PHYSICAL REVIEW B **67**, 174420 (2003)

Noether's theorem and conserved quantities for the crystal- and ligand-field Hamiltonians invariant under continuous rotational symmetry

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(Received 4 December 2001; revised manuscript received 26 December 2002; published 23 May 2003)

Applications of Noether's theorem to crystal-field (CF) and ligand-field Hamiltonians invariant under continuous rotational symmetry are discussed. Deeper meaning of the seemingly unrelated concepts of (i) Noether's theorems, (ii) the algebraic symmetry of Hamiltonians, and (iii) the rotational invariants and moments of CF Hamiltonians is considered and their interrelationships unraveled. Our investigations enable formulation of an important theorem and a conjecture on the conserved quantities stipulated by Noether's theorem for the CF Hamiltonians in question. Geometrical meaning of the second-order conserved quantities suggests feasibility of derivation of a conservation law encompassing all the conserved quantities identified. The existence of the conserved quantities has profound implications for interpretation of experimental CF parameter data sets, which are encapsulated in five corollaries. Our considerations reveal that various aspects require reinterpretation. This includes, e.g., (i) the feasibility of determination of CF parameters from fitting experimental spectra, and (ii) the reduction of the existing higher-order rotational invariants for hexagonal type-II and cubic symmetries to combinations of primary lower-order invariants. The approach presented in this paper enables adoption of better-fitting strategies utilizing the well-defined conserved quantities, which are invariant under continuous rotational symmetry.

DOI: 10.1103/PhysRevB.67.174420 PACS number(s): 75.10.Dg

I. INTRODUCTION

For reasons ranging from obtaining a deeper understanding of the underlying physics to practical implications for analysis of crystal-field (CF) [also referred to as ligand-field (LF)] spectra, it appears worthwhile to consider the deeper interrelationships that may exist between the seemingly unrelated concepts and aspects discussed in detail in Sec. II. This comprises, on one hand, Noether's theorems, which have profound theoretical significance to many areas of physics, since they utilize the geometrical symmetries of classical and quantum systems to obtain specific conservation laws as well as various associated conserved quantities, and, on the other hand, (i) the intricate properties of CF Hamiltonians invariant under continuous rotational symmetry, which have not to our best knowledge, been fully understood in the literature as yet, especially the underutilized concept of the algebraic symmetry of such CF Hamiltonians and its important implications for analysis of CF spectra, as well as (ii) the two interrelated general concepts, namely, (a) the CF rotational invariants and (b) the moments of CF Hamiltonians, which are defined for arbitrary symmetry CF Hamiltonians and which play a special role in the description of CF spectra. In brief, the canonical Noether's theorem implies, for given symmetry transformations of the coordinates, the existence of the associated conserved quantities, 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 continuous rotational symmetry, which includes five symmetry classes, namely, hexagonal II (C_6, C_{3h}, C_{6h}), tetragonal II (C_4, S_4, C_{4h}), trigonal II (C_3, S_6), monoclinic (C_2, C_{1h}, C_{2h}), and triclinic (C_i, C_1). Here, this problem will be discussed from another point of view.

It appears that researchers working in the CF-theory area (including one of the present authors, C.R.) have apparently not yet explored the potential interrelationships between the concepts and aspects outlined above. The algebraic symmetry of CF Hamiltonians invariant under continuous rotational symmetry has been considered for several symmetry cases by one of us as early as in 1985 (for references, see Sec. II). However, it had not been realized at that time that the ''invariant combinations'' of the CF parameters algebraically determined for specific symmetry cases may arise naturally as the conserved quantities stipulated by the canonical Noether's theorem applied to the CF Hamiltonians in question. On the other hand, it may be expected that such conserved quantities (invariant under continuous rotational symmetry) should be somehow related to the rotational invariants and hence the moments of CF Hamiltonians, which are defined for arbitrary symmetry and which are also conserved under rotations of the coordinates. One may also hope to arrive, as a direct consequence of Noether's theorem, at a general ''conservation law,'' which may possibly encompass all the conserved quantities in question.

