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Transition Metals in Coordination Environments

Computational Chemistry and Catalysis Viewpoints

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Preface

From its very foundation, quantum chemistry has been closely accompanying experiment in search of properties of a coordinate bond and structures of coordination compounds. The impact of the molecular orbital concept exerted on the model crystal field theory converted it to the ligand field theory which paved the way to investigate transition metal (TM) systems from first principles. Already early and of necessity simplified wave function methods were applied to study structures and other properties of transition metal complexes, but only after the advent of robust density functional-based methods, the number of quantitative applications dramatically increased. The number of theoretical works devoted to transition metal coordination compounds, dealing with their intricate electronic structures, spectral and magnetic properties, and related catalytic activity has already exceeded ten thousand, with recent contributions reaching over 500 papers each year. This is an obvious direction since the electronic properties of coordinated transition metals are largely responsible for unique activity of TM sites in materials and bio- or inorganic catalysis, and fine control of an intricate TM chemistry is vital for the progress of society and environmental safety.

Wide demand for theory-based practical guidelines for designing modern materials in the fields of medicine, electronics, and sustainable technology compelled the studies on transition metal compounds to verge upon the limits. However, it was soon recognized that the exact description of advanced electronic and magnetic properties of TM sites in materials required involvement of high-level theoretical approaches, more demanding than standard density functional theory (DFT). This prompted us to design this book as a collection of chapters, dealing with both the advancements in correlated wave function theory, making it still more accurate but less costly, and summarizing the attempts to upgrade DFT methods to make them sufficiently accurate to become robust and reliable tools for quantitative predictions. On the other hand, the quest for exact description of electron density-based properties of coordinated transition metals is challenging to both theory and experiment; thus, the interplay between these two areas remains in the focus of consecutive chapters devoted to selected subfields, here spin-related phenomena, spectroscopic, electrochemical, and catalytic properties of TM in

various coordination environments. In this spirit, the following chapters are not strictly ordered either according to the level of theory or along formal distinction with respect to the branch of chemistry or physics, but cover rather related fields, combining various levels of theory and experiment.

The initial batch of five chapters deals with magnetic interactions, untypical systems, and related dedicated theoretical approaches. Chapter "The Electronic Determinants of Spin Crossover Described by Density Functional Theory" by Kasper P. Kepp deals with spin crossover (SCO) phenomenon which plays a vital role in living systems and in many emerging technologies. In line with the introductory paragraphs, the accurate prediction and design of SCO systems are of high current priority, while SCO tendency is extremely sensitive not only to the level of theory but also to its ability to cover such physical effects as dispersion, relativistic effects, and vibrational entropy for large molecular systems. It is shown that the density functional theory (DFT) is the tool of choice that can be predictive for this purpose only if the study is carried out scrupulously. A similar approach is taken in Chapter "Anisotropic Magnetic Spin Interactions of Transition Metal Complexes and Metalloenzymes from Spectroscopy and Quantum Chemistry" where Matthias Stein on example of transition metal-containing model complexes and metalloenzymes discusses the advancement of DFT computational approaches to calculate the parameters of the effective Spin Hamiltonian such as the electronic g- and hyperfine tensors in order to support the analysis and interpretation of complex magnetic resonance spectra. Chapter "Non-covalent Interactions in Selected Transition Metal Complexes" by Filip Sagan and Mariusz P. Mitoraj discusses how DFT is able to describe non-covalent chemical interactions in transition metal complexes where routine DFT methods have been known to occasionally fail. The authors illustrate on several examples of nonstandard bonds that good separation of donation (ligand to metal) and back-donation (metal to ligand) charge transfer processes, which govern this type of bonding, may be done by proper analysis of the deformation density.

Different approach is taken by Vera Krewald and Dimitrios A. Pantazis (Chapter "Applications of the Density Matrix Renormalization Group to Exchange-Coupled Transition Metal Systems"). This chapter deals with inherently multireference problem, like oligonuclear transition metal complexes containing magnetically coupled open-shell ions, not always tractable by broken-symmetry DFT. In such cases, the use of multireference methods remains the deal to treat the exchange coupling. However, the applicability of these methods has been severely restricted due to their computational cost, and only in recent years, the introduction of the density matrix renormalization group (DMRG) to quantum chemistry has enabled the multireference treatment of exchange-coupled transition metal systems. The first detailed applications of DMRG-based methods to exchange-coupled systems are reviewed, and the lessons learned so far regarding the applicability, apparent limitations, and future promise of this approach are discussed. In the same spirit, Chapter "New Strategies in Modeling Electronic Structures and Properties with Applications to Actinides" is written by Aleksandra Leszczyk, Paweł Tecmer, and Katharina Boguslawski. After a short overview of relativistic Hamiltonians,

frequently applied to account for relativistic effects, the authors review conventional and unconventional single- and multireference approaches, developed to model the multireference nature of actinide compounds and their ground- and excited-state electronic structures, finishing with geminal-based approaches. In addition, concepts of quantum information theory are introduced, providing a qualitative understanding of complex electronic structures of actinide compounds using the picture of interacting orbitals.

The set of next four chapters is generally devoted to spectroscopic issues where the interplay between experiment and theory is frequently indispensable for the interpretation of the spectra and translates the gained information into chemical insights. In Chapter "Computational Versus Experimental Spectroscopy for Transition Metals" Maja Gruden, Wesley R. Browne, Marcel Swart, and Carole Duboc discuss a variety of examples where different spectroscopy techniques aided by computations allow to determine intricate and elusive properties, like the oxidation state, spin state, or coordination environment around redox-active metal ions such as iron, manganese, or nickel.

