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Higher-order field-dependent terms in spin Hamiltonians for transition ions – implications for high-magnetic field and high-frequency EMR measurements

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Abstract. An overview of theoretical background of the higher-order field-dependent (HOFD) terms in the generalized spin Hamiltonians for transition ions and current status of experimental studies of the HOFD terms is provided in the nutshell. The terms nonlinear in the magnetic field (B) of the type: $\boldsymbol{B}^2\boldsymbol{S}^2$, $\boldsymbol{B}^3\boldsymbol{S}$, $\boldsymbol{B}^5\boldsymbol{S}$ or $\boldsymbol{B}^2\boldsymbol{I}^2$, $\boldsymbol{B}^3\boldsymbol{I}$, $\boldsymbol{B}^5\boldsymbol{I}$, where $\boldsymbol{S}$ and $\boldsymbol{I}$ is the electronic and nuclear spin, respectively, are of particular importance as compared with the usual linear Zeeman term $\boldsymbol{B.g.S}$. This is due to the high B values, up to 100 T (pulsed fields), achievable at present in the high-magnetic field and/or high-frequency electron magnetic resonance (HMF-EMR) measurements of magnetic and spectroscopic properties. A blueprint for future theoretical and experimental studies of the HOFD terms is proposed taking into account their implications for HMF-EMR measurements.

Key words: electron magnetic resonance (EMR) • high-magnetic field and high-frequency EMR (HMF-EMR) • generalized spin Hamiltonians (GSH) • higher-order field-dependent (HOFD) terms • zero-field splitting (ZFS) terms • transition ions in crystals

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Introduction

Electron magnetic resonance (EMR) is a powerful technique for experimental characterization of materials containing transition-metal ($3d^N$) and rare-earth ($4f^N$) ions [14, 17, 27]. The novel areas, not fully explored as yet, concerns the high-magnetic field and/or high-frequency electron magnetic resonance (HMF-EMR) measurements of magnetic and spectroscopic properties [1, 3, 16, 25, 26]. These techniques are of importance in studies of the non-Kramers $S = 1$, e.g. Ni^{2+} ($S = 1$) systems [9–11] and especially $S = 2$ ions, which exhibit large zero-field splitting, e.g. Fe^{2+} ($S = 2$) systems [22].

This paper provides a nutshell overview of the theoretical background of the higher-order field-dependent terms in the generalized spin Hamiltonians for transition ions and the current status of relevant experimental studies. Theoretical consideration of implications of these terms for HMF-EMR measurements may potentially reveal new phenomena, thus providing a driving force for further studies.

Generalized spin Hamiltonians and HOFD terms at a conceptual level

Theoretical background of the spin Hamiltonian (SH) formalisms, forms of the Zeeman electronic (Ze) Hamiltonians and the zero-field splitting (ZFS) (or alternatively, fine structure) Hamiltonians used to de-

scribe EMR spectra for transition ions may be found in [18, 21], whereas modelling techniques for analysis and interpretation of EMR data at low symmetry sites in crystals were reviewed in [20]. The general SH form [14, 17, 18, 21, 27] can be expressed in the extended Stevens operators (ESOs) O_k^q (for references, see [18, 19, 21]) as

$$(1) \qquad H_{\text{spin}} = \mu_B \, \boldsymbol{B.g.S} + \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q \, O_k^q(S_x, S_y, S_z) + \{\text{higher order terms in GSH}\}$$

The usual Stevens operators were defined only for $q > 0$ [14, 17, 18, 21, 27] and are not suitable for triclinic (C_1 and C_i) symmetry cases, which by group theory require all q components in Eq. (1). The ESOs O_k^q [18, 21] were generalized to arbitrary rank k and higher values of S (L or J) [19].

