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Revealing the consequences and errors of substance arising from the inverse confusion between the crystal (ligand) field quantities and the zero-field splitting ones

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Czesław Rudowicz [a,*], Mirosław Karbowiak [b]

[a] Institute of Physics, West Pomeranian University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland
[b] Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

ABSTRACT

Survey of recent literature has revealed a doubly-worrying tendency concerning the treatment of the two distinct types of Hamiltonians, namely, the *physical* crystal field (CF), or equivalently ligand field (LF), Hamiltonians and the zero-field splitting (ZFS) Hamiltonians, which appear in the *effective* spin Hamiltonians (SH). The nature and properties of the CF (LF) Hamiltonians have been mixed up in various ways with those of the ZFS Hamiltonians. Such cases have been identified in a rapidly growing number of studies of the transition-ion based systems using electron magnetic resonance (EMR), optical spectroscopy, and magnetic measurements. These findings have far ranging implications since these Hamiltonians are cornerstones for interpretation of magnetic and spectroscopic properties of the single transition ions in various crystals or molecules as well as the exchange coupled systems (ECS) of transition ions, e.g. single molecule magnets (SMM) or single ion magnets (SIM). The seriousness of the consequences of such conceptual problems and related terminological confusions has reached a level that goes far beyond simple semantic issues or misleading keyword classifications of papers in journals and scientific databases. The prevailing confusion, denoted as the CF=ZFS confusion, pertains to the cases of labeling the *true* ZFS quantities as *purportedly* the CF (LF) quantities. Here we consider the inverse confusion between the CF (LF) quantities and the SH (ZFS) ones, denoted the ZFS=CF confusion, which consists in referring to the parameters (or Hamiltonians), which are the *true* CF (LF) quantities, as *purportedly* the ZFS (or SH) quantities. Specific cases of the ZFS=CF confusion identified in recent textbooks, reviews and papers, especially SMM- and SIM-related ones, are surveyed and the pertinent misconceptions are clarified. The serious consequences of the terminological confusions include misinterpretation of data from a wide range of experimental techniques and, most recently, have lead to pitfalls and errors of substance bearing on understanding of physical properties. Clarification of the incorrect terminology is timely in order to bring about better understanding of the physical principles and prevent further proliferation of the confusion.

1. Introduction

The present study elucidates the nature and properties of the two physically distinct types of Hamiltonians, which have confusingly been mixed each with the other in recent literature. Since these Hamiltonians underlie interpretation of the experimental data, this confusion has profound implications for magnetic measurements [1–9] as well as spectroscopic ones, both in the realm of optical spectroscopy [10–20] and electron magnetic resonance (EMR) spectroscopy [21–27]. The two types of Hamiltonians are: the *physical* crystal field (CF), i.e. equivalently 'ligand field (LF)', Hamiltonians, H_{CF} (H_{LF}), and the *effective* spin Hamiltonians (SH), which include as the major term the zero-field splitting (ZFS), i.e. equivalently 'fine structure', Hamiltonians, $\hat{H}_{SH}$ ($\hat{H}_{ZFS}$), as well as the Zeeman electronic (Ze) ones and some higher-order terms. Proper interpretation of experimental data is of outmost importance, since these Hamiltonians underlie vast areas of research, including the emerging fields of, e.g. spintronics and molecular magnetism as well as the well established ones, e.g. laser and magnetic materials, optoelectronics, and biological systems. The terminological confusion, which pertains to the cases of labeling the *true* ZFS quantities as *purportedly* the CF (LF) quantities, has been first identified and denoted as the CF=ZFS confusion [28]. It is the most widely spread type of the terminological confusions and has a long history as exemplified in the reviews [28–32]. An update on pertinent cases of the CF=ZFS

* Corresponding author.
E-mail address: crudowicz@zut.edu.pl (C. Rudowicz).

confusion together with their analysis and clarification has recently been provided in a dedicated review [33]. The focus therein [33] was on the cases identified in comprehensive critical survey of the recent textbooks, review articles, and papers dealing with the single molecule magnets (SMM) or the single ion magnets (SIM), which have been extensively studied in recent decades (see, e.g. the tutorial review by Sorace et al. [34]) as well as EMR related papers.

In this review we consider the confusion between the CF (LF) quantities and the ZFS ones, which consists in referring to the parameters (or Hamiltonians), which are, in fact, the *true* CF quantities, as *purportedly* the ZFS (or SH) quantities. This type of confusion represents the inverse confusion with respect to the CF=ZFS confusion and is denoted as the ZFS=CF confusion. Survey of recent literature has also revealed a doubly-worrying tendency. The number of studies, where either the CF=ZFS confusion or its more recent inverse version, i.e. the ZFS=CF confusion, have been identified, is rapidly growing, whereas the seriousness of the consequences of such conceptual problems is ever increasing. Both factors have reached alarming proportions as well as a level that goes far beyond simple semantic issues or misleading keyword classifications of papers in journals and scientific databases. Most recently, the confusions identified in our survey have lead to pitfalls and errors of substance bearing on understanding of the physical principles and thus the properties of the studied systems.

The considerations presented here together with those presented in [33] concern a wide range of fundamental aspects. Hence, these reviews should be of interest to broad readership ranging from condensed matter physicists to coordination chemists (see Section 2). The survey of specific cases of the CF=ZFS confusion [33] and the ZFS=CF confusion herewith as well as clarification of pertinent misconceptions have provided a thorough analysis of current situation at the CF (LF)↔SH (ZFS) interface. This analysis prepares solid grounds for the follow-up review aimed at systematization of nomenclature and bringing order to the zoo of different Hamiltonians and related notions [35].

