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Comment on ''Analytical expressions for zero-field splittings of $3d^5$ ions in low-symmetry fields and their applications''

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The aims of this paper are (i) to elucidate the properties of the physical Hamiltonians and the effective spin Hamiltonians used in electron magnetic resonance and (ii) to clarify the confusion in the microscopic spin Hamiltonian approach of Zhao *et al.* [Phys. Rev. B **52**, 10 043 (1995); **55**, 8955 (1997)]. The confusion consists in an *erroneous* identification (or ''approximate equivalence'') of the wave functions of the two Hamiltonians and leads to *invalid* relations for the zero-field-splitting parameters for the *S*-state $3d^5$ ions at axial symmetry and the spurious numerical results.

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I. INTRODUCTION

The concept of the spin Hamiltonian (SH)[1,2] used by Zhao *et al.*[3–6] is central to electron magnetic resonance (EMR).[7–11] The microscopic spin Hamiltonian (MSH) approach[1,2,12,13] enables derivation of the expressions relating the parameters of an effective spin Hamiltonian with those of the physical Hamiltonian. Hence the inter-relationships between the two types of Hamiltonians are crucial. Yet, as discussed in the comprehensive review[2] on the SH concept, some terms are often confused in the literature with each other, e.g., physical versus effective Hamiltonian, real versus effective versus fictitious spin, microscopic SH, zero-field-splitting (ZFS) Hamiltonian, generalized SH (GSH), and phenomenological SH (PSH). The general aim of this paper is to elucidate the properties of the physical Hamiltonians and the effective spin Hamiltonians, especially those relevant for the *S*-state $3d^5$ ions (Sec. II). The specific aim is to discuss critically the MSH approach for the transition-metal $3d^n$ ions proposed by Zhao *et al.* [3,4] and utilized for Mn^{2+} and $Fe^{3+}(3d^5)$ ions[3,4,6] and $Cr^{3+}(3d^3)$ ions[5] at axial symmetry (Sec. III). It appears that a serious confusion has occurred in Refs. 3–6 due to mixing up the properties of the wavefunctions of the physical Hamiltonian and those of the effective spin Hamiltonian. This has lead to (i) an *erroneous* identification (or ''approximate equivalence'' [3,4]) of the two sets of wave functions and hence (ii) the *invalid* relations derived using the MSH approach for the zero-field-splitting (ZFS) parameters for the *S*-state $3d^5$ ions at axial symmetry.[3,4]

II. EFFECTIVE NATURE OF SPIN HAMILTONIAN DERIVED USING MSH APPROACH

A brief overview of the pertinent notions and procedures is necessary for clarification of the confusion in question. The physical Hamiltonian $\mathcal{H}$ is defined as a full electronic Hamiltonian describing the various physical interactions involving the space and spin coordinates. It acts in its own basis of states. For the transition-metal ions with the $3d^n$ electronic configuration $\mathcal{H}$ is (for details see, e.g., Refs. 1, 2, 7–11):

$$\mathcal{H}=\mathcal{H}_e+\mathcal{H}_{\mathrm{SO}}+\mathcal{H}_{cf}=(\mathcal{H}_0=\mathcal{H}_e+\mathcal{H}_{cf})+(V=\mathcal{H}_{\mathrm{SO}}), \quad (1)$$

including, respectively, the electron-electron repulsion (represented, e.g., by the Racah parameters *B, C*), the spin-orbit (SO) interaction (represented by the SO parameter ξ_d), and the crystal-field (CF) potential (represented, e.g., by the CF parameters B_{kq}). Other interactions may be added to the total physical Hamiltonian in Eq. (1), e.g., the electronic spin-spin (H_{SS}) and the electronic Zeeman (H_{Ze}) interaction.[1,2,7–11] The explicit forms of the Hamiltonians involved depend on whether the calculations are carried out within a given ${}^{25-1}L$ multiplet of a free $3d^n$ ion, for which case simplified forms exists, or within the whole basis of states of a $3d^n$ configuration, e.g., $\{|{}^{2S+1}L,M_S,M_L\rangle\}$ in the intermediate CF-coupling scheme,[7–11] for which case more general forms must be used.[1,2,7–11] There are two methods of solving $\mathcal{H}$: (i) approximate solutions based on degenerate perturbation theory,[12] which consider specific restricted basis of states, and (ii) full numerical diagonalization, which is nowadays possible due to fast computers. The first method has resulted in the introduction of the concept of an effective SH[13] in the early years of EMR.

