Noether’s theorem and low symmetry aspects concerning the crystal (ligand) field Hamiltonians and spin Hamiltonians

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Abstract. This review presents a concise summary of major findings arising from our recent studies concerning the symmetry properties of crystal/ligand field (CF/LF) Hamiltonians and spin Hamiltonians (SHs). First we provide a bird’s-eye view of these studies. Then we overview (i) the pertinent basic concepts and notations, (ii) the algebraic symmetry (AS) of Hamiltonians for continuous rotational symmetry (CRS) cases, and (iii) the concepts of the rotational invariants and moments of CF Hamiltonians. This enables a new look from the point of view of the Noether’s theorem on the properties of CF/LF Hamiltonians and SHs invariant under CRS, i.e. hexagonal II, tetragonal II, trigonal II, monoclinic, and triclinic ones. An important theorem and a conjecture on the conserved quantities stipulated by Noether’s theorem for the Hamiltonians in question formulated by us helps to elucidate the interrelationships and deeper meaning of the concepts involved. Implications of the existence of the conserved quantities for interpretation of experimental CF parameter (CFP) datasets are encapsulated in five corollaries. These considerations reveal that the feasibility of determination of CFPs from fitting experimental spectra and the reduction of the existing higher-order rotational invariants for hexagonal type II and cubic symmetry require reinterpretation. This novel approach enables adoption of better fitting strategies utilizing well-defined conserved quantities, which are invariant under CRS. The advantages of this approach are illustrated using the CFP datasets reported in literature for RE3+(4fN) ions in LiYF4. This review deals also with the fundamental intricate aspects, hitherto not fully understood, concerning the CF Hamiltonians for the ‘low symmetry’ cases, including the CRS cases as well as orthorhombic ones. This includes: (1) selection of the axis systems, (2) types of CF parameters and their properties, (3) introduction of a new notion of a nominal axis system for the fitted CFP datasets, (4) implications of the Noether’s theorem and the AS of CF Hamiltonians, (5) correlation properties among CFP datasets, (6) the rotational degrees of freedom and the reduction of the number of independent CFPs, and (7) extension of the multiple correlated fitting technique. Clarification of these intricate aspects enables us to provide a general framework aimed at achieving an increased compatibility and reliability of CFP datasets for transition ions at low symmetry sites in crystals. The usefulness of this framework is illustrated by reanalysis of the CFP datasets for Nd3+(Pr3+) in NdGaO3 (PrGaO3) and RNiO3.

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1. Introduction
Spectroscopic properties of the transition ions, especially iron-group ions and lanthanides, at low symmetry sites in crystals play important role for various technologically important materials (for references, see [1-5]). The trivalent rare-earth (RE) $4f^N$ ions have been most extensively studied due to applications in laser host and optoelectronic materials. The experimental techniques employed to investigate the CF/LF effects, majority of which are ‘non-directional’ techniques - unlike those used in the EMR (electron magnetic resonance) studies [6,7], were discussed in [3]. During our recent CF/LF studies of transition ions in crystals [1-5] we have encountered several intricate low symmetry aspects. The motivation to clarify these aspects has prompted us to embark on a comprehensive project aimed at increasing the compatibility and reliability of the crystal field parameter (CFP) datasets. This review presents a concise summary of the major findings arising from our studies concerning the intricate low symmetry properties of CF/LF Hamiltonians and spin Hamiltonians (SHs). To facilitate broad understanding, a bird’s-eye view of these studies is given in Section 2, where the recent results [1-5] are briefly outlined, whereas our earlier pertinent studies [8-12] are put in perspective. To provide theoretical background for the underlying considerations, the pertinent basic concepts and notations are overviewed in Section 3. Our earlier studies on the algebraic symmetry (AS) of Hamiltonians for continuous rotational symmetry (CRS) cases as well as the existing concepts of the rotational invariants and moments of CF Hamiltonians are outlined in Section 4 and 5, respectively. Brief presentation of the Noether’s theorem applicable to CRS cases follows in Section 6. The various intricate ‘low symmetry’ aspects bearing on the compatibility and reliability of CFPs are dealt with in Section 7. The results presented in Sections 6 and 7 enable a new look at the properties of CF/LF Hamiltonians and SHs for CRS cases and consideration of practical applications in Section 8. Since this review is based on our published papers, especially the recent ones [1-5], instead of a full list of references and as a space saving measure, we provide here only pointers to the authors’ papers. Hence, these references shall be considered as sources of specific references to pertinent literature and not as mere self-citations. For completeness, the most recent relevant papers not cited in [1-5] are briefly commented on in Conclusions (Section 9).

