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Magnetic anisotropy in binuclear complexes in the weak-exchange limit: From the multispin to the giant-spin Hamiltonian

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This paper studies the physical basis of the giant-spin Hamiltonian, which is usually used to describe the anisotropy of single-molecule magnets. A rigorous extraction of the model has been performed in the weak-exchange limit of a binuclear centrosymmetric Ni(II) complex, using correlated *ab initio* calculations and effective Hamiltonian theory. It is shown that the giant-spin Hamiltonian is not appropriate to describe polynuclear complexes as soon as spin mixing becomes non-negligible. A relevant model is proposed involving fourth-order operators, different from the traditionally used Stevens operators. The new giant-spin Hamiltonian correctly reproduces the effects of the spin mixing in the weak-exchange limit. A procedure to switch on and off the spin mixing in the extraction has been implemented in order to separate this effect from other anisotropic effects and to numerically evaluate both contributions to the tunnel splitting. Furthermore, the new giant-spin Hamiltonian has been derived analytically from the multispin Hamiltonian at the second order of perturbation and the theoretical link between the two models is studied to gain understanding concerning the microscopic origin of the fourth-order interaction in terms of axial, rhombic, or mixed (axial-rhombic) character. Finally, an adequate method is proposed to extract the proper magnetic axes frame for polynuclear anisotropic systems.

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I. INTRODUCTION

Since the early 1990s,[1,2] single-molecule magnets (SMMs) have generated continuous interest of a large scientific community as their properties proved to be challenging from both technological and fundamental points of view. Their main remarkable property is the slow relaxation of their magnetization at low temperature,[3] which is interpreted in terms of a lift of degeneracy of the M_s components of the ground state of spin S and to a long lifetime of the $M_{s_{\max}}$ and $M_{s_{\min}}$ components. The relaxation is usually governed by direct or thermally assisted tunneling,[4,5] or is permitted thermally if the energy of the system is greater than the barrier required to reverse the magnetization.

From a theoretical point of view, the description of these systems is particularly difficult. In the first place, SMMs are magnetic systems with localized spin moments and in general highly correlated methods are required to calculate their properties. Second, the lift of degeneracy of the M_s components in absence of magnetic field is originated by relativistic effects and, in particular, by spin-orbit interaction. These facts, combined with the large size of most of the SMMs, makes practically impossible the use of the all-electron relativistic Hamiltonian, and normally model Hamiltonians are used both for the interpretation of experiments and to theoretically model their properties. Two models are commonly used: (i) the multispin Hamiltonian (MSH) and (ii) the giant-spin Hamiltonian (GSH). Both are phenomenological and their relevance should be validated by theoretical studies. As shown in previous studies,[6–8] it is possible to establish the relevance of any model Hamiltonian owing to the effective Hamiltonian theory. In combination with correlated *ab initio* calculations performed using the all-electron Hamiltonian, the effective Hamiltonian theory can also be used to propose a more appropriate model when the usual one is flawed.

This method has successfully been applied to Ni(II) and Co(II) mononuclear complexes[9] for which the appropriateness of the anisotropic spin Hamiltonian involving a second-order tensor has been confirmed. Recently, the method has also been used to check the validity of the multispin Hamiltonian to describe the magnetic properties of the $[Ni_2(en)_4Cl_2]^{2+}$ (en=ethylenediamine) binuclear complex.[10] This model Hamiltonian explicitly considers the anisotropy second-order tensor $\bar{\bar{D}}_i$ of the magnetic centers and their isotropic and anisotropic interactions.[11–13] The model deals with the energies and wave functions of all the states resulting from the interactions between the local spins. It has been shown[10] that the multispin Hamiltonian was not appropriate for the description of the anisotropy of the studied complex and a distinct Hamiltonian involving an anisotropic biquadratic operator has been proposed.

The present work is essentially focused on the giant-spin Hamiltonian. This model is more commonly used than the multispin, despite the fact that it neither explicitly considers the single-ion anisotropies nor their interactions and can therefore be considered as being less *microscopic* than the multispin Hamiltonian. Indeed, the model only describes the M_s components of the ground spin state and can be numerically solved for very large systems. As a consequence, anisotropy parameters of polynuclear SMMs determined from electron paramagnetic resonance spectroscopy are mostly (if not always) extracted using the giant-spin Hamiltonian, eventually involving standard Stevens operators up to order $2S$.[14] While the physical meaning of fourth-order operators is still a matter of debate in the literature,[15–19] it is usually considered that they account for the spin mixing between the ground state and low-lying excited states which are not explicitly included in the model.

The objective of the present work is twofold: in the first place, the most accurate effective Hamiltonian matrix working in the giant-spin model space will be extracted from *ab initio* calculations performed on the $[\mathrm{Ni}_2(\mathrm{en})_4\mathrm{Cl}_2]^{2+}$ complex and the relevance of the GSH (Refs. 3, 15, 20, and 21) will be discussed. In the second place, the GSH will be derived analytically from the MSH at the second order of perturbations and the role of the spin mixing between the ground quintet state and the excited singlet state will be studied. As a consequence of this analytical development, an appropriate GSH will be proposed. The physical nature of its constitutive interactions will be discussed, in particular, the physical link between the interactions appearing in the MSH and those appearing in this new GSH will be established.

II. METHODS OF EXTRACTION OF MODEL HAMILTONIANS AND COMPUTATIONAL INFORMATION

The effective Hamiltonian theory[22,23] can check the validity of any model Hamiltonian. It consists in the extraction from accurate *ab initio* calculations of the most rigorous effective Hamiltonian working in the same model space as the model Hamiltonian. This effective Hamiltonian is then compared to the model. In the des Cloizeaux formalism,[23] the general expression of the effective Hamiltonian is

$$\hat{H}^{eff} = \sum_i |\tilde{\Psi}_i\rangle E_i \langle\tilde{\Psi}_i|, \tag{1}$$

where $\tilde{\Psi}_i$ are the orthonormalized projections onto the model space of the all-electron Hamiltonian eigenvectors Ψ_i and E_i are the corresponding eigenenergies. This formulation ensures that the eigenvectors of the effective Hamiltonian are the projections onto the model space of the all-electron Hamiltonian eigenvectors and that its eigenvalues are the eigenenergies of the all-electron Hamiltonian such that

$$\hat{H}^{eff}|\tilde{\Psi}_i\rangle = E_i|\tilde{\Psi}_i\rangle. \tag{2}$$

The method provides more information than the spectrum of the energies only since it is possible to calculate all the matrix elements of the effective Hamiltonian as

$$\langle i|\hat{H}^{eff}|j\rangle = \langle i|\sum_i |\tilde{\Psi}_i\rangle E_i \langle\tilde{\Psi}_i|j\rangle. \tag{3}$$

The consistency of model Hamiltonians can be recognized by confronting these numerical matrix elements to their analytical expression in the model Hamiltonian.