Marcus Lundberg and Mickaël G. Delcey show in Chapter "Multiconfigurational Approach to X-ray Spectroscopy of Transition Metal Complexes" how close correlation between theoretical modeling and X-ray experiment allows for the identification of the electronic and geometric structure of transition metal system through their spectral fingerprint from the core excitation energies. Compared to ground state calculations, modeling of X-ray spectra is complicated by the presence of the core hole, which typically leads to multiple open shells and large effects of spin–orbit coupling. Thus, reliable fingerprinting requires a theoretical model that is accurate enough, and the authors show that multiconfigurational wave function approaches, recently extended to model a number of X-ray processes of transition metal complexes, are suitable for that purpose. Chapter "Assessing Electronically Excited States of Cobalamins via Absorption Spectroscopy and Time-Dependent Density Functional Theory" by Megan J. Toda, Pawel M. Kozlowski, and Tadeusz Andruniów is specifically devoted to one type of systems, B12 chemistry. Due to the complexity and the size of the cobalamins, the computational analysis is almost exclusively represented by DFT and time-dependent DFT (TD-DFT) methods; thus, the proper choice of exchange-correlation functional discussed by authors is of paramount importance in predicting electronic transitions and simulating the full spectrum reliably. Chapter "Photodeactivation Channels of Transition Metal Complexes: A Computational Chemistry Perspective" by Daniel Escudero which concludes this section deals with the fate of the excited states in a transition metal compound, deactivating via a plethora of interconnected relaxation processes, competing with each other and controlled by the subtle interplay of electronic and geometrical rearrangements. The author provides critical overview of the state-of-the-art quantum chemical and reaction dynamic methods to study the photodeactivation dynamics in transition metal compounds and illustrates the progress and challenges in this field with recent examples on a variety of excited states in photoactive iridium and ruthenium complexes.

Finally, the third section of the book is devoted to computational approaches to catalysis by transition metal compounds, with enzymatic and biomimetic systems allocated as the last, separate part. The section opens with Chapter "Mechanism and Kinetics in Homogeneous Catalysis: A Computational Viewpoint" where Jeremy N. Harvey critically reviews the use of computational methods based on electronic structure theory and statistical mechanics to study reaction mechanisms and kinetics in homogeneous catalysis, especially organometallic catalysis and organocatalysis. The chapter is based on suitably selected examples from the authors' own group, which are discussed in the perspective of progress and still open challenges for computational chemistry to model actual chemistry. A careful reading of this chapter may be especially recommended as a warning to researches pursuing this domain of computational modeling because it draws their attention to still existing (and occasionally even growing) number of doubts and pitfalls awaiting inexperienced users of "user-friendly" computational, half-automated tools. The main line set in the introductory chapter for this part is actually followed in consecutive three chapters which are devoted to complicated reaction patterns found in catalytic systems and summarize attempts to allow various extended environments into the modeling.

Chapter "Computational Modelling of Structure and Catalytic Properties of Silica-Supported Group VI Transition Metal Oxide Species" by Jarosław Handzlik deals with chromium, molybdenum, and tungsten oxides supported on amorphous silica, the catalysts for many reactions, including large-scale industrial processes. Although these systems have been extensively studied for many years, there are still unresolved issues, concerning mainly the nature of the active sites and mechanisms of their formation. Computational studies, using carefully selected cluster or periodic models to represent the catalyst surface, are helpful in interpretation of spectroscopic data and can provide complementary information about the catalytic process and lead to complex structure–activity relationships. Nevertheless, even if a great progress has been achieved in modeling of these systems, theoretical determining of complex reaction mechanisms using surface models with representative distribution of metal sites is still a challenge for computational catalysis. Chapter "Catalytic Properties of Selected Transition Metal Oxides—Computational Studies" by Witold Piskorz and Filip Zasada constitutes the review of computational methods applied specifically to transition metal oxides (most abundant in heterogeneous catalysis, used as bulk or supported oxides) and is focused on the influence of the environment on the transition metal cation properties. The shortcomings of the DFT level of theory, most commonly used for modeling, are discussed, and its extensions toward more realistic environment are presented. The modern reactive force field methods are also mentioned, and the embedding schemes most commonly found in the quantum chemical or classical description of the heterogeneous processes are discussed. It is shown that in all discussed systems, the appropriately applied Hubbard DFT GGA+U methods are successful provided that the Hubbard correction is carefully tuned for modeling of particular properties. In turn, Chapter "Molecular Electrochemistry of Coordination Compounds—A Correlation Between Quantum Chemical Calculations and Experiment" by

Piotr P. Romańczyk and Stefan S. Kurek describes the progress in efficient solvation models that helped to develop effective computational protocols allowing for accurate reproduction of experimental redox potentials of mono- and dinuclear complexes, including electrocatalytically relevant systems and mixed-valence compounds. Examples of such computational protocols that use DFT combined with continuum solvent models, as well as a mixed, discrete-continuum approach, are shown in this contribution. The ferrocenium/ferrocene system, widely used as an internal standard, is discussed, followed by the presentation of intriguing properties of mono- and bimetallic Mo/W scorpionates, in particular electrochemical communication between metal centers and a baffling dehalogenation, the mechanism of which was elucidated only owing to the application of DFT-D3 calculations.

The end section of the book entails four chapters and discusses enzymatic and biomimetic systems. The topic is singled out even if problems intrinsic to very large systems incorporating transition metals are generally common; nevertheless, transition metals in bio- or bioinorganic complexes share several specific properties and specific techniques common among them but distinctive from inorganic transition metal complexes. This part opens with Chapter "The Quest for Accurate Theoretical Models of Metalloenzymes: An Aid to Experiment" by Matthew G. Quesne and Sam P. de Visser. The chapter reviews two key computational approaches to metalloenzymes, namely quantum mechanics/molecular mechanics (QM/MM) on complete enzyme structures and QM cluster models on active site structures only. The former take the structure of the full enzyme with a solvent layer into consideration, whereas the latter only include key features of the first and second coordination sphere. The examples are discussed where the QM cluster approach worked well; however, for systems where substrate binding is tight and or a network of hydrogen-bonding interactions exists, a complete QM/MM approach may be more appropriate. The following Chapter "Applications of Computational Chemistry to Selected Problems of Transition-Metal Catalysis in Biological and Nonbiological Systems" by Hajime Hirao describes as well recent attempts to study the structure and catalytic properties of transition metal-containing systems of different sizes, including metalloenzymes but also metal–organic frameworks (MOFs). Similar techniques (DFT and hybrid techniques for embedding) are used, but examples are selected specifically and substantially broaden the spectrum of applications, increasing the pool for critical analyses and benchmarking. The same concerns Chapter "How Metal Coordination in the Ca-, Ce-, and Eu-Containing Methanol Dehydrogenase Enzymes can Influence the Catalysis: A Theoretical Point of View" written by Tiziana Marino, Mario Prejanò, and Nino Russo, where the pool of examples is farther enriched with studies on lanthanide-containing enzymes where relativistic effects played a significant role.

