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Theoretical determination of spin Hamiltonians with isotropic and anisotropic magnetic interactions

Rémi Maurice,[a] Coen de Graaf*[b,c] and Nathalie Guihéry[d]

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The determination of anisotropic magnetic parameters is both a task of experimental and theoretical interest. The added value of theoretical calculations can be crucial for analyzing experimental data by (i) allowing to assess the validity of the phenomenological spin Hamiltonians, (ii) allowing to discuss the values of parameters extracted from experiment, and (iii) proposing rationalizations and magneto-structural correlations to better understand the relations between geometry, electronic structure, and properties. In this review, we discuss the model Hamiltonians that are used to describe magnetic properties, the computational approaches that can be used to compute magnetic parameters, and review their applications to transition metal and (to a lesser extent) lanthanide based complexes. Perspectives concerning current methodological challenges will then be presented, and finally the need for further joint experimental/theoretical efforts will be underlined.

1 Introduction

The presence of unpaired electrons in molecules can give rise to a wide variety of phenomena. The study of such systems is appealing not only from a fundamental point of view but also in light of their potential technological applications. The improved control and possibilities to manipulate spin angular momenta (or spins, for short) and the interaction between them has been a key factor in the development of a new research area, nowadays known as spintronics. In this field, transition metal complexes and other materials with unpaired electrons have been used to design switching or sensing devices.[1] Interesting examples are the single molecule magnet behavior observed in polynuclear transition metal complexes[2] and the spin crossover process in which the total spin of a complex can be changed by external perturbations such as temperature or light.[3] A concise, accurate theoretical description of the interactions between spins (and in some cases, orbital angular momenta) is important to improve the understanding of these complex phenomena and eventually gain complete control over the magnetic properties of systems with unpaired electrons.

Although many important technological applications are based on organic radicals, we focus here on the magnetic interactions in transition metal complexes. In general, the description of magnetic phenomena is based on model Hamiltonians for which the parameters are fitted to experimental data such as the electron paramagnetic resonance (EPR) spectra,[4] temperature dependence of the magnetic susceptibility or the magnetization as function of an external field.[5] In such an approach, an *a priori* assumption has to be made about the dominant interactions. This is far from trivial and only by combining the input from various experimental studies with chemical intuition, the relative importance of the model interactions can be anticipated and values can be assigned from the fitting techniques. However, there is no guarantee that important physical effects remain hidden in the fitted parameters. Furthermore, problems can arise when various sets of parameters reproduce equally well the experimental data and no univocal model can be defined.

Most theoretical descriptions of the electronic structure of systems with magnetic properties start with the definition of the magnetic orbitals. As stated above, the presence of spin angular momenta is intimately related to the existence of unpaired electrons. The number of unpaired electrons and their distribution in the three-dimensional space are defined by the diagonalization of the hypothetical exact N-electron density matrix of the fundamental state of the system. The majority of the resulting eigenvalues (the occupation numbers) will be close to two or zero. The corresponding eigenvectors (natural orbitals) are known as the closed-shell or inactive orbitals, and the virtual orbitals, respectively. Additionally, there are n eigenvectors with eigenvalues close to one. These are the

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[a] *Department of Chemistry, Supercomputing Institute, and Chemical Theory Center, University of Minnesota*
207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, United States
[b] *Departament de Química Física i Inorgànica,*
Universitat Rovira i Virgili, Marcel·lí Domingo s/n,
43007 Tarragona, Spain. E-mail: coen.degraaf@urv.cat
[c] *Institució Catalana de Recerca i Estudis Avançats (ICREA)*
Passeig Lluis Companys 23, 08010 Barcelona, Spain
[d] *Laboratoire de Chimie et Physique Quantiques, Université de Toulouse III*
118, route de Narbonne, 31062 Toulouse, France

so-called magnetic orbitals, where n defines the number of unpaired electrons. In transition metal compounds, the magnetic orbital is normally strongly localized on the metal center with smaller tails on the surrounding atoms. The magnetic site is then atomic in nature and implies that the ligands are largely non-magnetic in character. Nevertheless, there are situations in which one or more magnetic orbitals are located on the ligand and delocalized over various atoms. In such cases, one normally refers to the magnetic site as a non-innocent ligand.

Given the fact that exact solutions are not available except for the most elementary systems, computational strategies to obtain accurate N-electron density matrices have to be used and will be discussed later on (see section 3), but before that we will shortly review in section 2 the important interactions between unpaired electrons and how these are covered in the most common model Hamiltonians. Whereas, the mechanisms for the isotropic coupling between spins on different centers have been studied in depth, are well understood and fully rationalized, the situation for anisotropic magnetic interactions is less well-established. Hence, we will shortly review the main mechanisms for the isotropic case and give a more detailed description of the mechanisms that control the anisotropic part of the magnetic interactions. Such insight eventually leads to a rational control over the main parameters, which may be of practical use when designing materials with interesting magnetic properties.

The large number of studies concerning magnetic interactions in compounds with transition or rare-earth metal ions makes impossible to fully cover all type of applications. Section 4 gives a few illustrative examples of different classes of magnetic materials (only $3d$ ions, (4,5)d, $4f$ metals, or combinations of these) and mentions the main peculiarities and prospective for further improvement of magnetic materials.

The last part of this article (section 5) is dedicated to the main challenges in the computational approaches to magnetic interactions. Although the theoretical description of magnetic materials has made important advances, there are still some major problems that have to be faced. The wave function based methods are notoriously difficult to be applied to systems with more than two transition metal centers or with bulky ligands. This problem is less important for calculations based on density functional theory, but the monodeterminantal nature of the Kohn-Sham implementation of density functional theory (DFT) makes necessary to introduce important approximations in the description of the electronic structure of magnetic systems, which is intrinsically multideterminantal in many cases. A different problem, already shortly mentioned above, is the validity of the commonly used model Hamiltonians. These models play a fundamental role in the understanding and rationalization of magnetic interactions, since they capture the highly complicated physics in simple concepts. However, there is no intrinsic guarantee that the model really parametrizes what is meant or that an important part of the physics is missing either in the model space or in the model operators. Standard extraction procedures cannot give an answer to this question, but the use of effective Hamiltonians provides a bridge between theoretical results based on the exact electronic Hamiltonian (and hence, including all possible interactions without any *a priori* assumption about their importance) and simpler model Hamiltonians to establish the validity of the latter.

2 Model Hamiltonians, effective Hamiltonians and quasi-degenerate perturbation theory

Model Hamiltonians are used to effectively describe the lowest-energy levels of a given system, *i.e.* the levels that largely determine the property of interest. Often the model Hamiltonian is constructed from some *a priori* assumptions about the dominant interactions, but they can also be derived from *ab initio* results using the effective Hamiltonian theory.[6] This theory establishes a one-to-one correspondence between the target space S' containing the *ab initio* states of interest and the model space S that spans the model Hamiltonian. The two spaces have dimension N. The effective Hamiltonian must be such that its eigenvalues E_i are those of the all-electron Hamiltonian $\hat{H}$ used in the *ab initio* calculation. After selecting the targeted N wave functions (Ψ_i) of the *ab initio* calculation with the largest projection on the model space, the corresponding projections are orthogonalized[7] ($\widetilde{\Psi}_i$) and the effective Hamiltonian is constructed by

$$\hat{H}^{eff} = \sum_{i}^{N} |\widetilde{\Psi}_i\rangle E_i \langle\widetilde{\Psi}_i| \tag{1}$$

All the matrix elements of the effective Hamiltonian can be calculated from this expression using the *ab initio* energies and wave functions. A comparison of this numerical matrix with the analytical matrix of the model Hamiltonian enables one to assign values to the various interactions of the model. The advantage of this procedure over the more usual fitting of the model parameters to reproduce only the *ab initio* energies is two-fold. In the first place, the norms of the projections provides information about the validity of the model space. The appearance of small norms is often an indication that the model space must be enlarged to accurately account for the physics of the problem. In the second place, much more information can be extracted from the calculation. While using the energies only, the information to extract the interactions is limited to $N-1$ (the number of energy differences), the information contained in the effective Hamiltonian can be as large as $N(N+1)/2-1$, corresponding to the maximum number of independent matrix elements for an Hermitian matrix. As will be shown in sections 3 and 4, this additional information is crucial to check the validity of a model Hamiltonian and to identify the missing operators when the model is not appropriate. It should however be noted that although this procedure is more rigorous than simple fitting techniques, it does not give analytical expressions for all operators necessary to reproduce the physics of the problem.

Complementary information about the operators that should be included in a model Hamiltonian is provided by quasi-degenerate perturbation theory (QDPT). QDPT enables one to derive analytically a model Hamiltonian from a more sophisticated Hamiltonian, yet simple enough to be handled analytically. In the context of isotropic magnetic interactions this Hamiltonian is often a generalized Hubbard Hamiltonian,[8] while it should contain the spin-orbit and spin-spin coupling operators when modelling anisotropic interactions. In practice, the zeroth-order Hamiltonian matrix is expressed in the basis of the model space. Then the effect of the perturbation $\hat{V}$ is taken into account at a given order of perturbation and the matrix is dressed by the interactions with the outer space determinants. Comparing this analytical matrix with that of the model Hamiltonian not only enables one to identify missing interactions, but also informs us about the physical content of the model Hamiltonian interactions. It therefore provides rationalization of the physical origin of each of the model operators. Ideally, in order to ensure an adequate interpretation, the ”bridge” should also be made between this more sophisticated but still simple representation of the system and a reference *ab initio* calculation, such that a clear connection is made between the *ab initio* Hamiltonian, a simpler Hamiltonian, and the model Hamiltonian.

In the rest of this section, we will introduce the commonly used model Hamiltonians adopted to the description of various types of systems including one or more magnetic centers, where magnetic centers here refer to open-shell $3d$, $4d$, $5d$ or $4f$ ions, as well as clues to derive the spin Hamiltonian parameters analytically.

