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Truncated forms of the second-rank orthorhombic Hamiltonians used in magnetism and electron magnetic resonance (EMR) studies are invalid—Why it went unnoticed for so long?

Czesław Rudowicz *

Modeling in Spectroscopy Group, Institute of Physics, West Pomeranian University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland

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ABSTRACT

This paper deals with the truncated forms of the second-rank orthorhombic Hamiltonians employed in magnetism and electron magnetic resonance (EMR) studies. Consideration of the intrinsic features of orthorhombic Hamiltonians reveals that the truncations, which consist in omission of one of three interdependent orthorhombic terms, are fundamentally invalid. Implications of the invalid truncations are: loss of generality of quantized spin models, misinterpretation of physical properties of systems studied (e.g. maximum rhombicity ratio and relative parameter values), and inconsistent notations for Hamiltonian parameters that hamper direct comparison of data from various sources. Truncated Hamiltonian forms identified in our survey are categorized and systematically reviewed. Examples are taken from studies of various magnetic systems, especially those involving transition ions, as well as model magnetic systems. The pertinent studies include magnetic ordering in three- and lower dimensions, e.g. $[(CH_3)_4N]MnCl_3$ (TMMC), canted ferromagnets, Haldane gap antiferromagnets, single molecule magnets exhibiting macroscopic quantum tunneling, e.g. Mn_{12} complexes with spin $S = 10$. Our study provides better insight into magnetic and spectroscopic properties of pertinent magnetic systems, which calls for reconsideration of the experimental and theoretical results based on invalid truncated Hamiltonians. The physical nature of Hamiltonians used in magnetism and EMR studies and other types of inappropriate terminology occurring, especially in model magnetism studies, require separate discussion.

1. Introduction

Ongoing surveys of magnetism and electron magnetic resonance (EMR) literature reveal that various orthorhombic Hamiltonians have often been employed in magnetism and EMR studies. Concerning the nature of Hamiltonians, most often the zero-field splitting (ZFS), or equivalently fine structure (FS), Hamiltonians $\mathbf{H}_{ZFS}$ have been invoked (see, e.g. Refs. [1–9]). For rare-earth ions also the crystal-field (CF), or equivalently ligand field, Hamiltonians may be invoked (see, e.g. Refs. [10–20]). Readers should beware of the confusion, which consists in labeling the *actual* ZFS quantities [1–9] as *purportedly* the CF quantities [10–20]. This type of confusion is denoted below as the CF = ZFS confusion. Recently, the CF = ZFS confusion in EMR studies has been reviewed in [21], whereas in magnetism literature dealing with specific compounds in [22] and model studies of spin systems in [23]. For readers' benefit, the nature of the CF = ZFS confusion is briefly explained in Section 2. In this paper as a representative Hamiltonian we adopt the ZFS Hamiltonian $\mathbf{H}_{ZFS}$, however, these considerations and thus conclusions apply to any orthorhombic second-rank Hamiltonians, regardless of their actual physical nature. The physical nature of Hamiltonians used in magnetism and EMR studies and other types of inappropriate terminology occurring, especially in model magnetism studies, require separate discussion.

Truncations of $\mathbf{H}_{ZFS}$ my be classified into three types: (i) some independent ZFS parameters allowed by symmetry of a paramagnetic complex are arbitrarily set to zero, (ii) some operator

* Tel.: +48 91 449 4286; fax: +48 91 449 4181.
E-mail address: crudowicz@zut.edu.pl

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parts in the independent ZFS terms are omitted, and (iii) one of several interrelated ZFS terms is omitted. In most cases truncations are driven by mathematical tractability of problems under study. Truncations of the type (i) are often used in EMR studies; especially if the available spectroscopic data do not warrant employment of full $\mathbf{H}_{ZFS}$ with a greater number of ZFS parameters. Such truncations affect, to a certain extent, the approximate values of fitted ZFS parameters. However, truncations of the type (ii) and (iii), occurring mostly in magnetism literature, have more serious consequences. Truncations of the type (ii) implicitly lead to modified meaning of ZFS parameters, so generally the same symbols are still used indicating that such modifications are not realized. Thus proper comparisons of the modified ZFS parameters and those commonly accepted in literature require specific conversion relations.