The *ab initio* calculations were performed using the spin-orbit state-interaction (SI) method[24] implemented in the MOLCAS package.[25] The method performs a variational treatment of the spin-orbit couplings between the lowest states and a collection of excited states. The preliminary spin-orbit free calculations account for both nondynamic and dynamic correlation effects. The complete active space self-consistent field method is used to determine nondynamically correlated wave functions. The spin-orbit free dynamically correlated energies used in the SI step are computed using (i) the highly accurate difference dedicated configuration interaction[26] method for the lowest singlet, triplet, and quintet states and (ii) the CASPT2 method[27] for the other excited states. More technical information is available in Ref. 10. The so-obtained *ab initio* low-energy spectrum of the $[\mathrm{Ni}_2(\mathrm{en})_4\mathrm{Cl}_2]^{2+}$ complex is represented in the central column of Fig. 1.

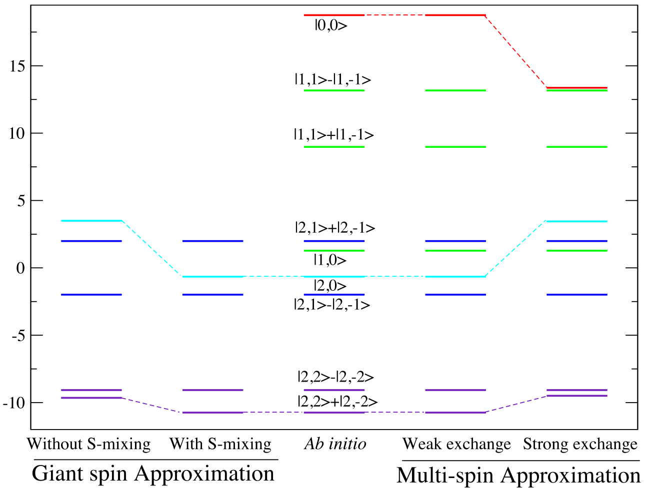

FIG. 1. (Color online) Comparison of model spectra obtained using different parameterizations with the *ab initio* spectrum.

III. MODEL HAMILTONIANS

A. Multispin Hamiltonian

Since the giant-spin Hamiltonian will be analytically derived from the multispin one, we first shortly review the commonly applied multispin Hamiltonian and the recently proposed modification to it. The multispin Hamiltonian has originally been proposed to rationalize the properties of copper binuclear complexes[28,29] and has later been generalized to magnetic systems involving spins larger than 1/2. For a binuclear complex, constituted of sites a and b, it has the following expression:

$$\hat{H}^{MS} = J\hat{S}_a\cdot\hat{S}_b + \hat{S}_a\bar{\bar{D}}_a\hat{S}_a + \hat{S}_b\bar{\bar{D}}_b\hat{S}_b + \hat{S}_a\bar{\bar{D}}_{ab}\hat{S}_b + \bar{d}_{ab}\hat{S}_a\times\hat{S}_b, \tag{4}$$

where J is the isotropic magnetic exchange, $\bar{\bar{D}}_a$ and $\bar{\bar{D}}_b$ are local zero-field splitting (ZFS) tensors, $\bar{\bar{D}}_{ab}$ is the symmetric anisotropic tensor and $\bar{d}_{ab}$ is the antisymmetric anisotropic term,[11–13] known as the Dzyaloshinskii Moriya vector. Since our studied complex exhibits a center of symmetry, both local tensors are equal and the antisymmetric term vanishes.

This Hamiltonian works on the basis of the $|M_{S_a}, M_{S_b}\rangle$ functions and is designed to reproduce the energy of all the states resulting from the coupling between the ground spin states of each magnetic sites. In the present study, the Hamiltonian should reproduce the energy of all M_s components of the singlet, triplet, and quintet states. Due to the parity rule, spin-orbit interactions cannot couple the triplet (of ungerade symmetry) and the singlet and quintet (of gerade symmetry), hence the spin mixing only concerns the quintet and singlet M_s components.

In the strong-exchange limit (i.e., when the isotropic exchange integral is large in comparison to the anisotropic interactions), the eigenvalues and eigenvectors of the model can be expressed analytically in a rather simple way leading to an easy extraction of the anisotropic axial D_a, D_{ab} and rhombic E_a, E_{ab} interactions.[11–13] These parameters are functions of the diagonal elements D_{xx}, D_{yy}, and D_{zz} of each tensor defined in its proper magnetic axes frame and for a traceless tensor,

$$D = D_{zz} - \frac{1}{2}(D_{xx} - D_{yy}) = \frac{3}{2}D_{zz}, \tag{5}$$

$$E = \frac{1}{2}(D_{xx} - D_{yy}). \tag{6}$$

In the weak-exchange limit (i.e., when the anisotropic parameters are of the same order of magnitude as the exchange integral), the extraction should be performed by solving analytically the model matrix built in the uncoupled $|M_{S_a}, M_{S_b}\rangle$ basis in order to accurately account for spin-mixing effects.[10,12,13] The parameters extracted from the *ab initio* energies only (i.e., without using the effective Hamiltonian matrix) lead to a perfect reproduction of the spectrum.[10] A comparison of the spectra obtained using the strong exchange approximation and this weak-exchange limit approach with the *ab initio* one is proposed in Fig. 1.

