



EMR-related problems at the interface between the crystal field Hamiltonians and the zero-field splitting Hamiltonians

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Abstract. The interface between optical spectroscopy, electron magnetic resonance (EMR), and magnetism of transition ions forms the intricate web of interrelated notions. Major notions are the physical Hamiltonians, which include the crystal field (CF) (or equivalently ligand field (LF)) Hamiltonians, and the effective spin Hamiltonians (SH), which include the zero-field splitting (ZFS) Hamiltonians as well as to a certain extent also the notion of magnetic anisotropy (MA). Survey of recent literature has revealed that this interface, denoted CF (LF) \leftrightarrow SH (ZFS), has become dangerously entangled over the years. The same notion is referred to by three names that are not synonymous: CF (LF), SH (ZFS), and MA. In view of the strong need for systematization of nomenclature aimed at bringing order to the multitude of different Hamiltonians and the associated quantities, we have embarked on this systematization. In this article, we do an overview of our efforts aimed at providing a deeper understanding of the major intricacies occurring at the CF (LF) \leftrightarrow SH (ZFS) interface with the focus on the EMR-related problems for transition ions.

Key words: crystal/ligand field (CF/LF) Hamiltonian • electron magnetic resonance (EMR) • magnetism • optical spectroscopy • transition ($3d^N$ and $4f^N$) ions • zero-field splitting (ZFS)

Introduction

The physical free ion Hamiltonians together with the crystal field (CF) Hamiltonians, or equivalently the ligand field (LF) Hamiltonians, H_{CF} (H_{LF}), are fundamental in optical spectroscopy (see, e.g. [1–5] and references therein), whereas the effective spin Hamiltonians (SH), $\tilde{H}_{\text{eff}} \equiv \tilde{H}_{\text{SH}}$, which include the zero-field splitting (ZFS) Hamiltonians, \tilde{H}_{ZFS} , and the Zeeman electronic (Ze) terms, \tilde{H}_{Ze} , are fundamental in electron magnetic resonance (EMR, equivalently electron paramagnetic resonance (EPR) or electron spin resonance (ESR)) [6–9] and magnetism [10–13] of transition ions in crystals, as well as their clusters. Importantly, these Hamiltonians are basic tools for the interpretation of magnetic and spectroscopic properties of the single-ion complexes in crystals, as well as the magnetic systems based on the transition metal (TM) or rare earth (RE) ions. Yet, the interface between the two physically distinct types of Hamiltonians, denoted CF (LF) \leftrightarrow SH (ZFS), has become a specific danger zone, especially for junior researchers.

The present situation regarding the definitions of the crucial notions, their interrelationships, and the operators existing in the EMR and optical spectroscopy area may be described as a maze difficult to follow, especially by experimentalists. To alleviate

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this situation, we have set ourselves the very challenging task of bringing order to the multitude of different Hamiltonians, especially those describing or parameterizing CFs and ZFSs, with the aim of correcting sloppy or incorrect usage. This minireview provides a brief summary of our ongoing work with the focus on the EMR-related problems occurring at the interface CF (LF) \leftrightarrow SH (ZFS). It may serve as an advanced warning for practitioners working in the area of EMR (EPR/ESR) of transition ($3d^N$ and $4f^N$) ions.

Overview of conceptual problems and related terminological confusions

Two major types of the terminological confusions exist in literature. The most widely spread is the CF=ZFS confusion, which pertains to the cases of labeling the true ZFS quantities as purportedly the CF (LF) quantities [14]. The inverse ZFS=CF confusion pertains to the cases of labeling the ‘true’ CF (LF) quantities as purportedly the ZFS quantities [15]. The associated quantities include effects, Hamiltonians, eigenfunctions, parameters, or energy level splittings. The consequences of these terminological confusions go far beyond simple semantic issues or misleading keyword classifications of papers in journals and scientific databases. More importantly, serious consequences include misinterpretation of data from a wide range of experimental techniques. Most recently, the confusions identified in our survey have led to pitfalls and errors of substance bearing on understanding of physical principles and thus the properties of the studied systems [14, 15].

The key topics dealt with in the review [14] are outlined in a nutshell below.