Truncations of the type (iii) that consist in omission of one of three interdependent second-rank ZFS terms for orthorhombic symmetry are considered in this paper. Other types of truncated ZFS Hamiltonian involving the fourth-rank ZFS terms require separate consideration. The paper is organized as follows. In Section 2 the intrinsic properties of the full orthorhombic ZFS Hamiltonians are considered. The truncated second-rank ZFS terms and adverse implications of such truncations are discussed in Section 3. Our analysis proves convincingly that the truncations in question are fundamentally invalid. Specific examples of truncated forms of ZFS Hamiltonians identified in magnetism and EMR studies are categorized into specific groups and systematically reviewed in Section 4. As a case study detailed analysis of ZFS data for Mn^{2+} in $[(CH_3)_4N]MnCl_3$ (TMMC) and related compounds is carried out in Section 5. Section 6 contains summary and conclusions. Since the truncations in question concern large class of magnetic materials involving transition ions as well as model magnetic systems, the present considerations may be of interest to wide research community.

2. Intrinsic properties of orthorhombic ZFS Hamiltonian

The definitions of the spin Hamiltonian forms and nomenclatures have recently been succinctly outlined in [24]. Thus here only the basic equations are provided to enable easier understanding of the nature of the intricacies involved in truncated orthorhombic ZFS Hamiltonians dealt with in Section 3. The full *conventional* form of $\mathbf{H}_{ZFS} = \boldsymbol{S.D.S}$ [1–9], most widely used in literature and suitable for paramagnetic species with the spin $S \geqslant 1$, may be expressed in the principal axis system (x, y, z) for monoclinic and triclinic symmetry as well as for orthorhombic symmetry as

$$\mathbf{H}_{ZFS} = D_x\boldsymbol{S}_x^2 + D_y\boldsymbol{S}_y^2 + D_z\boldsymbol{S}_z^2 \tag{1}$$

or equivalently as

$$\mathbf{H}_{ZFS} = D(\boldsymbol{S}_z^2 - \tfrac{1}{3}S(S+1)) + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2) \Leftrightarrow \mathbf{H}_{ZFS} = B_2^0O_2^0 + B_2^2O_2^2 \tag{2}$$

where the $\boldsymbol{D}$-tensor is traceless, see, e.g. [1,2], i.e. $Tr\ D_i = (D_x+D_y+D_z) \equiv 0$. In magnetism studies the constant $(1/3)S(S+1)$ in the first term in Eq. (2) is most often omitted.

For orthorhombic symmetry point groups (C_{2v}, D_2, D_{2h}) three mutually perpendicular and equivalent symmetry axes exist, which may be chosen as the symmetry-adapted axis system to obtain the simplest form of $\mathbf{H}_{ZFS}$. The different choices of assigning the axes (x, y, z) in Eqs. (1) and (2) to the orthorhombic symmetry axes have been defined in [25], whereas their structural meaning discussed in [26]. These choices yield six possible sets of orthorhombic ZFS parameters related by the standardization transformations Si (x', y', z'), defined in [25] with respect to the original axis system S1 (x, y, z), as follows: S2 (x, $-z$, y), S3 (y, x, $-z$), S4 (y, z, x), S5 (z, x, y), and S6 ($-z$, y, x). These alternative parameter sets are numerically distinct yet physically equivalent, i.e. they yield identical calculated energy levels. Note that the basic symmetry principles in question are essentially all simple consequences of the character tables of the orthorhombic point groups, which determine the invariant properties of orthorhombic Hamiltonians, like those in Eqs. (1) and (2).