Recently, the use of the effective Hamiltonian theory for a rigorous extraction of this model[10] has led to a revision of the MSH since the analytical matrix of the Hamiltonian of Eq. (4) and the numerical effective matrix extracted from the *ab initio* results were exhibiting numerous incompatibilities. Some matrix elements having the same analytical expression had different numerical values in the effective matrix. Moreover, some zero analytical elements were actually corresponding to quite large values in the effective Hamiltonian. It has been shown that a biquadratic anisotropic exchange tensor $\overline{\overline{\overline{\overline{D}}}}_{aabb}$ should be added to the usual Hamiltonian in order to accurately reproduce the matrix elements of the effective Hamiltonian. This new model is unfortunately not usable in a practical way due to the large number of parameters involved. Its determination is however of fundamental importance to understand the physics of polynuclear anisotropic molecules and will also be useful in order to derive an adequate GSH. Its analytical matrix elements are reported in Appendix A.

B. Giant-spin Hamiltonian

A second, simpler approach to describe the magnetic anisotropy in polynuclear systems is provided by the giant-spin approximation.[3,15,20,21] Instead of considering the anisotropy as resulting from the coupling of localized spin moments, the properties are interpreted as to arise from the spin of the ground state of the whole molecule, i.e., the giant spin. The basic assumption for using the GSH is that the lowest spin multiplet of the molecule is sufficiently separated in energy from the other spin multiplets such that the magnetic properties can be described using a single-spin ground state. The studied complex which pertains to the weak-exchange limit constitutes an interesting case to analyze the physical content of the model.

The GSH is commonly expressed in terms of the standard Stevens equivalent operators $\hat{O}_k^m(\hat{S}_z, \hat{S}_\pm)$,[14] i.e., as linear combinations of spin operators of symmetry m ($m=0$ is axial, $m=2$ is rhombic, and $m=4$ is tetragonal) and order k. The expansion up to fourth order gives

$$\hat{H}^1_{\mathrm{GSH}} = \sum_{k=0,2,4} \sum_{m=0}^{k} B_k^m \hat{O}_k^m, \tag{7}$$

where the operators O_k^m have the following expressions:

$$\hat{O}_0^0 = S(S+1) \quad \hat{O}_2^0 = 3\hat{S}_z^2 - S(S+1) \quad \hat{O}_2^2 = \frac{1}{2}(\hat{S}_+^2 + \hat{S}_-^2),$$

$$\hat{O}_4^0 = 35\hat{S}_z^4 + [25 - 30S(S+1)]\hat{S}_z^2 - 6S(S+1) + 3S^2(S+1)^2,$$

$$\hat{O}_4^2 = \frac{1}{4}\{[7\hat{S}_z^2 - S(S+1) - 5](\hat{S}_+^2 + \hat{S}_-^2) + (\hat{S}_+^2 + \hat{S}_-^2)[7\hat{S}_z^2 - S(S + 1) - 5]\},$$

$$\hat{O}_4^4 = \frac{1}{2}(\hat{S}_+^4 + \hat{S}_-^4). \tag{8}$$

The second-order terms are related to the axial and rhombic parameters of the ZFS $\overline{\overline{D}}$ tensor such that $D=3B_2^0$ and $E=B_2^2$. The fourth-order terms are usually attributed to spin mixing, i.e., the admixture of higher multiplets to the ground-state manifold. The model space of this Hamiltonian

TABLE I. Analytical matrix elements of the giant-spin Hamiltonian for high-spin binuclear Ni(II) complexes expressed in the proper magnetic axes frame.

$\lvert S,M_S\rangle$	$\lvert 2,-2\rangle$	$\lvert 2,-1\rangle$	$\lvert 2,0\rangle$	$\lvert 2,1\rangle$	$\lvert 2,2\rangle$
$\langle 2,-2\rvert$	$9B_2^0+60B_4^0$	0	$\sqrt{6}B_2^2+3\sqrt{6}B_4^2$	0	$12B_4^4$
$\langle 2,-1\rvert$	0	0	0	$3B_2^2-12B_4^2$	0
$\langle 2,0\rvert$	$\sqrt{6}B_2^2+3\sqrt{6}B_4^2$	0	$-3B_2^0+120B_4^0$	0	$\sqrt{6}B_2^2+3\sqrt{6}B_4^2$
$\langle 2,1\rvert$	0	$3B_2^2-12B_4^2$	0	0	0
$\langle 2,2\rvert$	$12B_4^4$	0	$\sqrt{6}B_2^2+3\sqrt{6}B_4^2$	0	$9B_2^0+60B_4^0$

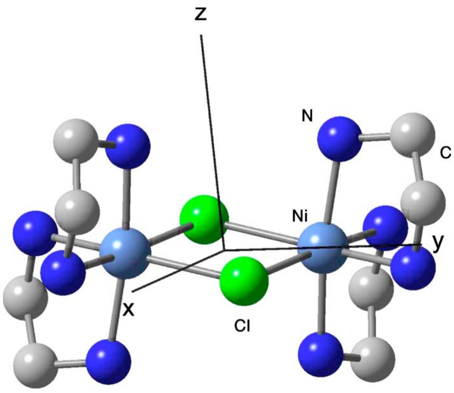

FIG. 2. (Color online) Ball and stick representation of $[Ni_2(en)_4Cl_2]^{2+}$. Hydrogen atoms are omitted for clarity. The proper magnetic axes are shown. The angle between the magnetic Z axis and the normal of the Ni-(Cl_2)-Ni plane is 12°.

is considerably smaller than for the MSH and is only spanned by the five $|2,M_S\rangle$ determinants for Ni(II) binuclear complexes. Table I shows the matrix representation of the GSH. Since we are only interested in state-energy differences, the trace of the matrix is an irrelevant parameter and the zero of energy has been chosen as the diagonal element of the $|2,\pm 1\rangle$ functions for convenience (see next section). It should be noted that these operators have been derived for the description of the crystal field around single magnetic centers. In the context of polynuclear systems, their relevance is not guaranteed and the physical content of the associated interactions B_k^m is not straightforward.

IV. RESULTS AND DISCUSSION

A. Determination of the proper magnetic axes frame

The proper magnetic axes frame is usually determined by diagonalizing the second-order ZFS tensor. This procedure implies that the GSH involving only the second-order tensor $S\cdot\bar{\bar{D}}\cdot S$ (i.e., only the B_2^0 and B_2^2 interactions) is appropriate for this purpose. Since higher-order terms are assumed to arise from spin mixing between the different spin states of the MSH, we have artificially removed the couplings between the singlet and quintet M_s components to extract the $\bar{\bar{D}}$ tensor and consequently to determine the proper magnetic axes frame. This switching off of the spin mixing will also help to obtain deeper insight in the origin of the higher-order terms in the GSH.