2. Bird’s-eye view of our studies of low symmetry aspects in the CF/LF and EMR area
For the purpose of these considerations the term ‘low symmetry’ includes hexagonal II, tetragonal II, trigonal II, monoclinic, and triclinic symmetry cases [8-10], which collectively can be termed as CRS cases, as well as orthorhombic [11] ones. The former symmetries have been studied by one of us (CZR) earlier from the point of view of the AS of CF Hamiltonians [8-10]. The fact that these symmetries fall in the realm of the Noether’s theorem and the arising consequences have only recently been realized [1]. The study [1] provides first consideration of the Noether’s theorem in application to CF Hamiltonians and has profound implications. As discussed in Section 6, the conserved quantities stipulated by the Noether’s theorem [1] are equivalent to the invariant combinations revealed earlier by the AS considerations [8-10]. Putting the studies [8-10] in perspective [1,3] provides a deeper meaning of the seemingly unrelated concepts: (i) the Noether’s theorem, (ii) the AS of Hamiltonians, and (iii) the rotational invariants and moments of CF Hamiltonians. Considerations of the Noether’s theorem [1] reveal hitherto unrealized implications for the properties of CFP datasets obtained from fitting the theoretical energy levels to the experimental data [3]. Utilizing the results [1], the CFP datasets for RE$^{3+}$ ions in LiYF$_4$ were thoroughly reviewed and systematized in [2] (see, Section 8).

An important question in CF studies is to what extent the CFPs obtained for the same ion/host system by various authors are compatible and reliable. The quantity, which bears on these aspects, is the ‘rhombicity’ ratio [10,11] defined as $\lambda = B_2^2 / B_0^0$ in the extended Stevens (ES) notation [6,12] and $\kappa = \text{Re}B_{22} / B_{20}$ in the Wybourne notation [6,7]. Due to the intrinsic property of orthorhombic [11] and lower symmetry CF Hamiltonians [10], this ratio can be confined to the standard range \{0, 1\} and
respectively, by choosing a proper axis system [10,11]. The standardization idea [11] was further extended to the higher-order CF terms and zero-field splitting (ZFS) terms [6,7] terms for orthorhombic [11] and monoclinic [10] symmetry. The computer package CST [13,14] was developed to facilitate (unit and notation) conversions [6,7,12], standardization [10,11], and transformations [12]. Since for any meaningful comparison the CFP and ZFSP datasets must be expressed in the same axis system, this package provides a useful tool for comparison of apparently different but physically equivalent datasets expressed in various notations and axis systems. Pertinent references for extensive applications of the standardization idea to ZFSP and CFP datasets can be found in [3].

Most recently, seeking an answer to the question: “Can the low symmetry crystal (ligand) field parameters be considered compatible and reliable?” posed in [3] we considered several fundamental aspects important for interpretation of the experimental and theoretical CFP datasets as well as their compatibility and reliability. The considerations [3] provide framework for re-consideration and clarification of various intricate ‘low symmetry’ aspects in CF studies, which have not been fully understood so far. These aspects are discussed in details in Section 7. The framework developed in [3] was utilized to reanalyse the CFP datasets for Nd$^{3+}$ in NdGaO$_3$ and Pr$^{3+}$ in PrGaO$_3$ [4] and rare-earth nickelates RNiO$_3$ [5]. Work is currently ongoing on the non-standard CFPs for the high temperature superconductors and related systems.

3. Overview of basic concepts and notations
For clarity, in this Section we define in the nutshell the basic concepts and notations pertinent for the considerations in the following Sections. Detailed discussion of the general properties of CF (ZFS) Hamiltonians and CF (ZFS) parameters and pertinent references can be found in [1,3] ([6,7]).

The concept of crystal-field was introduced to describe the effect of the electric field due to the surrounding ligands acting on the paramagnetic ion [1,3]. Within a given $J$- (or $L$-) multiplet the general form of the CF Hamiltonians can be expressed in terms of the ES operators [6,12] as:

$$H_{CF} = \sum_{kq} B_{kq}^B O_{kq}^B (J_x,J_y,J_z)$$

where the nature of the ES operators $O_{kq}^B$ in equation (1) is explicitly indicated as being the functions of the total angular $J$ (or total orbital $L$) momentum operators. The Wybourne notation utilizing the spherical tensor operators $C_{kq}$ [1,3,6] is more widely used in the optical spectroscopy area. Within a given $nl^m$ configuration $H_{CF}$ in the compact form (as defined in Ref. 6) is given by:

$$H_{CF} = \sum_{kq} B_{kq}^B O_{kq}^B$$

whereas in the expanded form [6] using explicitly the pairs of the operators with $\pm q$, $H_{CF}$ is given by:

$$H_{CF} = \sum_k \left[ B_{k0} C_{k0} + \sum_{q=1}^k \left( \text{Re} B_{kq} \left[ C_{kq} + (-1)^q C_{k-q} \right] + \text{Im} B_{kq} \left[ C_{kq} - (-1)^q C_{k-q} \right] \right) \right]$$

Note that the CFPs $B_{kq}^B$ in the ES notation are real, whereas the CFPs $B_{kq}$ in the Wybourne notation are complex, i.e. involve both real (Re) and imaginary (Im) parts. Conversion relations between the ES, Wybourne, and several other operator notations existing in the literature are provided in the comprehensive review [6].