Two additional points are worth mentioning. First, taking the axes (x, y, z) in Eqs. (1) and (2) arbitrarily, yields a triclinic-like $\mathbf{H}_{ZFS}$ with all D_{ij} components non-zero, even if the *actual* site symmetry is orthorhombic or higher. In such cases, the low-symmetry ZFS terms are not *actual* but *apparent* only [24]. Second, for monoclinic and triclinic site symmetry, the orthorhombic-like form of $\mathbf{H}_{ZFS}$ as in Eqs. (1) and (2) may be obtained if the original low-symmetry $\mathbf{H}_{ZFS}$ is expressed in the principal axes (x, y, z) of the second-rank ZFS terms. However, than the orientation of the principal axes (x, y, z) with respect to the crystallographic or laboratory axis system (X, Y, Z) must be provided for meaningful data comparison [8,27].

The second form in Eq. (2) is given in the extended Stevens operators $O_k^q(\boldsymbol{X} = \boldsymbol{S})$ defined in [28], and the associated ZFS parameters, B_k^q(or b_k^q), now prevailing in EMR and magnetism studies [1–9]. For systems with the spin $S \geqslant 2$ the higher-rank ZFS terms are required [1–9]. Hence, instead of the *conventional* notation in Eqs. (1) and (2), various spherical tensor operators and tesseral tensor operators (including the extended Stevens operators [28]) have been used in EMR as reviewed in [8,9]. Note that the extended Stevens operators $O_k^q(\boldsymbol{X})$ [28] have been generalized in [29] to any rank k and value of the angular momentum operator $\boldsymbol{X} = \boldsymbol{S}$, $\boldsymbol{J}$, or $\boldsymbol{L}$.

Relations between the *conventional* orthorhombic ZFS parameters in Eqs. (1) and (2) and $B_k^q(b_k^q)$ in the extended Stevens (ES) operator notation [28] are [2,8]

$$\begin{aligned} D &= b_2^0(ES) = 3B_2^0(ES) = (3/2)D_z \\ 3E &= b_2^2(ES) = 3B_2^2(ES) = (3/2)(D_x - D_y) \end{aligned} \tag{3}$$

Relations between the D_{ij} tensor components and the ZFS parameters B_k^q(ES) for triclinic symmetry derived in [30,31] may also be found in [24]. Importantly, a recent controversy concerning incorrect relations between the conventional ZFS parameters and those in the extended Stevens operator notation used in EMR for orthorhombic and lower symmetry has been clarified in [32].

It is worth to explain briefly the nature of the CF = ZFS confusion mentioned in Introduction, since it bears on analysis of the truncation cases in later Sections. This confusion arises partially because $\mathbf{H}_{CF}$ and $\mathbf{H}_{ZFS}$ are often expressed in terms of the same (mathematically) tensor operators. Similar mathematical form of both Hamiltonians does not entail their identical physical nature. The major distinctions are: (i) the operators are functions of different angular momentum—for $\mathbf{H}_{CF}$ of the orbital $\boldsymbol{L}_{\boldsymbol{\alpha}}$ ($\alpha = x, y, z$) or total angular momentum $\boldsymbol{J}_{\boldsymbol{\alpha}}$ for $3d^N$ or $4f^N$ ions, respectively, whereas for $\mathbf{H}_{ZFS}$ of the 'spin' (electronic, effective, or fictitious [8,9]) angular momentum $\boldsymbol{S}_{\boldsymbol{\alpha}}$ for given 'spin' systems, (ii) their nature is different since it is determined by the respective distinct basis of states. These distinctions appear to be forgotten in a number of papers implying the incorrect identification of the CF and ZFS quantities. The confusing terminology mixing up physically different CF and ZFS quantities, i.e. either $\mathbf{H}_{CF}$ and $\mathbf{H}_{ZFS}$ Hamiltonians, CF and ZFS parameters, or respective CF and ZFS energy level splittings (or transitions), is unacceptable considering the different physical nature of $\mathbf{H}_{ZFS}$ and $\mathbf{H}_{CF}$. The surveys of the pertinent confusion cases [21–23] have also revealed inappropriate nomenclature used for the *actual* axial and rhombic (so truncated) second-rank ZFS terms labeled as the '*longitudinal*' and