First we discuss the second method. Within the entire nl^n $(=3d^n$ or $4f^n)$ configuration in, e.g., the intermediate CF-coupling scheme,[7–9] the basis of states formed by the multi-electron Slater determinant wave functions[7] can be denoted as $\{|{}^{2S+1}L,M_S,M_L\rangle\}$.[14–16] Although the calculations are fairly tedious, the physics behind is rather straightforward. Several computer programs are now available to do the job (see, e.g., Refs. 14–17, and references therein) and to enable analysis of optical spectroscopy data. In this method, calculating the matrix elements of the physical Hamiltonian $\mathcal{H}$, as, e.g., in Eq. (1), within the basis $\{|{}^{2S+1}L,M_S,M_L\rangle\}$ and carrying out numerical diagonalization, one obtains the *full* set of eigenvalues and eigenfunctions of $\mathcal{H}$. For certain spectroscopic techniques, especially EMR,[7–11] only the energies of the ground orbital singlet (well separated from the excited states) are of importance. The basis of states consists in this case of the subset of real $2S+1$ states $\{|\Gamma_\alpha\rangle|S,M_S\rangle\}\equiv|\alpha\rangle$ arising from the ground ${}^{2S+1}L(3d^n)$ multiplet split by $\mathcal{H}_{cf}$. The energy levels of the physical Hamiltonian, ϵ_i, within the ground orbital singlet describe, what can be defined as, *the* *zero-field splitting* (see below). Here the eigenvalues ϵ_i of $\mathcal{H}$, within the restricted basis of states $\{|\Gamma_\alpha\rangle|S,M_S\rangle\}$ of the ground-state orbital singlet, are obtained numerically as functions of the parameters of the physical Hamiltonian considered, e.g., B, C, ξ_d, and B_{kq} as defined in Eq. (1).

The links between the results of numerical diagonalization[3,4,14–16] of a physical Hamiltonian $\mathcal{H}$ and those of perturbation method leading to an effective SH (Refs. 1, 2, 12 and 13) are not so straightforward. In order to elucidate these links below we briefly recap the MSH method originated by Pryce,[13] which has lead to an effective spin Hamiltonian for a ground orbital singlet well separated from the excited states. The effective Hamiltonian of Pryce[13] involves *only* the *spin* operators[1,2,7–11] and hence later it become known as the spin Hamiltonian:

$$\tilde{H}_{\text{spin}}=\tilde{\mathbf{S}}\cdot\mathbf{D}\cdot\tilde{\mathbf{S}}+\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\tilde{\mathbf{S}}\equiv\tilde{H}_{\text{ZFS}}+\tilde{H}_{\text{Zs}}. \tag{2}$$

The matrix elements of the orbital operators, arising from the perturbation $V=\mathcal{H}_{\text{SO}}=\lambda\mathbf{L}\cdot\mathbf{S}$, and the energy denominators, $\Delta_\beta\equiv E(\Gamma_\beta)-E(\Gamma_\alpha)$, within the ground multiplet ${}^{2S+1}L(3d^n)$, were lumped in Eq. (2) into the tensor $\Lambda_{ij}\equiv\langle\Gamma_\alpha|\mathbf{L}_i|\Gamma_\beta\rangle\langle\Gamma_\beta|\mathbf{L}_j|\Gamma_\alpha\rangle/\Delta_\beta$. Then the components of D_{ij} and g_{ij} are obtained (see, e.g., Refs. 7–11) as

$$D_{ij}=-\lambda^2\Lambda_{ij}\quad\text{and}\quad g_{ij}=(g_e\delta_{ij}-\lambda\Lambda_{ij}), \tag{3}$$

where $i,j=(x,y,z)$ and $|\Gamma_\alpha\rangle,|\Gamma_\beta\rangle$ are the orbital parts of the wave functions of the ground orbital singlet and the excited orbital states, respectively. The *conventional*[1,2] ZFS term,[7–11] $\tilde{\mathbf{S}}\cdot\mathbf{D}\cdot\tilde{\mathbf{S}}$ in Eq. (2), describes the splitting of the spin states of the ground orbital singlet in the absence of an external magnetic field. Hence the components D_{ij} represent the *zero-field splitting* (ZFS) or the fine structure parameters. The ZFS Hamiltonian and its parameters have been represented explicitly in various forms in the literature[2,18] and often confusingly named as the ''crystal field'' ones.[2] The conventional form of ZFS Hamiltonian,[1,2,7–11] $\mathcal{H}_{\text{ZFS}}$, for the $3d^n$ ions with the spin $S\geqslant 2$ at tetragonal symmetry sites with the cubic axes (ξ, η, ζ) along the tetragonal axes (x, y, z). is:

$$\begin{aligned}\mathcal{H}_{\text{ZFS}}=&D\left[S_z^2-\frac{1}{3}S(S+1)\right]\\&+\frac{a}{6}\left[S_\xi^4+S_\eta^4+S_\zeta^4-\frac{1}{5}S(S+1)(3S^2+3S-1)\right]\\&+\frac{F}{180}[35S_z^4-(30S(S+1)-25)S_z^2-6S(S+1)\\&+3S^2(S+1)^2].\end{aligned} \tag{4}$$