The section is finalized by Tomasz Borowski and Maciej Szaleniec in Chapter "Challenges in Modelling Metalloenzymes" which gives a critical summary of the entire process of constructing a reliable computational model for metalloenzymes. This contribution, complementary to preceding chapters, nicely illustrates and validates the key decisions and steps one has to take in such projects: validating

X-ray structures, re-refining metal sites, determining residues protonation state, modeling missing loop regions or whole proteins by comparative modeling, performing MD simulations, choosing representative snapshots and constructing QM models. While this list is by no means exhaustive, the content of this chapter, combined with the material covered in other chapters of this book offers a more comprehensive view on modeling metalloenzymes and may supply additional suggestions for modeling other systems related to modern materials.

In the closing paragraph of this Preface, the reader deserves some remarks justifying the need for publishing (and reading!) still new book on modeling transition metals in various coordination environments despite that many works on the topic have already appeared. We hope we succeed in constructing the book as a collection of chapters well obeying the balance between methodological and practical information. The first nine chapters deal with advancements in correlated wave function and DFT methods making them applicable to nonstandard problems, whereas the next eight contributions bring as well instructive examples of their applications as practical guidance (and warnings!) to prospective users of modeling protocols in related disciplines.

We are very grateful to all authors for their contributions shaping this book and for their patience.

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The Electronic Determinants of Spin Crossover Described by Density Functional Theory

Kasper Planeta Kepp

Abstract Spin crossover (SCO) plays a vital role in living systems and in many emerging technologies, and the accurate prediction and design of SCO systems is of high current priority. Density functional theory (DFT) is the state-of-the-art tool for this purpose due to its ability to describe large molecular electronic systems with an accuracy that can be predictive if carried out correctly. However, the SCO tendency, i.e., the free-energy balance of high- and low-spin states, is extremely sensitive to the theoretical description and physical effects such as dispersion, relativistic effects, and vibrational entropy. This chapter summarizes the recent fundamental insight into SCO gained from DFT and efforts that approach the accuracy needed (~10 kJ/mol) for rational design of SCO to become reality.

1 Introduction

Spin crossover (SCO) is the process, whereby two electronic states of different quantum-mechanical spins interconvert upon perturbation such as chemical bonding, temperature, light, or applied pressure [1–9]. Since its discovery in coordination complexes [10], it has emerged as one of the most important chemical processes [1–3, 11]. If this importance is not immediately appreciated, please consider that without SCO, the reader would suffocate within 2–3 min due to the absence of O_2 binding to hemoglobin within the honorable reader's lung arteria.

Some chemical systems can undergo transition between the two spin states without any change of chemical composition, whereas others only do so upon interaction with other molecules, such as ligand binding to a metal. The term "SCO system" or "SCO complex" is mainly used if the transition occurs relatively near standard conditions of temperature and pressure. Thus, thermal SCO systems are particularly notable as those where SCO occurs close to atmospheric pressure and within the range of room temperature by a few hundred Kelvin. Such systems are central to life

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processes via the management of $^3O_2$ by hemes [12–14]. They are also important to many emerging technologies [1, 3], as they manifest as two distinct quantum states that can be interconverted by external stimuli. This makes them suitable for, e.g., molecular electronics [3, 15–17], sensors [18–20], and nano-mechanical behavior such as molecular motors [3, 7, 21–27].

For convenience, we will write the SCO process as a conversion from a low-spin state (LS) to a high-spin state (HS),

$$LS \rightleftharpoons HS \tag{1}$$

where the HS state has the highest spin quantum number or, if this number is not well-defined, the largest magnetic moment due to parallel alignment of electron spins. The fundamental requirement of SCO is then that the free energy difference of the two electronic spin states approaches zero [2, 28, 29]:

$$\Delta G_{SCO} = \Delta H_{SCO} - T \, \Delta S_{SCO} \approx 0 \tag{2}$$

The enthalpy ΔH_{SCO} largely derives from changes in the ground-state electronic structure during SCO. These effects can be obtained from electronic energy calculations using standard quantum-mechanical programs and a suitable Hamiltonian, but it includes various energy terms not always considered that systematically contribute to ΔH_{SCO}, most notably the differential zero-point energy, dispersion forces, and relativistic effects of the two states [28, 30]. In contrast, the entropy of the process ΔS_{SCO} to a large extent (but not completely) arises from changes in the vibrational state functions [2, 30, 31] and favors the weaker and longer M–L bonds of the HS state [24, 28, 32, 33]. The electronic degeneracy contribution to this entropy is somewhat less important than the vibrational entropy of the involved chemical bonds [28, 30, 34, 35], as first recognized by Sorai and coworkers [24, 32].

Written as in (1) and (2), because ΔS_{SCO} is positive, higher temperature will favor the right-side HS state via $-T\Delta S_{SCO}$ of (2), and thus conversion from an initial LS state to HS is induced by raising the temperature [24, 29]. It turns out by inspection of experimental data for iron SCO systems, but it remains to be confirmed as a general law, that the entropy and enthalpy terms of (2) tend to compensate each other substantially, as also seen in some other processes [36]. This would suggest that SCO may be a true entropy–enthalpy compensation process not just with entropy favoring reaction toward the right, but with the two terms canceling over a broad range of enthalpies and entropies; this possibility is explored further in the present chapter as it has direct implications for accurate prediction of the SCO tendency.

Transition metal ions of the middle of the first row of the d-block, specifically Mn, Fe, and Co, are particularly common in SCO systems: SCO has been observed in d^4, d^5, d^6, d^7 and arguably in some Ni(II) d^8 systems [37]. This is partly because the ligand field stabilization energy has a magnitude that makes the vibrational entropy cancel the energy terms almost perfectly. However, the balance is a compromise between the metal ion and ligand field strength, as both contribute to the SCO tendency. This is

illustrated by the spectrochemical series of the ligands and the corresponding series of the metal ions [38, 39]. Thus, for example, most SCO systems contain moderate-field nitrogen-donor ligands combined with Fe(II), as exemplified by the much studied, first synthetic iron(II) SCO system $Fe(Phen)_2SCN_2$ [40–43]. However, Fe(III) and Co(II) are also relatively common SCO metal ions, with the first-reported Fe(III) SCO systems being those of Cambi et al. [10] and the first Co(II) SCO system being that of Stoufer et al. [44].

In this chapter, the basis for describing SCO accurately by chemical–physical principles and the role of various contributions to the SCO tendency will be discussed. These include important systematic energy terms, i.e., the zero-point vibration energy, relativistic contributions to SCO, and dispersion forces that modulate the HS–LS equilibrium already at the single-molecule level. The importance of modeling the vibrational entropy contribution in the theoretical study of SCO systems is emphasized. The difference between the spectrochemical series and the "thermochemical series" of spin-state propensities are discussed. The performance of DFT and various ingredients of the functionals that affect the accuracy are analyzed.