The concept of effective spin Hamiltonian (SH) has been introduced to describe the splitting to the lowest orbital singlet ground state with the electronic spin $S$ of a paramagnetic ion [6,7]. The derivation procedure and the effective nature of SHs were thoroughly discussed in [6,7]. Various meanings of ‘spin’ may apply for a particular ‘spin’ system: electronic (real), effective, or fictitious ‘spin’. Within a given effective spin $S$ multiplet the SH form [6], including the second-order conventional ZFS term ($D$-tensor) and the Zeeman electronic term ($g$-tensor) is given by:
\[ H_{\text{spin}} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mu_{B} g_{\text{B}} \mathbf{S} = \mathbf{H}_{\text{ZFS}} + \mathbf{H}_{\text{Ze}} \]  

(4)

In terms of the ES operators [12] the general form of the ZFS term is nearly identical with \( H_{\text{CF}} \) in equation (1), except for the odd-order terms admissible only for \( H_{\text{CF}} \) [6,7] and replacement of \( B_{k}^{q} \) (CF) by \( B_{k}^{q} \) (ZFS) and \( J_{i} \) by appropriate ‘spin’ components \( \tilde{S}_{i} \). Hence, the physical nature of the CF and ZFS quantities is completely different. However, there is a wide-spread confusion in the literature between the CF and spin Hamiltonians as well as the respective quantities. Various degrees of this confusion were discussed in the review [6] and more recently in [7,15].

Several theoretical models to compute the CFPs for transition ions in crystals exist in the literature [3]. A formula relating various CF components has often been employed to reduce the number of free parameters for fittings [4,5]:

\[ B_{n}^{m(\alpha)} = \left( \gamma_{n}^{m(\alpha)} \right) B_{n}^{0}, \]

(5)

where \( \alpha = c \) and \( s \) denotes CFP components \( B_{k}^{q} \) (ES) and \( B_{k}^{-q} \) (ES) [12], respectively. The geometrical coordination factors \( \gamma_{n}^{m(\alpha)} \) (\( \alpha = c, s \), s) equivalent to Hutchings’ \( \gamma_{n}^{\alpha m} \) [4], are to be calculated from the crystallographic data using, e.g. point charge model (PCM) or equivalent models reviewed in [3].

4. Algebraic symmetry (AS) of Hamiltonians for continuous rotational symmetry (CRS) cases

CRS cases comprise the following symmetry classes: hexagonal II (\( C_{6}, C_{3h}, C_{6h} \)), tetragonal II (\( C_{4}, S_{4}, C_{4h} \)), trigonal II (\( C_{3}, S_{6} \)), and monoclinic (\( C_{2}, C_{1h}, C_{2h} \)), i.e. the so-called uni-axial symmetries, as well as triclinic (\( C_{i}, C_{1} \)) symmetry. The concept of AS of Hamiltonians has been introduced by Clark in 1971 (Ref. 57 in [1]) to describe the symmetry of the characteristic equation of Hamiltonians [8-10,1]. Regrettably, the concept of the AS has been underutilized - apart from the applications [8-10,1] the Clark’s paper [8,1] remains largely forgotten as revealed by a SCI citation search.

Considerations of the AS of CF Hamiltonians were carried out for tetragonal II [8], hexagonal II and trigonal II [9], and monoclinic [10] symmetry. These considerations revealed the existence of some conserved quantities (CQs) invariant under rotations around the axis specifying the given CRS. CQs are in fact invariant combinations (ICs) of the CFPs. The following ICs were identified explicitly [8-10]: the first-order ICs, which comprise the CFPs with \( q = 0 \):

\[ B_{2}^{0}, B_{4}^{0} \text{ and } B_{6}^{0}, \]

(6)

the second-order ICs of two types:

- type (i): \( \left( B_{k}^{+q} B_{k}^{-q} \right)^{2} + \left( B_{k}^{+q} B_{k}^{-q} \right)^{1/2} = \| \mathbf{v}_{kq} \| \]

(7)

- type (ii): \( B_{k}^{+q} B_{k}^{+q} + B_{k}^{-q} B_{k}^{-q} = \mathbf{v}_{kq} \cdot \mathbf{v}_{kq} = v_{kq} \cos(\beta_{k}^{+q} q) \).

(8)

The higher nth-order (n>2) ICs exist for the cases which require solution of the characteristic equations of the order greater than 2. The third- (n=3) and fourth-order (n=4) ICs were explicitly derived for trigonal II [9] and monoclinic [10] symmetry and their basic types were discussed in [1]. The 2nd-order CQs have a geometrical meaning [8-10,1]: type (i) - the length of a ‘vector’ \( \mathbf{v}_{kq} \), the type (ii) - the angle between any two possible vectors \( \mathbf{v}_{kq} \) and \( \mathbf{v}_{k'q} \) (see, also Section 6.1).

The fact that the ICs, and not separate CFPs involved in the ICs, appear in the coefficients of the characteristic equation of CF Hamiltonian has an important consequence for fitting experimental spectra to the theoretical energy levels. Three approaches to fitting the experimental spectra for RE ions at sites exhibiting one of the five symmetry types in question exist in the literature [8-10,1]. In the approximated (A) approach the actual point-symmetry group is approximated by a higher group, thus omitting the CFPs with negative q in Eq. (1) (or equivalently the Im parts of CFPs in Eqs (2) and (3)). In the reduced (R) approach one component of a pair of CFPs with +q and -q is set to zero. In the complete (C) approach all CFPs admissible by group theory for a given site symmetry are allowed in the fittings. Various conventions and implications regarding each approach were discussed in [1].

Critical examination of the literature reveals various inconsistencies in the experimental determination...
of the low symmetry CFPs [8-10,1-5]. The studies [8-10] established that determination from fitting experimental spectra of the magnitudes and relative signs of all CFPs predicted by group theory is impossible for CRS cases. However, the relationship between the Noether’s theorem [1] and the AS of CF Hamiltonians has only recently been noticed (see, Section 6).