In the Pryce[13] MSH approach the components of the ''tensor'' D_{ij} and the ''matrix'' g_{ij} in Eq. (3) are expressed directly in terms of the *microscopic* quantities, i.e., the parameters of the physical Hamiltonian $\mathcal{H}$, comprising in the above case the energy-level splittings Δ_α within the ground multiplet ${}^{2S+1}L$ and the spin-orbit coupling parameter λ. Hence the Pryce's[13] method constitutes a derivation of the microscopic spin Hamiltonian (MSH). The readers may benefit from the *general* definition of an ''effective Hamiltonian'' by Stevens (Ref. 1, p. 70) as ''an operator which acts only within the lowest unperturbed manifold and yet which has eigenvalues that coincide with those expected to come from it when the perturbation is switched on.'' The meaning of the ''effectiveness'' of the spin operators in the spin Hamiltonian is also well reflected by Atherton (Ref. 19, p. 35/36): ''What the spin Hamiltonian does is to mimic these energy levels (Cz.R.: i.e., of the full electronic Hamiltonian), and comparison of the two calculations leads to identification of the structure of the coupling coefficients used in the spin Hamiltonian. In some case the coefficients can be understood as integrals of the full Hamiltonian over the electronic wave functions which would imply that the operators in the spin Hamiltonian are the true spin operators. However, this is not generally true: strictly speaking the operators in the spin Hamiltonian are effective spin operators which give *the right number of energy levels* whose disposition is such as to account for the observed spectrum.''

The Pryce[13] method can be used only for the special case of the lowest orbital singlet $|\alpha\rangle$ being well separated in energy (by Δ_β) from the excited states $\{|\Gamma_\beta\rangle|S,M_S\rangle\}\equiv|\beta\rangle$ within the ground state ${}^{2S+1}L$ multiplet. This *conventional* method[13] was later extended.[12] A more general method of derivation of MSH from perturbation theory[12] has been proposed for the $3d^4$ and $3d^6$ transition ions with an orbital singlet ($S=2$) ground state arising from the ${}^5D$ multiplet.[20–22] The methods[12,13,20–22] are not applicable for the *S*-state ($3d^5$:Fe^{3+},Mn^{2+};$4f^7$:Gd^{3+};Eu^{2+}) ions characterized by the orbital angular momentum $L=0$ in the ground state. For these systems the MSH derivations must be carried out within the basis of states of the entire nl^n ($=3d^n$ or $4f^n$) configuration.[23] Hence the procedure is much more complex than that for a ground multiplet ${}^{2S+1}L(3d^n)$,[13,20–22] since then calculations require using, instead of the simplified forms of the physical Hamiltonians,[2,7–11] the respective general forms,[7,14–17] which involve the individual electronic spins $\mathbf{s_i}$. Hence for the *S*-state ions it is not possible, using either the conventional perturbation[12,13,7–11] or the tensor method,[20–22] to derive directly an explicit form of $\tilde{H}_{\text{spin}}$ in terms of the total effective spin $\tilde{\mathbf{S}}$ corresponding to the total electronic spin $\mathbf{S}=\Sigma\mathbf{s_i}$.

Nevertheless the concept of the effective SH applies also to the *S*-state ions. The final result of derivation of MSH can be considered as a ''replacement,'' for the purpose of description of the *fine structure* within any ground orbital singlet with true spin *S*, of the physical Hamiltonian, $\mathcal{H}_0+V$, by the effective spin Hamiltonian, $\tilde{H}_{\text{spin}}$ as defined above. The mathematical structure of $\tilde{H}_{\text{spin}}$ can be represented in a general form as:[1,2,18]

$$H_0+V\rightarrow\tilde{H}_{\text{spin}}=\tilde{H}_{\text{ZFS}}+\tilde{H}_{Ze}\equiv\sum_{1,m}X_{1m}\chi_{1m}(\tilde{\mathbf{S}})+\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}, \tag{5}$$

where X_{1m} denote the ZFS parameters associated with a given *generic* type of the tensor operators, χ_{1m}, which here are functions of the components of the effective spin operator $\tilde{\mathbf{S}}$, with the rank 1 even $(1=2,4,6$, depending on the value of spin $\tilde{S}$) and the components $-1 \leqslant \mathrm{m} \leqslant 1$ (m depending on the site symmetry) with specific restrictions on 1, m for a given symmetry case.[2,18] *Generic* symbol χ_{1m} and X_{1m} in Eq. (5) represents any tensor operators and associated parameters, respectively, thus these symbols *do not* define yet another tensor-operator notation, an abundance of which already exists in literature.[2,18] The spherical-tensor and tesseral-tensor operator notations as well as the conventional notations used in EMR and related areas have been classified in Refs. 2 and 18.