- 1) Basic aspects concerning the notion CF (LF) and the notion SH (ZFS), including (a) the nature of both types of Hamiltonians and (b) notations used for parameters.
- 2) Major aspects and problems concerning the orthorhombic and lower symmetry standardization, including (a) meaning of orthorhombic standardization, (b) problems arising from implications of standardization, and (c) specific problems concerning the rhombicity ratio.
- 3) Problems and confusions identified in the tutorial review by Sorace *et al.* [16] of the magnetic properties of single molecule magnets (SMM) based on the RE ions in molecular magnets, including (a) distinct properties of the CF (LF) parameters expressed in the Stevens and Wybourne notations, (b) conversion relations between the CF (LF) parameters expressed in the Stevens and Wybourne notations, (c) distinct physical nature of H_{CF} (H_{LF}) and \tilde{H}_{SH} (\tilde{H}_{ZFS}) and interrelationships between the CF (LF) parameters and the SH (ZFS) ones, (d) confusion of the type CF=ZFS between the CF (LF) and SH (ZFS) quantities, and (e) misprinted and misinterpreted conversion relations.
- 4) Confusion between the CF (LF) and SH (ZFS) quantities in recent textbooks.
- 5) Confusion between the CF (LF) and SH (ZFS) quantities in recent literature, including (a) problems and confusions concerning the multispin Hamiltonians and the effective total SHs, and (b) confusion between the CF (LF) and SH (ZFS) quantities in the recent EMR-related literature and in the recent magnetism studies.

The reviews [14, 15] have prepared grounds for the extensive compendium [17]. For easy reference, the crucial notions and aspects concerning the CF (LF), SH (ZFS), and related quantities that are pertinent for single transition ions and exchange coupled systems have been systematically defined and their logical interrelationships outlined [17]. The reviews [14, 15] and the compendium [17] are intended to simplify the navigation through the maze of the complex web of interrelated notions involved in this interface, which has become entangled over the years. The focus here is on the EMR-related problems occurring at this interface with special consideration of the single-ion complexes of transition ($3d^N$ and $4f^N$) ions in crystals. The single molecule magnets (SMM) or molecular nanomagnets (MNM) and single-ion magnets (SIM) based on the RE and TM ions and other exchange coupled complexes (ECS) have been discussed in [14, 15, 17].

The key definitions and aspects dealt with in the compendium [17] are outlined in a nutshell below.

 - 1) Physical Hamiltonians for single transition ions, including (a) the free-ion Hamiltonians H_{FI} for transition ions, (b) total Hamiltonians for single transition ions in crystals, (c) crystal field and ligand field Hamiltonians H_{CF} (H_{LF}), (d) quenching of the orbital angular momentum by CF, and (e) rare-earth ions with the Russell–Saunders ground multiplet.
 - 2) Effective Hamiltonians for single transition ions, including (a) the spin operators for single transition ions: (i) true electronic spin \mathbf{S} , (ii) effective spin $\tilde{\mathbf{S}}$, and (iii) fictitious ‘spin’ \mathbf{S}' ; (b) effective spin Hamiltonians $\tilde{H}_{eff} \equiv \tilde{H}_{SH}$ for single transition ions: (i) generic ‘spin’ Hamiltonians, (ii) effective single-ion SHs ($\tilde{H}_{ZFS} + \tilde{H}_{Ze}$), (iii) origin and nature of single-ion ZFS; and (c) the two approaches to SH: (i) the microscopic SH and (ii) the generalized spin Hamiltonian (GSH).
 - 3) Exchange coupled systems (ECS) of transition ions and single molecule magnets, including (a) exchange interactions (EI) and Hamiltonians, (b) multispin Hamiltonians H_{MH} for ECS, (c) effective total (giant) SHs H_{GS} ($\equiv \tilde{H}_{SH}^T$) for ECS, and (d) relationships between H_{MH} and H_{GS} ($\equiv \tilde{H}_{SH}^T$) and origin of the total ZFS Hamiltonian \tilde{H}_{ZFS}^T .
 - 4) The Stevens, Wybourne, and other operators, including (a) historical perspective and origin of the Stevens and Wybourne operators, (b) usual Stevens operators vs. the extended Stevens operators (ESO), (c) adoption of the Stevens operators and other notations in EMR studies, and (d) Hamiltonians vs. operators.
 - 5) Forms of Hamiltonians and definitions of the associated parameters, including (a) H_{CF} (H_{LF}) and relations between the CF (LF) parameters expressed in the Stevens and Wybourne nota-