2 Fundamentals of Spin Crossover

2.1 The Dilemma and Choice Between LS and HS

As taught in basis inorganic chemistry, when ligands are placed around a metal ion, the energies of the d-orbitals split into several energy levels due to the symmetry breaking, i.e., the d-orbitals experience different environments. If the ligand field is octahedral (O_h symmetry), two levels occur: The two high-lying degenerate e_g orbitals are aligned toward the ligands and thus experience more electronic repulsion, and the threefold degenerate low-lying t_{2g} orbital level becomes less repelled as these orbitals (originating from d_{xy}, d_{xz}, and d_{yz}) distribute further from the ligands.

Depending on the energy splitting Δ_o between the two levels, the electrons face a dilemma after occupying the three t_{2g} orbitals by one electron according to Hund's Rule: Either the additional electrons distribute in the normal fashion by pairing with the three first t_{2g} electrons or, if the energy distance is small, they may in fact move to the next level, e_g. The solution to this dilemma partly (but not completely, as discussed below) lies in resolving the relative magnitude of the penalty of moving up to the e_g orbitals, i.e., Δ_o, versus the penalty of occupying a t_{2g} orbital where another electron is already residing close in space, i.e., the spin-pairing energy penalty P. This situation is also entropically unfavorable, to be discussed below. If the fourth and fifth electron decide to move to e_g, the system will experience more aligned electron spins; this state is the HS state. If it is more favorable to pair with the t_{2g} electrons first, the resulting spin and magnetic moment becomes smaller; this is the LS state.
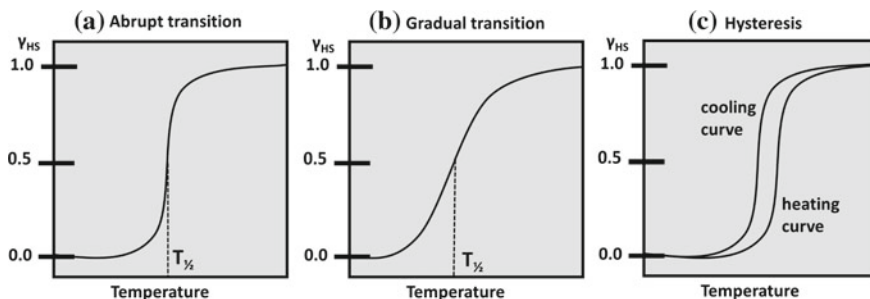
Fig. 1 Schematic representation of the transition from a low-spin electronic state with zero or little magnetism, which dominates at low temperature, to a more magnetic high-spin state, which dominates at higher temperature. **a** Abrupt transitions increase magnetism quickly near the transition temperature; **b** gradual transitions display smaller temperature gradients of the magnetism near transition; **c** hysteresis involves different transition temperatures upon heating and cooling

The question now arises: What happens if this dilemma remains unsolved, in other words, if the energy cost of pairing in the same orbitals and the entropy loss associated with this more compact LS state is almost perfectly outweighing the benefits of the lower orbital energies? If this is the case, the two possible occupations may be realized not far from standard conditions, as speculated by Pauling in his third paper in the series on the chemical bond, where he discussed the magnetic criterion for transition between HS and LS states [45]; these systems are the SCO systems.

The temperature at which the conversion in (1) takes place is referred to as the transition temperature, $T_{1/2}$, the temperature at which half of the system is in the HS state (the most magnetic), written as $\gamma_{HS} = \frac{1}{2}$, and the other half is in the LS state (the least magnetic or even diamagnetic state, as in, e.g., Fe(II) LS), written as $\gamma_{LS} = \frac{1}{2}$. Accordingly, at higher temperature, the fraction of HS, γ_{HS}, exceeds ½. This situation is shown schematically in Fig. 1a for an abrupt transition. The process can also be considerably more gradual, as shown schematically in Fig. 1b, characterized by a smaller magnetic susceptibility gradient at $T_{1/2}$. For abrupt processes, hysteresis is commonly observed (Fig. 1c), as discussed in detail in this chapter. At $T_{1/2}$, the isobaric heat capacity C_p displays a major peak reflecting the transition, being either narrow and steep or broader depending on whether the transition is abrupt or gradual [24].

Under actual equilibrium conditions, which are rarely realized in practice, the equilibrium constant K_{SCO} is equal to unity and the free energy of the process is then $\Delta G_{SCO} = 0$. However, due to the nonequilibrium nature of the actual transition, one can hardly consider this definition exact. Still it is theoretically meaningful to separate contributions to the free energy and transition temperature, as the following discussion shows. Simply put, the core premise of theoretical studies of SCO is that if the relationship holds, we should be able to predict $T_{1/2}$ from an estimate of $\Delta G_{SCO} = 0$, determined by electronic structure calculations. Under such conditions,

$T_{½} = \Delta H_{SCO}/\Delta S_{SCO}$, which can, as discussed below, be obtained from quantum-chemical computations at variable accuracy.

2.2   The Spectrochemical Series

In text books, the spectrochemical series [38, 46, 47] is traditionally used to estimate the preference for either HS or LS in a given coordination complex. This series is based on spectroscopic measurements of the absorption peak for the d–d transitions of cobalt(III) complexes and ranks common coordinating ligands according to Δ_o in an octahedral field. A rough rule-of-thumb order is:

$I^- < Br^- < Cl^- < F^- < S$ σ-donor $< O$ σ-donor $< N$ σ-donor $< π$-acceptors

Although sometimes forgotten, this series is mainly based on Co(III), and the series, more specifically, the ligand field stabilization energy calculated from Δ_o, estimates the relative preference for HS versus LS *if this preference was only due to electronic energy* as measured by the absorption spectroscopy. The series, moreover, reflects a non-thermal electronic excitation, whereas the SCO systems of interest involve the thermal excitation of typically two electrons. Although widely used and displayed in textbooks, the estimates based on the spectrochemical series thus miss vibrational relaxation, spin pairing, and entropic effects, and they do not necessarily accurately convey the spin-state preference in a real chemical system at thermal equilibrium. Still, because the energy described by absorption maximum is a large part of the typical thermodynamic preference between the spin states, it is often accurate when applied to trend predictions, which largely explains its success [48–51].