Two indirect approaches: (i) and (ii), exist to relate the parameters of the physical Hamiltonian to those of the effective one for the *S*-state ions. Both approaches are based on the equivalence of the actual and the corresponding effective quantities. *Each approach* requires *assuming* certain form for the effective SH usually characterized by the same, or as an approximation, higher, symmetry as that of the full physical Hamiltonian. In this sense, both approaches are based on a prior knowledge of the ZFS part (and the Ze part) of SH, which have been obtained either from the MSH derivations discussed above or from the generalized SH method.[1,2] In *each approach* the derivation follows the *three similar stages* outlined below, however, they differ in the ''equivalence'' used.

First, the eigenvalues, ϵ_j, of the physical Hamiltonian as, e.g., in Eq. (1), $\mathcal{H}=\mathcal{H}_0+V$, are calculated either exactly by numerical diagonalization or approximately by degenerate perturbation theory. The solutions include the eigenvalues, ϵ_i with $i=1$ to $(2S+1)$, corresponding to the states $\{|\Gamma_\alpha\rangle|S,M_S\rangle\}$ within the ground orbital singlet; some energy levels may turn out to be degenerate. In order to explain the observed ZFS, various mechanisms are taken into account, including admixtures of higher-lying states into the ground state orbital singlet due to crystal field and/or spin-orbit coupling, relativistic effects responsible for the mixing of states with different spin multiplicity, and overlap and covalency effects.[7–9,17] Most MSH applications for the spin systems considered in the literature deal with the ZFS part of SH with $S \geqslant 1$, whereas the Ze part applicable to $S \geqslant 1/2$ has been considered only in a few cases.

Second, the $(2S+1)\times(2S+1)$ matrix elements of the *assumed* effective SH, $\tilde{H}_{\mathrm{spin}}$, in its own basis $\{|\tilde{S},\tilde{M}_S\rangle\}$ (or using the symmetry-adopted combinations of $|\tilde{S},\tilde{M}_S\rangle$) are calculated in parametric form, since the values of the ZFS parameters are not known at this point. Then solving algebraically the characteristic equation for $\tilde{H}_{\mathrm{spin}}$, its eigenvalues, E_i, $i=1$ to $(2\tilde{S}+1)$, with some energy levels being degenerate, can be obtained for some cases. For example, for transition-metal ions at tetragonal symmetry one obtains E_i in terms of the ZFS parameters, e.g., $E_i \propto (B_k^q$ or $b_k^q)$ in the extended Stevens notation[24,2,18] with $k=2$, $q=0$; $k=4$, and $q=0,4$, or $E_i \propto (D,a,F)$ in terms of the conventional notation.[24,2,18] Eqs. (7) and (8) below derived by Zhao *et al.*[3,4] serve as an example. To obtain similar expressions for orthorhombic or lower symmetry additional approximations are required.

Third, by comparing the actual quantities with the corresponding effective ones the microscopic relations can be obtained. The major difference between the approaches (i) and (ii) lies in the actual and the corresponding effective quantities used.

The *particular details of each approach* are now described. *Approach* (i) uses the equivalence (or ''comparison,'' see, Ref. 19, p 36, as quoted above) of *eigenvalues*: actual=the *zero-field splitting energy levels* of the physical Hamiltonian, ϵ_i, obtained either by numerical diagonalization or degenerate perturbation theory, i.e., its eigenvalues within the restricted basis of states $\{|\Gamma_\alpha\rangle|S,M_S\rangle\}$ of the ground orbital singlet as explained above, *and* effective=the *eigenvalues*, E_i, of the *assumed* ZFS Hamiltonian in the basis $\{|\tilde{S},\tilde{M}_S\rangle\}$. *Approach* (ii) uses the equivalence of *matrix elements*: actual=the matrix elements of the physical Hamiltonian in the basis $\{|\Gamma_\alpha\rangle|S,M_S\rangle\}$ *and* effective=the *matrix elements* of the *assumed* effective ZFS Hamiltonian in the basis $\{|\tilde{S},\tilde{M}_S\rangle\}$. The derivations are then more cumbersome than those in the approach (i).