5. Rotational invariants and moments of CF Hamiltonians
Since various authors often use different axis systems for the same ion/host system, the rotational invariants $S_k$ have been introduced by several authors [1,3] to measure the strength of the CF terms; in the Wybourne notation:

$$ (S_k)^2 = \frac{1}{2k+1} \sum_q |B_{kq}|^2. \quad (9) $$

Equivalent expressions in the ES notation exist [1,3,10,11]. The quantities $S_k$ are the 2nd-order rotational invariants [1] and provide an additional check of compatibility of the original and transformed CFPs [12-14]. The 3rd- and 4th-order rotational invariants, i.e. combinations of three and four CFPs, respectively, were also introduced [1]. However, as shown in [1] such hexagonal and cubic invariants carry no new information, since they are reducible to the first-order ICs in Eq. (6).

The $n^{th}$-order CFPs rotational invariants are related to the $n^{th}$-order (spectral) moments $\sigma_n(\alpha LSJ)$ of $H_{CF}$ as follows [1]:

$$ (\sigma_n(\alpha LSJ))^n = (1/(2l+1))\text{Tr}(H_{CF})^n. \quad (10) $$

It appears that the invariant properties of the $n^{th}$-order moments as well as their relationships with the CFPs and the CQ predicted by the AS of CF Hamiltonians and stipulated by the Noether’s theorem have not been explicitly considered so far [1]. For a more detailed discussion of the rotational invariants and moments of CF Hamiltonians we refer to [1].

6. New look at the CRS cases in CF studies from the point of view of the Noether’s theorem
6.1. Noether’s theorem and continuous rotational symmetries
In [1] we considered generalization of CF and ZFS Hamiltonians in the form of a generic Hamiltonian:

$$ H = \sum A_{lm} \chi_{lm}(X), \quad (11) $$

where $A_{lm}$ denote the parameters associated with a given generic type of the tensor operators $\chi_{lm}(X)$ of the specific angular momentum $X(X_x, X_y, X_z)$ operators, expressed in a given axis system (x, y, z). Note that the generic symbols $\chi_{lm}$ and $A_{lm}$ used in Eq. (11) do not define yet another tensor-operator notation, an abundance of which already exists in literature [6,7] but may represent any of the various sets of tensor operators and associated parameters. Since the arguments [1] are based on symmetry requirements, which apply to all types of Hamiltonians (11), the general conclusions concerning the implications of the Noether’s theorem are valid for all such Hamiltonians.

The symmetry aspects inherent in each of the CRS cases were discussed in details in [1]. Various formulations of Noether’s theorems, which utilize the geometrical symmetries, from introductory ones to advanced mathematical ones, available in the literature were discussed in [1]. Most pertinent for our consideration is the formulation given by Hill & Lederman (2001; Ref. 2 in [1]): “For every continuous symmetry of the laws of physics, there must exist a conservation law. For every conservation law, there must exist a continuous symmetry.” Hence, the canonical Noether’s theorem implies, for given symmetry transformations of the coordinates, the existence of the associated CQs, which are functions of the parameters describing a given classical or quantum system. This theorem should, in principle, apply also to any CF Hamiltonian invariant under CRS.

Here we can only afford to recap the major findings achieved in [1]. As argued in [1] for the CRS cases there must exist associated conserved quantities, i.e. polynomial functions of the CFPs; in general, the generic $A_{lm}$ ones in Eq. (11). Existence of such quantities ensures the physical equivalence of the CFP datasets interrelated by the CRS transformations applicable to the cases in question. The
central idea put forward in [1] and arising from the canonical Noether’s theorem for the CF and equivalent Hamiltonians invariant under CRS is encapsulated in Theorem 1:

If the CF Hamiltonian defined in Eq. (1) (and (2) & (3); in general, any Hamiltonian of the type in Eq. (11)) is invariant under CRS, then several quantities of various order in the CF parameters $B_i^q$ (and equivalent ones; in general, the associated $A_{im}$ ones) are conserved.

By ‘conservation’ we mean the invariance of such quantities under the CRS operations. Analytical rigorous derivations of the CQs in question may be appealing to algebraists and quantum mechanical theorists. Instead, we have exploited [1] the AS results [8-10], which provide a direct proof of Theorem 1 for all symmetry cases in question, except of triclinic symmetry not dealt with in a similar way yet. The studies [8-10] have, in fact, revealed the existence of several “invariant combinations” (ICs) in the characteristic equations of monoclinic or higher CRS CF Hamiltonians. ICs are polynomial functions of CFPs of the form: $f\{(B_i^q)^j \cdot (B_k^q)^m \cdot (B_l^q)^{l}\}$, with various values of $(k, q)$ in each term and the power coefficients $(i, j, m, l)$. Theorem 1 and the AS considerations enable us [1] to put forward Conjecture 1:

The “invariant combinations” (ICs) revealed by the AS considerations and categorized above are the CQs stipulated by the canonical Noether’s theorem applied to the CF Hamiltonians in question (Theorem 1).