It turns out that application of Noether's theorem and the associated conserved quantities stipulated by Noether's theorem, which should, as it seems intuitively obvious, be inherent for the CF Hamiltonians for each of the five symmetry classes involving continuous rotational symmetry, have not been explored as yet. Driven by both theoretical curiosity and the profound implications Noether's theorem may have for the CF studies, we attempt to fill this gap. The main aims of this paper are to unravel the interrelationships between the crucial concepts in question and discuss their implications. To achieve these aims, first in Sec. II we provide sufficient background for the present considerations by presenting in a nutshell the crucial concepts drawn from various areas of theoretical physics. Next we outline the basic properties of CF Hamiltonians in Sec. III, and in Sec. IV we consider the algebraic symmetry of CF Hamiltonians from the point of view of Noether's theorem. The relationships between the predictions of Noether's theorem as well as of the algebraic symmetry considerations, the concepts of CF rotational invariants, and the moments of CF Hamiltonians are considered in Sec. V. Comparative analysis and consequences of Noether's theorem for interpretation of the CF parameter (CFP) data sets for S_4 symmetry occurring, e.g., for rare-earth (RE) RE^{3+} ions in LiYF_4 revealed by our survey of recent literature, will be presented in a future paper. The systematic method of interpretation of experimental data proposed here may in turn bring about increased reliability of the CF parameter data sets for the future.

II. AN OVERVIEW OF CRUCIAL CONCEPTS AND ASPECTS

The geometrical symmetries of classical and quantum systems have been widely studied and exploited to simplify various theoretical problems. Various formulations of Noether's theorem(s), which utilize geometrical symmetries, from introductory[1,2] to advanced mathematical ones,[3–5] can be found in the literature. Formulations especially pertinent in the present context are ''If a system has a continuous symmetry property, then there are corresponding quantities whose values are conserved with time.''[3] and ''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.''[2] In classical mechanics, Noether's theorem leads to conservation of linear momentum, total energy, and angular momentum for the continuous symmetry being spatial displacement, time displacement, and rotation about an axis, respectively.[2,3] The distinction between various variants of Noether's theorems is not clear-cut in the literature. Some authors (see, e.g., Refs. 6–8, and references therein) use the following nomenclature concerning applications of Noether's theorems in classical theories: (i) Noether's first theorem establishes the connection between global symmetries and the conservations laws, and (ii) Noether's second theorem refers to the local symmetry of a system and implies existence of Noether's identities, whereas (iii) the connection between canonical continuous symmetry and conservations laws is referred to as the canonical Noether's theorem. Various applications of Noether's theorem(s) to specific classical and quantum-mechanical systems exist; see, e.g., Refs. 6–9, and references therein. According to Castaños *et al.*,[9] Noether's theorem asserts that, under certain conditions satisfied by a Lagrangian of the system $L = L(x_i, \dot{x}_i, t)$, to the symmetry transformation of the coordinate, x_i corresponds a conserved quantity (called also the Noether charge). These authors have derived explicit forms of the associated conserved quantities for several quantum-mechanical systems. Noether's inverse theorem can be used to establish the associated symmetry transformation.[9] Attempts have also been made using various methods, not involving Noether's theorems, to construct exact invariants for a variety of classical dynamical systems (see, e.g., Ref. 10, and references therein).

In the realm of CF (or LF) theory (see, e.g., Refs. 11–19, and references therein), numerous cases of CF Hamiltonians invariant under continuous rotational symmetry exist (see, e.g., Refs. 20–22, and references therein). Yet to the best of our knowledge, as a recent Science Citation Index (SCI) search indicates, no application of Noether's theorem(s) to such CF Hamiltonians has so far been discussed in the literature. Out of 11 Laue-symmetry classes (see, e.g., Refs. 12, 17, and 23), five classes yield CF Hamiltonians invariant under continuous rotational symmetry. The cases of transition ions at sites having such symmetry are also referred to as the low-symmetry cases, since the respective CF Hamiltonians involve so-called ''imaginary'' or ''low-symmetry'' CF parameters.[24] This includes the following point-symmetry groups (in descending symmetry order): hexagonal type-II (C_6, C_{3h}, C_{6h}), tetragonal type-II (C_4, S_4, C_{4h}), trigonal type-II (C_3, S_6), monoclinic (C_2, C_{1h}, C_{2h}), and triclinic (C_1, C_i) symmetries. A detailed consideration of the intricacies of the CF theory for the RE ions at low-symmetry sites in various crystals and a review the CF parameters (CFP's) appearing in the literature up to 1985 for the tetragonal II, trigonal II, hexagonal II, and monoclinic have been dealt with in Refs. 20–22. Several pertinent monoclinic, triclinic,[25] and tetragonal cases[26] have recently been under consideration by us. Note that the triclinic symmetry require separate consideration, since no symmetry-related coordinate axes exist for these cases.[25] Some pertinent references for low-symmetry CF studies may also be found in Refs. 12 and 14–17.