tions, (b) \tilde{H}_{SH} (\tilde{H}_{ZFS}) and relations between the ZFS parameters expressed in the ESO and conventional notations, and (c) higher-order terms in the generalized spin Hamiltonians.

- 6) Distinctions and interrelationships between the CF (LF) and SH (ZFS) quantities, including (a) distinct physical nature of H_{CF} (H_{LF}) and \tilde{H}_{SH} (\tilde{H}_{ZFS}) and (b) interrelationships between the CF (LF) and SH (ZFS) parameters.
- 7) Current status of applications, importance and usage of the ESOs in recent literature.
- 8) Finally, with the hindsight of the precise definitions provided for basic notions, we formulate the generalized definitions of the full and restricted Hamiltonians vs. the effective and fictitious ones. For each major topic, pertinent general comments concerning particular terminology are pro-

vided [17], which list additional references but may be skipped on first reading. For visualization of the problems at the CF (LF) \leftrightarrow SH (ZFS) interface for single transition ions and the interrelationships and distinctions between the pertinent crucial notions, several concept maps and diagrams have been devised. As an example, the visualization of the notion CF (LF) pertinent for single transition ions in crystals and molecules is presented in Fig. 1. Note that the symbol D in Fig. 1, which has been used in the early CF theory (see, e.g. [1, 4]), shall not be confused with the axial ZFS parameter D used in SH theory (see, e.g. [6–10]).

Let us recall two basic definitions. The CF (LF) Hamiltonians, H_{CF} (H_{LF}), parameterize the effect of the electric field due to the surrounding n ligands (L) acting on a paramagnetic ion (M) in a given ML_n com-