The ICs (CQs) identified by the explicit AS considerations [8-10] as specific combinations of CFPs arise naturally from the Noether’s theorem. Theorem 1 and Conjecture 1 establish a direct link between the Noether’s theorem and the AS of CF Hamiltonians invariant under CRS. The geometrical meaning of the 2nd-order ICs in Eqs (7) and (8) was illustrated in [1] using a two- and three-dimensional representation in the CFP space, respectively. The vexing question if a single conservation law can sum up all the ICs has also been discussed in [1]. The ramifications of Theorem 1 and Conjecture 1 are considered in Section 6.2.

6.2. Implications of the canonical Noether’s theorem and the conserved quantities

The existence of the CQs stipulated by Theorem 1 and Conjecture 1 has profound practical implications for interpretation of experimental CFP datasets for the CRS cases. For example, for tetragonal II symmetry [8] only the ‘length of the vector’ $|v_{44}| = (\{B_4^q\}^2 + \{B_4^{-q}\}^2)^{1/2}$, equation (7), can be experimentally determined. Hence, the approach C, which attempts to determine independently the values of both $B_4^q$ and $B_4^{-q}$, appears inappropriate. Since $|v_{44}|$ is nothing else but one of the CQs stipulated by the Noether’s theorem, this limitation is a direct implication of this theorem.

The properties of the CQs and their implications were summarized in Corollaries [1] listed below. Corollaries 1 to 3 generalize the conclusions arising from the AS considerations [8-10] and bear on interpretations of the experimental CFPs and fitting procedures. Implications specific for interpretation of the approach C and R were summarized in Corollaries 4 and 5 thus providing new deeper meaning of these approaches.

**Corollary 1.** The coefficients of the characteristic equations of the CF Hamiltonians described by the Theorem 1 are functions of the admissible CQs defined by Conjecture 1 only.

**Corollary 2.** Only the CQs can be directly and independently determined from fitting the experimental energy level structure to the theoretical energy levels.

**Corollary 3.** The CQs of the order $n = 1$ determine directly the magnitudes and the signs of the CFPs $B_i^q$ with $q = 0$, whereas those of the order $n \geq 2$ determine the magnitudes of the allowed combinations of the CFPs and the relative signs of $B_i^q$ with $q \neq 0$.

**Corollary 4.** There exists one to many correspondence between the CQs and the magnitudes of the CFPs with $q \neq 0$ determined in the approach C.
**Corollary 5.** There exist one to one correspondence between the CQs and the magnitudes of the CFPs with \(q \neq 0\) determined in the approach \(R\) for each specific choice of the CF parameter reduced to zero.

Corollary 1 establishes the link between the coefficients of the characteristic equations of the CF Hamiltonians and the CQs. The consequences of the invariance of CF Hamiltonians under CRS stipulated by the Noether’s theorem and encapsulated in Corollaries 2 to 5 provide a new insight into the symmetry properties of such Hamiltonians and CFPs. The ramifications of the present considerations provide a solid basis for interpretation of experimental CFP datasets appearing in the literature. Our considerations reveal that various aspects not fully realized in the literature as yet require reinterpretation, e.g. the feasibility of determination of CF parameters from fitting experimental spectra and the reduction of the existing higher-order rotational invariants for hexagonal type II symmetry and cubic symmetry to combinations of primary lower-order invariants. The novel approach presented in [1] enables adoption of better fitting strategies utilizing the well-defined CQs, which are invariant under CRS. The considerations enable also to solve the long-standing problem, i.e. which CF parameters can be determined from fitting the experimental energy level structure to the theoretical energy levels [1].

7. **Re-consideration and clarification of various ‘low symmetry’ aspects in CF studies**

As continuation of the studies [1,2] we considered the fundamental, yet hitherto not fully understood, intricate properties of CF Hamiltonians. The studies [3-5] are briefly summarized below. Clarification of the intricate aspects in question has enabled us to provide a general framework aimed at achieving an increased compatibility and reliability of CFP datasets for transition ions at low symmetry sites in crystals. This framework may be especially useful for trivalent lanthanides in technologically important low symmetry hosts for which only limited energy-level data are available.

7.1. **Selection of the axis systems for various symmetry cases and their implications**

The crystallographic axes \((a, b, c)\), the local site symmetry axes, and the ‘natural’ choices of the axis system \((x, y, z)\) for the CF Hamiltonian were discussed for various symmetries in [3]. In short, for given site symmetry: hexagonal type II \((C_6, C_{3h}, C_{6h})\) - there exist only one sixfold axis \((C_6)\); axial type II, i.e. tetragonal II \((C_4, S_4, C_{4h})\) and trigonal II \((C_3, S_3)\) - there exist only one fourfold and one threefold local site symmetry axis, respectively; orthorhombic \((D_2, C_{2v}, D_{2h})\) - there exist three \(C_2\) mutually perpendicular local site symmetry axes, which may or may not coincide with the axes \((a, b, c)\). This leads to additional complications discussed in [3].