Independent developments in the CF-theory area, which potentially may be (and as we shall show in this paper, in fact, are) linked to the general aspects of Noether's theorems, are twofold. Of particular relevance are the concepts of the rotational invariants, including the equivalent one of the *norms* N_k, and the moments of CF Hamiltonians. The CF rotational invariants S_k, quadratic in the CFP's have been introduced by several authors.[27–33] Yet no formal derivation from ''first principles'' has been provided in the papers.[27–33] Independently, in the electron magnetic-resonance (EMR) area (for a review, see Refs. 34 and 35) the norms N_k of the zero-field splitting (ZFS) parameters have been introduced[36] and later related to the transformation properties of the normalized Stevens operators.[37] These quantities, which are conserved under arbitrary rotations of the coordinates, arise as a consequence of the transformation properties of the CF and ZFS Hamiltonians. The norms N_k have been used to a rather limited extent in the EMR area—see, e.g., Refs. 38–40. The quadratic CF rotational invariants S_2, S_4, and S_6 of CFP's as well as a combined quantity, namely, their average, representing the ''strength of the crystal field,'' have been used to a moderate extent by several authors (see, e.g., Refs. 41–52). The third- and higher-order invariants in CFP's have also been introduced[43] and discussed but only for the simplest symmetry cases, i.e., cubic and hexagonal, as reviewed by Yeung.[53] On the other hand, the rotational invariants of a given kth order have been shown to be in general related to the kth-order moments of CF Hamiltonians, thus not within the whole nl^N configuration but within an approximation of a given J multiplet.[29–31,42,47,53] The moments of Hamiltonians have also been defined in a general way for any Hamiltonian and have found useful applications in statistical spectroscopy in various areas, e.g., atomic, nuclear, and vibrational spectroscopies (see, e.g., Refs. 54–56, and references therein). The moments of N-particle Hamiltonians are also invariants of the unitary transformations of the basis in the model space.[56]

Another development in CF theory and related areas, which is potentially related to Noether's theorems, concerns another type of symmetry, namely, the algebraic symmetry of CF Hamiltonians defined, in general, as the symmetry of the characteristic equation of a Hamiltonian.[57] The concept of the algebraic symmetry has been applied originally by Clark[57] to the second-order Hamiltonians of a ''spin-Hamiltonian type'' having the form $H=\mathbf{A}\cdot\mathbf{J}+\mathbf{J}\cdot\mathbf{B}\cdot\mathbf{J}$, which occurs in many areas of physics and chemical physics. The first term may represent interaction with magnetic field, whereas the second term represents, e.g., nuclear hyperfine interactions (considered in detail in Ref. 57) or the ZFS terms studied by EMR.[34,35] For such a simple Hamiltonian it has been feasible to carry out analytical considerations of the algebraic symmetry. This has enabled[57] to derive polynomials in the ''symmetrized parameters,'' being combinations of the Hamiltonian parameters A_{ij} and B_{ij}. Clark[57] has shown that any polynomial function of the matrix elements of the Hamiltonian, which is invariant under all transformations of the frame of reference, can be written as a polynomial in the ''symmetrized parameters.'' One advantage of the algebraic symmetry considerations[57] was that the number of matrix elements to be calculated could be reduced. Other useful general properties arising from the existence of several invariant quantities being functions of the Hamiltonian parameters A_{ij} and B_{ij} have been discussed in Ref. 57. In particular, Clark[57] has provided solid theoretical justification for the axes conventions for reporting the principal values V_{ii} of the electric-field gradient used in nuclear magnetic resonance. The concept of ordering the principal values of interaction ''tensors'' is equivalent to the standardization of the orthorhombic second-order ZFS parameters introduced independently in the EMR area as reviewed in Ref. 58. The standardization idea, which is applicable both to the CF and ZFS Hamiltonians, has been extended to the fourth- and sixth-order terms[58] as well as to monoclinic and triclinic symmetries.[22] In relation to Noether's theorems we note that the standardization of the orthorhombic and lower-symmetry Hamiltonians (including CF, ZFS, and related ones) involves continuous permutational symmetry, and not rotational symmetry, being the focus of this paper, and hence requires separate consideration.