2.3   The Thermochemical Spin Series

The real thermochemical spin-state preference and thus the adequate tool for rationalizing and predicting SCO can be argued to be a "thermochemical series" of spin-state propensity [52]. This series takes into account ground-state geometry relaxation of the HS state and entropy terms that also favor HS [31, 52, 53]. This series is straightforward achievable from DFT computations of the fully relaxed ground-state geometry of the HS state, which corrects the spectrochemical series based on electronic transitions in which the HS state features as an excited state. Furthermore, DFT can compute the vibrational entropy term with decent accuracy [36, 52, 54] so that the real preference as given by the free energy in (2) is honored. The series is importantly independent on the functional used [52], because the trend of interest involves cancellation of the major systematic errors in DFT that are discussed below.

The resulting thermochemical series resembles the spectrochemical series, but notably differs in several aspects. One of the most interesting differences is that Cl^- and Br^- have similar spin-state propensity once the thermochemical, spin-pairing, and vibrational-structural corrections are accounted for [52]. In the spectrochemical series, they separate clearly in the halide trend. Another difference is the preference for negatively charged versus neutral π-acceptors such as CN^- and CO, which change place in the thermochemical series depending on the oxidation state of the metal ion. A third difference relates to coordination isomers such as $\underline{S}CN^-$ and $\underline{N}CS^-$ that also change relative position depending on metal oxidation state [52], of relevance to the much studied SCO system $[Fe(SCN)_2(Phen)_2]$ and its derivatives.

The thermochemical series is quantitative and includes vibrational relaxation and entropy terms directly [52]. Thus, one can predict that Mn(III) systems will have relatively similar ligand preferences as Fe(II) in order to induce SCO, whereas Fe(III) should have a slightly weaker total ligand field; Co(II) SCO systems are predicted to be realized with stronger ligand fields than for Mn(III), Fe(III), and Fe(II), and even stronger ligand fields are required for Mn(II) such that even CO and CN^- become relevant. In contrast, Co(III) requries very weak ligands due to its strong LS preference, with SCO most likely occuring between F^- and weak O-donor ligands such as water, ethers, and alcohols [52]. Examples of SCO systems that illustrate these preferences are shown in Fig. 2, with 6N coordination for Fe(II) (Fig. 2a), weaker 4N2O coordination for Fe(III) (Fig. 2b), tunable ligand fields for porphyrins with Fe(II)/Fe(III) (Fig. 2c), 6N coordination for Co(II) (Fig. 2d), and correspondingly weaker 6O ligand field for Co(III) (Fig. 2e).

2.4 The Oxidation State on the Central Metal Ion

The metal ion's oxidation state plays a major role in defining the spin-state propensity, with higher oxidation state favoring LS. This effect ("the spectrochemical series of the central ions") was originally formulated by Jørgensen on the basis of spectroscopic data [39], but its fundamental truth is easily recovered and even quantified using modern DFT [52]. Specifically, a difference in LS preference of Fe(II) and Fe(III) of ~50 kJ/mol has been estimated [52]; for Co(III) versus Co(II), the difference is even higher and can reach 100 kJ/mol [52]. This effect clearly needs to be considered if SCO systems of variable metal oxidation states are to be developed by rational screening.

The fact that Fe(III) favors LS more than Fe(II) is easily understood from the stronger and shorter metal–ligand bonds formed in the higher oxidation states, which increases the σ-donation and thus the ligand field splitting and tendency toward low spin. Because of this, the most common coordination structure for Fe(II) SCO systems is 6N [55], whereas for Fe(III) SCO systems, the 4N2O coordination structure is common [6], where two nitrogen donors have been changed into weaker oxygen donor atoms. There are many exceptions to this preference: For example, some 4N2O iron(II) systems have been reported [56], and an Fe(II) 5N1S system has been made
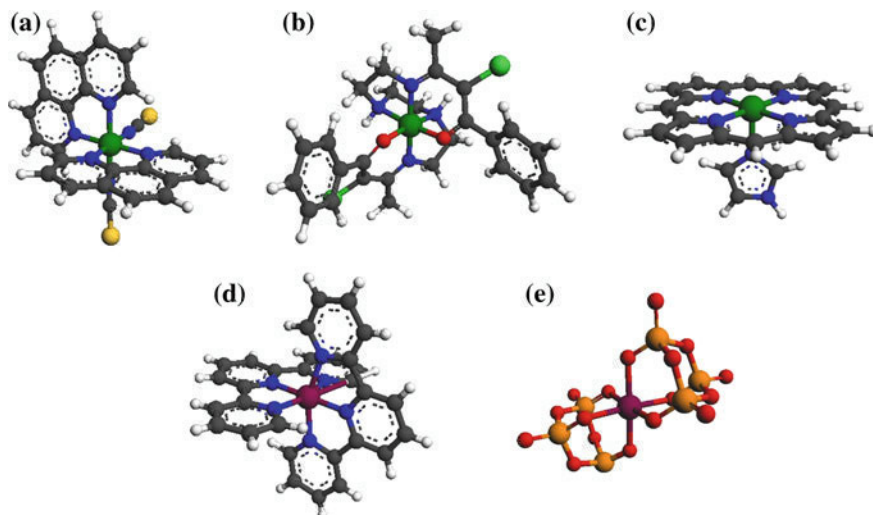
Fig. 2 Some examples of mononuclear SCO coordination complexes: **a** the iron(II) compound $[Fe(SCN)_2(Phen)_2]$; **b** the iron(III) compound $[Fe(bzacCl)_2trien]^+$ (bzac = benzoylacetonate-triethylenetetramine); **c** deoxyiron(II)porphine as a generalized representation of porphyrins and hemes; **d** the cobalt(II) compound $[Co(terpy)_2]^{2+}$; **e** the cobalt(III) compound $[Co(P_3O_9)_2]^{3-}$

[57]. This is possible because the constraints imposed by the thermochemical spin preference of the monodentate ligands can be broken in more complex coordination environments where the σ-donation is modulated electronically either by induction effects to the donor atom or by strained geometries, as commonly seen in SCO systems using multidentate ligands.

2.5 Homoleptic SCO Complexes and the Case of $Co^{3+}(aq)$

Very few, if any, real SCO systems possess O_h symmetry (one candidate is $[NiF_6]^{3-}$). Even if the complex is homoleptic (sharing chemically identical ligand donor atoms) as is reported in few cases [58, 59], Jahn–Teller distortion will cause the t_{2g} and e_g levels to split for the d^4 HS and LS configurations, for the d^6 HS configuration, and for the d^5 and d^7 LS configurations. Thus, the O_h symmetry is broken in almost all real cases to a variable extent. In fact, it would be an interesting academic challenge to identify a homoleptic SCO system that possesses almost perfect, unstrained O_h symmetry without Jahn–Teller distortion in one of its spin states, i.e., d^5 HS or d^6 LS. This state would represent an intrinsic, unstrained fit of the ligand and metal to enable SCO, something that puts major restriction on the exact ligand fields' strength of the six identical donor atoms.