For monoclinic site symmetry \((C_2, C_{1h}, C_{2h})\) three complications occur [3]: (i) the vectors \((a, b, c)\) may not form a Cartesian coordinate frame - then an approximate \(c^*\) axis is chosen perpendicular to the plane \((a, b)\); (ii) only one local site symmetry \((C_2)\) axis (or plane) exists defining the unique monoclinic direction \((C_M)\) – this yields three choices of labeling the \(C_M\) direction: \(C_M \parallel z\), \(C_M \parallel y\), or \(C_M \parallel x\), each corresponding to different yet physically equivalent form of the CF (ZFS) Hamiltonian; (iii) once a specific axis is fixed along the \(C_M\) direction, a problem arises how to select the other two axes, e.g., \(x\) and \(y\) in the case of \(C_M \parallel z\) - consequently, the remaining two axes may be selected arbitrarily and hence for monoclinic symmetry an infinite number of distinct yet physically equivalent CFP datasets may be generated in two independent ways.

For triclinic site symmetry \((C_1, C_i)\) there exist no single local site symmetry axis, whereas for triclinic space groups the crystallographic axes \((a, b, c)\) do not form a mutually perpendicular set. This renders the choice of the axis system \((x, y, z)\) completely arbitrary. Due to the lowest symmetry, a number of specific intricacies concern triclinic CF Hamiltonians. They are dealt with in a separate section in [3] and are too extensive to cover in details here. The major point is that there exist an infinite number of identical and physically equivalent forms of triclinic CF Hamiltonians each associated with a distinct yet physically equivalent CFP dataset.
7.2. Types of CF parameters and their properties
In [3] we identified three types of CFPs occurring in the CF/LF studies: (i) **symbolic CFPs** and two types of **numerical CFPs**: (ii) **theoretical CFPs** and (iii) **fitted CFPs**. Each type has specific intrinsic properties and general ones in regard to the axis system in which the CFPs are (presumably) expressed [3]. This novel classification helps to clarify the related intricate aspects.

The **symbolic CFPs** are defined by the CF Hamiltonians employed for a given ion-host system and hence underlie both the theoretical calculations and fitting procedures. Most often the symmetry-adapted (x, y, z) axis systems are adopted explicitly or implicitly in CF/LF studies since they yield the smallest number of the non-zero symbolic CFPs. The axis systems defined for CF Hamiltonians and hence the symbolic CFPs serve as “input” necessary to set up the CF calculations. The **theoretical CFPs** are computed using model calculations. Clear definitions of the axis system (x, y, z) in which the positions of ligands are given, e.g. w.r.t. to the axes (a, b, c), are indispensable for any model calculations. The existence of equivalent theoretical CFP datasets in the literature arise from ‘different (implicit) choices of coordinate system’ [3].

The **fitted CFPs** are obtained from fitting the experimental CF energy levels and/or intensity data to the theoretical predictions based on the symmetry-adapted CF Hamiltonians. Our extensive survey of CF data and their analysis have enabled us to make the following statements [3]. (A) It is feasible to specify clear definitions of the axis system (x, y, z) only for the CF Hamiltonians and thus the symbolic and theoretical CFPs. (B) The conventional techniques employed to determine CFPs for the transition ions in crystals provide information primarily about the experimental CF energy levels and in some cases also about the intensity of the transitions. These techniques provide no ‘directional’ information, unlike most of EMR techniques [6,7]. (C) Our survey reveals two kinds of attitudes concerning the axes for the fitted CFP datasets for a given ion/host system. By implication, the more theoretically inclined researchers seem to share the presumption that such axes are just identical with the axes (x, y, z) adopted initially for the CF Hamiltonian. Another attitude manifested by majority of researchers, especially experimentalists, consists in simply avoiding any explicit mention of the axis system adopted for their fitted CFP datasets. It turns out that the interpretation of the axis systems for the fitted CFP datasets amounting to their tacit equivalence with the axis systems pertinent for the symbolic or theoretical CFPs (see the statement (A) above) does not stand up to the truth. In fact, no such equivalence exists, since no particular axis system can be obtained from fitting the experimental CF energy levels determined by ‘non-directional’ techniques (see the statement (B) above).

7.3. Introduction of a new notion of a nominal axis system for the fitted CFP datasets
The apparent dilemma that there is no prescription how to assign an axis system to the fitted CFPs bears on the compatibility of CFP datasets since the knowledge of the axes is essential for any meaningful comparison. To solve this dilemma we have introduced [3] a novel notion of a ‘nominal’ axis system defined by the statement: any CFP dataset fitted using non-directional techniques must initially be considered as expressed in an undefined ‘nominal’ axis system denoted, e.g. by (x₀, y₀, z₀).

Ample justification for this statement coming from the intrinsic properties of the CF Hamiltonians in question and the nature of the CF calculations carried out using the least-squares fitting procedures was provided in [3]. The orientation of a ‘nominal’ axis system w.r.t. the crystallographic axes is not known and cannot be assigned based on the axes used for $H_{CF}$. In conclusion, the fitted CFP datasets reported in the literature cannot be automatically assigned to any, even well defined, specific axis systems. Conversely, one cannot determine any axis system from fittings. These findings represent a marked difference with the wide-spread perception that the axis system once defined as “input” can be carried over and assigned to the fitted CFPs. The notion of the ‘nominal’ axis system solves the existing confusion concerning the fitted CFPs.