An important point is that the resulting effective SH in Eqs. (2), (4), or (5) no longer acts within the basis of states of the Hamiltonian in Eq. (1). The eigenstates of the *full* Hamiltonian in Eq. (1), denoted $\{|\Gamma_\beta\rangle|S,M_S\rangle\}$, are linear combinations of the eigenstates of $\mathcal{H}_0=\mathcal{H}_e+\mathcal{H}_{cf}$, i.e., $\{|^{2S+1}L,M_S,M_L\rangle\}$. The effective spin Hamiltonian acts within its own basis of states, i.e., $|\tilde{S},\tilde{M}_S\rangle$ of the *effective* spin $\tilde{\mathbf{S}}$. This fact is denoted by the tilde (∼) to distinguish the *effective* spin operator $\tilde{\mathbf{S}}$ and its states $|\tilde{S},\tilde{M}_S\rangle$ from the *real* total electronic spin operator $\mathbf{S}$ and its states $|S,M_S\rangle$. This distinction can be made more evident comparing the multielectron Slater determinant wave functions,[7,14–17] defining the basis of states pertinent to the physical Hamiltonian in Eq. (1), with the basis of states $\{|\tilde{S},\tilde{M}_S\rangle\}$, as, e.g., in Eq. (7) below, of the effective SH in Eqs. (2), (4), or (5). As an example we consider the results[23] for Mn^{2+} $(3d^5;\ S=5/2)$ at the Nb site in LiNbO_3. The CF program[14–16] has been used to diagonalize within the basis states $|^{2S+1}L,M_S,M_L\rangle$ the full Hamiltonian,[23] similar to the one in Eq. (1), including $\mathcal{H}_{cf}$ possessing C_3 symmetry and additionally the Trees correction.[14–16] Then the six actual spin states defining the ^6S ground multiplet and the corresponding six lowest energy levels can be obtained.[23] These states can be *denoted* by their dominant components $|^6S,M_S,M_L=0\rangle \equiv |^6S,M_S\rangle$ with $-5/2 \leqslant M_S \leqslant 5/2$. For illustration, we reproduce here the state $|^6S,+5/2\rangle$ and $|^6S,+1/2\rangle$, being an admixture of the states $|^{2S+1}L,M_S,M_L\rangle$, obtained on a computer using the parameter values (in cm^{-1}) pertinent for the full *physical* Hamiltonian:[23] Racah parameters $B=911$, $C=3273$, the Trees correction parameter $\alpha=65$, the spin-orbit coupling parameter $\xi=337$, and CF parameters in Wybourne's notation[14–16] $B_{20}=-1524.3$, $B_{40}=-14225.4$, $\mathrm{Re}\,B_{43}=21882.1$, and $\mathrm{Im}\,B_{43}=-370.3$:

$$
\begin{aligned}
|{}^6S,+5/2\rangle = {} & (0.005495-i0.000186)|{}^6S,-0.5,0\rangle+(0.999338-i0.0016917)|{}^6S,2.5,0\rangle\\
& +(0.029379-i0.000497)|{}^4P,1.5,1\rangle+(0.008012-i0.000271)|{}^4G,1.5,-2\rangle\\
& -(0.006212-i0.000105)|{}^4G,1.5,1\rangle-(0.006118+i0.000000)|{}^4G,1.5,4\rangle;\\
|{}^6S,+1/2\rangle = {} & (0.005491-i0.000279)|{}^6S,-2.5,0\rangle+(0.998882-i0.033828)|{}^6S,0.5,0\rangle\\
& +(0.009297-i0.000315)|{}^4P,1.5,-1\rangle+(0.023425-i0.000793)|{}^4P,0.5,0\rangle\\
& +(0.016095-i0.000545)|{}^4P,-0.5,1\rangle+(0.007171-i0.000364)|{}^4G,0.5,-3\rangle\\
& +(0.004378-i0.000223)|{}^4G,-0.5,-2\rangle-(0.003421-i0.000116)|{}^6G,-0.5,1\rangle\\
& +(0.002531-i0.000043)|{}^4G,1.5,2\rangle+(0.007184-i0.000122)|{}^4G,0.5,3\rangle-(0.003342-i0.000057)|{}^4G,-0.5,4\rangle,
\end{aligned}
\tag{6}
$$

where $L=0,1,2,3,4,5,...$ are denoted as S, P, D, F, G,..., and $i=\sqrt{-1}$. The effective-spin representation ($\tilde{S}=5/2$) for the effective Hamiltonians $\tilde{H}_{\mathrm{ZFS}}$ and $\tilde{H}_{\mathrm{Ze}}$, suitable for C_3 symmetry, has also been employed for a general derivation[23] of the microscopic SH using the approach (i) described above. In no case the labeling based on the dominant component of the states $|{}^{2S+1}L,M_S,M_L\rangle$ implies any ''equivalence'' of the actual states $|{}^6S,M_S,M_L=0\rangle\equiv|{}^6S,M_S\rangle$ and the effective states $\{|\tilde{S}=5/2,\tilde{M}_S\rangle\}$. The six states of the physical Hamiltonian, labeled $\{|{}^6S,M_S\rangle\}$ and partially listed in Eq. (6), are of quite different nature than the six spin states $\{|\tilde{S}=5/2,\tilde{M}_S\rangle\}$ of the effective SH$\tilde{H}_{\mathrm{spin}}$, denoted[23] as $\{|M_S\rangle'\}\equiv\{|\pm 1/2\rangle',|\pm 3/2\rangle'$ and $|\pm 5/2\rangle'\}$.