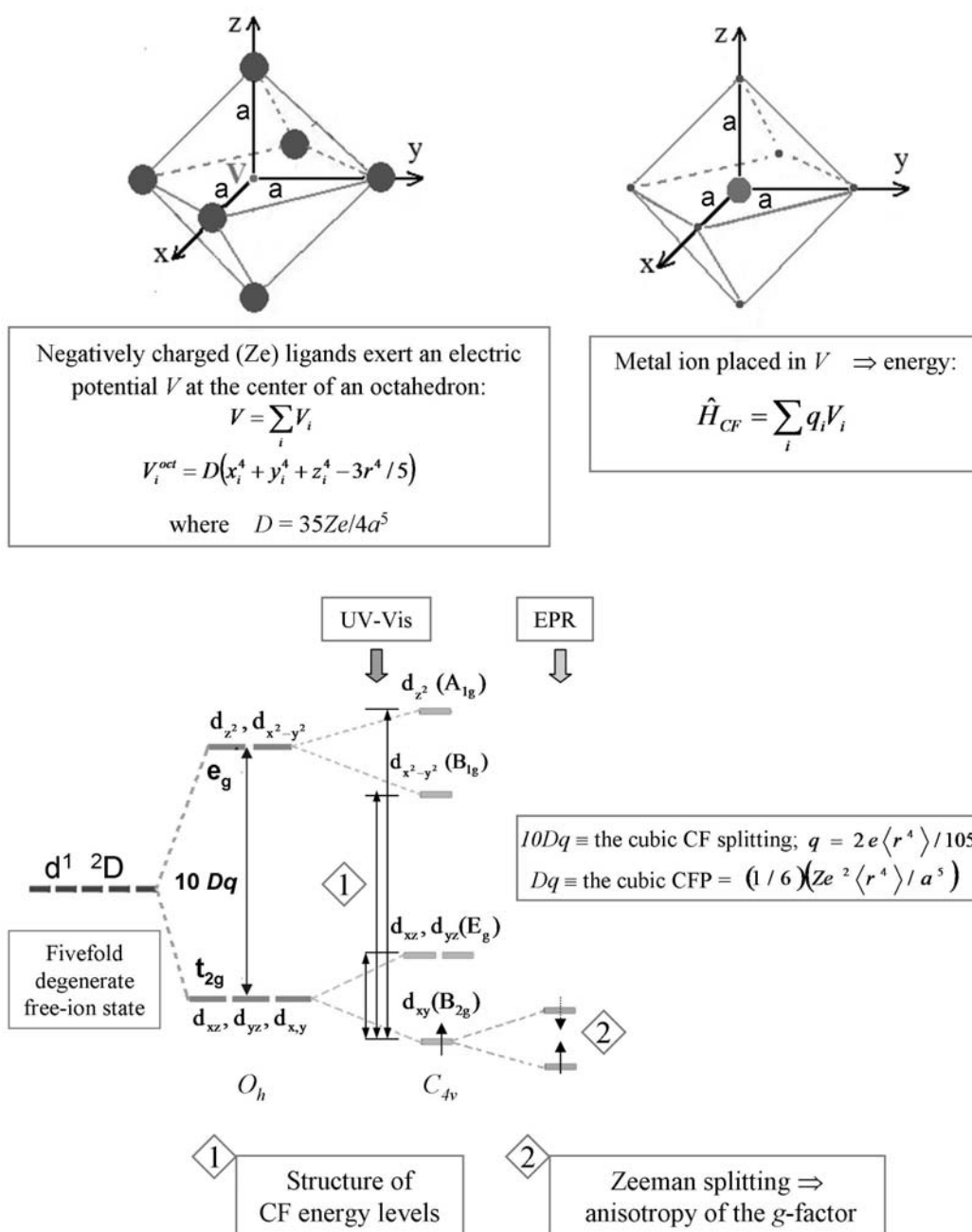


Fig. 1. Visualization of the notion CF (LF) pertinent for single transition ions in crystals and molecules (adapted from [17]).

plex in crystal or in a molecule (see Fig. 1). The ZFS term, \bar{H}_{ZFS} , in the effective spin Hamiltonians (SH), $\bar{H}_{\text{eff}} \equiv \bar{H}_{\text{SH}}$, describes the splitting within the basis of the effective spin \mathbf{S} states at zero external magnetic field (or magnetic induction \mathbf{B}). The splitting of the spin levels within the orbital singlet ground state is due to the combined action of the CF (LF) interactions, H_{CF} (H_{LF}), and the electronic spin-orbit (SO) coupling, H_{SO} , and, to a lesser extent, the electronic spin-spin (SS) coupling, H_{SS} . Hence, this splitting is appropriately called the ‘zero-field splitting’ (ZFS), or equivalently ‘fine structure splitting’. Note that the latter name is strictly appropriate only for single transition ions, whereas it is rather inappropriate for the ECS. The transitions between the spin levels are observed using EMR techniques, whereas those between the ground states and the states belonging to the higher lying ^{2S+1}L terms or $^{2S+1}L_J$ multiplets are observed using optical spectroscopy techniques. Keeping in mind the prevailing definitions of the crucial notions [1–12] should dispel any doubts about the incorrectness of naming the ‘true’ ZFS quantities as ‘purportedly’ the CF (LF) ones or *vice versa*. For the reasons exposed in [14, 15, 17], any idea of identification of the true ZFS quantities with the true CF quantities is fundamentally wrong.

Summary of EMR-related problems

The pertinent examples of various types of terminological confusions identified in the recent textbooks (see, e.g. [13]), review articles (see, e.g. [16]), and regular papers dealing with the single molecule/ion magnets (see, e.g. [18]) and EMR studies of transition ions in crystals (see, e.g. [19]) are briefly outlined and the nature of confusion is elucidated. As discussed in [20, 21], the detrimental consequences of the problems in question include misinterpretation of data from a wide range of experimental techniques and, most recently, the pitfalls and errors of substance bearing on understanding of physical properties. Here, for illustration of the scope of the confusions, we summarize the key EMR-related problems and provide pertinent references.