Homoleptic coordination complexes for a range of different simple monodentate ligands with these d-electron configurations for Mn(II), Mn(III), Fe(II), Fe(III), Co(II) and Co(III) have been studied by DFT [52] and can help to suggest how such an "ideal" symmetric homoleptic system may be realized. Using the functionals known to be more accurate for the purpose (e.g., B3LYP* [60, 61] or TPSSh [62], e.g., as shown previously [63, 64]), one sees that some combinations of metal ions and ligands can bring a homoleptic complex very close to SCO. Co(III) has the strongest LS preference of all first-row d-block metal ions up to the III oxidation state as it has maximal ligand field stabilization energy in LS due to its t_{2g}^6 configuration and has higher charge than the iso-electronic Fe(II) LS. Thus, Co(III) SCO systems are rare and require very weak total ligand field strengths to reach SCO; the 6O coordination structures by Kläui and associates are notable in this regard [65–67]. Examples of Co(III) SCO may also exist in mixed-metal oxides [68], and a new example of a bistrimetaphosphate Co(III) complex with probable SCO properties was reported recently (Fig. 2e) [69]. In contrast, Co(II) SCO systems are relatively common and often feature 6N-coordination structures, e.g., bis-terpyridines (Fig. 2d) [70], consistent with the discussion above [71–73].

This raises an interesting and important question, namely how far above the LS state is the HS state of Co(III)(aq)? All other M(aq) systems of the first row of the d-block are HS due to water's weak ligand field, and their spin states were recently studied by CASPT2 [74]. Standing out alone, Co(III) is known to be LS under typical conditions studied (which are very acidic, because Co(III)(aq) readily undergoes reductive hydrolysis to Co(II) at neutral pH). Moreover, $[CoF_6]^{3-}$ is known to be HS, and this makes the range to HS very small since H_2O is close-by in the spectrochemical series [38]. The Co(III)(aq) is assumed (and has been shown in older data) to feature LS, but this produces several anomalies such as a much faster self-exchange electron transfer rate and faster ligand substitution than expected. Recent DFT computations [75] of the relative self-exchange rates of hydrated transition metal ions accurately recover the experimental 10^5 anomaly of Co(II)/Co(III) when plotting the trend in reorganization energies versus experimental rate constants and using LS Co(III) as commonly assumed. When doing the same correlation for HS Co(III)(aq), the anomaly disappears almost completely. DFT can also be used to correct previous spectroscopic estimates of the HS–LS gap with entropy and vibrational geometry relaxation showing that Co(III)(aq) is very close to SCO. In conclusion, this analysis converges on the view that the HS state is probably active during much of the chemistry of the hydrated Co(III), in stark contrast to text book consensus based on early NMR and absorption spectroscopy measurements in strong acid [76–78], but explaining the anomalous high ligand substitution and electron transfer capabilities of Co(III)(aq) [79, 80]. Indeed, several SCO systems of Co(III) with O-donor ligands are known [66, 68]. Future exploration of the SCO properties of Co(III) in water-like coordination environments should therefore be of interest.

2.6 Geometry Preferences and Changes During SCO

In the HS state, e_g occupation and associated ligand d-electron repulsion expands the metal–ligand bond lengths [52, 81]. Accordingly, LS states are generally more compact than HS states, and the system tends to expand upon SCO to the HS state [2], as schematically shown in Fig. 3a. However, despite the increased molar volume, the crystal symmetry is typically unaffected [24]. The longer, weaker, and more entropic metal–ligand bonds largely explain why HS is favored by temperature, viz the $T\Delta S$ term in (2). It is also the main reason why applied pressure tends to often favor the more compact LS state. In a crystal state, expansion of the core system leads to a larger unit cell and to a change in the intermolecular crystal packing forces. In a solution state, the expansion can affect the solvation energy of the two states differently, since the HS state will tend to be a slightly larger solute [28]. Not only the bond lengths but also the bite angles and the distances between the N-donor atoms of multidentate ligands may change accordingly, and the different geometric preferences of the two electronic states can thus sometimes be used to predict spin-state preferences by simple geometric inspections [58].

To put approximate numbers to this geometry effect, one can again turn to systematic studies of homoleptic mononuclear octahedral coordination complexes [52]. A summary of this analysis is shown in Fig. 3b. It turns out that the geometry changes upon the conversion of spin state are very dependent on the involved ligands and metal ion. Importantly, the geometry change scales almost monotonically with the ligand field strength such that weak-field halides give small geometry changes of the order of 0.02–0.12 Å (depending on metal ion), whereas larger changes of 0.15–0.40 Å occur for strong-field π-acceptor ligands [52]. Furthermore, the *variation* in geometry relaxation also scales with ligand field strength. This implies that the metal ion effect on HS–LS geometric relaxation upon SCO is much larger for strong-field
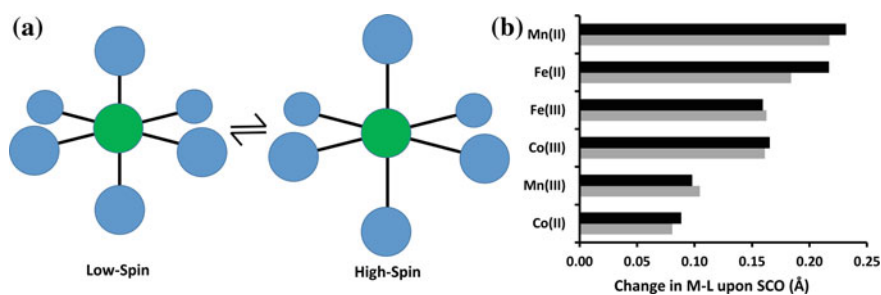
Fig. 3 **a** Schematic representation of the change in geometry associated with a transition from a LS state to a HS state in a mononuclear coordination complex; **b** DFT-computed changes in average metal–ligand bond lengths for d^4–d^7 configuration systems. The present figure is made from previously published data [52]: black color shows results for hexamine complexes, whereas gray color shows the average over a range of ligand types (halides, O-, and N-donor, and strong π-acceptors)

ligands than for weak-field ligands. The largest structural effects are, interestingly, seen for Mn(II) and Fe(II). A change of 0.2 Å or 0.3 Å is considerable; it occurs on average for all six bonds in a six-coordinate complex. For Fe(II) SCO systems with N-donor ligands, one can expect a typical average increase in Fe–N bond length of ~0.2 Å, as shown in black color for Fe(II) in Fig. 3b [52].