In the first place, the effective matrix of the MSH has been calculated. Then, the off-diagonal elements that couple M_s components of different spin states have been set to zero, and finally, the GSH effective matrix has been extracted from the spin-mixing free MSH effective matrix. The ZFS tensor has been determined from the resulting GSH effective matrix and diagonalized to obtain the proper magnetic axes frame. The numerical matrix of the GSH extracted from *ab initio* calculations performed in the so-obtained axes frame (see Fig. 2) is reported in Table II while the analytical matrix of the $S\cdot\bar{\bar{D}}\cdot S$ Hamiltonian in the proper magnetic axes frame can be obtained by keeping only the B_2^0 and B_2^2 interactions in the matrix of the GSH given in Table I, or by keeping only the diagonal components D_{ii} of the $\bar{\bar{D}}$ tensor in Appendix B.

From the comparison of the numerical and analytical matrices, we conclude that most of the fourth-order interactions in the GSH are zero (or smaller than the numerical precision) when the spin mixing is eliminated. The origin of these terms when nonzero in a full treatment should therefore be essentially attributed to spin mixing. Furthermore, the matrix element $\langle 2,-2|\hat{H}^{\text{GSH}}_{spin\text{-}mixing\ free}|2,2\rangle$ is nonzero and can only be caused by the fourth-order interaction B_4^4. Therefore, this fourth-order interaction has a different origin than the spin mixing between the singlet and the quintet. As shown in the Appendix A, this interaction is not included in the usual MSH, actually it comes from the fourth-order tensor $\bar{\bar{\bar{\bar{D}}}}_{aabb}$ of the recently proposed MSH. Finally, the so-determined axes frame leads to a numerical Hamiltonian matrix in which all the off-diagonal elements of the $\bar{\bar{D}}$ tensor vanish. The procedure therefore provides a rational way to extract the proper magnetic axes frames of polynuclear anisotropic molecules.

The main contribution to the anisotropy of a polynuclear complex is usually attributed to the local anisotropy of the metal ions for systems with $S > 1/2$, i.e., to the $\bar{\bar{D}}_a$ and $\bar{\bar{D}}_b$ tensors of the MSH. For noninteracting sites or for an isotropic interaction of the anisotropic centers, the anisotropy of the resulting Hamiltonian would be provided by the sum of the local $S_a\cdot\bar{\bar{D}}_a\cdot S_a$ terms. Related to this, it is interesting to note that there is a strict proportionality between the $\bar{\bar{D}}$ tensor of the GSH and the $\bar{\bar{D}}_a$ tensors of the local centers,

$$\bar{\bar{D}} = \frac{1}{6}\bar{\bar{D}}_a \tag{9}$$

as can be seen by comparing the analytical matrices of the $S\cdot\bar{\bar{D}}\cdot S$ and $S_a\cdot\bar{\bar{D}}_a\cdot S_a + S_b\cdot\bar{\bar{D}}_b\cdot S_b$ Hamiltonians expressed in

TABLE II. Giant-spin effective Hamiltonian matrix (in cm^{-1}) without spin-mixing effects in the $|S,M_S\rangle$ space extracted for the $[Ni_2(en)_4Cl_2]^{2+}$ complex computed in the proper magnetic axes frame.

(H^{eff})	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	−9.13	0.00	1.63	0.00	−0.06
$\langle 2,-1\|$	0.00	0	0.00	1.99	0.00
$\langle 2,0\|$	1.63	0.00	3.05	0.00	1.63
$\langle 2,1\|$	0.00	1.99	0.00	0	0.00
$\langle 2,2\|$	−0.06	0.00	1.63	0.00	−9.13

TABLE III. Giant-spin effective Hamiltonian matrix (in cm^{-1}) including spin-mixing effects in the $|S,M_S\rangle$ space extracted for the $[\mathrm{Ni_2(en)_4Cl_2}]^{2+}$ complex computed in the proper magnetic axes frame.

(H^{eff})	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	−9.19	$0.00+0.01i$	$2.49+0.01i$	$0.00+0.01i$	−0.12
$\langle 2,-1\|$	$0.00-0.01i$	0	$-0.01+0.05i$	1.99	$0.00-0.01i$
$\langle 2,0\|$	$2.49-0.01i$	$-0.01-0.05i$	−2.09	$0.01-0.05i$	$2.49+0.01i$
$\langle 2,1\|$	$0.00-0.01i$	1.99	$0.01+0.05i$	0	$0.00-0.01i$
$\langle 2,2\|$	−0.12	$0.00+0.01i$	$2.49-0.01i$	$0.00+0.01i$	−9.19

an arbitrary frame (see Appendices B and C). As a consequence, the proper magnetic axes frame of a centrosymmetric polynuclear complex is also a proper magnetic axes frame for the independent magnetic centers. One should also note that, as shown in Ref. 10, the symmetric anisotropic tensor $\bar{\bar{D}}_{ab}$ of the multispin Hamiltonian is also diagonal in the same axes frame.

B. Rigorous extraction of the effective matrix of the GSH

The effective matrix of the GSH has also been extracted including the spin mixing. It is reported in Table III. The optimization of the orbitals for the singlet, triplet, and quintet states leads to slightly different expressions of the spatial part of the wave function for these states. Consequently, the three states do not interact in the same way with the excited states and the magnetic axes frame does not strictly coincide for the three states. Hence, the introduction of spin mixing causes small contributions to off-diagonal elements of the $\bar{\bar{D}}$ tensor. Since these terms never exceeds 0.05 cm^{-1}, they have not been considered in the following extractions.