Regrettably, the concept of algebraic symmetry has been underutilized and the paper[57] remains largely forgotten, as revealed by a SCI citation search. The only applications of the algebraic symmetry are those by one of us to CF Hamiltonians invariant under continuous rotational symmetry for the RE ions at tetragonal II,[20] trigonal II and hexagonal II,[21] and monoclinic[22] symmetry sites. The considerations of the algebraic symmetry of such CF Hamiltonians have been carried out[20–22] not in an analytical way[57] but by using a ''brute-force'' method. By employing a computer algebraic programming, explicit solutions of the characteristic equation of the CF Hamiltonian within various J multiplets of RE ions at various symmetry sites could be obtained.[20–22] This has enabled to study the properties of the coefficients in the characteristic equations, which by their nature were combinations of the CFP's involved. The major findings arising from the algebraic symmetry considerations[20–22] concern the following aspects. First, several conserved quantities, being polynomial functions of first and up to third order in CFP's have been explicitly identified in the characteristic equations of CF Hamiltonians invariant under continuous rotational symmetry. Secondly, implications of the existence of the conserved quantities for the feasibility of determination of CFP's from spectral data have been elucidated. It has turned out that independent determination of the magnitudes and relative signs of all CFP's admissible by group theory for a given symmetry was not possible. Thirdly, the three approaches (C, R, and A—for definitions, see Sec. IV C) used in the literature in this regard have been critically examined[20–22] and various inconsistencies in the experimental determination of the low-symmetry CFP's have been pointed out. As revealed by SCI and literature searches, although these findings have been utilized so far by several authors[59–75] (see also Ref. 17), inconsistent CFP data sets for RE ions at low-symmetry sites still do appear in a number of papers.

III. GENERAL PROPERTIES OF CF HAMILTONIANS AND PARAMETERS

Here we discuss only the major aspects, which bear on the present considerations. Other pertinent theoretical aspects of the CF Hamiltonians, which parametrize the effect of the electric field due to surrounding ligands acting on the central paramagnetic ion, as well as the ZFS ones, which describe effectively the splitting of the spin states of the lowest orbital singlet in the absence of an external magnetic field, have been reviewed in Ref. 34 and more recently in Ref. 35. This includes a succinct description of the physical nature of the two Hamiltonians as well as clarification of the crucial terms, which are often confused with each other.[34,35] Especially widespread in the literature is the confusion between the actual ZFS and CF parameters as recently reviewed.[76] As a reference notation we use the general forms of the intraconfigurational CF Hamiltonian[11–19] $H_{CF'}$. Within a given J or L multiplet $H_{CF'}$ can be expressed[12,34,35] in terms of the extended Stevens' (ES) operators[37] as

$$H_{\mathrm{CF}}=\sum_{kq} B_k^q O_k^q(\mathbf{J_x},\mathbf{J_y},\mathbf{J_z}), \tag{1}$$

where the nature of the ES operators[37] $O_k^q(\mathbf{J_x},\mathbf{J_y},\mathbf{J_z})$ in Eq. (1) is explicitly indicated as being the functions of the total angular $\mathbf{J}$ (or total orbital $\mathbf{L}$) momentum operators. The Wybourne notation[11,34] is more widely used in the optical spectroscopy area.[11–19,47,53] Within a given nl^m configuration H_{CF}, in the *compact* form (as defined in Ref. 34) is given by[11,16,17]

$$H_{\mathrm{CF}}=\sum_{kq} B_{kq}C_{kq}\,, \tag{2}$$

whereas in the *expanded* form, i.e., using explicitly the pairs of the tensor operators with $\pm q$, H_{CF} is given by[34]

$$H_{\mathrm{CF}}=\sum_k \left(B_{k0}C_{k0}+\sum_{q=1}^{k}\{\mathrm{Re}\,B_{kq}[C_{kq}+(-1)^q C_{k-q}] + i\,\mathrm{Im}\,B_{kq}[C_{kq}-(-1)^q C_{k-q}]\}\right). \tag{3}$$