2.1 One magnetic center

In complexes with $3d$, $4d$ or even $5d$ ions, the electron-electron interactions and the ligand-field potential created by the charge and charge-density interactions with the ligand atoms have a significantly more important effect on the energy levels than the spin-orbit interaction.[9] As a consequence, when the ground state is orbitally non-degenerate, and all other excited states are high enough in energy, the problem may be reduced to just the spin degrees of freedom, *i.e.* one can use the spin Hamiltonian approach.

A mononuclear complex[‡] with a total spin angular momentum of $S = 1/2$ can be considered as one of the simplest expressions of a magnetic system. In absence of interaction with other complexes, such a complex only becomes magnetically interesting when an external magnetic field is applied. The lowest electronic state, a Kramers doublet, is split by the magnetic field $\mathbf{B}$ in two non-degenerate levels with $M_S = 1/2$ and $M_S = -1/2$.

$$\hat{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{S} \tag{2}$$

Transitions between the two levels can be measured in EPR experiments and the $\mathbf{g}$-tensor can be determined.[10] On the contrary, in the absence of an external field only systems with $S \geq 1$ can show magnetic anisotropy. This zero-field splitting (ZFS) of the $2S+1$ levels of the ground state are commonly described with a Hamiltonian that is quadratic in the spin operator:[11]

$$\hat{H} = \hat{S} \cdot \mathbf{D} \cdot \hat{S} \tag{3}$$

where $\mathbf{D}$ is called the ZFS tensor. When $S \geq 2$, the spin Hamiltonian also contains quartic terms.[11] These quartic spin operators have usually a much smaller effect on the lowest energy levels than the quadratic ones, since they mainly originate from spin-orbit coupling at fourth order of perturbation. In cases of near orbital degeneracy, these terms may however become larger,[12,13] and should be considered in the model Hamiltonian.

Both spin-spin and spin-orbit interactions contribute to the ZFS tensor at first and second order of perturbation, respectively.[14] Higher-order terms and other relativistic effects also affect the ZFS, but the spin-spin and spin-orbit terms are usually the leading ones. Although in the general case both individual contributions to the ZFS tensor do not lead to the same principal axes, it is always possible to define the principal axes of the ZFS tensor when both contributions are simultaneously considered. Conventions are then applied to define the magnetic anisotropy axes: the z axis should be the most different one and x should be a harder magnetization axis than y.[5] One should note that another convention for differentiating x and y is also often used in the literature: x should be more similar to z than to y. These conventions can be summarized as $|D| > 3E$ and $E \geq 0$ in the first case, and $|D| > 3E$ and $\frac{E}{D} \geq 0$ in the second case, where D and E are the axial and rhombic ZFS parameters, respectively.

$$\begin{aligned} D =& D_{zz} - \frac{1}{2}\left(D_{xx} + D_{yy}\right) \\ E =& \frac{1}{2}\left(D_{xx} - D_{yy}\right) \end{aligned} \tag{4}$$

When D is positive, the most distinguishable magnetic axis is a hard axis of magnetization, while for negative D the most distinguishable one is an easy axis of magnetization. In the present review, we will use the convention $E > 0$, meaning that a positive D is associated with an intermediate x axis, and that a negative D is associated with a hard x axis. If x and y

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[‡] Mononuclear is used here in the significance of a polynuclear complex with one magnetic center, usually the transition metal ion

are equivalent by symmetry, E is zero and the anisotropy is axial. If x, y and z are equivalent, as in an octahedral case, D is also zero and there is no magnetic anisotropy. When $|D| = 3E$ the system is in the rhombic limit, where one of the magnetic anisotropy axis is the perfect intermediate of the other two axes. Although one can define an easy, intermediate and hard axis of magnetization, it makes no sense to label the z-axis as easy (negative D) or as hard (positive D) magnetization axis. Hence, the sign of D is only defined when $|D| > 3E$.

In lanthanide complexes, *i.e.* complexes based on 4f ions, the electron-electron interactions and the spin-orbit coupling have a more important effect on the energy levels than the crystal field potential.[9] The radial extension of the 4f orbitals is small and as a consequence, the crystal field potential should be considered as a perturbation of the free-ion Hamiltonian. Hence, equivalent operators (also known as Stevens operators) effectively describe the ZFS of the fundamental spectroscopic term $^{2S+1}L_J$ of the perturbed free-ion.[15] It is important to note that even if in lanthanide complexes the equivalent operators are applied to $|J, M_J\rangle$ functions (with $J = L+S$), they physically represent the effect of the crystal field potential on the orbital part of the wave functions.

The 5f ions present a more complex situation. Because of the larger spatial extension of the 5f orbitals, the electrons in these orbitals are more strongly influenced by the neighboring atoms in actinide-complexes. Hence, the ligand field potential and the spin-orbit coupling have an effect of the same order of magnitude on the energy levels. It is not possible in the general case to reduce the problem of the ZFS of the lowest spin-orbit states to an effective spin Hamiltonian, as in d ions, or to an effective crystal field Hamiltonian, as in 4f ions. One can however define a pseudo-spin Hamiltonian to reproduce the energy levels for these cases.[16]

The crystal-field Hamiltonian acting on a $^{2S+1}L_J$ spectroscopic term of a given ion or atom can be expressed as

$$\hat{H}_{CF} = \sum_k \sum_q c_k B_k^q \hat{O}_k^q \tag{5}$$

where c_k is a prefactor specific of a given $^{2S+1}L_J$ spectroscopic term and depending on the order k of the operator, and where q indicates the symmetry of the field. In practice, $k = 0$ is omitted since it corresponds to a spherical field and does not split the components of the $^{2S+1}L_J$ term. Hence, only the values $k = 2, 4, 6$ need to be considered. The c_k prefactors are given for the ground terms of the lanthanide free-ions in the original article of Stevens.[15] Methods to determine these prefactors in excited $^{2S+1}L_{J'}$ terms and for ground and excited terms of other configurations exist and are given in the reference book of Abragam and Bleaney,[10] as well as tables for the $\hat{O}_k^q$ operators.

To rationalize the ZFS in d complexes, a two step approach can be used. In the first step, crystal-field states are built by applying the crystal field Hamiltonian given above to the ground ^{2S+1}L term of the free-ion. In a second step, the spin-orbit coupling (SOC) is introduced:

$$\hat{H}_{SOC} = \lambda \hat{L} \cdot \hat{S} \tag{6}$$

where λ is the polyelectronic spin-orbit coupling constant, and $\hat{L}$ and $\hat{S}$ refer to the orbital and spin momentum operators. The (perturbed) spin-orbit levels of the ground state arise from the diagonalization of the following matrix obtained at the second order of perturbation in the SOC:

$$\begin{aligned}
&\langle \Psi_0(M_S(i)) | \hat{H}_{CF} + \hat{H}_{ee} + \hat{H}_{SOC} | \Psi_0(M_S(j)) \rangle = \\
&\delta_{ij} \langle \Psi_0(M_S(i)) | \hat{H}_{CF} + \hat{H}_{ee} | \Psi_0(M_S(j)) \rangle \\
&+ \sum_{k,l} \frac{\langle \Psi_0(M_S(i)) | \hat{H}_{SOC} | \Psi_l(M_S(k)) \rangle \langle \Psi_l(M_S(k)) | \hat{H}_{SOC} | \Psi_0(M_S(j)) \rangle}{E_j - E_l}
\end{aligned} \tag{7}$$

$\Psi_0(M_S(i))$ and $\Psi_0(M_S(j))$ are M_S components of the (non-degenerate) crystal-field ground state Ψ_0, and $\Psi_l(M_S(k))$ is one of the components of an excited crystal-field state Ψ_l. Note that Ψ_0 and Ψ_l are solutions of the crystal-field Hamiltonian obtained in the first step, and thus, are linear combinations of M_L configurations of the considered ^{2S+1}L spectroscopic term. E_j and E_l are the spin-orbit free energies obtained with $\hat{H}_{CF}$ and $\hat{H}_{ee}$ accounts for the electron-electron interactions.

Such derivations for various d^n configurations and symmetries of the ligand field are presented in the book of Abragam and Bleaney.[10] Working with the global orbital momentum and the polyelectronic SOC operator complicates the inclusion of other (excited) $^{2S'+1}L'$ terms, either with the same spin as the ground state, or with S'=$S \pm 1$. These states can also play an important role in the ZFS,[17] and hence, it can be advantageous to include such states in the derivations from the beginning, and work in the basis of configurations expressed in terms of the real d orbitals with the following spin-orbit coupling operator:

$$\hat{H}_{SOC} = \sum_i \zeta_i \hat{l}_i \cdot \hat{s}_i \tag{8}$$

One way of doing this consists of including the electron-electron repulsion with the Racah parameters B and C, and introduce crystal field parameters that split the d orbitals.[18] Such rationalizing works are particularly important to reach a certain control over the way how to tune the anisotropy of complexes of a given configuration.