The magnitude of all the GSH interactions was determined from the set of independent linear equations obtained by imposing the equality of the analytical and numerical matrices. The values are reported in Table IV and show nonnegligible fourth-order interactions apparently accounting for the spin mixing and significantly different values for the second order interactions. While such an extraction leads at first sight to the conclusion that the GSH is appropriate, a deeper analysis of the effective matrices extracted with and without spin mixing reveals some inconsistencies. In the present case, a consistent extraction should give identical values of the second-order interactions B_2^0 and B_2^2 with and without spin mixing while a quite large discrepancy is observed. However, the numerical values derived from the two extractions are rather different. If we look in some more detail, it can be observed that the $\langle 2,\pm 1|\hat{H}^{\mathrm{GSH}}|2,\mp 1\rangle$ matrix element has the same value (1.99 cm^{-1}) in both numerical matrices while the $\langle 2,\pm 2|\hat{H}^{\mathrm{GSH}}|2,0\rangle$ element is substantially different (1.63 versus 2.49 cm^{-1}). The fourth-order interaction B_4^2, which contributes to both elements, cannot reproduce by itself these incompatible changes in the matrix elements, and hence, the B_2^2 interaction is artificially enhanced to keep constant the $\langle 2,\pm 1|\hat{H}^{\mathrm{GSH}}|2,\mp 1\rangle$ matrix element. Renormalizations of second-order interactions are only possible when higher-order terms affect the same matrix elements as the second-order ones. Since this is not the case in the present study, spin mixing cannot renormalize the second-order interactions and introduces distinct physics.

TABLE IV. Magnetic anisotropy parameters (in cm^{-1}) extracted for the GSH of Eq. (7) with and without spin-mixing effects and for the GSH of Eq. (13). Values have two significant figures, close to 5 third ones are given in parenthesis.

	$\hat{H}^1_{\mathrm{GSH}}$ spin-mixing free	$\hat{H}^1_{\mathrm{GSH}}$	$\hat{H}^2_{\mathrm{GSH}}$
B_2^0	−1.01(4)	−0.77(6)	−1.01(4)
B_2^2	0.66(5)	0.86(6)	0.66(5)
$60B_4^0$	$<10^{-3}$	−2.22	$<10^{-3}$
$3\sqrt{6}B_4^2$	$<10^{-3}$	0.37(5)	$<10^{-3}$
$12B_4^4$	−0.06	−0.12	−0.06
B_4^{ax}			−5.14
B_4^{rh}			−0.06
$B_4^{ax,rh}$			0.86

From this analysis, one may conclude that the operators usually introduced in the GSH in order to describe deviations to the $S\cdot\bar{\bar{D}}\cdot S$ Hamiltonian are not physically based for the studied complex. The assumption of spherical Stevens operators, which were proposed to reproduce these deviations in mononuclear species, is not valid for polynuclear complexes.

C. Proposal of a consistent GSH Hamiltonian

In order to propose a consistent Hamiltonian accurately accounting for spin mixing, the GSH has been derived analytically at the second order of perturbation from the MSH including the fourth-order tensor proposed in Ref. 10. One should note that since the energies of the $|2,0\rangle$ and $|2,\pm 2\rangle$ are different, the use of the exact denominators would lead to a non-Hermitian matrix that could only be compared to the Bloch effective Hamiltonian matrix (i.e., not to the des Cloizeaux one). Since our purpose is to use the perturbation theory as a guideline to determine adequate fourth-order operators, the denominators have been chosen to be the analytical spin-orbit free energies and this leads to the Hermitian matrix reported in Appendix D.

The perturbative terms involve the anisotropic biquadratic operators of the multispin Hamiltonian and are functions of the anisotropic parameters (D_a, D_{ab}, E_a, and E_{ab}). In order to specify the nature of the additional operators that will be

TABLE V. Matrix elements of the proposed giant-spin Hamiltonian in the proper magnetic axes frame.

$\|S,M_S\rangle$	$\|2,-2\rangle$	$\|2,-1\rangle$	$\|2,0\rangle$	$\|2,1\rangle$	$\|2,2\rangle$
$\langle 2,-2\|$	$9B_2^0+B_4^{rh}$	0	$\sqrt{6}B_2^2+B_4^{ax,rh}$	0	$12B_4^4+B_4^{rh}$
$\langle 2,-1\|$	0	0	0	$3B_2^2$	0
$\langle 2,0\|$	$\sqrt{6}B_2^2+B_4^{ax,rh}$	0	$-3B_2^0+B_4^{ax}$	0	$\sqrt{6}B_2^2+B_4^{ax,rh}$
$\langle 2,1\|$	0	$3B_2^2$	0	0	0
$\langle 2,2\|$	$12B_4^4+B_4^{rh}$	0	$\sqrt{6}B_2^2$	0	$9B_2^0+B_4^{rh}$

defined hereafter, their associated interactions will be called according to the nature (axial, rhombic or mixed) of the interactions appearing in the perturbation. Three different terms are obtained: (1) the spin-mixing term that affects the $\langle 2,-2|\hat{H}^{\mathrm{GSH}}|2,-2\rangle$, $\langle 2,2|\hat{H}^{\mathrm{GSH}}|2,2\rangle$ and $\langle 2,-2|\hat{H}^{\mathrm{GSH}}|2,2\rangle$ by the same quantity. This perturbative term involves the E_a and E_{ab} rhombic anisotropic parameters of the multispin Hamiltonian, it is noted B_{rh} and its expression is

$$B_4^{rh} = \frac{[2E_a - E_{ab} + 2(2) - (3)]^2}{9J}. \tag{10}$$

(2) The matrix elements $\langle 2,0|\hat{H}^{\mathrm{GSH}}|2,0\rangle$ are affected by the spin mixing through an interaction that involves the D_a and D_{ab} axial anisotropic parameters, B_4^{ax} is defined by

$$B_4^{ax} = \frac{2[2D_a - D_{ab} + (1) - (6) + (8) - (9)]^2}{27J}. \tag{11}$$

(3) The matrix elements $\langle 2,\pm 2|\hat{H}^{\mathrm{GSH}}|2,0\rangle$ are affected by an interaction involving both axial and rhombic parameters, $B_4^{ax,rh}$ is

$$B_4^{ax,rh} = \frac{\sqrt{6}[2(2) - (3) + 2E_a - E_{ab}][(1) + 2D_a - D_{ab} - (6) + (8) - (9)]}{27J}, \tag{12}$$

where terms (1), (2),…, (9) are interactions of the fourth-order tensor given in Appendix A. In these expressions the physical content of the interactions is given at the second order of perturbation. It is worth noting that the effective Hamiltonian theory provides interactions extracted at an infinite order of perturbation. Following this derivation a consistent GSH Hamiltonian can be defined. Its expression is