III. CRITICISM OF THE ZHAO *et al.* APPROACH TO MICROSCOPIC SPIN HAMILTONIAN

The method used by Zhao *et al.*[3–6] is a modification of the approach (i) described in Sect. II, where apart from the *valid* ''equivalence'' of the eigenvalues also an *incorrect* ''equivalence'' of the wave functions, as explained below, has been invoked. Firstly, solving the secular equation for $\mathcal{H}_{\mathrm{ZFS}}$ in Eq. (4), the eigenenergies $E(m_s)\propto(D,a,F)$ and the eigenvectors were obtained[3] as in their Eqs. (6)–(8); for example:

$$E(\pm 5/2)\propto(D,a,F)\quad \text{and its wave function:}$$

$$|\psi_3\rangle=\cos\alpha|\pm 5/2\rangle+\sin\alpha|\pm 3/2\rangle, \tag{7}$$

together with the relation for $\tan 2\alpha$ in terms of (D,a,F) [their Eq. (9)]:

$$\tan 2\alpha=\sqrt{5}a/[2(a+2F/3+2D)]. \tag{8}$$

The ZFS transitions were defined[3] as $\Delta_1=E(\pm 5/2)-E(\pm 1/2)$ and $\Delta_2=E(\pm 3/2)-E(\pm 1/2)$. This has enabled to derive[3] the relations: Δ_1 and $\Delta_2\propto(D,a,F,\tan 2\alpha)$ [their Eqs. (10) and (11)].

Secondly, the complete diagonalization procedure (CDP) has been employed[3] to solve within the basis of states of the $3d^5$ configuration the physical Hamiltonian[1,2] in Eq. (1), $\mathcal{H}=\mathcal{H}_e+\mathcal{H}_{SO}+\mathcal{H}_{cf}$. No explicit notation for the wave functions of the Hamiltonian in Eq. (1) was provided in Ref. 3, however, the ''CPD ground state'' was given as:

$$
\begin{aligned}
&|5/2\rangle(\mathrm{CDP}=a_1|{}^6S,5/2\rangle+a_2|{}^6S,-3/2\rangle\\
&\qquad +\text{smaller contributions arising from the}\\
&\qquad S=3/2\ \text{ and }\ S=1/2\text{states.}
\end{aligned}
\tag{9a}
$$

As ''an equivalent approximation'' [supposedly to Eq. (9a)] the following wave functions were stated:

$$|5/2\rangle\mathrm{CDP}\cong(a_1/N)|{}^6S,5/2\rangle+(a_2/N)|{}^6S,-3/2\rangle \tag{9b}$$

with the normalization constant $N=[(a_1)^2+(a_2)^2]^{1/2}$. The CDP wave functions in Eq. (9b) and the SH wave functions like those in Eq. (7) were then apparently treated as physically identical entities. This presumption was used[3] to obtain ''by means of the approximate equivalence between the SH and CDP'' the relations [their Eqs. (17) and (18)] between the mixing coefficients of the wavefunctions of the two physically different Hamiltonians:

$$\cos\alpha\cong a_1/N,\quad \sin\alpha\cong a_2/N. \tag{10}$$

This procedure has lead to the identity [their Eq. (19)]:

$$T\equiv\tan 2\alpha=2a_1a_2/[(a_1)^2-(a_2)^2], \tag{11}$$

which has been used in the derivation of the ''the analytical expressions'' [their Eqs. (20)–(22)] for the conventional ZFS parameters for tetragonal symmetry: D, $a+2F/3$, and a, in terms of the ZFS transitions Δ_1,Δ_2, and the coefficient T defined by the right-hand side of the Eq. (11). The authors[3] claim that ''these expressions are general ones which are independent of the specific interaction model.''

The same approach has been used in Ref. 3 for the $3d^5$ ions at trigonal symmetry to derive the analogous expressions [their Eqs. (40)–(42)] for the trigonal ZFS parameters D, $a-F$, and a in terms of the corresponding ZFS transitions Δ_1,Δ_2 and the coefficient T defined for this case [their Eq. (43)] as:

$$T=-2a_1a_2/[(a_1)^2-(a_2)^2]. \tag{12}$$

The microscopic relations for the ZFS parameters[3] involving the coefficient T in Eqs. (11) and (12) were then applied for Mn^{2+} in the tetragonal ABF_8 and $\mathrm{A}_2\mathrm{BF}_4$ crystals, and Fe^{3+} in the trigonal α-$\mathrm{Al}_2\mathrm{O}_3$, respectively. The latter relations[3] were also reproduced in Ref. 4 and used for Mn^{2+} at trigonal symmetry sites in LiNbO_3. The ''approximate equivalence between the SH and CDP'' has also been invoked in Refs. 5 and 6. Note that Holliday *et al.*[25] pointed out the errors of different nature in the *ab initio* calculations[5] for Cr^{3+} in LiNbO_3.

The physical framework set in Sec. II helps clarifying the following misconceptions in Refs. 3–6.