(1) Confusion between the CF (LF) and SH (ZFS) quantities, mainly the CF=ZFS confusion exemplified by consideration of the two notions: the CF parameters (CFPs) and the ZFS parameters evidently as synonymous, occurs in recent EMR-related papers, e.g., [22–32]; for critical comments, see [14]. Apart from the problems and confusions identified in the review on molecular magnets [16], serious forms of the CF=ZFS confusion occur also in the EMR and SMM/MNM related textbook [13].

(2) Other less serious misconceptions have been also revealed in the recent EMR-related textbooks [33–39]. This includes, for example, (i) inappropriate consideration of the ZFS term (or Hamiltonian) as an ‘interaction’ or ‘coupling’ or (ii) inadequate presentation of the origin of ZFS as well as (iii) incomplete explanation of the standard convention: $0 \leq E/D \leq 1/3$ [14]. The first terminological misconception represents a specific case of the confusion

between the exchange interactions (EI) quantities and the ZFS quantities, denoted EI=ZFS, examples of which have been discussed in [40–42].

On the positive side, Rieger’s book [43] on ESR analysis and interpretation is a commendable example of correct terminology, while Lund *et al.* [44] provided an introductory description of the principles and applications of ESR spectroscopy from an experimentalist perspective and may be commended on a few points, whereas in the book edited by Brustolon and Giamello [45] only minor problems occur.

(3) Confusion between the ZFS and CF (LF) quantities, mainly the ZFS=CF confusion exemplified by naming the true CFPs as purportedly the ZFSPs, occurs in recent magnetism related papers, especially dealing with trivalent rare earth (RE) ions in various systems, e.g., [18, 46–54], whereas that exemplified by referring to the true CF Hamiltonians as purportedly the ZFS ones in, e.g., [55–58]; for critical comments, see [15, 59]. Note that a very serious case of the ZFS=CF confusion has most recently been identified in the study of the LF splittings and magnetic properties of the Er^{III} SIMs [58].

(4) Invalid direct conversions between the CF parameters and ZFS ones have recently been identified. The implied usage of the invalid conversion relations occurs in the tutorial review [16] and in the recent EMR and magnetism related papers [18, 60–66]. The most serious case of the factual invalid usage of the conversion relations occurs in [19] and in a descriptive way, also in the papers [18, 60–63] utilizing the software package SIMPRE [18]. The latter cases have been critically commented on in [20] and [21], respectively.

The elucidation of problems arising from misinterpretations of the crucial notions or the operators’ definitions, which have been exposed in [14, 15, 17, 20, 21], may stimulate EMR researchers to look more deeply into the intricacies involved. Clarification of the incorrect terminology may prevent further proliferation of the problems and confusions in literature. In longer terms, a better understanding of the physical principles as well as the major intricacies involved in the CF (LF) \leftrightarrow SH (ZFS) interface may be achieved within the scientific community. Problems and confusions that are beyond the scope of this minireview concern, for example, the multispin Hamiltonians and the effective total spin Hamiltonians for the ECS, as well as the confusion between the CF (LF) and SH (ZFS) quantities in the recent magnetism studies. These topics will be dealt with in a separate review.

Conclusions

Efforts aimed at providing a deeper understanding of the major intricacies identified at the interface between the physical Hamiltonians, which include the crystal (ligand) field (CF/LF) Hamiltonians, and the effective spin Hamiltonians (SH), which incorporate the zero-field splitting (ZFS) Hamiltonian, have been briefly overviewed. The EMR-related problems occurring at the CF (LF) \leftrightarrow SH (ZFS)

interface have been summarized, whereas for full details, Refs. [14, 15, 17, 20, 21] may be consulted.

We have exposed the misinterpretations of the crucial notions, which have created serious terminological confusions and have led to pitfalls and errors of substance that bear on understanding of physical properties of magnetic systems. These considerations are of importance to researchers working in the areas of EMR (EPR/ESR), optical spectroscopy, and magnetism. It is hoped that the in-depth clarifications provided therein [14, 15, 17, 20, 21] will also enable better interpretation of experimental results. Major conclusion is that scientific community should strive for a consensus view on the proper meaning of the crucial notions, for example, by producing a glossary of terms under the auspices of an international body.

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