$$\hat{H}^2_{\mathrm{GSH}} = B_2^0\hat{O}_2^0 + B_2^2\hat{O}_2^2 + B_4^4\hat{O}_4^4 + B_4^{ax}\hat{O}_4^{ax} + B_4^{ax,rh}\hat{O}_4^{ax,rh} + B_4^{rh}\hat{O}_4^{rh}, \tag{13}$$

where

$$\hat{O}_4^{ax} = \frac{1}{96}(M_S+2)(M_S+1)(M_S-1)(M_S-2)(\hat{S}_+^2\hat{S}_-^2 + \hat{S}_-^2\hat{S}_+^2),$$

$$\hat{O}_4^{ax,rh} = \frac{1}{4\sqrt{6}}(\hat{S}_-\hat{S}_z^2\hat{S}_- + \hat{S}_+\hat{S}_z^2\hat{S}_+),$$

$$\hat{O}_4^{rh} = \frac{1}{24}[\hat{S}_+^4 + \hat{S}_-^4 + (M_S-1)(M_S+1)(\hat{S}_z\hat{S}_+\hat{S}_z\hat{S}_- + \hat{S}_z\hat{S}_-\hat{S}_z\hat{S}_+)]. \tag{14}$$

The analytical matrix of this Hamiltonian is given in Table V and is perfectly consistent with the numerical matrix of the effective GSH. Numerical values of the interactions of this new Hamiltonian are reported in Table IV. The second-order interactions are equal to those obtained in the spin-mixing free GSH, as required. The dominant fourth-order interaction is B_4^{ax}, reflecting the strong stabilization of the $|2,0\rangle$ function through the spin-mixing effects, next comes the $B_4^{ax,rh}$ interaction which couples the $|2,0\rangle$ and the $|2,\pm 2\rangle$ functions and finally the B_4^{rh} interaction is the smallest one. The B_4^{rh} interaction has almost the same value as B_4^4, and hence, a consistent model should include both for cases where the interaction becomes important. These two interactions contribute less than 5% to the energy difference between the $|2,-2\rangle + |2,2\rangle$ and $|2,-2\rangle - |2,2\rangle$ functions at the bottom of the spectrum (see Fig. 1). The energy difference is dominated by the $B_4^{ax,rh}$ interaction. The numerical contribution of the spin mixing to the energy difference is 1.08 cm^{-1}. Since this difference is proportional to the tunnel splitting, it governs the relaxation of the magnetization and plays therefore an important role in the anisotropic properties as already mentioned in other works.[18,19]

The spectra extracted using different approximations are reported in Fig. 1. The important effect of the spin mixing appears clearly when comparing the spectra obtained with and without spin mixing. The interactions with the singlet state strongly stabilizes the $|2,0\rangle$ function which is lower in energy that the $|2,1\rangle - |2,-1\rangle$ one and dominates the energy difference between the $|2,2\rangle + |2,-2\rangle$ and $|2,2\rangle - |2,-2\rangle$ functions. Furthermore, the spectrum of the quintet components obtained in absence of spin mixing resembles the spectrum obtained in the strong exchange approximation as expected.

Finally, we mention that some of the second-order GSH interactions contain fourth-order MSH interactions. For example, the $\langle 2,-2|\hat{H}_{\mathrm{GSH}}|2,-2\rangle$ matrix element is equal to

$9B_2^0+B_4^{rh}$. Comparing this with the expression of the matrix element in Appendix D and the expression of B_4^{rh} in Eq. (10), it is obvious that B_2^0 contains fourth-order interactions of the MSH Hamiltonian, namely term (1) of Appendix A.

V. SUMMARY AND PERSPECTIVES

The main objectives of this work were to study the effect of the spin mixing in the weak-exchange limit and to evaluate the validity of the giant-spin Hamiltonian. We found that when the effective giant-spin Hamiltonian matrix is extracted from a multispin Hamiltonian matrix in which the spin mixing has been removed, the system can reasonably be reproduced using the second-order $\bar{\bar{D}}$ ZFS tensor and perfect agreement is achieved when introducing the fourth-order interaction B_4^4. One may therefore conclude that even if the main contribution to fourth-order interactions is due to spin mixing, some of the fourth-order interactions also account for effects that have a different origin than the spin mixing. Furthermore, the second-order interactions of the GSH contain part of the fourth-order interaction of the MSH including an anisotropic biquadratic exchange operator, Appendix C.

The proper magnetic axes frame has been extracted from the $\bar{\bar{D}}$ tensor determined in absence of spin mixing. In centrosymmetric complexes, the local $\bar{\bar{D}}_i$ tensor, the symmetric anisotropic $\bar{\bar{D}}_{ij}$ tensor of the interaction between the magnetic centers, and the global $\bar{\bar{D}}$ tensor are diagonal in this proper magnetic axes frame. Since this procedure works well in the weak-exchange limit (worst case scenario), it can safely be used to theoretically determine the proper magnetic axes frame of other polynuclear complexes.

The use of the effective Hamiltonian theory made possible to switch on and off the spin mixing and therefore to separate spin-mixing effects from other anisotropic effects. The procedure of extraction also leads to numerical estimates of both. It appears that the spin-mixing effects can be of the same order of magnitude as the direct anisotropic interactions and accurate models should imperatively account for both. Indeed, as illustrated by the spectra obtained using different approximations, the relative energies are strongly affected by the spin mixing which may induce a different energetic order of the states. As already discussed in Refs. 18 and 19, the spin mixing also affects the energy difference between the lowest-energy functions $|M_{s_{\max}} \pm M_{s_{\min}}\rangle$ of the giant spin, which is proportional to the tunnel splitting and therefore also governs the relaxation of the magnetization.

This on and off switching of the spin mixing also shows that the usual giant-spin Hamiltonian involving standard equivalent Stevens operators is not physically based for polynuclear systems as soon as this spin mixing is non-negligible. A different giant-spin Hamiltonian has been derived from the multispin Hamiltonian. The origin of its constitutive interactions has been characterized according to the axial, rhombic, or mixed nature of the interactions of the multispin Hamiltonian from which they have beenextracted. This new giant-spin Hamiltonian perfectly reproduces the spectrum of the giant-spin components including both spin-mixing effects and effects of the fourth-order $\bar{\bar{\bar{D}}}_{aabb}$ tensor.