2.2 Two (or more) magnetic centers

2.2.1 Isotropic spin interactions. In nearly all cases, magnetic centers do not exist as isolated units but show interactions with other centers in their surrounding. Although

$4f$ ions can be involved in complexes with other $4f$ or d ions, the present section focusses on spin Hamiltonians, and hence is more specific to d ions. Usually, the leading interaction is isotropic in nature and couples the spins on two interacting centers in a co-linear fashion, either parallel (ferromagnetic) or anti-parallel (antiferromagnetic). The lowest energy states of a collection of magnetic centers connected through isotropic interactions of the local spin moments can be described with the Heisenberg-Dirac-van Vleck Hamiltonian (HDVV).[19–21]

$$\hat{H} = -\sum_{i>j} J_{ij}\hat{S}_i \cdot \hat{S}_j \tag{9}$$

where J_{ij} parametrizes the magnetic coupling strength between site i and j. At least four different definitions of this Hamiltonian exist in the literature, differing in the prefactor (positive, negative; one or two). In the present definition, a negative J indicates antiferromagnetic coupling and positive values correspond to a ferromagnetic situation. The values taken from other sources may have been converted to ensure the use of a single definition of the HDVV Hamiltonian. For a system with two magnetic sites, the energy eigenvalues of the HDVV Hamiltonian are regularly spaced following the Landé pattern: $E(S-1)-E(S) = JS$, where S is the total spin of the system running from S_1+S_2 to $|S_1-S_2|$. Deviations to the Landé pattern may appear in the energy levels when $S_1 \geq 1$ and $S_2 \geq 1$. This behaviour can be described by adding extra exchange terms to the model Hamiltonian which, for instance for two magnetic sites of spin $S=1$, is written as:

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 + \kappa\left(\hat{S}_1 \cdot \hat{S}_2\right)^2 \tag{10}$$

where κ is the biquadratic exchange parameter.[22] For systems with three or more magnetic centers, biquadratic terms involving spin operators acting on three different magnetic centers have to be considered as part of the (isotropic) biquadratic exchange.[22]

2.2.2 Mechanism of the isotropic coupling. The analysis of the isotropic magnetic coupling strength and the understanding of antiferromagnetic interactions goes back to the pioneering work of Anderson and Nesbet in the 1950s. Based on the observation of Kramers that magnetic ions may interact by the action of an intermediate closed-shell (non-magnetic) ion,[23] Anderson introduced the concept of superexchange in 1950.[24] Analyzing the coupling in MnO, it was shown how the O-2p to Mn-3d excitations favor the anti-parallel coupling of the spins on the magnetic sites. Almost ten years later, the concept was put a more firm basis[25] and numerical estimates of the coupling strength were published by Nesbet shortly after.[26,27]

Qualitative relationships between coupling strength and geometry were provided by the Goodenough-Kanamori-Anderson (GKA) rules[28,29] and the Kahn-Briat model.[30] Both reasonings are based on the overlap of non-orthogonal orbitals, where larger overlaps are indicative of stronger antiferromagnetic interactions. Whereas the GKA rules were derived using strongly localized orbitals of the magnetic centers and the bridging ligand(s), the Kahn-Briat model only considers the magnetic orbitals, which in turn have significant delocalization tails on the ligand that bridges the magnetic centers.

A similar valence-only model was developed by Hay, Thibeault and Hoffmann (HTH).[31] Since this approach is based on delocalized orthogonal molecular orbitals, it is especially suitable for implementation in computer codes. The HTH model predicts the following magnetic coupling strength for centro-symmetric systems with two $S=1/2$ magnetic centers A and B

$$J = 2K_{ab} - \frac{(\varepsilon_g - \varepsilon_u)^2}{J_{aa} - J_{ab}} \tag{11}$$

where the ε's represent the orbital energies of the symmetry adapted magnetic (delocalized) orbitals, and K_{ab}, J_{aa} and J_{ab} are exchange and Coulomb integrals, respectively. This relation has been used extensively to rationalize magnetostructural correlations, although the intuitive valence-bond picture of the GKA rules and Kahn-Briat model is not easily recovered.

The quantitative analysis of the isotropic magnetic coupling beyond the valence-only description[§] was described in a series of papers by Malrieu and co-workers. After the construction of accurate multiconfigurational wave functions for the lowest electronic states (see Section 3), the contribution of the different classes of determinants was determined by perturbation theory[32] or variationally in a class-partitioned configuration interaction (CI).[33–35] The valence-only description gives rise to two antagonist contributions; the direct exchange K_{ab}, which favors high-spin ground state (ferromagnetic) and the kinetic exchange, which is antiferromagnetic in nature. The latter process arises from the electron transfer between the magnetic centers and is related to the ratio of the hopping integral t_{ab} and the on-site repulsion $U = J_{aa} - J_{ab}$ as $-4t_{ab}^2/U$.

However, the magnitude of both contributions is far too small in the bare, unscreened valence-only description and additional mechanisms play an important role in the coupling. The most important ones are (i) the dynamic charge polarization arising from single electron replacements from inactive to virtual orbitals combined with single excitations among the magnetic orbitals; (ii) the spin polarization, involving the combination of single inactive-to-virtual excitations with a change of the spin in the magnetic orbitals; and (iii) the ligand-to-metal charge transfer (LMCT) and metal-to-ligand CT (MLCT)excitations. Working with canonical high-spin orbitals, these configurations cannot interact directly with the valence configurations due to the generalized Brillouin theorem and their effect arise from higher-order coupling

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[§] The valence space is restricted to the magnetic orbitals and the unpaired electrons only with other excited configurations. In combination with other smaller contributions, a full decomposition of the isotropic coupling can be obtained and one can look for factors that specifically affect one of the contributions to modify the overall coupling in the desired direction.

All these effects can be mapped on the simple valence-only description by the use of effective Hamiltonian techniques. This converts the direct exchange integral K_{ab} in an effective parameter with contributions from the spin polarization. The kinetic exchange is mainly enhanced by the effect of the dynamic charge polarization, which lowers U and the coupling of LMCT with determinants that relax the orbitals for these configurations, resulting in an increase of t_{ab} and K_{ab}. In this way the simple picture of the qualitative models is recovered, although it should be mentioned that the effective parameters can adopt counterintuitive values such as a negative K_{ab} in systems with large negative spin polarization.

2.2.3 Isotropic biquadratic exchange.

The analysis of the deviations to the Heisenberg behavior is mostly performed for $S = 1$ systems,[36–38] concentrating on the physical content of the interactions that must be added to the Hamiltonian. The orthogonal localized magnetic orbitals in such dinuclear complexes are a_1, a_2 on center A and b_1, b_2 on center B. Due to the local direct exchange K between the electrons in a_1 and a_2 (idem for b_1 and b_2), the local ground state of each center is a triplet obeying the Hund's rule. The isotropic magnetic coupling at the second order of perturbation has the same physical content as the magnetic coupling between two electrons in two orbitals. Assuming that a_1 can only interact with b_1 through the hopping integral t_1 (and a_2 with b_2 through t_2), the second order expression of the magnetic coupling is

$$J^{(2)} = \sum_{i,j=1}^{2} K_{a_i b_j} - \frac{t_1^2}{U} - \frac{t_2^2}{U} \tag{12}$$

The microscopic origin of the effective interactions responsible for the deviations can only be obtained at the fourth order of perturbation. The most important interactions come from the local excited states,[37] called the non-Hund states. These states have the same orbital occupation as the local ground state, but differ by their spin multiplicity. In $S = 1$ systems, the non-Hund state is a singlet, which lies only at $2K$ ($K \sim 0.6$ eV) above the ground triplet. The analytical derivation of the spin Hamiltonian from a generalized Hubbard Hamiltonian at the fourth order of perturbation shows that the non-Hund states introduce an additional interaction, the biquadratic exchange κ, and also affect the physical content of the magnetic exchange coupling J. The fourth order expressions of these interactions are

$$\kappa = \frac{F^2}{K} - \frac{1}{4K}\left(\frac{t_1^2}{U} + \frac{t_2^2}{U}\right)^2 \tag{13}$$

$$J = \sum_{i,j=1}^{2} K_{a_i b_j} - \frac{t_1^2}{U} - \frac{t_2^2}{U} - \frac{F^2}{K} \tag{14}$$

where

$$F = \frac{t_1^2}{U} - \frac{t_2^2}{U} \tag{15}$$

The magnitude of J and κ strongly depends on electron correlation. However, since κ is a fourth order interaction, its magnitude is always small. In case of systems involving more than two magnetic centers, the non-Hund states are also responsible for the appearance of three-center operators in the model spin Hamiltonian.[36] It was recently shown that this operator accounts for the most important part of the deviation in nickelate materials.[36] The main contribution to the interaction of the three-center operator is proportional to F. As a consequence one may only expect important deviations when t_1 is significantly different from t_2.

2.2.4 Anisotropic spin interactions.

The anisotropic part of the interaction between two $S = \frac{1}{2}$ magnetic centers A and B can be separated in a symmetric and an anti-symmetric contribution and is generally modelled with the following spin Hamiltonian:[39]

$$\hat{H} = \hat{S}_A \cdot \mathbf{D}_{AB} \cdot \hat{S}_B + \vec{d}_{AB} \hat{S}_A \times \hat{S}_B \tag{16}$$

The second interaction is related to non-colinear local spin moments and can introduce small ferromagnetic contributions to the magnetic properties of materials with antiferromagnetically coupled spin moments. This Dzyaloshinskii-Moriya interaction can only become effective in the absence of an inversion center between the magnetic sites[39] and has been invoked to explain the appearance of spiral ordering of the spin moments in ferroelectric materials. The $\mathbf{D}_{AB}$-tensor of the symmetric anisotropic interaction can be decomposed in an axial (D_{AB}) and a rhombic (E_{AB}) term. Except for isolated magnetic centers, the interaction is non-zero due to the symmetry properties of the binuclear complexes. The highest symmetry point group than can be found for any binuclear complex is $D_{\infty h}$. In this point group, the z direction is different from all other directions perpendicular to it. As a consequence, the zz component of $\mathbf{D}_{AB}$ always differs from the xx and yy components. For less symmetric point groups than $D_{\infty h}$, other symmetric and antisymmetric components can become symmetry allowed. An overview of the symmetry rules for the symmetric part and antisymmetric part of the anisotropic interactions can be found elsewhere.[40]

The simplest extension of the binuclear system with two $S = 1/2$ magnetic centers is obtained when S_B=1 and S_B=$\frac{1}{2}$. To correctly described the magnetism of such system, an anisotropy tensor $\mathbf{D}_A$ has to be added to the Hamiltonian to account for the local anisotropy on site A:

$$\hat{H} = \hat{S}_A \cdot \mathbf{D}_A \cdot \hat{S}_A + \hat{S}_A \cdot \mathbf{D}_{AB} \cdot \hat{S}_B + \vec{d}_{AB} \hat{S}_A \times \hat{S}_B \tag{17}$$

Usually, the description of systems with two $S = 1$ magnetic centers relies on the extension of the previous model Hamiltonian with a second local anisotropy term:[22,41]

$$\hat{H} = \hat{S}_A \cdot \mathbf{D}_A \cdot \hat{S}_A + \hat{S}_B \cdot \mathbf{D}_B \cdot \hat{S}_B + \hat{S}_A \cdot \mathbf{D}_{AB} \cdot \hat{S}_B + \vec{d}_{AB} \hat{S}_A \times \hat{S}_B \quad (18)$$

However, as for the isotropic interactions, biquadratic terms can appear in this case. Hence, a more complete description of the spin system includes also the biquadratic symmetric exchange[42] and the biquadratic antisymmetric exchange[43] in the model Hamiltonian. The presence of local spins higher than 1 may also result in higher rank intersite anisotropy tensors, further complicating the model Hamiltonian.

