</td>
<td>−0.02</td>
</tr>
<tr>
<td>$^1T_1/^5E$</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>$^3T_1/^5T_2$</td>
<td>0.05</td>
<td>0.07</td>
</tr>
<tr>
<td>$^3T_1/^5E$</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>$^3T_2/^5T_2$</td>
<td>−0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>$^3T_2/^5E$</td>
<td>0.22</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$^a$ from ref. 19.

**Table A5:** Comparison of the TD-B3LYP* and CASPT2-calculated values of minimum energies corresponding to the potentials of the metal-centered electronic states of [Fe(bipy)$_3$]$^{2+}$. Values are given in eV relative to the minimum of the B3LYP* or CASPT2 $^1A_1$ potential (from ref. 19).

<table>
<thead>
<tr>
<th>Electronic state</th>
<th>TD-B3LYP*</th>
<th>CASPT2$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_1$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>$^1T_1$</td>
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<td>2.30</td>
</tr>
<tr>
<td>$^3T_1$</td>
<td>0.92</td>
<td>1.24</td>
</tr>
<tr>
<td>$^1T_2$</td>
<td>1.48</td>
<td>1.77</td>
</tr>
<tr>
<td>$^5T_2$</td>
<td>0.54</td>
<td>0.69</td>
</tr>
<tr>
<td>$^5E$</td>
<td>1.93</td>
<td>2.22</td>
</tr>
</tbody>
</table>

$^a$ from ref. 19.


**Table A6:** Linear fit parameters obtained for the $\delta = (\rho(0) - c) + \beta$ calculation of isomer shifts.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\alpha$ (au$^3$mms$^{-1}$)</th>
<th>$\beta$ (mms$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>GTO-CP(PPP) basis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>$-0.458\pm0.017$</td>
<td>$12.86\pm0.46$</td>
</tr>
<tr>
<td>OLYP</td>
<td>$-0.466\pm0.019$</td>
<td>$4.55\pm0.17$</td>
</tr>
<tr>
<td>B3LYP</td>
<td>$-0.431\pm0.009$</td>
<td>$7.66\pm0.15$</td>
</tr>
<tr>
<td>B3LYP*</td>
<td>$-0.439\pm0.011$</td>
<td>$6.75\pm0.15$</td>
</tr>
<tr>
<td>TPSS</td>
<td>$-0.463\pm0.015$</td>
<td>$10.33\pm0.32$</td>
</tr>
<tr>
<td>TPSSh</td>
<td>$-0.443\pm0.011$</td>
<td>$9.38\pm0.22$</td>
</tr>
<tr>
<td><strong>STO-TZP basis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPBE</td>
<td>$-0.464\pm0.018$</td>
<td>$16.36\pm0.63$</td>
</tr>
<tr>
<td>OLYP</td>
<td>$-0.367\pm0.020$</td>
<td>$7.97\pm0.41$</td>
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<tr>
<td>B3LYP</td>
<td>$-0.419\pm0.008$</td>
<td>$10.40\pm0.20$</td>
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<tr>
<td>B3LYP*</td>
<td>$-0.433\pm0.010$</td>
<td>$9.34\pm0.21$</td>
</tr>
<tr>
<td>TPSS</td>
<td>$-0.485\pm0.016$</td>
<td>$17.79\pm0.59$</td>
</tr>
<tr>
<td>TPSSh</td>
<td>$-0.452\pm0.012$</td>
<td>$16.28\pm0.44$</td>
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</tbody>
</table>
**Table A7:** Linear fit parameters obtained with the application of the COSMO for the \( \delta = (\rho(0) - c) + \beta \) calculation of isomer shifts.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \alpha ) (au(^3)mms(^{-1}))</th>
<th>( \beta ) (mms(^{-1}))</th>
</tr>
</thead>
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<tr>
<td></td>
<td>GTO-CP(PPP) basis</td>
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</tr>
<tr>
<td>RPBE</td>
<td>(-0.459\pm0.014)</td>
<td>(12.91\pm0.38)</td>
</tr>
<tr>
<td>OLYP</td>
<td>(-0.448\pm0.014)</td>
<td>(4.40\pm0.13)</td>
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<tr>
<td>B3LYP</td>
<td>(-0.424\pm0.007)</td>
<td>(7.55\pm0.12)</td>
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<tr>
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<td>(-0.439\pm0.008)</td>
<td>(6.77\pm0.12)</td>
</tr>
<tr>
<td>TPSS</td>
<td>(-0.462\pm0.012)</td>
<td>(10.33\pm0.26)</td>
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<tr>
<td>TPSSh</td>
<td>(-0.442\pm0.008)</td>
<td>(9.39\pm0.17)</td>
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<td></td>
<td>STO-TZP basis</td>
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<td>(10.47\pm0.16)</td>
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<td>(9.42\pm0.17)</td>
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<td>TPSS</td>
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<td>(18.25\pm0.54)</td>
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<tr>
<td>TPSSh</td>
<td>(-0.459\pm0.011)</td>
<td>(16.54\pm0.38)</td>
</tr>
</tbody>
</table>
Table A8: Comparison of experimental and COSMO-TPSSh/STO-TZP calculated $\delta$, $\Delta E_Q$ (both given in $\text{mms}^{-1}$), and $\eta$ values

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{4,2K}$ (exp.)</th>
<th>$\delta$ (calc.)</th>
<th>$\Delta E_Q$ (exp.)</th>
<th>$\Delta E_Q$ (calc.)</th>
<th>$\eta$</th>
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</thead>
<tbody>
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<td>0.77</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>+3.83</td>
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</tr>
<tr>
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</tr>
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<td>+0.91</td>
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</tr>
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<td>+2.87</td>
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<td>69</td>
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