By the higher order terms in Eq. (1) we mean any higher-rank terms in the electronic spin (S) and/or the nuclear spin (I) in the generalized spin Hamiltonians (GSHs) [18, 21]. Specifically, by the higher-order field-dependent (HOFD) terms, we mean the higher-rank terms in $\boldsymbol{S}$ and $\boldsymbol{I}$, which are nonlinear in the magnetic field (B), e.g. terms of the type: $\boldsymbol{B}^2\boldsymbol{S}^2$, $\boldsymbol{B}^3\boldsymbol{S}$, $\boldsymbol{B}^5\boldsymbol{S}$ or $\boldsymbol{B}^2\boldsymbol{I}^2$, $\boldsymbol{B}^3\boldsymbol{I}$, $\boldsymbol{B}^5\boldsymbol{I}$ [18, 21]. In general, group theory predicts the admissible terms of the type $\boldsymbol{S}^a\boldsymbol{I}^b\boldsymbol{B}^c$, where $(a + b + c)$ must be an even integer due to time reversal symmetry [13], so the mixed terms like $\boldsymbol{SIB}^2$ are also admissible. The HOFD terms have so far been barely explored in experimental characterization of materials containing transition ions. However, in view of the recent advances in high-magnetic field techniques [1, 3, 16, 25, 26] studies of the HOFD terms become timely and of prime scientific significance. The steady state magnetic field of over 20 T are nowadays achievable for HMF-EMR measurements [16]. Especially useful are the variable-frequency and the pulsed magnetic fields techniques. For example, an EMR system which covers the magnetic field region up to 16 T, the quasi-continuous frequency region from 60 to 700 GHz, the temperature region from 1.8 to 4.2 K, and the hydrostatic pressure region up to 1.1 GPa has been developed [23]. High-field EMR has enabled direct determination of the single-ion anisotropy parameters D and E (actually the ZFS parameters [18, 21]) in $S = 1$ bond alternating system [11]. Moreover, the pulsed magnetic fields of up to 55 T with a long duration time of the pulse are now achievable for HMF-EMR measurements with the frequencies up to about 2 THz [9, 12]. The pulsed magnetic fields of up to even 100 T are also achievable, so with a shorter duration time of the pulse, e.g. variable-frequency HMF-EMR was performed in the Haldane gap system Y_2BaNiO_5 over a wide magnetic field range up to 100 T [10]. Such high $\boldsymbol{B}$ values make the HOFD terms with higher powers in $\boldsymbol{B}$ significant in comparison with the usual linear Zeeman term $\boldsymbol{B.g.S}$, even if the associated parameters may be small.

There exist two approaches to the SH formalism – the historically first developed derivational SH approach, which yields the microscopic SH (MSH), and the constructional SH approach, which yields the GSHs; for references, see [18, 21]. The conceptual frameworks for each SH approach and their interrelationships are illustrated in the concept map in Fig. 1. The HOFD terms have originally been introduced based on the constructional SH approach, which can provide only the explicit forms of generalized SHs for the various combinations of the operators ($\boldsymbol{S}$, $\boldsymbol{I}$) and external fields ($\boldsymbol{B}$, $\boldsymbol{E}$ – electric field) involved. On the other hand, microscopic SH theory of the HOFD terms, which require higher orders of perturbation theory (PT), have proved to be very cumbersome, so only in a few cases such MSH derivations have been carried out [18, 21].