The model Hamiltonians presented so far are part of the 'multispin' Hamiltonian class, since they explicitly deal with local spin operators. The 'block spin' and 'giant spin' Hamiltonians belong to another class of Hamiltonians, in which the local spins operators are not used anymore, but instead the spin operators act on the coupled spin states, ranging from $|S_A - S_B|$ to $S_A + S_B$. In the giant spin picture, only the lowest (coupled) spin state with $S \geq 1$ is considered, while the block spin picture accounts for all the coupled states. Such pictures are thus particularly indicated when the coupled spins can be considered as good quantum numbers, *i.e.* when the isotropic interactions are much larger than the anisotropic ones, resulting in large energy separations between the levels that enter the giant spin model and those that are left out, or in a clear separation between the spin components belonging to different spin levels in a block spin picture. This situation is referred to as the 'strong-exchange limit', which should not be confounded with the 'strong-coupling scheme' in spin-broken symmetry approaches (see Section 3). When only $\mathbf{D}_A$, $\mathbf{D}_b$ and $\mathbf{D}_{ab}$ tensors are considered (which may be a crude approximation in some cases), simple expressions relate the $\mathbf{D}_S$ tensors (with $|S_A - S_B| \leq S \leq S_A + S_B$) to the local $\mathbf{D}_A$ and $\mathbf{D}_B$, and intersite $\mathbf{D}_{AB}$ tensors.[22,41,44]

When the isotropic and anisotropic interactions are of the same order of magnitude, the system belongs to the 'weak-exchange limit'. In such cases, the spin components of the different coupled spin states strongly mix under the influence of antisymmetric and symmetric interactions. In order to get insight in this so-called 'spin mixing', it is very informative to derive the giant or block spin Hamiltonians from the multispin ones. The easiest approach to perform such a transformation consists of building the model Hamiltonian matrix of the multispin Hamiltonian in the uncoupled $|S_A, M_{S_A}, S_B, M_{S_B}\rangle$ basis, and rotating it to the coupled $|S, M_S\rangle$ basis by using the appropriate Clebsch-Gordan coefficients to construct the transformation matrix.[22] Several important conclusions from this type of work can be formulated:

- If the spin mixing is negligible, the block spin model Hamiltonian only has to consider a second-rank ZFS tensor per spin state S and possibly additional higher rank terms for $S \geq 2$ that are associated with the corresponding Stevens operators for the considered spin state; fourth order terms for $S = 2$ and $S = \frac{5}{2}$, fourth and sixth order terms for $S = 3$ and $S = \frac{7}{2}$, *etc.*
- When $S_A = \frac{1}{2}$ or $S_B = \frac{1}{2}$, the antisymmetric exchange is the only responsible for spin mixing, coupling the spin components of two adjacent spin blocks ($S' = S \pm 1$).
- When $S_A \geq 1$ and $S_B \geq 1$, both the local anisotropy tensor(s) and the symmetric exchange cause spin mixing. For moderate spin mixing, the block spin or giant spin pictures can still be considered, and second order perturbation theory shows that the contribution of the local anisotropy tensor(s) and of the symmetric exchange can be effectively represented by operators acting on the coupled spins. Although Stevens operators are usually used for such purpose, these operators do not have the correct symmetry to account for the spin mixing, and one should rather define a new set of operators compatible with the representation of the multispin Hamiltonian in the coupled basis.[45]

The definition of magnetic anisotropy axes is rather straightforward when $S_A = \frac{1}{2}$ or $S_B = \frac{1}{2}$, or when the local anisotropy axes are collinear (as in complexes with an inversion center). Indeed, in such cases the anisotropy axes of the block spin and giant spin ZFS tensors correspond to the axes of the local anisotropic tensor(s), if applicable.[45] The existence of nonzero noncollinear anisotropy in system with S_A and $S_B \geq 1$, makes that the global anisotropy axes (those obtained with giant/block spin approaches) differ from the local anisotropy axes. It is necessary to account for the mismatch between the local anisotropy axes when building a coupled model matrix with a multispin model Hamiltonian.[46] The collinear approximation, commonly used to fit magnetic data, should not be used in such cases. This is crucial in the weak-exchange limit, since in this case the mismatch between the local anisotropy axes is responsible for coupling between spin components of adjacent spin blocks ($S' = S \pm 1$), as the antisymmetric exchange, and not only between every second spin block ($S' = S \pm 2$), as in the case of centro-symmetric complexes.[42]

2.2.5 Mechanism of the anisotropic coupling. The mechanism for the anisotropic interactions have been first exposed in the pioneering work by Bleaney and Bowers concerning the symmetric exchange,[47] and Moriya[39] for the antisymmetric exchange. Since then these works have been slightly refined,[48–51] but the conclusions derived from these early works remain valid even with more sophisticated models. In both cases, a subtle interplay between the spin-orbit free interactions and the spin-orbit coupling is involved:

- The symmetric exchange does not depend on the isotropic coupling between the lowest-lying electronic states, the ones considered in the HDVV Hamiltonian. It can only be non-vanishing when the isotropic coupling between orbitally excited states (where an electron is promoted to a higher energy *d* orbital) is different from zero.[47–49] Consequently, if the magnetic sites are magnetically isolated in the excited states , the symmetric exchange goes to zero. In other words, although the symmetric exchange is always symmetry allowed in binuclear systems, it requires specific interactions between the magnetic sites to be non-vanishing, numerically speaking.

- The antisymmetric exchange also vanishes for isolated magnetic sites. As stated by Moriya,[39] based on an atomic orbital picture derivation, the antisymmetric exchange is nonzero if the two magnetic centers are coupled via anisotropic superexchange[24] interactions. Even if the contribution from the bridging atoms is explicitly considered,[50,51] this condition is still a necessary condition for the antisymmetric exchange to be nonzero.

3 Computational approaches

The success of computational approaches to provide useful information is critically dependent on the ability to accurately reproduce the small energy differences that determine the magnetic properties of the systems of interest. These energy differences range from a few cm^{-1} (or less) for anisotropic interactions to approximately 1000 cm^{-1} ($\sim$0.1 eV) for the larger isotropic couplings. Preferably the computational strategy correctly reproduces trends when comparing different molecules, and provides values in reasonable agreement with experimental ones. Additionally, the computational cost of the theoretical method should not be too high to avoid being restricted to small model compounds. Finally, the calculation should ideally not only give numbers but also the possibility to analyze, decompose and interpret the results in terms of simple concepts in order to facilitate the interaction between theory and experiment. Here we will highlight the most commonly applied computational approaches to calculate and analyze (an-)isotropic magnetic interactions and discuss their strengths and weaknesses concerning the mentioned requirements, which are not easily united in one specific computational approach. For wave function theory (WFT) and DFT based methods, we will start the discussion focussing on the isotropic magnetic coupling and then give some additional information that is more specific to calculate anisotropic interactions.

3.1 Wave function based methods

In almost all cases, the electron distribution of the states that are relevant to the isotropic couplings of a system can be described with a single electronic configuration, but this does not mean that a single determinantal representation suffices. Except for the states with maximum expectation value of the $\hat{S}^2$ and $\hat{S}_z$ operators (all spins aligned ferromagnetically), it is necessary to adopt a multideterminantal wave function to ensure the spin symmetry of the (open-shell) spin states. Therefore, a good starting point is the complete active space self consistent field (CASSCF) method,[52] which combines a full CI expansion of the wave function in the valence space with a self-consistent optimization procedure of all the molecular orbitals. In magnetic problems the valence (or active) space typically contains the magnetic orbitals and the unpaired electrons. In this way, the spin symmetry can be imposed and in addition to the main electronic configuration with one unpaired electron per localized magnetic orbital, some other configurations are present in the wave function. An important extra group of configurations are those with one or more electrons transferred from one magnetic center to another one. These configurations play a central role in the kinetic exchange mechanism and their presence in the wave function makes that the CASSCF estimates of the isotropic magnetic coupling usually have the correct sign. It has however been observed in numerous applications that CASSCF severely underestimates the strength of both ferro- and antiferromagnetic coupling.[33,53–58] This is caused by the limited description of the electron correlation effects and the complete neglect of some of the mechanisms described in Sec. 2.2.2, which should be repaired by considering more complex wave function based approaches. Extending the active space with more orbitals (other metal-*d* orbitals, ligand orbitals, doubling the *d*-shell) does not systematically lead to significant improvements.[59] The key lies in the dynamic correlation.

3.1.1 Perturbation theory. The multideterminantal nature of the electronic structure makes standard many body perturbation theory approaches based on Hartree-Fock references less useful for magnetic compounds. Among the different multiconfigurational reference implementations of perturbation theory, the complete active space second-order perturbation theory (CASPT2)[60] and the *n*-electron valence second-order perturbation theory (NEVPT2)[61] have been used regularly to calculate isotropic magnetic coupling parameters in many different systems. Both approaches use a CASSCF wave function as zeroth-order description and estimate the effect of dynamic correlation with second-order perturbation theory including single and double excited configurations with respect to the configurations of the CAS. The main difference lies in the definition of the zeroth-order Hamiltonian. CASPT2 is based on an effective one-electron Fock type operator and

NEVPT2 uses the Dyall Hamiltonian,[62] which contains all two-electron interactions between the active orbitals. This has certain advantages concerning the occurrence of intruder states, but the results of both perturbation schemes are similar in most cases.