As discussed below, metal ions with large structural relaxation upon SCO are expected to also show more abrupt transitions with hysteresis. Accordingly, DFT as summarized in Fig. 3b largely explains why Fe(II) SCO systems commonly display high hysteresis but also predicts that Mn(II) systems should have similar or even larger ability to do so, of course under a modulating influence of other effects outside the first coordination sphere.

Since the geometric and environmental effects required to cause SCO can be subtle, SCO may be induced by adsorption of one molecular system to another, as the adsorbed state affects the molecular environment of the SCO system. The classic example is the host–guest systems [82], such as that of Halder and Kepert et al. [83] Supramolecular cages with SCO properties constitute one class of systems [84], whereas a recent example of "on-surface" SCO is that of Kumar et al. [85] Hemes, which are well known to change spin state upon changes in coordination environment, also seem to undergo on-surface SCO upon relatively weak adsorption to, e.g., gold surfaces [86], although this finding needs stronger experimental bearing.

2.7 The Nature of the SCO Transition

The actual transition from one spin state to the other can occur either gradually, or abruptly, and be subject to small or large hysteresis, as shown in Fig. 1. It is also possible, although not shown in Fig. 1, to have a multistep transition, and two-step processes have recently been studied by DFT [27]. Such multistep processes typically arise from a heterogeneous SCO sample, i.e., the presence of two or more the individual and distinct sites undergoing SCO, or possibly from restructuring of the system (including solvent) near the transition temperature.

The SCO transition curve has a sigmoidal form characteristic of a cooperative process. The cooperativity can be partly due to magnetic alignment as seen in an Ising model, and partly to structural phase transitions occurring locally: If the molecules interact closely, the intermolecular interactions produce free energy minima distinct to the larger HS and smaller LS volume. Accordingly, the conversion into a given spin state of one molecule makes it more favorable for neighbor molecules to attain the same spin state [27]. The extent of cooperativity, and accordingly the abruptness of the transition, thus depends greatly on the surroundings of the single molecule. In a solid, each magnetic center has contact with several neighbors, and thus the geometric spin-state preference induces a friction in the tendency to change spin state, which is greatly influenced by intermolecular interactions. In a solvent, cooperative interactions can be modulated by the presence of counter ions and solvent molecules, and the solvent can separate the SCO solutes so well that the spin transition becomes

gradual. Accordingly, the transition behavior is typically very different in solid and solution [2, 3], and largely influenced by electrostatic interactions of molecules [87]. Covalent linkers and hydrogen bonds can be introduced to enhance the cooperativity [2, 3, 25, 88].

Hysteresis, defined as magnetization curves that differ upon heating and cooling *for the same molecular composition*, is shown schematically in Fig. 1c. Hysteresis is a priori expected during SCO because of the change in molar volume associated with the more expanded HS state. In case of hysteresis, one has to distinguish two transition temperatures, $T_{1/2}$ ($\uparrow$) for heating and $T_{1/2}$ ($\downarrow$) for cooling. Because of the "friction" due to the distinct cooperative interactions in each state of distinct molar volumes, it generally holds that $T_{1/2}$ ($\downarrow$) < $T_{1/2}$ ($\uparrow$) (Fig. 1c). The difference in these two values,

$$\Delta T_{1/2} = T_{1/2}(\uparrow) - T_{1/2}(\downarrow) \tag{3}$$

defines the extend of hysteresis. For the purpose of theoretical modeling, the *single* molecule $T_{1/2}$ can be assumed to be

$$T_{1/2} \approx (\ T_{1/2}(\uparrow) + T_{1/2}(\downarrow)\ )\ /\ 2 \tag{4}$$

The *intermolecular* correlations causing $\Delta T_{1/2}$ should then be modeled separately [89]. Hysteresis may be utilized technologically because it produces a molecular "memory" to the system near the transition region [88]. Accordingly, large hysteresis is rare but desired for the purpose of switchable materials [4, 90].

2.8 True Hysteresis and Intrinsic Hysteresis

True hysteresis is defined only for systems where the composition is identical before and after transition. However, many SCO systems are prepared as hydrates, or with other co-crystallized molecules. Many transitions of interest occur at temperatures where these molecules begin to evaporate from the complexes, and this process is irreversible. Accordingly, if $T_{1/2}$ provides thermal energy enough to release these molecules, a large separation in the first heating and subsequent cooling curves will be observed which is *not* hysteresis, but simply reflects two different molecular systems being studied. Thus, several of the SCO systems reported to have large hysteresis may in fact reflect different molecular systems rather than true hysteresis [24]. Any technological application of hysteresis obviously requires microscopic reversibility, which is only obtained with stable systems of the same composition. This requirement substantially narrows down the number of observed cases of very large "true" hysteresis.

Inspection of $\Delta T_{1/2}$ values suggests a natural or *intrinsic* hysteresis of 0–20 K for many studied cases, which for some SCO systems is augmented by additional hysteresis. Although not discussed there, this can be inferred from the data compiled

by Sorai [24]. The intrinsic hysteresis probably reflects the simple volume reordering effects of the first coordination sphere, which is approximately similar for all SCO systems (although the expansion depends on ligand and metal type as discussed above). Additional contributions to $\Delta T_{1/2}$ can arise from larger reorganizations due to bulky groups or intermolecular interactions beyond the local volume changes of the first coordination sphere that is generic to all SCO systems; this distinction between two parts of the hysteresis (which is, as a disclaimer, only the author's view) probably warrants further exploration.

As shown in Fig. 3b, Fe(II) systems exhibit some of the largest geometric changes upon SCO among d^4–d^7 systems [52]. Consistent with the volume-friction interpretation discussed above, this probably explains why Fe(II) more commonly displays hysteresis in comparison with other SCO systems [2]. This observation seems to confirm that hysteresis at least partly arises from the geometric friction of the heating and cooling processes caused by the different free energy minima at different molar volumes for HS and LS. The intermolecular interactions that define the transition are diverse and harder to systematize than the electronic structure of the molecule itself, but the intrinsic contribution from the first coordination sphere, as discussed above, seems to be predictable by DFT, which computes geometric changes with good accuracy.