In addition to the ES operators[37] and Wybourne operators,[11,34] several other types of operators have also been employed in the literature as reviewed in Ref. 34.

Since the ES operators[37] belong to the class of tesseral tensor operators, whereas the Wybourne operators[11] belong to the class of spherical tensor operators,[34,35] the CFP's defined in Eq. (1) are all real, whereas, those in Eq. (2) are in general complex. Note that the negative components B_k^{-q} of the CFP's in Eq. (1) correspond to the imaginary parts of the CFP's in Eq. (3), $\mathrm{Im}\,B_{kq}$, whereas the positive ones B_k^{+q} to the real parts, $\mathrm{Re}\,B_{kq}$.[20,34] Since H_{CF} must be invariant under a given local site symmetry group G of a paramagnetic ion in crystal, the number of the admissible nonzero CFP's in Eqs. (1)–(3) can be determined by group theory.[11–19] A question arises as to whether all CFP's predicted by group theory can be independently determined. Full discussion of the forms of H_{CF} for the symmetry cases in question[20–22] and the intricacies involved has been given in Ref. 25. In brief, the CFP's can be experimentally determined by optical-absorption spectroscopy, inelastic neutron-scattering, and infrared spectroscopy techniques (see, e.g., Refs. 16–19), whereas the ZFS ones by the EMR techniques (see, e.g., Refs. 12, 13, 34, and 35), as well as by related spectroscopic and magnetic techniques, including magnetic susceptibility, magnetic anisotropy, and Mössbauer spectroscopy. The major difference between the various experimental techniques in question is the ability to determine the directional properties of a given transition ion located at a particular site in crystal. The EMR techniques, which, like electron paramagnetic resonance (EPR) and electron spin resonance, apply the external magnetic field with orientation varying in several different crystallographic planes, offering a deeper insight into the local site symmetry. This enables determination of the orientation of the symmetry axes at transition ion sites from the observed EMR spectra. However, the techniques, which probe the energy levels and the intensity of transitions only at zero external magnetic field, cannot provide such "directional" information. Thus the above CF experimental techniques can yield the values of the CFP's but cannot determine the orientation of the symmetry axes.[11,16–19] Likewise the zero-field EPR (Refs. 77 and 78) yields only the values of the ZFS parameters. This inherent limitation, which is most important for low-symmetry cases involving a large number of the parameters, is often not realized by experimenters. As a consequence, the low-symmetry CFP's have often been determined as if the orientation of the symmetry axes could be obtained from the least-squares fitting of the experimental and theoretical energy levels (see Sec. IV). These widespread-in-the-literature ambiguities in the CF parametrization make the CFP data sets unreliable and hamper reliable interpretation of the CFP data sets. The general methods employed in the CF/LF studies of determination of the axis systems for the CF Hamiltonians invariant under continuous rotational symmetry as well as the implications of various choices for interpretation of the CFP data sets appearing in the literature have recently been considered.[25] A general framework to achieve increased compatibility and reliability of CFP data sets for RE ions at low-symmetry sites in crystals has also been proposed[25] and applied to the apparently incompatible CFP data sets reported for Nd^{3+} (Pr^{3+}) in $\mathrm{NdGaO_3}$ ($\mathrm{PrGaO_3}$).