7.4. Implications of the Noether’s theorem and the AS of CF Hamiltonians
The existence of several CQs stipulated by the Noether’s theorem and AS of CF Hamiltonians invariant under CRS bears on the feasibility of determination of CFPs from fitting experimental
spectra. The novel approach [1] enables adoption of better fitting strategies utilizing the well-defined CQs for these symmetry cases [2,3]. The constraints inherent in any least-squares fitting of CFPs can be classified as (i) ‘computational’ - related to the sufficient number of experimental CF energy levels available for meaningful fitting, and (ii) ‘physical’ - applicable to CF Hamiltonians invariant under CRS. The considerations of the AS [8-10,1] reveal that for such Hamiltonians not all the non-zero CFPs predicted by group theory for a given symmetry, of total number \( N_G = \sum_k N_G(k) \), where \( N_G(k) \) is the number of independent k-th order CFPs, can be determined independently from least-squares fittings of experimental data. Only certain combinations of CFPs (see Section 4) can be independently determined for such symmetry cases due to the intrinsic CF Hamiltonian properties. In the set of all vectors \( v_{kq} \) formed by the possible pairs (+q and -q) of the non-zero k-th order CFPs admissible for a given symmetry, only one component of one vector \( v_{kq} \) at a time may be set to zero. This ‘(\( N_G -1 \))’ constraint limits the number \( N_D \) of the independently determinable CFPs to \( (N_G -1) \) for the uni-axial symmetry as well as for triclinic symmetry cases [3]. The approach utilizing \( (N_G -1) \) CFPs for fitting correspond to the approach R. The \( (N_G -1) \) physical constraint holds irrespective of the computational constraint. Hence, even if a sufficiently large number of experimental CF energy levels is available for fittings, one cannot meaningfully determine all \( N_G \) CFPs for these symmetry cases. This may render the CFP datasets obtained using the approach C potentially unreliable [3]. Various approximations concerning the non-zero CFPs adopted to reduce the number of CFPs involved in fitting procedures have also been discussed in [3].

7.5. Correlation properties among CFP datasets and the standardization idea

An infinite number of physically equivalent CFP datasets of any type can be obtained by applying arbitrary transformations to the original CFPs. Such transformed and original CFPs are mutually ‘correlated’. However, the symmetry-adapted form of CF Hamiltonian is preserved only for specific transformations. The transformations preserving CF Hamiltonian form and yielding equivalent CF Hamiltonian forms [3] have special importance since they generate easily identifiable physically equivalent CFP datasets. Correlation properties of such CFP datasets can be utilized to improve their overall compatibility and reliability [3]. Three types of such transformations were identified for low symmetry cases [3]: (I) the standardization transformations (see Section 2) for the orthorhombic and monoclinic symmetry cases [10,11] as well as triclinic ones [3], (II) transformations applicable to \( H_{CF} \) for continuous uni-axial rotational symmetry, and (III) transformations applicable to the three forms of monoclinic \( H_{CF} \). In relation to the Noether’s theorem [1] we note that the standardization [10,11] of the orthorhombic and lower symmetry Hamiltonians (including CF, ZFS, and related ones) involves continuous permutational symmetry, and not rotational symmetry, whereas the transformations type (II) and (III) represents implications of the Noether’s theorem and AS of CF Hamiltonians.

As a consequence of the transformations type (I) to (III), there exist several equivalent CF Hamiltonians with numerically different values of CFPs, while each CFP set must yield identical energy levels. Hence fittings may yield several equivalent CFP datasets in various regions of the multidimensional CF parameter space. The question how to identify such distinct yet correlated CFP datasets was discussed in details in [3] for each type of transformations (I) – (III). Keeping in mind the possibility that the least-squares fittings may return both global and local minima, the problem arises how to correlate the various data points resulting from independent fittings. The notion of a ‘common’ nominal axis system meant as any transformed nominal axis system required to yield, after transformation of an original non-standard CFP dataset, the transformed standardized dataset located in the standard region in the CF parameter space, plays an important role in these considerations.

The interrelationships between physically equivalent CFP datasets located in different regions in the CF parameter space were graphically visualized [3]. The advantages of the standardization [10,11] call for a wider acceptance of unified guidelines for presentation of CFP datasets proposed in [3].
7.6. The rotational degrees of freedom and the reduction of the number of independent CFPs

These aspects are of special importance for triclinic symmetry cases and have aroused some controversy in the literature. To summarize the extensive discussion [3], for each CRS, including triclinic symmetry, the number of independent rotational degrees of freedom $W = 1$. The physical constraint discussed above for these cases yields a reduction of the number ($X$) of CFPs which can be independently fitted from experimental data. Even if there is sufficient number of experimental CF energy levels, i.e. when the computational constraint is satisfied, we have the relation: $X = N_\text{G} - W = N_\text{G} - 1$ [3].

7.7. Extension of the multiple correlated fitting technique

The idea of utilization of additional information contained in the intrinsically correlated CFP datasets underlies the multiple correlated fitting technique (MCFT) originally proposed in [10]. MCFT has, for the first time, been practically implemented using the experimental CF energy levels for Nd$^{3+}$ in YAG and LaF$_3$ [16]. The study [16] has also revealed misinterpretations of the original CFPs due to inadvertent choices of different ‘representations’, i.e. different nominal axis systems [3] corresponding to different regions in the CF parameter space. MCFT provides also guidance on the selection of most appropriate ‘representation’ for the final fitted CFP dataset. The three types of physically equivalent CFP datasets discussed in Section 7.5 enable further extension of the capabilities of MCFT [3]. The extension includes a quantitative method for CFP datasets comparison based on the closeness parameters defined for the CFP “vectors” [3]. Hence the degree of correlation between independently fitted CFP datasets and expressed in the same nominal axis system may be quantitatively measured.