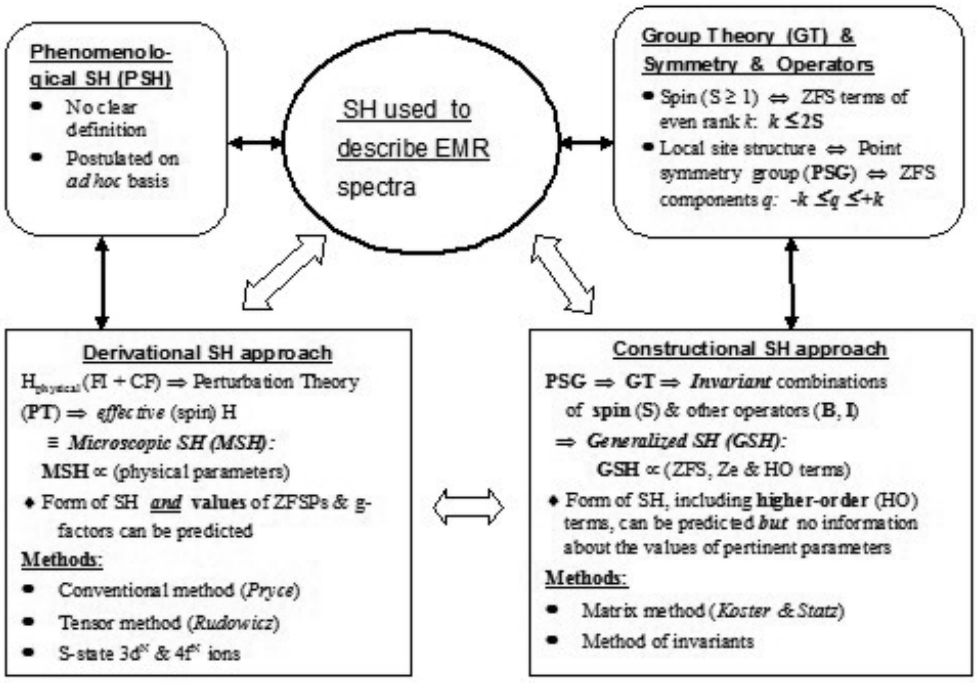

Fig. 1. The conceptual framework underlying the spin Hamiltonian formalisms and relationships between the constructional approach and the derivational one (for definitions of abbreviations, see text; for detailed explanations and references, see [18, 21]).

Importantly, the constructional approach and the derivational one should, in principle, yield compatible SH forms for each specific ion-host system. Unfortunately, each approach has a drawback. GSH formalism can provide no information on the values of SH parameters, unlike MSH formalism. However, in view of the computational complexity, especially for the *S*-state transition ions, the higher-order SH terms can hardly be derived using perturbation theory and MSH approach. The advantage of the GSH approach is that it has enabled first predictions of the form of various higher-order SH terms admissible by group theory (GT), e.g. the higher-order Zeeman electronic terms (i.e. nonlinear terms depending on the magnetic field B and the electronic spin $\boldsymbol{S}$: $\boldsymbol{B}^2\boldsymbol{S}^2$, $\boldsymbol{B}^3\boldsymbol{S}$, $\boldsymbol{B}^5\boldsymbol{S}$) and the higher-order hyperfine terms (i.e. nonlinear terms depending on $\boldsymbol{B}$ and the nuclear spin $\boldsymbol{I}$: $\boldsymbol{B}^2\boldsymbol{I}^2$, $\boldsymbol{B}^3\boldsymbol{I}$, $\boldsymbol{B}^5\boldsymbol{I}$). Experimental determinations of the higher-order SH parameters from detailed fittings to EMR spectra are still hampered due to the lack of suitable theory and computer fitting programs [1, 3, 16, 18, 21, 25, 26].

Experimental evidence of HOFD terms in EMR studies of transition ions

Here we provide only two key illustrative examples of experimental evidence of HOFD terms detected in EMR studies of transition ions [2, 13].

Pioneering study of the $\boldsymbol{B}^3\boldsymbol{S}$ terms has been carried out by Kuroda *et al*. [13] using EMR of cobalt ammonium Tutton salt $(NH_4)_2Co(SO_4)_2\cdot 6H_2O$ at high pulsed B up to 40 T (400 kOe) and submillimeter waves (337 μm of HCN laser and 119 μm of H_2O laser). The transitions between the spin states of Co^{2+} ions at tetragonal sites split by the spin-orbit coupling have provided first experimental observation of the nonlinear $\boldsymbol{B}^3\boldsymbol{S}$ term in ionic crystals with the $3d^N$ ions. Interestingly, a recent SCI search has indicated only 16 citations of the paper [13] with the last one in 2004; no new experimental or theoretical efforts on HOFD terms of the type $\boldsymbol{B}^3\boldsymbol{S}$ could be identified. The observed substantial frequency dependence of the g value (Fig. 2) could be explained by the $\boldsymbol{B}^3\boldsymbol{S}$ term [13].