The important quantities employed in the CF and ZFS studies are the *rotational invariants* S_k (Refs. 29–33) and the equivalent *norms* N_k of the CF (ZFS) parameters.[34,36,37] For the normalized Stevens' operators[34–36] $O_k'^{q}$, N_k are defined as

$$N_k=\sum_q \{B_k'^{q}\}^2=\sum_q [B_k'^{q}]^2, \tag{4}$$

where $-k\leqslant q\leqslant +k$, whereas for the ES operators,[37] which are not "normalized," [34,37] they are defined as[22]

$$N_k=\{B_k^0\}^2+\sum_{q=1}^{k}\left(\frac{1}{c_q^k}\right)^2(\{B_k^q\}^2+\{B_k^{-q}\}^2). \tag{5}$$

The coefficients c_q^k are listed in Refs. 34 and 37. For the Wybourne notation the CF *rotational invariants* S_k are defined[22,29–33,47,53] as

$$(S_k)^2=\frac{1}{2k+1}\sum_q |B_{kq}|^2=\frac{1}{2k+1}N_k\,, \tag{6}$$

whereas the *norms*[26] are defined as

$$N_k=\sum_q |B_{kq}|^2=\{B_{k0}\}^2+2\sum_{q=1}^{k}[(\mathrm{Re}\,B_{kq})^2+(\mathrm{Im}\,B_{kq})^2]. \tag{7}$$

The quantities S_k and N_k in Eqs. (4)–(7) are invariant with respect to an arbitrary rotation of the axis system (see Sec. V). Hence, they were employed to measure the "strength" of the CF (Refs. 29–33, 47, and 53) and ZFS.[38–40] Another useful property of the quantities S_k is that they provide an additional check of the reliability of fitting of the experimental CFP's as well as of the consistency of the transformed CFP's expressed in different axis systems by various authors (see, e.g., Ref. 25). The necessary rotations of the coordinates are facilitated by the recently developed[24,79,80] computer package for Conversions, Standardization, and Transformations (CST). The CST package[24,79,80] is useful for general manipulations of the ZFS and CF parameters for various systems, especially for transitions ions at orthorhombic and lower-symmetry sites in crystals. Automatic calculation of the rotational invariants S_k for all major tensor operator notations has been provided in the extended version of the CST package.[80]

The quantities S_k are actually the second-order rotational invariants of the ranks $k=2$, 4, and 6, whereas, in general, a given nth order in CFP rotational invariants has also been defined. The latter quantities are related, within an approximation of a given J multiplet, to the nth-order (spectral) moments of CF Hamiltonians[29–31,41,42] defined as[53]

$$[\sigma_n(\alpha LSJ)]^n=[1/(2J+1)]\mathrm{Tr}(H_{\mathrm{CF}})^n. \tag{8}$$

Yeung[53] has provided the general relations for the moments of the second through fourth order in terms of the corresponding nth-order rotational invariants. It appears that the existence of the first-order moments and their invariant properties have not been explicitly considered so far. Using Eq. (8) and the Wigner-Eckart theorem we obtain the relation

$$[\sigma_1(\alpha LSJ)]=[1/(2J+1)]\sum_k B_k^0\langle\alpha LSJ\|C^{(k)}\|\alpha LSJ\rangle \times\begin{pmatrix} J & J & k\\ -M_J & M_J & 0\end{pmatrix}, \tag{9}$$

which is utilized in Sec. V. Since the moments of N-particle Hamiltonians, including CF Hamiltonians, are invariants of the unitary transformations of the basis in the model space,[56] the quantity $\sigma_n(\alpha LSJ)$, including $\sigma_1(\alpha LSJ)$, is also invariant. Although used only occasionally in CF studies, the quantities S_k play a specific role as a handy but approximate tool in interpretation of the optical spectra for transition ions (see, e.g., Refs. 29–31, 41, 42, 47, and 53). The relationships between the two interrelated quantities, i.e., S_k in Eq. (6) and $[\sigma_2(\alpha LSJ)]^2$, and the second-order conserved quantities stipulated by Noether's theorem discussed in Sec. IV provide a deeper meaning for the former quantities as discussed in Sec. V.