The basic steps involved the MCFT procedure [16] are summarized in [3].

8. Application of the Noether’s theorem and low symmetry aspects to CFP datasets

The CQs stipulated by the Noether’s theorem were utilized in [2] for comparative analysis of the CFP datasets for the RE$^{3+}$ ions at tetragonal type II $S_4$ symmetry sites in LiYF$_4$, for which sufficiently large amount of data is available across the whole 4f$^N$ series. Five CQs stipulated by the Noether’s theorem for $S_4$ symmetry, namely, $B_{20}$, $B_{40}$, $B_{60}$, $|v_{44}|$, $|v_{64}|$, and the angle $\beta_{44}^{64}$ as well as the ratio $\text{Im} B_{64}/\text{Re} B_{64}$ and the 2nd-order rotational invariants $S_k$ were considered. Pertinent CFP datasets together with the calculated associated quantities were tabularized and the variations of $B_2^0$, $B_4^0$, $B_6^0$, $|v_{44}|$, and $|v_{64}|$ vs $N$ were presented in graphs [2].

This systematics facilitated consideration of trends across the 4f$^N$ series among the CFPs and derived quantities. Knowledge of such trends enables identification of unreliable CFPs and prediction of CFPs for ions for which no or little data are available. The major observations for RE$^{3+}$:LiYF$_4$ are as follows [2]. The available data show for most ions a very large spread of the original CFP values for the same 4f$^N$ ion, thus indicating inconsistency of several CFP datasets. Since the ratio $\text{Im} B_{64}/\text{Re} B_{64}$ used earlier in the literature is not a CQ it is inadequate for comparative purpose, whereas the angle $\beta_{44}^{64}$ as a CQ is more convenient to deal with than the ‘scalar product’ $v_{44} \cdot v_{64}$. The values averaged over the available data points for each ion show no well-defined trends across the RE$^{3+}$ series in $B_k^0$, whereas a weak diminishing trend with increasing $N$ in $|v_{44}|$ and $|v_{64}|$. Various aspects bearing on the erratic CFP behavior were discussed [2]. The intricacies concerning the approach R and C were also clarified providing guidelines for identification of the CFPs and associated quantities reliably determinable from fitting the experimental CF spectra to the theoretical energy levels.

The applications [2] of proposed method of analysis and presentation of experimental and theoretical data [1] amply illustrate the usefulness of the CQs stipulated by the Noether’s theorem and their advantages over other derived quantities used in the literature as well as the advantages of the approach R and the disadvantages of the approach C and A. The systematics presented in [2] has
implications for interpretation of the published CFP datasets and their reliability and thus may bring about an increased reliability of the CFP datasets in future.

Concerning other practical applications of the results presented in Sections 6 and 7, better understanding of the intricate properties of low symmetry CF Hamiltonians has enabled consideration of specific important aspects bearing on compatibility and reliability of the CFP datasets for Nd$^{3+}$ in NdGaO$_3$ and Pr$^{3+}$ in PrGaO$_3$ [4] and rare-earth nickelates $R$NiO$_3$ ($R$ = Pr, Nd, Sm, Eu, and Pr$_{1-x}$La$_x$, $0 \leq x \leq 0.7$) [5]. This includes: (i) clear definition of the axis systems, (ii) relevant coordination factors used in the point charge model, (iii) multiplicative factors missing in some CFP datasets, (iv) reduction of the number of the independent CF parameters, and (v) conserved quantities existing for monoclinic symmetry [4,5].

9. Conclusions and further readings
The summary of major findings arising from our recent studies concerning the symmetry properties of crystal/ligand field Hamiltonians and spin Hamiltonians presented in this review offers several advantages. This review provides all-in-one concise yet comprehensive treatment of the important problems dealt previously with in separate papers. The aspects considered here are crucial for better understanding of the procedures used to obtain the experimental CFP values, especially for low symmetry cases, and hence interpretation of the CFP datasets available in the literature. Clarification of these intricate aspects has enabled us to provide a general framework aimed at achieving an increased compatibility and reliability of CFP datasets for transition ions at low symmetry sites in crystals. It may be hoped that by making this general framework more accessible to general practitioners more meaningful interpretation and comparison of the CFP datasets may be carried out in future studies.

Concerning recent pertinent literature we note the following papers. Optical absorption spectroscopy in geosciences has been reviewed with focus on the basic concepts of crystal field theory [17] and quantitative aspects of crystal fields [18]. Generalization of the extended Stevens operators to higher ranks and spins and systematic review of the tables of the tensor operators and their matrix elements are provided in [19].

The paper by Mulak [20] proposing a parameterization scheme in which the number of the k-even triclinic CF parameters $N_c(k) = 5$, 9, and 13 can be reduced by 4, 8, or 12 for $k = 2$, 4, or 6, respectively, has been critically commented on in [3]. The inapplicability of such parameterization has recently been admitted [21]. However, the paper [21] adds more to the controversies concerning the low symmetry properties of CF Hamiltonians, which will be discussed separately.

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