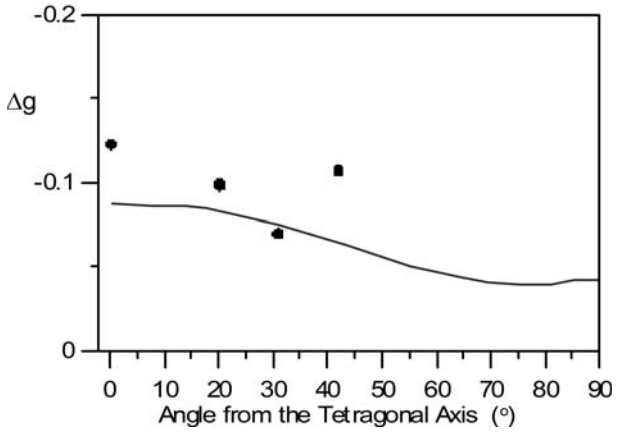

Fig. 2. Sketch of the theoretical prediction for the g shift due to the $\boldsymbol{B}^3\boldsymbol{S}$ term (solid line) and the first experimental evidence of this term (solid circles) measured at 119 μm for $(NH_4)_2Co(SO_4)_2\cdot 6H_2O$ (adapted from [13]).

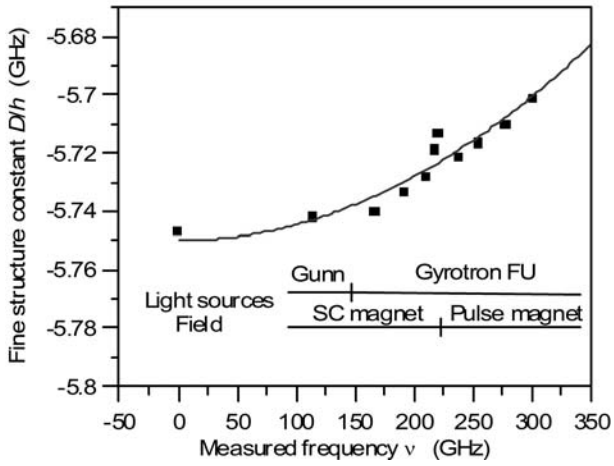

Fig. 3. Sketch of the recent experimental evidence of the $\boldsymbol{B}^2\boldsymbol{S}^2$ term; the solid curve shows the best fit curve obtained by using Eq. (2) (adapted from [2]).

The transitions between the spin states of Cr^{3+} ions at trigonal sites in ruby Al_2O_3 have recently provided experimental observation of the $\boldsymbol{B}^2\boldsymbol{S}^2$ term [2]. EMR measurements have been carried out at room temperature using pulsed high magnetic fields up to 24 T and a gyrotron as a radiation source in a millimeter to submillimeter wave range with frequency (ν) step-tunable up to 300.94 GHz. The Zeeman energy in this frequency range was large enough compared with the ZFS parameter D, i.e. the fine structure constant [2]. The theoretical prediction for the frequency dependence of D was derived as [2]:

$$D(\nu) = D(1 + a\nu^2)\, S^2 \qquad (2)$$

The observed frequency dependence of D (Fig. 3) has been well explained by the nonlinear $\boldsymbol{B}^2\boldsymbol{S}^2$ term [2]. Interestingly, a recent SCI search has indicated only 2 self-citations of the paper [2] with the last one in 2002; both concerned with equipment aspects and not with the HOFD terms.