A. The spurious nature of the ''approximate equivalence between SH and CDP''

The authors have not explained or defined the ''approximate equivalence between SH and CDP'' used in their derivation of the MSH relations. However, in view of the quantum mechanical properties of the wave functions and Hamiltonians involved[1,2] (see Sec. II), it turns out that the wave functions of the two types of Hamiltonians, i.e., those of the effective spin Hamiltonian and those of the physical Hamiltonian, *cannot be made equivalent*, irrespective of any approximation used in obtaining either type of the wavefunctions, as, e.g., in Eqs. (5a) and (5b). The wave functions in Eq. (7) and those in Eq. (9) constitute *different* basis of states. The major point overlooked in Refs. 3–6 is that the wave functions in Eq. (9), i.e., $|\alpha\rangle \equiv \{|\Gamma_\alpha\rangle |S,M_S\rangle\}$ in the notation used here, *do include* the orbital parts, i.e., $\{|\Gamma_\alpha\rangle\}$, which cannot be arbitrarily neglected as done by Zhao et al.[3–6]

B. The erroneous identification of the two sets of wave functions

In the microscopic approach, the orbital parts of the wave functions ''disappear'' only after the integration over the orbital variables, which results in the effective Hamiltonian expressed only in the spin variables. Only if one neglects, erroneously so, the orbital parts $\{|\Gamma_\alpha\rangle\}$ in the wave functions obtained from the CDP calculations, as e.g., in Eqs. (9) and (6), it is possible to make the ''approximate equivalence between SH and CDP'' leading to Eqs. (10) and (11) as done in Refs. 3 and 4. The convenient labeling used in both cases as described above, although resembles ''equivalency,'' does not entitle a replacement of the wave functions of one type by those of the other type. The two types of the wave functions should not be confused with each other. Hence, the ''equivalence'' used by Zhao et al.[3–6] amounts to a serious confusion, which consists in mixing up the properties of the wave functions of the effective spin Hamiltonian and those of the physical Hamiltonian. This confusion has lead to an *erroneous* identification of the two sets of wave functions, which is evident e.g., in the statements pertinent for tetragonal symmetry in Ref. 3: ''In the SH approximation, the effective spin ground state approximately equals $|5/2\rangle$. However, it is an admixture of $|5/2\rangle$, $|3/2\rangle$, and $|1/2\rangle$ states in the framework of CDP.'' In fact, in the effective SH approach for the d^5 ions, ''the effective ground-state spin'' is exactly $\tilde{S}=5/2$, whereas it is not true that ''the effective spin ground state approximately equals'' $|5/2\rangle$. The ground state of SH in Eq. (1) depends on the sign of the parameter D and, as it follows from Eqs. (6) to (8) in Ref. 3, it may be either $|\pm 1/2\rangle$ for $D>0$ or a combination of $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$ for $D<0$—see Eq. (7) above, but not even approximately $|5/2\rangle$. The states of any half-integer spin are the so-called Kramers doublets and can be split only by the magnetic field. Hence the Kramers pair states, $|\pm M_s\rangle$, being the eigenstates of SH in Eq. (4) must have the same energy and thus ''the effective spin ground state'' is double degenerate, not just $|5/2\rangle$ or $|1/2\rangle$. Such confusing terminology on the part of the authors[3] may be partially blamed for the resulting more substantial misinterpretations.

The consequences of the above misconceptions[3,4] are as follows.

1. The invalid relations for the ZFS parameters

The coefficient T obtained from the ''complete diagonalization procedure'' (CDP) and defined in Eq. (11) for tetragonal symmetry and in Eq. (12) for trigonal symmetry, appears *erroneously* in the relations for the effective ZFS parameters in terms of the ZFS transitions Δ_1, Δ_2, and T, i.e., in their Eqs. (20)–(22) and Eqs. (40)–(42), respectively. This makes these relations *invalid*, in spite of the authors[3] claim that ''these expressions are general ones which are independent of the specific interaction mode.'' On the other hand, Eqs. (12)–(14) of Ref. 3 for the tetragonal symmetry: $\{D, a+2F/3, a\} \propto (\Delta_1, \Delta_2, \tan 2\alpha)$, are given correctly in terms of the ZFS transitions Δ_1, Δ_2, and $\tan 2\alpha$ obtained from the effective SH calculations and defined in Eq. (8). The corresponding relations for trigonal symmetry, i.e., Eqs. (40)–(42) of Ref. 3 for D, $a-F$, and a, are given directly in terms of Δ_1, Δ_2, and T. The major reason for the *inadmissible* replacement in the relations for the effective ZFS parameters[3] of ''$\tan 2\alpha$'' by ''T'' is that otherwise these relations could not be used for determination of the ZFS parameters, since $\tan 2\alpha$ is itself a function of D, a, and F. Here for the d^5 ions at axial symmetry there are three ZFS parameters but only two ZFS transitions Δ_1 and Δ_2, which can be determined either experimentally or from the CDP calculations. Hence it is not possible to solve analytically Eqs. (10) and (11) of Ref. 3, i.e., Δ_1 and $\Delta_2 \propto (D, a, F, \tan 2\alpha)$ without some approximations. For the d^5 ions at trigonal symmetry the expressions for the two ZFS transitions $\Delta\mathcal{E}(2\rightarrow 3)=\Delta_1-\Delta_2$ and $\Delta\mathcal{E}(1\rightarrow 2)=\Delta_2$ have been derived earlier[23] in terms of the extended Stevens parameters (Ref. 24) b_k^q. These expressions[23] could not be solved analytically and have been rather used to verify the correctness of the values of the ZFS transitions obtained from the simulation of the experimental data. After conversion to the same form, the expressions[23] could be compared with those in Eqs. (40)–(42) for D, $a-F$, and a of Ref. 3, provided an explicit definition of T in terms of Δ_1, Δ_2 was given in Ref. 3, which is not the case. Resorting to the physically *inadmissible* replacements used in Refs. 3 and 4, see Eqs. (11) and (12) above, does not make it possible to solve these equations, even in an approximate way. Note that for $3d^4$ and $3d^6$ ions with spin $S=2$ at orthorhombic symmetry[26] there are five ZFS parameters but only four ZFS transitions. Suitable mathematical approximations have been proposed[26] in this case to determine the ZFS parameters from the values of ZFS transitions.