Multiconfigurational perturbation theory largely improve the CASSCF results and is therefore efficient to evaluate trends in the coupling in a wide spectrum of compounds. However, it should be kept in mind that it does in general not fully reproduce the couplings as deduced from experimental measurements. A semi-quantitative agreement can be obtained when the reference wave function is calculated with a large active space. While this is doable for some systems with a small number of unpaired electrons such as dinuclear complexes with Cu^{2+} or Ni^{2+} ions, this becomes cumbersome for larger systems and may rapidly be prohibitive. A second drawback is the fact that perturbation theory does not reproduce the regular energy spacing between the spin eigenfunctions as predicted by the Heisenberg Hamiltonian.[63–66] This is not a problem of the model Hamiltonian but a matter of numerical precision of the computation. NEVPT2 appears to be less sensitive to this problem than CASPT2.

3.1.2 Difference Dedicated CI.

An alternative to perturbation theory is the variational treatment of the dynamic correlation by means of configuration interaction (CI). Multiconfigurational reference CI with singly and doubly excited determinants (MR-SDCI) suffers from size-consistency errors and rapidly becomes intractable, and hence, cannot be applied but to small model systems. An important reduction of the CI space can be obtained by excluding all the doubly excited determinants that do not involve electron replacements in the active orbitals. This has important consequences for the total energies, but quasi-degenerate perturbation theory shows that these determinants do not affect the energy difference between the states of interest at second order of perturbation. The reduction of the CI expansion also leads to smaller size consistency errors. The resulting CI is known as difference dedicated CI (DDCI)[67] and has shown its potential to accurately estimate isotropic magnetic coupling parameters in many occasions.[33,68–73] The method can, however, not be applied to determine energy differences for states at different geometries, for example the high-spin low-spin energy difference in spin crossover compounds.

Despite the important reduction, DDCI is still a rather expensive method, computationally speaking. It scales as $N_{CAS} \cdot N_{occ} \cdot N_{virt} \cdot N$ (N_{CAS} is the number of active orbitals; N is the sum of the number of occupied (N_{occ}) and virtual (N_{virt}) orbitals) and cannot be applied to systems with a large number of unpaired electrons (large CAS) or with bulky ligands (large number of occupied and virtual orbitals). Therefore, several modifications have been developed in order to widen the applicability range of the method. The DDCI2 and CAS+S (or DDCI1) variants further restrict the number of determinants in the CI expansion, which result in smaller interaction parameters.[33,35] Other approaches restrict the molecular orbital space to reduce the computational cost. Taking the orbital energies as selection criterion is not convenient, instead it is more effective to first make an orbital transformation based on the density matrices difference of the states under study and then eliminate the orbitals with the smallest eigenvalues.[74] Further reductions can be obtained when the molecular orbital set is transformed to localized orbitals and a combination of restriction is applied. Among them, one may quote physically justified truncations of the reference space, *e.g.* by eliminating the determinants in which the number of electrons per magnetic site changes by two or more compared to the dominant configuration. The subsequent calculation of dynamic correlation can be achieved with a lower computational cost.[75,76] A considerable gain in computational effort is also achieved when applying restrictions in the in the orbital space based on topological arguments (orbitals localized far away from the magnetic center can be kept frozen) and restrictions in the generation of the CI expansion by selecting the determinants based on the size of the exchange integral among the orbitals involved in the excitation. This excitation selected CI (EXSCI)[77] has recently been applied to relatively large polynuclear systems.[72,78,79]

3.1.3 Spin-orbit coupling, spin-spin coupling, and anisotropic interactions.

As stated in section 2, the ZFS has a relativistic origin, being essentially due to spin-orbit and spin-spin couplings. Other relativistic effects, either spin-free or spin-dependent terms,[80] also influence the ZFS, and therefore a rigorous treatment of the effect requires a coupled relativistic and correlated computational approach. Four and two components formalisms are the methods of choice for treating relativistic effects, but soon lead to a prohibitively expensive treatment of electron correlation within a WFT framework.

Since the spin-orbit interaction is less important than the electron-electron and ligand-field interactions in most d complexes,[9] decoupled two-step approaches are popular for this type of applications. In a first step, the spin-free interactions are treated, while the spin-orbit and/or spin-spin couplings are treated *a posteriori*. The spin-orbit and spin-spin interactions are treated as perturbations to the spin-free ones. In $4f$ complexes the situation is different: the spin-orbit interaction has a larger impact on the spectrum than the ligand field interaction. Nevertheless, since both interactions are much smaller than the electron-electron interaction, two-step approaches can also be used successfully in such cases. Methods to treat simultaneously the spin-orbit coupling and the electron correlation are available,[81,82] but their computational cost prevents the application to large TM complexes. Therefore, we limit the discussion to the more commonly used two-step methods.

In the first part, scalar relativistic effects and spin-orbit free interactions are treated. The former are accurately accounted for by the Douglas-Kroll-Hess Hamiltonian.[83,84] This treatment only affects the mono-electronic part of the electronic Hamiltonian and hence is easily implemented and used in standard wave function based methodologies.[85] In 3*d* complexes the effect of the scalar relativistic effects on ZFS is small,[86] but in 4*d* and 5*d* it becomes essential to include these effects. The description of the spin-orbit free ground state and a relevant set of excited states is often based on a CASSCF wave function followed by a post-CASSCF treatment of the remaining electron correlation. The minimal active space to be considered in the CASSCF calculation consists of the magnetic orbitals and unpaired electrons, extended with all the orbitals involved in the excitations that dominate the excited states. Normally, this includes all *d* or *f* orbitals of the metal, and sometimes a limited set of orbitals localized on the ligands. Such a minimal active space usually provides good semi-quantitative estimates of the ZFS, although further extensions of the active space may slightly improve the results.[87] CASPT2, NEVPT2 or DDCI calculations can then be performed to account for dynamic correlation in the ground and excited states.

The second part of the two-step procedure to calculate the ZFS introduces the spin-orbit and spin-spin couplings. Two approaches can be used for this purpose. The first one gives a variational treatment of the couplings by adding the spin-orbit and spin-spin operators to the standard non-relativistic Hamiltonian and diagonalizing the resulting matrix expressed in the basis of the M_S components of the CASSCF wave functions of ground and excited states. The second approach involves a perturbative description of the spin-orbit and spin-spin interactions. Both approaches count with their own advantages that will be discussed below. Dynamic correlation can be accounted for by replacing the CASSCF energies with those obtained with methods that account for a larger part of the dynamic correlation as proposed by Llusar *et al.* in the context of a variational treatment of the spin-orbit coupling.[88]

Concerning the state interaction (variational) approach, two possibilities exist to extract the ZFS tensor, (i) use the effective Hamiltonian theory,[87] described in section 2, or (ii) use the pseudospin approach.[16] For the cases in which the spin Hamiltonian approach is relevant, both approaches lead to very similar results. However, both approaches are significantly different in their philosophies. The effective Hamiltonian only uses the information contained in the lowest energy projected eigenvectors, while the pseudospin approach also takes profit of the information contained in the higher energy solutions of the state interaction matrix. Note that in the first approach an initial guess concerning the model space has to be done, although the initial guess can be rigorously refined, if necessary. More emphasis and examples concerning the effective Hamiltonian approach and the refinement of model operators will be presented in Section 4. Although these approaches are rigorous and accurate, it is not straightforward to analyze the factors governing the ZFS. This is the reason why it is still useful to apply QPDT to obtain the ZFS parameters.

Equations to obtain the ZFS tensor at second order of perturbation were derived several years ago to include not only the effect of spin components of spin-free states with same spin quantum numbers S as the ground state, but also spin quantum number $S' = S \pm 1$.[17,89] The ZFS tensor is constructed as a sum of individual contributions of the different M_S components of the spin-orbit free states, which provides direct access to the contributions of the different states to D and E to rationalize the nature and magnitude of the ZFS. The first-order contribution coming from the spin-spin coupling can also be introduced in the treatment.[89,90] While the state interaction approach can be used to extract any type of anisotropic interactions, the perturbative approach is in practice restricted to symmetric second-rank ZFS tensors, *i.e.* single-ion anisotropy or to giant spin approaches. The extension to other effective interactions would require further derivations, which could be a perspective in this field.

In addition to factors as the basis set, the size of the active space, and the treatment of the dynamic correlation, the calculated ZFS depends on the number of states considered in the state interaction or perturbative treatment. It is crucial to understand that the number of spin states considered cannot be completely arbitrary: the excitations have to be well balanced in all the orientations of space to avoid artefacts. An easy choice on the safe side consist of including the entire d^n or f^n manifold. However, this may result in a very large number of spin-free states in the first step of the calculation, and due to averaging effects, can lead to a poor representation of the ground states and the lowest-lying excited states, which most contribute to the ZFS. Therefore, it is often better to restrict the state-interaction/external space to a fraction of the d^n or f^n manifolds. No unique choice can be recommended. A balanced selection of the spin-free states depends on the considered electronic configuration, the coordination of the metal ion, and the ligand field strength.

3.2 Density functional theory

3.2.1 Isotropic interactions. The Kohn-Sham implementation of DFT requires the use of a single determinant. It is therefore in general not possible to respect the spin symmetry for magnetic systems. The use of DFT based calculations has of course the big advantage that is rather easily applicable to large, real-world molecules and it is highly desirable to have a way to address the isotropic magnetic interactions within this approach. This can be done by exploiting the broken symmetry solution.

Broken symmetry (BS) approaches, first introduced by Ginsberg and Noodleman,[91,92] have intensively been used for the extraction of magnetic couplings from DFT calculations. Since magnetic states are multideterminantal functions (except for the highest spin (HS) state), the extraction of the magnetic coupling values cannot proceed through a direct identification of the DFT solutions to the Heisenberg wave functions. The BS approaches usually consist in a mapping of the DFT energies of the spin-unrestricted determinants to the energies of the Ising Hamiltonian, *i.e.* to the diagonal elements of the Heisenberg Hamiltonian. In the case of a two-electrons in two-orbitals problem, the magnetic coupling is evaluated from the energy difference between the $M_S = 1$ and $M_S = 0$ solutions and more generally, for systems involving several unpaired electrons per center, J is calculated from the $M_{S_{max}}$ and $M_{S_{min}}$ solutions. The procedure can easily be generalized to calculate magnetic interactions in extended systems, such as polynuclear complexes and extended materials, eventually optimizing intermediate M_S solutions. This approach is valid in the 'weak-coupling' limit, *i.e.* when the $M_{S_{min}}$ spin-broken-symmetry solution can be considered as an ideal weighted average of the different spin states ranging from S_{min} to S_{max}, with the weights being obtained from the square of the appropriate Clebsch-Gordan coefficients.