IV. APPLICATION OF NOETHER'S THEOREM TO CF HAMILTONIANS INVARIANT UNDER CONTINUOUS ROTATIONAL SYMMETRY

A. General considerations

With the background presented in Sec. II and III in mind, we set out to consider the deeper interrelationships between the concepts outlined above: the canonical Noether's theorem and the algebraic symmetry on the one hand, and the properties of CF Hamiltonians invariant under continuous rotational symmetry, including the rotational invariants and the moments of CF Hamiltonians, on the other hand. We start with a generalization of CF Hamiltonians defined in Eqs. (1)–(3) and consider a generic Hamiltonian of the form

$$H=\Sigma A_{lm}\chi_{lm}(\mathbf{X}), \tag{10}$$

where A_{lm} denote the parameters associated with a given generic type of the tensor operators $\chi_{lm}(\mathbf{X})$ of the specific angular momentum $\mathbf{X}(X_x,X_y,X_z)$ operators, expressed in a given axis system (x, y, z). Note that the generic symbols χ_{lm} and A_{lm} used in Eq. (10) do not define yet another tensor-operator notation, an abundance of which already exists in the literature,[34,35] but may represent any of the various sets of tensor operators and associated parameters. As discussed in Refs. 34 and 35 such generic Hamiltonians accounts for (i) the CF interaction, if $\mathbf{X}$ is taken as the orbital angular momentum, either $\mathbf{l_i}$ or $\mathbf{L}$, as well as the total angular momentum, $\mathbf{j_i}$ or $\mathbf{J}$ when only the one-electron CF Hamiltonian is considered and the spin-correlated CF terms are neglected, and (ii) the ZFS splitting, if $\mathbf{X}$ is taken as either the *effective* spin, $\tilde{\mathbf{S}}$, or the *fictitious* spin, $\mathbf{S}'$, as well as (iii) any other mathematically similar higher-order interactions being functions of physically different angular momentum operators, e.g., the nuclear spin $\mathbf{I}$. Other more sophisticated variants of the CF Hamiltonian, e.g., the correlation CF or the spin-correlated CF Hamiltonians,[16,17] may be treated in a similar way as the CF Hamiltonians, Eqs. (1)–(3), dealt with in Sec. IV B. However, the amount of work involved in rigorous derivations of the associated conserved quantities would be prohibitive. Since the present arguments are based on symmetry requirements, which apply to all types of CF Hamiltonians, the general conclusions concerning the implications of Noether's theorem should be valid for these CF Hamiltonians as well.

Next we consider the continuous rotational symmetry aspects inherent in each of the following symmetry cases: tetragonal II (C_4,S_4,C_{4h}), trigonal II (C_3,S_6), hexagonal II (C_6,C_{3h},C_{6h}), and monoclinic (C_2,C_{1h},C_{2h}). For each case there exists a unique symmetry axis $\mathbf{u}$ (or direction). An arbitrary rotation $\phi/O\mathbf{u}$ leaves the form of a given CF (in general, generic) Hamiltonian invariant. However, as concerns the CF parameters, only the $q=0$ ($l=0$) components are invariant, whereas the CFP's with $q\neq 0$ (the associated A_{lm} ones with $l\neq 0$) acquire different values for each specific transformation $\phi/O\mathbf{u}$. Hence, one may generate an infinite number of distinct yet physically equivalent CFP data sets. For triclinic symmetry no symmetry-related coordinate axes exist and the choice of the CF axes is completely arbitrary.[25] For this case, unlike that for the monoclinic one, any choice of the CF axes yields an identical and physically equivalent form of the CF Hamiltonian with a distinct yet physically equivalent CFP data set for each specific choice of the CF axes. Hence, one may generate an infinite number of distinct yet physically equivalent CFP data sets by applying different Euler angles (α, β, γ). Each transformed CF Hamiltonian involves all CFP's with components $-k\leqslant q\leqslant +k$ for a given rank $k=2$, 4, and 6 as defined in Eqs. (1)–(3). However, all CFP's, including $q=0$ (the associated A_{lm} ones with $l=0$), acquire different values for each specific transformation (α, β, γ). The physical equivalence of the CFP data sets generated in this way implies that the corresponding energy levels and also the intensity of CF transitions are identical for each related CFP data set. Hence, it appears that the transformations in question correspond to "the equivalence transformations among physical states" generated by independent generators of the gauge transformation considered for various dynamical systems.[8] Likewise for Lagrange's variables,[6–9] a crucial question arises, namely, what identities or interrelationships between the CFP's must be obeyed in order to ensure that the physical equivalence is, in fact, fully preserved?