It should also be mentioned that the low-energy spectrum of weak-exchange limit complexes may exhibit states of different spin multiplicity intercalated in between the M_s components of the giant-spin ground state. In such cases, the use of the giant-spin Hamiltonian may be questionable since the low-temperature properties of the compounds would also depend on these intercalated states that do not form part of the GSH model space. The use of a multispin Hamiltonian which reproduces all the states generated by the interaction between the local spin moments is recommended for these cases.

This work shows the limits of the use of the usual GSH. The proposed Hamiltonian is however not a universal Hamiltonian for the treatment of polynuclear complexes. A more detailed analysis is still necessary to define a complete set of operators that accounts for spin mixing in polynuclear complexes having any symmetry point group and is valid for all metal d^n configurations, and of course for an arbitrary number of magnetic centers.

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APPENDIX A: ANALYTICAL MATRIX ELEMENTS OF THE MULTISPIN HAMILTONIAN EXPRESSED IN THE $|S,M_s\rangle$ BASIS OF THE QUINTET AND SINGLET COMPONENTS, IN THE PROPER MAGNETIC AXES FRAME

$$\begin{aligned}
\langle 2,-2|\hat{H}|2,-2\rangle &= (1)+\tfrac{2}{3}[D_a+D_{ab}]+J\\
\langle 2,-2|\hat{H}|2,-1\rangle &= 0\\
\langle 2,-2|\hat{H}|2,0\rangle &= \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}]\\
\langle 2,-2|\hat{H}|2,1\rangle &= 0\\
\langle 2,-2|\hat{H}|2,2\rangle &= (4)\\
\langle 2,-2|\hat{H}|0,0\rangle &= \tfrac{1}{\sqrt{3}}[2(2)-(3)+2E_a-E_{ab}]\\
\langle 2,-1|\hat{H}|2,-1\rangle &= -\tfrac{D_a}{3}-\tfrac{D_{ab}}{3}+(5)+(6)+J\\
\langle 2,-1|\hat{H}|2,0\rangle &= 0\\
\langle 2,-1|\hat{H}|2,1\rangle &= -(3)+E_a+E_{ab}+(7)\\
\langle 2,-1|\hat{H}|2,2\rangle &= 0\\
\langle 2,-1|\hat{H}|0,0\rangle &= 0\\
\langle 2,0|\hat{H}|2,0\rangle &= \tfrac{1}{3}[(1)-2D_a-2D_{ab}-4(6)+(8)+2(9)]\\
&\quad +J
\end{aligned}$$

$$
\begin{aligned}
\langle 2,0|\hat{H}|2,1\rangle &= 0\\
\langle 2,0|\hat{H}|2,2\rangle &= \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}]\\
\langle 2,0|\hat{H}|0,0\rangle &= \tfrac{\sqrt{2}}{3}[(1)+2D_a-D_{ab}-(6)+(8)-(9)]\\
\langle 2,1|\hat{H}|2,1\rangle &= -\tfrac{D_a}{3}-\tfrac{D_{ab}}{3}+(5)+(6)+J\\
\langle 2,1|\hat{H}|2,2\rangle &= 0\\
\langle 2,1|\hat{H}|0,0\rangle &= 0\\
\langle 2,2|\hat{H}|2,2\rangle &= (1)+\tfrac{2}{3}[D_a+D_{ab}]+J\\
\langle 2,2|\hat{H}|0,0\rangle &= \tfrac{1}{\sqrt{3}}[2(2)-(3)+2E_a-E_{ab}]\\
\langle 0,0|\hat{H}|0,0\rangle &= \tfrac{1}{3}[2(1)+4(6)+2(8)+(9)]-2J
\end{aligned}
$$

$$
\begin{aligned}
(1) &= \tfrac{1}{4}(D_{xxxx}+D_{yyyy})+\tfrac{1}{2}D_{xxyy}+D_{xxzz}+D_{yyzz}\\
&\quad +D_{zzzz}\\
(2) &= \tfrac{1}{4}(D_{xxxx}-D_{yyyy})+\tfrac{1}{2}(D_{xxzz}-D_{yyzz})\\
(3) &= \tfrac{1}{2}(D_{xzxz}-D_{yzyz})\\
(4) &= \tfrac{1}{4}(D_{xxxx}+D_{yyyy})-\tfrac{1}{2}D_{xxyy}-D_{xyxy}\\
(5) &= \tfrac{1}{2}(D_{xxxx}+D_{yyyy})+D_{xxyy}+D_{xxzz}+D_{yyzz}\\
(6) &= \tfrac{1}{2}(D_{xzxz}+D_{yzyz})\\
(7) &= \tfrac{1}{2}(D_{xxxx}-D_{yyyy})\\
(8) &= \tfrac{1}{4}(D_{xxxx}+D_{yyyy})+D_{xyxy}-\tfrac{1}{2}D_{xxyy}\\
(9) &= D_{xxxx}+D_{yyyy}+2D_{xxyy}
\end{aligned}
$$

APPENDIX B: ANALYTICAL MATRIX OF THE $S\cdot\bar{\bar{D}}\cdot S$ HAMILTONIAN, EXPRESSED IN AN ARBITRARY AXES FRAME

$\lvert S,M_S\rangle$	$\lvert 2,-2\rangle$	$\lvert 2,-1\rangle$	$\lvert 2,0\rangle$
$\langle 2,-2\rvert$	$D_{11}+D_{22}+4D_{33}$	$-3D_{13}-3iD_{23}$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}+2iD_{12})$
$\langle 2,-1\rvert$	$-3D_{13}+3iD_{23}$	$\frac{5}{2}(D_{11}+D_{22})+D_{33}$	$-\frac{\sqrt{6}}{2}(D_{13}+iD_{23})$
$\langle 2,0\rvert$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}-2iD_{12})$	$-\frac{\sqrt{6}}{2}(D_{13}-iD_{23})$	$3(D_{11}+D_{22})$
$\langle 2,1\rvert$	0	$\frac{3}{2}(D_{11}-D_{22}-2iD_{12})$	$\frac{\sqrt{6}}{2}(D_{13}-iD_{23})$
$\langle 2,2\rvert$	0	0	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}-2iD_{12})$