One problem of these extractions comes from the spin contamination of the spin unrestricted determinants, which does not correspond in the general case to the ideal mixture of the various spin states observed in the 'weak-coupling' limit. Various methods have been proposed to adequately decontaminate the BS solutions in order to get reliable estimates of the real spin states energies. One of the most popular spin decontamination techniques has been proposed by Yamaguchi resulting in the following expression of the magnetic coupling parameter:[93]

$$J = \frac{2\,(E_{BS} - E_{HS})}{\langle S^2 \rangle_{HS} - \langle S^2 \rangle_{BS}} \tag{19}$$

Note that this formula is compatible with the 'weak-coupling' limit, decribed above, and the 'strong-coupling' limit, described below. This procedure can be extended to polynuclear systems with a large number of magnetic centers, either by using the generalized spin projection technique,[94,95] or by considering pairs of magnetically active centers such that equation 19 can be used for each pair calculation.[96]

In the 'strong-coupling' limit, the $M_{S_{min}}$ spin-broken-symmetry solutions of binuclear systems are considered to be true S_{min} spin states.[97] In the case of an even number of electron and S_A=S_B, the M_S=0 state would thus correspond to a true singlet state; in other words, a strong covalent interaction between the "magnetic" centers can lead to a true singlet spin state, supposedly ground state. One should note that the 'strong-coupling' qualification here refers to covalent coupling, and should not be confused with the 'strong-exchange' limit of section 2.2.4.

Many papers have been published dealing with the dependence of the calculated magnetic coupling strength on the degrees of freedom of the DFT calculation, such as the functional, the self-interaction error corrections, the percentage of exact exchange in hybrid functionals, the value of U in DFT+U methods, *etc.*[98–106] In most cases, the values are largely overestimated, although some recent functionals tend to perform better.[104,105] The tendency to produce too large couplings has been explained by the exceeding delocalization of the magnetic orbitals which results in an overestimation of both the direct exchange (dominant in ferromagnetic systems) and the kinetic exchange contributions (dominant in antiferromagnetic systems). Nevertheless, trends are usually accurately reproduced allowing interpretations and rationalizations of the observed trends in families of systems. While during a long time, the decomposition of the magnetic coupling was the prerogative of wave function based methods, decomposition schemes for DFT approaches have recently been proposed.[107] These analyses start from the spin restricted high spin state orbitals and optimize separately the delocalization of the magnetic orbitals and the spin polarization of the core orbitals in constrained BS solutions. From the energy differences between the various optimized solutions, it is possible to evaluate the direct exchange, the kinetic exchange and the spin polarization contributions to the magnetic coupling in a consistent manner. The relevance of the decomposition scheme can be checked by comparing the sum of the separated contributions to the value of the magnetic coupling calculated from equation 19.

Another issue of the BS approach is the extraction of complex interactions, such as four-spin cyclic exchange, biquadratic exchange and double exchange interactions from spin unrestricted DFT calculations. While the strength of the first interaction can be determined from the energy differences of the $M_{S_{max}}$, $M_{S_{min}}$ and intermediate M_S determinants,[108], this is no longer possible for the other two interactions. Recent papers propose to first extract the interactions of a generalized Hubbard Hamiltonian.[109–111] Since analytical expressions of these complex interactions can be expressed as functions of the Hubbard interactions, it is then possible to numerically calculate their values from the estimates of the Hubbard interactions.

3.2.2 Anisotropic interactions.

The first main DFT approach for the ZFS was proposed in the late 1990's by Pederson and Khanna.[112] First a spin unrestricted calculation of a given spin configuration is performed, followed by a perturbative treatment of the spin-orbit coupling to obtain a second-rank symmetric ZFS tensor. Similar approaches appeared over the years, for instance by Aquino and Rodriguez,[113] and by Neese.[89] These approaches were recently reviewed by van Wüllen and coworkers,[114,115] clarifying the discrepancy between the prefactors associated with the spin-flip approaches of Pederson and of Neese. These approaches can only incorporate the effect of singly-excited configurations, and the excitation energies are estimated from the corresponding (spin-)orbital energy differences. As for the method described in Section 3.1.3, the truncation should be done carefully to avoid any artefact. Note that if high energy excitations are considered, the truncation is not problematic in practice since the second-order contributions to the ZFS tensor of the last included and first missing configurations are negligible.

An alternative that avoids truncation problems consists in using linear response theory. In 2007, Neese solved the coupled-perturbed equations for a second-rank symmetric ZFS tensor,[116] allowing a linear response theory implementation including both spin-orbit and spin-spin couplings. Even though this approach is more sophisticated than the perturbative ones, it also suffers from the degrees of freedom of DFT calculations. In particular, various functionals may lead to different ZFS parameters, and this approach appears to be less robust than the WFT ones described in Section 3.1.3.

Perturbation and linear response approaches may lead to very different results, none of which being necessarily in good agreement with experiment.[117] Therefore, there is still a need for clarifying the problems of these approaches for eventually improving them. This point will be discussed in detail in Section 5.

4 Applications

4.1 Single-ion anisotropy

Single ion anisotropies are expected to be the most important contribution to the overall magnetic anisotropy of polynuclear systems and in particular to polynuclear single molecule magnets,[41] although intersite anisotropies can also play a non-negligible role.[118] In order to increase the magnetic anisotropy of a single paramagnetic ion, people have pursued various strategies. A first successful idea, which actually led to a new class of single molecule magnets, was to conceive molecules containing a single paramagnetic lanthanide center.[119] In these systems, the large magnetic anisotropy stems from the strong spin-orbit coupling associated with the f-element ion and a relatively smaller ligand-field effect. Another strategy consists of synthesizing TM complexes in which the paramagnetic transition metal ion exhibits exotic coordinations such as penta or hepta coordination. While up to now the corresponding complexes did not show any blocking of the magnetization, relatively large values of the axial parameters D were obtained.[120–125] Finally, a very promising mean to improve the property was to design complexes having an unquenched angular orbital momentum in their high spin ground state. In such cases, extremely large values of D were observed in Ni and Fe TM complexes for instance.[126,127] Note that in some cases it is possible to obtain slow relaxation of the magnetization in complexes with positive D parameters,[128] and thus complexes with positive D values can be interesting building blocks to build larger architectures, although usually building blocks with negative D values are used in bottom-up approaches.[122,129]

From a theoretical point of view, the study of complexes with a single anisotropic ion has been particularly fruitful.[13,124–126,130–135] This has allowed to develop appropriate *ab initio* methods and to determine the level of correlation needed to reach accuracy as discussed in section 3. Various methods of extraction of anisotropic parameters have also been proposed and tested on mononuclear complexes.[16,87,89,116] They can lead to significantly different values for a same *ab initio* method. ZFS tensors have traditionally been calculated from first principles using sum-over-states formulas based on second-order perturbation theory. Recently, an extraction procedure based on the effective Hamiltonian theory has been proposed and successfully applied to Ni, Co, and Mn TM complexes.[12,87] The parameters are of variational quality, *i.e.* correct to an infinite order and the comparison with the perturbative extractions shows that PT2 may lead to overestimates of D and E by up to 20%.[125,136] One should also mention that the effective Hamiltonian theory which gives access to numerical evaluation of all the matrix elements of the model spin Hamiltonian has confirmed the validity of the anisotropic spin model Hamiltonian for the description of single ion anisotropy and can be used to evaluate the magnitude of higher than 2 order terms in systems with more than 2 unpaired electrons.[12]

Finally, another important contribution from theory was the rationalization of both the nature and magnitude of single ion anisotropy. Indeed, the sensibility of the anisotropic parameters to structural, chemical (ligand field strength) and even electrostatic factors makes it difficult to anticipate their magnitude from the chemical intuition and there is a real need for understanding how to control magnetic anisotropy if one wants to propose new systems with improved properties. The first extensive rationalizations of the anisotropic parameters were provided by Abragam and Bleaney through analytical derivations of the spin orbit interactions between the ground and lowest in energy excited terms.[10] These derivations bring interesting information when the considered wave functions can easily be anticipated, i.e. for relatively simple geometrical structures such as elongated or compressed octahedra, for instance. Nevertheless, for most of the real strongly anisotropic systems, the geometries are of very low symmetry and the lowest wave functions are multiconfigurational. In such cases, it is hardly possible to predict the most important determinants and their relative weight in the wave functions of the lowest states without performing an *ab initio* calculation. Recently several works have proposed rationalizations for the magnitude and nature of the anisotropic parameters, based on the analytical derivation of the spin orbit interactions between the calculated wave functions and the quasi-degenerate perturbation theory at second order.[12,13,126,137,138] The analysis of the physical content of the most contributing excited states also brings the opportunity to determine the chemical and structural factors (the ligand field strength and effect of specific geometrical distortions) that determine the features of the single ion anisotropy in a specific compound or a series of compounds. In the same philosophy, one should quote the Angular Overlap Model (AOM),[139] which provides a ligand field based analysis. The method builds a ligand field matrix (5 by 5) for the 5 *d* orbitals that depends on two parameters e_σ and e_π for each ligand and angular factors which account for the real geometry (for which the overlap between the metal and ligand orbitals may not be optimal). The two parameters for each ligand-metal orbital pair, can be fitted either from experiment or theoretical results, providing useful interpretations of the D and E values as functions of the chemical and geometrical factors.[120,121,140] However, in some cases the number of parameters may be too large, preventing the extraction of a unique set of ligand field parameters from a direct fit to the *ab initio* results. The study of model systems can provide magneto-structural correlations and tendencies,[12,135,137,141] further improving our chemical intuition on the relation between structure and property.