2. Survey of the role of the crucial notions in the area of coordination compounds

The interplay between Hamiltonians H_{CF} (H_{LF}) and the *effective* spin Hamiltonians (SH) as well as the paramount role of both types of Hamiltonians for description of the magnetic properties (e.g. magnetic anisotropy) and spectroscopic ones (e.g. electronic transitions, spectral characteristics) of various coordination compounds is well evident in the recent reviews. The coordination compounds in question include the single transition ions in various crystals or molecules as well as the magnetic systems based on the transition metal (TM) and rare-earth (RE), i.e. either bulk magnets or the exchange coupled systems (ECS) of transition ions, especially SMM or SIM. Adequate and precise terminology regarding the CF (LF) quantities, the ZFS ones, and the quantities that describe magnetic anisotropy is crucial for proper interpretation of the properties of these systems. Results of survey of a sample selection of the recent pertinent reviews are presented below.

Sun et al. [36] proposed strategies towards single-chain magnets utilizing the strong uniaxial magnetic anisotropy arising from the tetragonal ligand fields acting on the transition ions, the spin–orbit interaction, the antiferromagnetic exchange, and the topology of the chain. Armelao et al. [37] considered design of luminescent lanthanide complexes: from molecules to highly efficient photo-emitting materials taking into account, among others, the electronic spectra of lanthanide-doped single crystals

and lanthanide salts, which have been interpreted within the frame of the Russell–Saunders coupling scheme. In the review of targeted synthesis, high-field EPR and pulsed-field magnetization of tetranuclear complexes in molecular magnetism Chaudhuri et al. [38] invoked prominently the notions of CF, ZFS as well as the single ion anisotropy (SIA). A note of caution is pertinent since the axial ZFS parameter *D* of the Ni(II) ions was named in [38] as the SIA quantity [31–33].

Both types of Hamiltonians H_{CF} (H_{LF}) and the *effective* SH are also considered in the density functional theory (DFT) as evidenced by the following reviews. Atanasov et al. [39] have developed theoretical approaches that combine ligand field theory with DFT-based methods and applied these approaches for a rational design of SMM based on cyanometalate-bridged oligonuclear transition metal complexes. Neese [40] presented method for prediction of molecular properties and molecular spectroscopy with DFT, which heavily relies on the interplay between the notions H_{LF} and SH. Pertinently, Neese [40] pointed out that it is, quote: '*of utmost importance to not "mix up" the levels of argumentation between the spin-Hamiltonian, ligand field arguments and numerical quantum chemical calculations*'. Pronounced role of LF theory for providing background for DFT is well exposed in [40]. Schäffer et al. [41] reviewed Kohn–Sham DFT results projected on ligand-field models and have shown that using DFT may supplement ligand-field descriptions and supply ligand-field parameters.

Pertinent examples of other spectroscopic and EMR studies may also be provided. Sessoli et al. [42] presented strategies towards SMM based on lanthanide ions, which utilize the notion of LF for description of electronic structure that are of importance for condensed matter physicists as well as coordination chemists. Alonso et al. [43] have consistently utilized the notions 'CF' and 'ligand(s)' in the study of the ground state Kramers doublet of low-spin heminic system and provided a comprehensive description of the EPR and Mössbauer spectra. Krzystek's et al. [44] review of applications of multi-frequency, high-field EPR for accurate determination of ZFS in high-spin transition metal coordination complexes may be commended for proper terminology. Gatteschi et al. [45] reviewed EPR of molecular nanomagnets and invoked the notions CF and ZFS in various contexts. A note of caution is pertinent since, as discussed in [33], some misinterpretations occur in [45]. They concern the nature of the *effective* total ZFS term $\tilde{H}_{ZFS}^{T}$ in the *effective* total SH $\tilde{H}_{SH}^{T}$ (or alternatively, giant SH), which describes the ground multiplet with the total (giant) spin S_T of SMM complexes; for definitions, see the review [35].

3. Inverse confusion of the type ZFS=CF between the CF (LF) parameters and the SH (ZFS) ones

Here we adopt the prevailing conventions utilized in the main textbooks [1–5,10–27] and the general reviews [28–32]. Definitions of the crucial notions and the essential notations used for H_{CF} (H_{LF}) and $\tilde{H}_{SH}$ ($\tilde{H}_{ZFS}$) as well as clarifications of the nature of Hamiltonians and definitions of parameters have recently been provided in the review [35]. The basic aspects concerning the CF (LF) parameters and SH (ZFS) ones have recently been discussed [33] in the context of the CF=ZFS confusion. For clarity, it is worth to recap a few basic points concerning H_{CF} (H_{LF}) and $\tilde{H}_{SH}$ ($\tilde{H}_{ZFS}$) as well as the operators involved in each type of Hamiltonians [35]. H_{CF}(H_{LF}) within a restricted basis of CF (LF) states of a given *L*- or *J*-multiplet, whereas $\tilde{H}_{SH}$ ($\tilde{H}_{ZFS}$) within the *effective* spin $\tilde{S}$ states for a given spin $\tilde{S}$ system, may be, and often are, expressed in terms of the extended Stevens operators (ESO) $O_k^q(\boldsymbol{X})$ [46,47]. The ESO may be, in general, functions of the respective operators $\boldsymbol{X}$ representing either the orbital $\boldsymbol{L}$ or total $\boldsymbol{J} \equiv (\boldsymbol{L}+\boldsymbol{S})$ angular momentum, where $\boldsymbol{S}$ is here the *true* electronic spin of a single transition ion, or the