The sample results presented above indicate that the HOFD terms are definitely worth further studies since they provide an opportunity to explore new phenomena, e.g. the novel spin excitations that may arise due to the energy level crossings between the higher and lower lying states induced by high magnetic fields [9, 10]. The major obstacle in the studies of the HOFD terms is the lack of suitable theoretical predictions and computer fitting programs.

Key research aspects underlying the studies of HOFD terms

The following key research aspects should be tackled in order to advance our understanding of the HOFD terms and their implications for HMF-EMR measurements. Starting point is a systematic review of available experimental data on HOFD terms for isolated transition ions with $S \leq 7/2$ in order to (i) assess the values of HOFD parameters and contributing mechanisms, (ii) consider their effect on the observed spectroscopic and magnetic properties of various specific systems, (iii) reveal new physical effects induced by HOFD terms, (iv) identify

best candidate ion-host systems for detailed studies. In parallel, a review of the pertinent theoretical literature dealing with specific HOFD terms is to be carried out to (i) enable identification and comparative analysis of the existing GSH forms and (ii) provide information on the operators and their matrix elements necessary for further theoretical development. A review of the older literature has been partially carried out and search for relevant recent literature is ongoing. Our extensive literature database covering all major journals and spanning over 60 years, which has been developed to facilitate research in optical and EMR spectroscopy as well as magnetism of transition ions, contains at present nearly 120 records relevant to the studies of the HOFD terms. It appears, however, that since till recently low magnetic field B techniques were predominantly used, HOFD terms are barely explored even for the otherwise well-studied transition ions with $S \leq 7/2$ [14, 17, 27]. Consequently, no consistent and comprehensive theoretical framework for presentation of the generalized spin Hamiltonians, which would incorporate all admissible HOFD terms, has been worked out as yet.

Hence, the next major task is the development of GSH theory based on group theory methods, which would lead to derivation of explicit forms of the admissible HOFD terms. For completeness, various values of the 'effective' spin S and selected symmetry cases, which may be of relevance for transition ions in crystals as well as for the exchanged coupled systems, should be considered. This is an enormous task, so a step by step approach for selected specific cases is suggested. Note that for the isolated transition ions the highest spin is $S = 7/2$ for Gd^{3+} and Eu^{2+} ions, which requires the usual ZFS terms of even rank only $k = 2$, 4, and 6 [14, 17, 27]. However, the exchanged coupled systems exhibit a much higher total spin. Very interesting systems are the single-molecule magnets (SMMs), e.g. Mn_{12}-acetate exhibiting the high-spin $S = 10$ arising from the exchange coupling of four Mn^{4+} ($S = 3/2$) and eight Mn^{3+} ($S = 2$) ions [4–7]. For spin $S = 10$ systems, not only the ZFS terms with $k = 2$–6 used so far, but also the higher-order ZFS (HOZFS) terms with k-even up to $2S$, i.e. $k \leq 20$ are admissible [18, 21]. However, no adequate methods for dealing with high-spin $S > 7/2$ systems exist. Thus, partial and inadequate methods are used for high-spin SMMs, see, e.g. [4–7]. Notably, SMMs with a total spin higher than $S = 10$ have become available [4–7]. With increasing applications of the high-B techniques [1, 3, 16, 25, 26] studies of high-spin SMM behaviour under HMF conditions, including the role of unexplored HOFD and HOZFS terms, become important and attractive.