4.2 Isotropic interactions

A key ingredient for the existence of non-zero net magnetic moments at room temperature is the strength of the isotropic coupling of the spins localized on the magnetic centers. If the spins are only loosely coupled, temperature effects will destroy any long-range order of the spins and lead to a paramagnetic phase in the absence of an external field. Therefore many efforts have been dedicated to the design of materials with strongly coupled spin moments. This is in general not so difficult for antiferromagnetic coupling. By properly choosing the magnetic core of the system (magnetic centers and bridge), the kinetic exchange mechanism can induce a delocalization of the spin density to effectively connect the two magnetic centers. To name one example, we mention the interaction of the Cu(II) ions in the CuO_2 planes of the copper oxides, parent compounds of the high-T_c superconductors.[69,142] Actually, stronger and stronger antiferromagnetic coupling leads in the end to the formation of a covalent bond between the magnetic centers with the 'unpaired' electrons occupying bonding orbitals.

In contrast, strong ferromagnetic coupling between localized magnetic moments are intrinsically more difficult. Strong interactions require a certain degree of delocalization of the spin density, but this normally favors antiferromagnetic coupling. Hence, ferromagnetic order with molecule-based materials at room temperature is not easily achieved,[143–147] although defects in graphene[148] or semiconductors can induce robust ferromagnetism. A way to circumvent the kinetic exchange mechanism, but still establish contact between the magnetic centers is the use of 4d or 5d TM ions instead of the more common 3d TM ions. The spatial extent of the 4d and 5d orbitals is much larger than the 3d orbitals, and hence, stronger interactions may be expected for systems with such ions.[149,150] A nice illustration is given by comparing the coupling of Cu(II) with Cr(III) and with Re(IV) through the same cyanide bridge. The latter coupling (+57 cm^{-1}, claimed to be a record for ferromagnetic coupling through CN)[151] almost doubles the first one, determined to be +32 cm^{-1}.[152] It would be interesting to see how the magnetic coupling changes when the Cu(II) ions in the complexes recently reported by Colacio and collaborators[153] by 4*d* or 5*d* ions. These Cu(II) complexes show extremely strong ferromagnetic coupling of the order of 200 cm^{-1}.

An alternative to ferromagnetic isotropic coupling is the antiferromagnetic coupling of unlike spin moments. The disadvantage of smaller spin moments is compensated by the larger versatility of the antiferromagnetic couplers. There are many examples of molecule-based magnets constructed with ferrimagnetic materials.[143,154,155]

The role of theory and computation in this aspect of molecular magnetism is three-fold. In the first place, the decomposition of the calculated isotropic magnetic coupling provides important insights into the relative importance of the different coupling mechanisms such as the direct and kinetic exchange, spin polarization and other electron correlation effects.[32,33,107,156,157] This information is important to rationalize the coupling strengths observed for different compounds. Secondly, computational experiments can be performed to obtain information about the relation between geometrical factors and the interaction strength. These magnetostructural correlations go back to the work of Hay, Thibeault and Hofmann[31] and many examples may be found in the literature.[54,158–162] An illustration of the information that can be derived from these computational experiment, we mention the proposal of some bridges that could possibly give rise to strong ferromagnetic coupling.[163,164] Finally, theory is especially useful to unravel the magnetic structure of polynuclear systems with several magnetic interaction pathways.[72,165,166] In these cases, the fitting of the magnetic susceptibility data cannot by itself provide conclusive results due to the fact that the curves can be fitted equally well with different parameter sets.

4.3 Anisotropic interactions in polynuclear systems

4.3.1 Multispin Hamiltonian. Polynuclear TM complexes with several magnetic centers constitute an important group of systems in the field of molecular or molecule-based magnetism. Among the many examples, we quote here the single-molecule magnets, the metal-organic frameworks (MOFs) and extended materials as the TM oxides. The description of the magnetic phenomena with the multispin Hamiltonian covers local single-ion anisotropy and intersite anisotropic terms in addition to the standard, previously described isotropic interactions.

The simplest approach to compute single-ion anisotropy in polynuclear systems consists in treating explicitly only one magnetic center. This approach neglect the role of intersite electron correlation on the local single-ion anisotropy. However, assuming that the single-ion anisotropy is largely dominated by the local ligand field, this approach allows to compute quite accurately the magnitude of the local anisotropy, and in a similar way as in mononuclear complexes. If other magnetic ions are located close to the magnetic center of interest, for instance in the second coordination sphere, the charge and charge density of these ions may affect the ligand field felt by the ion of interest, and thus, the single-ion anisotropy. These effects can be accounted for by point charges, model potentials, or diamagnetic ions of similar ionic radii as the replaced ions. The last two options give more accurate results and are preferable above the crude description with point charges. Recently, several studies addressed local anisotropies in this way. One may quote the work concerning a mixed-valence cobalt heptanuclear wheel,[167] which allowed to explain the lack of SMM behaviour of this system. We estimated the D_A and E_A parameters in the binuclear complex $[Ni_2(en)_4Cl_2]^{2+}$ (en=ethylenediamine) in a similar way.[42] Note that this system was used to further discuss the multispin and giant spin Hamiltonians, and thus will be used as an example in the remainder of this section. Recent works using an embedded cluster approach allowed to estimate the local ZFS in $Cd_2Os_2O_7$,[168] and a cluster approach was used to compute the single-ion anisotropy in the Fe_2(dobdc) MOF.[136]

The determination of intersite anisotropic terms is particularly challenging from a theoretical point of view, and the literature on this topic is much less extensive than that on mononuclear complexes or even single-ion anisotropy. A pioneering work on $H_2Ti(\mu\text{-}H)_2TiH_2$ by Webb and Gordon[169] appeared already in 1998, based on a two-step wave function based approach, as explained in Section 3.1.3. In this particular case, *i.e.* two $S=\frac{1}{2}$ sites and C_i symmetry, the D_{AB} and E_{AB} parameters can be simply extracted from the ZFS parameters of the triplet state.[22] As a consequence, although the D_{AB} and E_{AB} parameters were not explicitly highlighted in this article, since the spin-orbit splitting of the triplet state was determined, these parameters could have been extracted. Similarly, we determined with high-level calculations the ZFS of the triplet state in copper acetate monohydrate,[49] and had access to the intersite anisotropic terms of the multispin Hamiltonian. Still in the case of two $S=\frac{1}{2}$ site, when the Dzyaloshinskii-Moriya interaction is symmetry allowed, the energies are not sufficient to extract the intersite parameters. We showed that all the parameters of the multispin Hamiltonian can be extracted in an arbitrary frame with the effective Hamiltonian theory,[51] and that a spin-orbit calculation considering only the lowest-lying open-shell states (the ones corresponding to the model states of the HDVV Hamiltonian) allows one to obtain a good estimate of the antisymmetric exchange.[51,170] This approach was used to determine the antisymmetric exchange in cuprates.[170,171]

As explained in Section 2.2.4, the multispin Hamiltonian becomes rapidly intractable, starting with the case of two $S = 1$ local spins. As a consequence, trials to extract the full set of multispin Hamiltonian parameters from the spin-orbit coupled states have been unsuccessful so far.[42] The strategy outlined in the previous paragraph for antisymmetric exchange can, however, be used for any local spin state(s), and was also applied to the $Cd_2Os_2O_7$ system within an embedded cluster approach.[168]

4.3.2 Block spin and giant spin Hamiltonians. In relation with SMMs and the DFT implementations for the ZFS, the literature on the giant spin Hamiltonian is more extensive than the one on the multispin Hamiltonian. The first application concerned the well-known Mn_{12} complex,[172] experimentally studied for its magnetic properties in the 1990s.[173–175] This system possesses a S=10 ground spin state, whose spin components are split and mixed under the effect of spin-orbit coupling and an anisotropic ligand field. This system was theoretically studied by Pederson and Khanna, as an illustrative example of their method to compute ZFS.[112] A very good agreement between the computed and experimentally derived giant spin D and E parameters was found, motivating several other studies of this type with the same methodology.[176–182]

The giant spin approximation is generally considered as a good approximation when the spin-mixing is negligible, *i.e.* when other spin states are well separated from the ground state. This happens for example in the strong-exchange limit. Spin-mixing can be accounted for by introducing higher (than second) order terms in the spin Hamiltonian.[183,184] Since there are certain limitations inherent to the giant spin approximation,[185] a detailed theoretical study was performed on the $[Ni_2(en)_4Cl_2]^{2+}$ dinuclear unit. In order to clearly assess the magnitude of the potential effective interactions, wave function approaches were used together with the effective Hamiltonian theory.[42,45,137] A first important result was that in centrosymmetric complexes the magnetic anisotropy axes defined with the giant spin Hamiltonian correspond to the ones of the block spin approach and also to those of the multispin Hamiltonian. A second finding was that when the spin-mixing is switched off, the Stevens operators can be used within a block or giant spin approach. After introducing the spin mixing in the effective Hamiltonian matrix, it became clear that at second order of perturbation, the spin-mixing cannot be treated with the Stevens operators. New operators were designed to account for the spin mixing in centrosymmetric S=1 binuclear complexes,[45] clarifying the controversy about high-order Stevens terms and spin-mixing in giant spin and block spin approaches. Note that the extension of this work to other configurations is still a perspective in the molecular magnetism field.