2. The spurious numerical results

Using the values of the coefficient *T*, which involves the mixing coefficients between the states of the physical Hamiltonian, instead of $\tan 2\alpha$, which involves the mixing coefficients between the states of the effective Hamiltonian *is not justified*. Yet, since in both cases the mixing coefficients, if properly normalized, obey similar constraints and in view of the number of adjustable parameters: B, C, ξ_d, B_{kq}, which determine *T*, one may obtain apparently acceptable numerical results using the wrong method.[3,4] However, the scientific value of the method and the results[3–6] remains *spurious*. The erroneous premise, on which the derivations and calculations[3–6] are based, makes the expressions of Ref. 3 for the ZFS parameters in Eqs. (20)–(22) for tetragonal symmetry and Eqs. (40)–(42) for trigonal symmetry *invalid*. The latter point can be verified by considering the consequences of such equations[3] and the properties of each type of the mixing coefficients. The mixing coefficients of the effective SH: $\cos\alpha$ and $\sin\alpha$ in Eq. (7), are *real* and obey exactly the normalization condition: $\cos^2\alpha+\sin^2\alpha=1$, whereas those of the physical Hamiltonian in Eq. (9) are generally *complex*, as it can be seen from Eq. (6). For trigonal symmetry the ground state of the physical Hamiltonian was given in Ref. 3 [their Eq. (49)] as:

$$|1/2\rangle(\mathrm{CDP})=a^1|{}^6S,1/2\rangle+a_2|{}^6S,-5/2\rangle + \text{small contributions arising from the } S=3/2 \text{ and } S=1/2 \text{ states}, \tag{13}$$

which structurally corresponds to the first line for the state $|{}^6S,+1/2\rangle$ in Eq. (6). However, the ‘‘norm’’ of the truncated wave functions in Eqs. (9b) and (13): $(a_1/N)^2+(a_2/N)^2$, may significantly vary from 1 depending on the approximations used. Some coefficients at the omitted terms in Eq. (13), e.g., 0.016095 at $|{}^4P,-0.5,1\rangle$, may be much larger than those included in Eq. (13), e.g., the real part of $a_1=0.005491$. It follows from Eq. (8) that to obtain the ZFS parameter *a* vanishing for tetragonal symmetry requires no mixing of the states of the effective SH i.e., $\cos\alpha=1$ and $\sin\alpha=0$. No corresponding equation for trigonal symmetry has been given in Ref. 3, but our calculations show the same applies for this case. On the other hand, it follows from Eq. (19) of Ref. 3 [Eq. (11) above] and Eq. (43) of Ref. 3 [Eq. (12) above] defining the coefficient *T* for tetragonal and trigonal symmetry, respectively, that to obtain *a* vanishing requires either (a_1/N) or (a_2/N) to be zero. The latter situation is rather unphysical in view of the nature of the mixing coefficients obtained from full diagonalization of the physical Hamiltonian as illustrated by the states given in Eq. (6).

IV. CONCLUSIONS

The present paper explains the intricacies concerning the properties of the physical Hamiltonians and the effective spin Hamiltonians used in EMR.[1,2,7–11] This has enabled clarification of the confusion in Refs. 3–6 consisting in mixing up the properties of the wavefunctions of the two Hamiltonians, i.e., an erroneous identification (or ‘‘approximate equivalence’’) of the two sets of wave functions. The consequences of this confusion are the invalid relations for the ZFS parameters derived in the MSH approach for the $3d^5$ ions[3,4] and the spurious numerical results.[3–6] It is hoped that this paper may help reducing the confusion concerning the not-too-well-understood properties of spin Hamiltonian, still being proliferated in various ways in the literature as reviewed in Ref. 2.

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