Development of GSH approach [18, 21] dealing with HOFD and HOZFS terms for high spins S and higher ranks k presents considerable challenges. The derivation of somewhat simpler higher-order linear Zeeman terms, BJ^n ($n = 3$, 5) or higher-order hyperfine terms of the type $J_1^n J_2$ and $J_1 J_2^n$, where J_1 and J_2 represent the operators $\boldsymbol{S}$ or $\boldsymbol{I}$ [15] illustrates the complexity involved in such derivations. Even the terms $\boldsymbol{BS}^3$ turn out to be very complicated for low symmetry cases [15]. Definitions of the operators are crucial and hence methodology requires selection of suitable tensor operators for derivation of explicit listings of GSH forms. We propose utilizing the generalized extended Stevens operators (ESO), which have recently been worked out [19], instead of the tesseral spherical tensor operators proposed in [15]. Note that the extended Stevens operators (ESO), for references, see [18, 19, 21], have extensively been used in magnetism [5, 24] and EMR [14, 17–19, 21] studies. Adoption of the generalized ESO [19] would greatly facilitate (i) the development of algebraic methods and suitable programs, e.g. Mathematica programs, for calculations of matrix elements of the generalized ESO with rank $k > 6$ for arbitrary spin S and (ii) derivations of algebraic expressions for transformations of the generalized ESO of higher ranks k for arbitrary spin S and development of suitable programs.

An important task is also the development of MSH approach in order to predict the values of HOFD parameters and analyse the contributing mechanisms. The MSH approach seems best suited for the non-Kramers ions, e.g. $3d^4$ and $3d^6$ ($S = 2$) exhibiting large ZFS [22], as well as for $3d^2$ and $3d^8$ ($S = 1$) [10, 11]. Hence, we envisage explicit derivations, using the MSH methods in the ^5D approximation, of MSH expressions for HOFD terms for $3d^4$ and $3d^6$ ions for various symmetry cases and subsequent development of programs for modelling of HOFD parameters. Applications for Fe^{2+} and Mn^{3+} ($S = 2$) and Ni^{2+} ($S = 1$) ions may be of special importance in order to evaluate the strength of the HOFD parameters involved.

Practical applications of the theoretical GSH framework require suitable computational tools for dealing with HOFD and HOZFS terms for the high-spin S and higher-rank k terms. This necessitates development of programs, or modules to be incorporated into existing programs, for (i) diagonalization of GSH to obtain energy levels and resonance transitions and (ii) simulation of resonance characteristics in X/Q-band EMR and HMF-EMR spectra. No such computer programs suitable for $S > 7/2$ systems exist at present. Extended computer programs for simulation and fitting of EMR spectra would greatly facilitate collaborative experimental studies of HOFD and HOZFS terms for transition ions and the exchanged coupled systems.

Summary and conclusions

Development of the generalized spin Hamiltonian (GSH) approach including the higher-order field-dependent (HOFD) terms and the higher-order zero-field splitting (HOZFS) terms for high-spin S systems and higher ranks k proposed above would have a significant impact on the future EMR studies of transition ions in crystals and the exchanged coupled systems. This would open up new horizons well beyond the single-molecule magnets field, including the high-magnetic field and/or high-frequency electron magnetic resonance (HMF--EMR) measurements of magnetic and spectroscopic properties. The proposed research would enable extending the applications of HMF-EMR spectroscopy in studies of magnetic, optoelectronic, and laser materials by offering new perspectives arising from the theoretical GSH framework. Hence, the new opportunities offered by novel experimental techniques involving extreme conditions in the external quantities, i.e. magnetic field

(B), frequency (ν), pressure (p), and temperature (T), would be more efficiently utilized.

It should be kept in mind that studies of the HOFD and HOZFS terms for high spins S and higher ranks k presents considerable challenges since suitable computer modelling techniques are still to be worked out. Such techniques are indispensable to (i) help extracting structural information about the actual site symmetry and symmetry axes, (ii) enable studies of low symmetry effects, (iii) correlate EMR and optical spectroscopy data, (iv) predict measurable parameters, and (v) provide reliable experimental data on HOFD and HOZFS parameters.

This preliminary feasibility study of the role of the HOFD and HOZFS terms in HMF-EMR provide solid foundations for a future large scale project aimed at direct applications of these terms for improving spectroscopic characterization of technologically important materials and advancement of our knowledge in the emerging area. It may be hoped that the blueprint for future theoretical and experimental studies of the HOFD and HOZFS terms presented above may be successfully implemented due to international collaboration in not so distant future.

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