5 Challenges and perspectives

5.1 Wave function methods: Limits and prospects.

Computational schemes based on a single reference determinant can be used to treat rather large molecules. In many cases a (nearly) linear scaling can be obtained. However, the intrinsic multideterminantal nature of the electronic structure of most magnetic systems puts serious restrictions on the application of wave function based methods. One of the bottlenecks is the rapid increase of the number of determinants in the reference wave function with increasing number of unpaired electrons. The reference wave function is commonly expanded following the complete active space procedure, which is at present limited to approximately 16 orbitals and 16 electrons for low-spin states. Instead of a CAS reference, one can also opt for a restricted active space approach, which have become specially interesting when the RASPT2 approach[186] became available to treat the remaining dynamic correlation. The active space is divided in three sub-blocks and restrictions are imposed on the excitations between different blocks.[187] This method is promising but suffers from some convergence problems in the wave function optimization and necessarily neglects some matrix elements among the sub-blocks of the active space. Other ways of selecting configurations have been recently developed, namely using the generalized active space concept,[188] and partitioning techniques can also help in reducing the computational cost.[189,190]

A second bottleneck is the number of determinants external to the reference space that has to be considered in order to reach a satisfactory description of the dynamic electron correlation. The previously discussed DDCI approach eliminates a large part of the external determinants from the standard MR-SDCI wave function, but is rather demanding already for medium-sized molecules with few unpaired electrons, and when the number of unpaired electrons increases only small systems can be addressed. However, there are several ways to stretch the applicability range of DDCI. In the first place, the number of MO's can be reduced to $\sim$50% of the original size at virtually no loss of accuracy by an orbital transformation based on the diagonalization of difference density matrices[74,191] or using improved virtual orbitals as proposed by Barone and co-workers.[192] Secondly, one can introduce additional selection criteria for including determinants in the CI expansion when working in localized orbitals. Chemically less important orbitals can be excluded right away and the remaining external determinants are filtered on the basis of the exchange integrals between the orbitals involved in the excitation, including only those above a certain threshold.[72,77–79] The third approach is based on a combination of variational and perturbative treatment of the external determinants. In the complementary space perturbative approach a division is made in the improved virtual space based on the orbital energies. The determinants with one or two electrons in the lower part of the virtual space are treated variationally, while the effect of the remainder is estimated with second-order perturbation theory.[71] The spectroscopy oriented CI follows a similar scheme,[193] albeit that the division variational/perturbative is done by screening the determinants based on perturbative estimates of the coefficients and energy contributions, inspired by the CIPSI approach of Malrieu and collaborators.[194]

Concerning more specifically the anisotropic interactions, the size of the active space is limiting in practice the maximum size of systems that can be treated, except if only the antisymmetric exchange is targeted (see Section 4). For instance, for binuclear TM systems, the minimal active space contains the d electrons and the 10 d orbitals. Although restrictions of the CI space may lead to more tractable calculations, *e.g.* by using the RASSCF/RASPT2 approach, the computation of the giant spin Hamiltonian in Mn_{12} with WFT is far from being a realistic short term objective. Another limitation of the two-step sum-over-states and state-interaction approaches arises from the necessity of defining the external and state-interaction spaces, respectively. Although in standard TM complexes with SOC essentially dominated by the TM atom and with only a moderate mixing of the TM d and ligands AOs, *i.e.* for weak to moderately covalent coordination bonds, it is easy to select such spaces, it may not be more problematic in some cases. In particular, with heavy atom ligands, the SOC near these ligand nuclei can also play an important role on the ZFS. In this case, one cannot simply restrict to crystal-field excited states if the coordination bond show moderate covalent interactions between the TM and ligand orbitals. The progressive increase of the active space and the state interactions space can in principle solve this problem. However, attempts to treat such situations in this way were unsuccessful.[134] One elegant way to avoid this problem would be to avoid truncation and averaging artefacts, *e.g.* by using linear response theory, or by treating simultaneously electron correlation and SOC.

The development of a general approach aiming to treat any mononuclear system accurately and at a moderate computational cost with WFT has yet to be achieved.

5.2 Density functional methods: Recent progress, limits, and outlook.

The application of DFT to transition metal based systems, despite its long-standing history, still deserves further development. As pointed out in a recent review, some applications have been performed with not so reliable functionals, however, ongoing development of new functionals and new application fields may lead to further improvements in the future.[195] Isotropic magnetic couplings obtained with broken-symmetry calculations, despite the choice of the extraction scheme and other computational details, essentially depend on the functional choice. Recently, benchmarks have been performed on transition metal complexes,[104,105] assessing the reliability of standard and new functional to compute isotropic couplings. The very popular B3LYP[196] and PBE0[197] hybrid functionals tend to largely overestimate moderate to large magnetic couplings.[104] Although these functionals are widely used for chemical applications, they are therefore not recommended in general to compute isotropic magnetic couplings. The M06 meta generalized gradient approximation (GGA) hybrid functional[198] usually provide better magnetic couplings than the B3LYP and PBE0 ones,[104] and thus can be recommended to compute isotropic interactions. Higher accuracy can be obtained with range-separated functionals, such as the Heyd-Scuseria-Ernzerhof (HSE)[199] and long range corrected (LC) hybrid LC-ωPBE[200] ones. Note that the HSE functional is however less robust than the LC-ωPBE one, which provides a close correlation between experimental and computed values.[105] One may conclude at this stage that some recently developed functionals tend to better behave than standard ones, which is a significant progress in the field.

A second important point of attention is the way to connect the energies of the different Kohn-Sham determinants with the magnetic coupling parameters.[69] As mentioned in Section 3.2, various schemes exist to extract J from broken symmetry calculations. None of this scheme is perfect in the general case, and these different schemes would lead to different coupling constant values in a practical case. Hence, the extracted values are not uniquely defined, contrary to the WFT approaches which ensure proper spin symmetries. One should also note that it is not easy to access other types of isotropic interactions such as biquadratic exchange, although it is in principle possible to extract relevant information by using an appropriate set of spin-broken-symmetry solutions.[109] Spin-flip time-dependent DFT (SF-TDDFT) allows to extract unambiguously magnetic couplings,[201–203] and would deserve further testing. Multiconfigurational hybrid density-functional theory[204] appears as an attractive route by combining the advantages of both WFT and DFT approaches in an efficient and accurate way, and may lead to some significant progress in the next few years.

Despite recent reviews of the available approaches for computing ZFS parameters based on DFT, including the corrections of some prefactors,[114,115] a recent article pointed out difficulties to compute the ZFS in Ni(II) mononuclear complexes.[117] It is in particular very surprising and quite puzzling to observe that sum-over-state and linear response theory based approaches lead to completely different answers in the tested molecules, *i.e.* different D signs. This fact could indicate a problem in either or both approaches, and thus a more detailed study on the origin of this discrepancy is necessary. Even more surprising, is the fact that the computed values are far off compared to experiment (more than a factor of 10), while these complexes are correctly treated with WFT and other d^n configurations are less problematic for DFT. It would be crucial to understand the reasons of such failures in order to improve the DFT methods for the magnetic anisotropy, and one may hope that these recent articles and the present article will motivate further theoretical work on this problem.

5.3 Interpretation of experimental data: Comments and perspectives

Until now, this review mostly focused on the zero-field Hamiltonians from theoretical and computational points of view. The experimental component is however crucial in this field, and we now want to underline the role of joint or independent experimental and theoretical/computational efforts to understand how to extract and interpret relevant magnetic parameters.

The copper acetate monohydrate case underlines the difficulty of extracting magnetic parameters from experiment. After being considered positive for decades,[47,48] new experiments allowed recently to determine unambiguously that the D parameters of the first excited triplet state is actually negative.[205] Shortly after, high-level quantum mechanical calculations supported this latter experimental study,[49] nearly 60 years after the first magnetic study[206] of this compound! One can conclude from this that the extraction of magnetic parameters from experiment is not trivial, and that theoretical and computational studies can be helpful in confirming the values of experimentally extracted parameters.

In solid state or polynuclear systems, it is often possible to find various sets of parameters allowing to fit with similar accuracy a same data set. One may quote the $LiCu_2O_2$ case as an example, for which two potential parameter sets were discussed in the literature.[207–211] By performing *ab initio* calculations on embedded clusters, it was eventually possible to discriminate between these two parameters sets.[171]

Similar examples concern the magnetic interactions in Cu(II) cubanes, discussed by Calzado[72] and the polynuclear Mn clusters treated by Ruiz and co-workers.[95,212]

It is often hard to extract unambiguously antisymmetric interactions from experiment due to a too large number of parameters to be simultaneously extracted.[213] In some cases however, the norm of the Dzyaloshinskii-Moriya can be extracted after some approximations in the model.[214] Since there is clearly a need for more understanding of the role of the Dzyaloshinskii-Moriya interaction in molecular magnetism,[215] the possibility of computing *ab initio* the magnitude of this interaction is an important step in this direction.

Theory can also help in rationalizing the magnitude of the ZFS parameters, which is an important perspective in the field for some years.[216] Magneto-structural correlations can of course be obtained by analyzing only experimental data,[217] but computational chemistry can be even more powerful in the sense that model systems can be studied.[141] Theoretical predictions concerning the various mechanisms leading to an effective parameters can also be confirmed, such as the role of bridging oxygen atoms on the antisymmetric interaction in cuprates.[50,51]

In many cases, high-field/high-frequency electron paramagnetic resonance (HF-EPR) is a powerful tool to determine ZFS parameters,[218] allowing to perform *definitive* extractions.[219] However, in some cases, a discrepancy appears between the model used in the experimental extraction[220] and the one derived from *ab initio* calculations and the effective Hamiltonian theory.[42] Such a situation is problematic in the sense that the experimental extraction is in this case potentially invalidated, while it is not clear how to experimentally probe the validity of the different models. Theoretical and experimental efforts are then still required to solve this discrepancy which concerns the multispin Hamiltonian in bi- and poly-nuclear complexes.

More generally, two approximations are often used to extract experimental information in bi- and poly-nuclear systems, (i) the collinear approximation, and (ii) the strong-exchange limit approximation. While it is clear that these two approximations should not be used in non-collinear situations, or under the weak-exchange limit, at least one of these two approximations cannot be removed in standard programs used to simulate magnetic data, *i.e.* fit magnetic data. Theoretical determinations of magnetic parameters can then be very helpful in such cases, and still more theoretical and experimental work is necessary to better understand and characterize such complex situations. We hope that the present review will stimulate more efforts in this direction.

6 Concluding remarks

Spin Hamiltonians are used to interpret experimental magnetic data for many decades. Many breakthroughs in the molecular magnetism field are related with magnetometric studies and EPR spectroscopy, notably evidencing isotropic couplings between electrons located in different magnetic centers, as well as zero-field splitting in many mononuclear and polynuclear transition metal complexes. The interpretation of these experiments first relied on simple models, and more recently also on accurate computational quantum chemistry studies. Not only the parameter values can be discussed, but also the validity of the model Hamiltonians. Moreover, more interpretative information can be obtained, which is crucial to understand how to control the property, and thus how to design rationally new systems and materials in view of applications. Many methodological and interpretative challenges remain, and further theoretical and experimental efforts are necessary.

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