3   Important Contributions to Single-Molecule SCO

3.1   Zero-Point Vibrational Energy

The vibrational zero-point energy (ZPE) is one of the electronic effects that always contribute to the SCO tendency regardless of the environment. It has been known for a long time, and was described clearly in the pioneering DFT work on SCO by Paulsen et al. [34], that the differential ZPE of the HS and LS states is an important contribution to the SCO process. This paper also reported the strong bias toward LS of the non-hybrid GGA functionals and the preference for HS for the hybrid B3LYP functional, an important observation that, for example, motivated the later development of the B3LYP* functional by Reiher et al. with a smaller 15% HF exchange [60].

The importance of ZPE lies both in the fact that its magnitude is of the order of 10 kJ/mol [34, 64], similar to the typical values of the full ΔH_{SCO} [36], and it is systematic, as it almost exclusively favors the HS state. This favoring follows directly from the longer and weaker M–L bonds of the HS state, which accordingly have smaller ZPEs than the LS states. Not only the SCO process but also a general chemical process involving multiple spin states will experience this effect. On an energy profile of competing spin states, neglect of ZPE will tend to provide an artificial bias in favor of the LS states in the reaction coordinate diagram.

More systematic studies of the ZPE contribution indicate that the differential ZPE is very dependent on the type ligand and to a lesser extent the type of metal ion [52]: Typical differential ZPEs in favor of HS range from 5 to 25 kJ/mol and grow more or less monotonically with the ligand field strength. Accordingly, for weak ligands such as halides, the differential ZPE can be almost neglected, whereas for strong-field π-acceptor ligands such as CN^- and CO, the ZPE dramatically favors HS by more than 20 kJ/mol. Thus, the importance of remembering the ZPE correction depends very much on the system of interest. This follows trivially from the fact that the ZPE scales monotonically with the overall strength of the M–L bond, which again scales with the ligand field strength. In the middle range, typical ligands relevant to SCO systems have differential ZPEs of 10–15 kJ/mol [52]. The ZPE can also vary by >10 kJ/mol due to metal ion and d^q configuration. This also affects the bond strengths of the M–L bonds in the two spin states, but since these d^q configurations vary substantially in terms of electronic structure and some, such as HS Mn(III) and LS Co(II) induce strong Jahn–Teller distortions, this metal effect is not trivial to interpret.

3.2 Dispersion Contributions to the Spin Crossover Equilibrium

Dispersion effects are the second-order interaction of instantaneously induced dipole moments of electron densities that affect bonding in all systems. Dispersion is not intrinsically included in most modern density functionals, and the most popular way to do so is by using an empirically parameterized correction to the electronic energies computed by the functional, such as the popular D3 correction by Grimme and coworkers [91]. Within the last decade, dispersion corrections have become increasingly mandatory in DFT calculations of chemical structure and reactivity.

Since the dispersion forces contribute substantially to the intermolecular interactions, their inclusion is important if one wants to understand the transition behavior [92, 93]. Dispersion interactions also affect $T_{1/2}$ itself, by favoring either HS or LS. Depending on the nature of the ligands and their packing, dispersion forces will either compress or expand the first coordination sphere, shifting the potential energy surface either toward longer M–L bonds to favor HS or to shorter M–L bonds favoring LS. The favoring of HS or LS may be very dependent on the intermolecular ligand–ligand interactions.

A priori, dispersion effects might not be expected to contribute to the SCO tendency of *single* molecules in solution with simple monodentate ligands having no systematic steric strain. Dispersion would be expected to mainly affect closely interacting parts of different molecules, or bulky parts of the same molecule. With the advent of empirical dispersion corrections of DFT, one could explore whether dispersion forces also contribute to this important process *even* at the single-molecule level, i.e., if there is a generic first coordination sphere contribution from dispersion

to the SCO thermodynamics. This question can be directly addressed by dispersion-corrected DFT [91], because the dispersion energy correction is calculated explicitly and is separated from the remaining electronic energy of the system [54].

Strained five-coordinate iron(III)porphyrins with variable substituted axial ligands have been studied with and without dispersion forces included [54]. It was found that dispersion forces contribute already for the single molecule by affecting the free energy gap of (2) by often 10 kJ/mol or more. Considering that the total ΔH_{SCO} is in the order of 5–20 kJ/mol, this makes account of the dispersion forces critical. Four of the porphines had axial phenyl ligands attached directly by Fe–C bonds with 3–5 fluorides as phenyl substituents. This produces unusual short-range interactions and clashes between the fluorine and hydrogen atoms and the porphyrin ring in these particular systems.

However, with the advent of computational dispersion corrections to DFT, it was discovered that also in most other, unstrained single molecules, intramolecular dispersion tends to favor LS due to the stronger electronic stabilization of the more compact LS state [52]. This suggests that there is a generic, intrinsic contribution of dispersion interactions to the SCO tendency arising for the first coordination sphere of any complex of typically 5–15 kJ/mol which contributes to the real, observed $T_{\frac{1}{2}}$ [36, 52]. This contribution may then be compensated or increased by other ligand–ligand interactions. In bulky systems with ligand–ligand strain from close contacts, which tend to expand the first coordination sphere and favor HS, dispersion will further remedy some of the strain and reduce the expansion, and thus by itself favor LS.

This discovery of a generic first coordination sphere dispersion contribution to SCO arises because the attractive close-range dispersion energy favors the more compact LS state more than the HS state. As an example of consequence, if dispersion is included in B3LYP (as in B3LYP-D3), the SCO prediction becomes better because the intrinsic first coordination sphere contribution to SCO is included and counteracts the HS bias, and thus B3LYP-D3 is generally more accurate than B3LYP [36, 94].

It has now been found repeatedly that the dispersion forces of the SCO process work to favor the LS state of the single-molecule first coordination sphere [36, 95, 96]. The effect can easily reach 15–20 kJ/mol and averages 10 kJ/mol for the 30SCOFE database [36]. Thus, in order to model and predict the relative thermodynamics, SCO tendency, and $T_{\frac{1}{2}}$ of a series of compounds, dispersion forces need to be explicitly included.

3.3   Relativistic Stabilization of LS

Most studies of first-row transition metal systems do not include relativistic contributions to the energy. This is probably because relativistic effects are relatively less important for Sc–Zn, and partly because relativistic computations can be very demanding in terms of computational resources. However, relativistic effects can be substantial already for the first row of the d-transition series [97], and, e.g., for