$\lvert S,M_S\rangle$	$\lvert 2,1\rangle$	$\lvert 2,2\rangle$
$\langle 2,-2\rvert$	0	0
$\langle 2,-1\rvert$	$\frac{3}{2}(D_{11}-D_{22}+2iD_{12})$	0
$\langle 2,0\rvert$	$\frac{\sqrt{6}}{2}(D_{13}+iD_{23})$	$\frac{\sqrt{6}}{2}(D_{11}-D_{22}+2iD_{12})$
$\langle 2,1\rvert$	$\frac{5}{2}(D_{11}+D_{22})+D_{33}$	$3D_{13}+3iD_{23}$
$\langle 2,2\rvert$	$3D_{13}-3iD_{23}$	$D_{11}+D_{22}+4D_{33}$

APPENDIX C: ANALYTICAL MATRIX OF THE $S_a\cdot\bar{\bar{D}}_a\cdot S_a+S_b\cdot\bar{\bar{D}}_b\cdot S_b$ HAMILTONIAN EXPRESSED IN AN ARBITRARY AXES FRAME; $\bar{\bar{D}}_a=\bar{\bar{D}}_b$ ARE THE LOCAL ZFS TENSORS OF THE MULTISPIN HAMILTONIAN

$\lvert S,M_S\rangle$	$\lvert 2,-2\rangle$	$\lvert 2,-1\rangle$	$\lvert 2,0\rangle$
$\langle 2,-2\rvert$	$D_{a11}+D_{a22}+2D_{a33}$	$-D_{a13}-iD_{a23}$	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}+2iD_{12})$
$\langle 2,-1\rvert$	$-D_{a13}+iD_{a23}$	$\frac{1}{2}(3D_{a11}+3D_{a22}+2D_{a33})$	$-\frac{1}{\sqrt{6}}(D_{a13}+iD_{a23})$
$\langle 2,0\rvert$	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}-2iD_{a12})$	$-\frac{1}{\sqrt{6}}(D_{a13}-iD_{a23})$	$\frac{1}{3}(5D_{a11}+5D_{a22}+2D_{a33})$
$\langle 2,1\rvert$	0	$\frac{1}{2}(D_{a11}-D_{a22}-2iD_{a12})$	$\frac{1}{\sqrt{6}}(D_{a13}-iD_{a23})$
$\langle 2,2\rvert$	0	0	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}-2iD_{a12})$

$\lvert S,M_S\rangle$	$\lvert 2,1\rangle$	$\lvert 2,2\rangle$
$\langle 2,-2\rvert$	0	0
$\langle 2,-1\rvert$	$\frac{1}{2}(D_{a11}-D_{a22}+2iD_{a12})$	0
$\langle 2,0\rvert$	$\frac{1}{\sqrt{6}}(D_{a13}+iD_{a23})$	$\frac{1}{\sqrt{6}}(D_{a11}-D_{a22}+2iD_{a12})$
$\langle 2,1\rvert$	$\frac{1}{2}(3D_{a11}+3D_{a22}+2D_{a33})$	$D_{a13}+iD_{a23}$
$\langle 2,2\rvert$	$D_{a13}-iD_{a23}$	$D_{a11}+D_{a22}+2D_{a33}$

APPENDIX D: ANALYTICAL MATRIX ELEMENTS OF THE GIANT-SPIN HAMILTONIAN DERIVED FROM THE MULTISPIN HAMILTONIAN AT THE SECOND ORDER OF PERTURBATION

$$\langle 2,-2|\hat{H}|2,-2\rangle = (1)+\tfrac{2}{3}[D_a+D_{ab}]+J+\frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,-2|\hat{H}|2,-1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,0\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,-2|\hat{H}|2,1\rangle = 0$$

$$\langle 2,-2|\hat{H}|2,2\rangle = (4)+\frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,-1|\hat{H}|2,-2\rangle = 0$$

$$\langle 2,-1|\hat{H}|2,-1\rangle = -\frac{D_a}{3}-\frac{D_{ab}}{3}+(5)+(6)+J$$

$$\langle 2,-1|\hat{H}|2,0\rangle = 0$$

$$\langle 2,-1|\hat{H}|2,1\rangle = -(3)+E_a+E_{ab}+(7)$$

$$\langle 2,-1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,0|\hat{H}|2,-2\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,0|\hat{H}|2,1\rangle = 0$$

$$\langle 2,0|\hat{H}|2,0\rangle = \tfrac{1}{3}[(1)-2D_a-2D_{ab}-4(6)+(8)+2(9)]+J + \frac{2[(1)+2D_a-D_{ab}-(6)+(8)-(9)]^2}{27J}$$

$$\langle 2,0|\hat{H}|2,1\rangle = 0$$

$$\langle 2,0|\hat{H}|2,2\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,1|\hat{H}|2,-2\rangle = 0$$

$$\langle 2,1|\hat{H}|2,-1\rangle = -(3)+E_a+E_{ab}+(7)$$

$$\langle 2,1|\hat{H}|2,0\rangle = 0$$

$$\langle 2,1|\hat{H}|2,1\rangle = -\frac{D_a}{3}-\frac{D_{ab}}{3}+(5)+(6)+J$$

$$\langle 2,1|\hat{H}|2,2\rangle = 0$$

$$\langle 2,2|\hat{H}|2,-2\rangle = (4)+\frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

$$\langle 2,2|\hat{H}|2,-1\rangle = 0$$

$$\langle 2,2|\hat{H}|2,0\rangle = \sqrt{\tfrac{2}{3}}[(2)+(3)+E_a+E_{ab}] + \frac{\sqrt{6}[2(2)-(3)+2E_a-E_{ab}][(1)+2D_a-D_{ab}-(6)+(8)-(9)]}{27J}$$

$$\langle 2,2|\hat{H}|2,1\rangle = 0$$

$$\langle 2,2|\hat{H}|2,2\rangle = (1)+\tfrac{2}{3}[D_a+D_{ab}]+J+\frac{[2(2)-(3)+2Ea-Eab]^2}{9J}$$

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