The answer is provided by the canonical Noether's theorem and the algebraic symmetry considerations discussed in the next section.

B. The canonical Noether's theorem and the conserved quantities

In the spirit of the canonical Noether's theorem[1–9] we argue that for the continuous symmetry cases in question there must exist associated *conserved quantities*, i.e., polynomial functions of the CFP's (in general, the generic A_{lm} ones). Existence of such quantities ensures the physical equivalence of the CFP data sets interrelated by the continuous symmetry transformations discussed in Sec. IV A. The central idea put forward here may be encapsulated in the canonical Noether's theorem for the CF and equivalent Hamiltonians invariant under continuous rotational symmetry as follows.

a. Theorem 1

If the CF Hamiltonian defined in Eq. (1) [and Eqs. (2) and (3); in general, any Hamiltonian of the type in Eq. (10)] is invariant under continuous rotational symmetry, then several quantities of various order in the CF parameters B_k^q (and equivalent ones; in general, the associated A_{lm} ones) are conserved.

By "conservation" we mean here the invariance of such quantities under the continuous rotational symmetry operations. We attempt to provide a clear exposition of the pertinent aspects at the level comprehensible to the CF practitioners. Analytical rigorous derivations of the conserved quantities in question are beyond the immediate scope of the present work. Such derivations (see, e.g., Ref. 57) may be particularly appealing to algebraists and quantum-mechanical theorists because Hamiltonians of the type in Eq. (10) are far less complex than those considered using Noether's theorems in particle physics, high-energy physics, and field theories.[6–10]

Instead of rigorous derivations of the conserved quantities here we fully exploit the results of the algebraic symmetry studies of the CF Hamiltonians invariant under continuous rotational symmetry.[20–22] Although it had not been realized at that time, it turns out that the algebraic symmetry considerations[20–22] provide a direct proof of theorem 1 for all symmetry cases in question, except triclinic symmetry, which has not been dealt with in a similar way so far. The studies[20–22] have, in fact, revealed for monoclinic or higher continuous symmetry the existence in the characteristic equations of CF Hamiltonians of several "*invariant combinations*" (IC's) being polynomial functions of CFP's of the form $f\{(B_k^q)^i(B_k^q)^j(B_k^q)^m(B_k^q)^l\}$, with various values of $(k,\, q)$ in each term and the power coefficients $(i,\, j,\, m,\, l)$. The possible IC's, which have been explicitly identified in Ref. 20 for tetragonal II, in Ref. 21 for hexagonal II and trigonal II, and in Ref. 22 for monoclinic symmetry cases, can be classified as follows. In terms of the ES operators,[34,37] provided that the special symmetry axis or direction is taken as the quantization z axis of the ES operators, the explicit forms of the admissible IC's are as follows:

(a) The first-order IC's are simply the parameters B_k^q with $q=0$, i.e., B_2^0, B_4^0, and B_6^0.

(b) Two types of second-order IC's exist and have the following meaning:

  (i) The second-order IC's of the type (i) have the meaning of the "length of a vector" $\mathbf{v}_{kq}$ formed by the pairs $(+q$ and $-q)$ of the CFP's with a given k and are defined by

$$(\{B_k^{+q}\}^2+\{B_k^{-q}\}^2)^{1/2}\equiv|\mathbf{v}_{kq}|. \tag{11}$$

  Invariance of the quantity $|\mathbf{v}_{kq}|$ under continuous symmetry transformations discussed in Sec. IV A arises from the conservation of the "magnitude," i.e., "length of the vector" $\mathbf{v}_{kq}=(B_k^{+q},B_k^{-q})$.

  (ii) The second-order IC's of the type (ii) have the meaning of the "scalar product" of any two possible vectors $\mathbf{v}_{kq}$ and $\mathbf{v}_{k'q}$ in Eq. (11) and are defined by

$$B_k^{+q}B_{k'}^{+q}+B_k^{-q}B_{k'}^{-q}\equiv\mathbf{v}_{kq}\cdot\mathbf{v}_{k'q}=|\mathbf{v}_{kq}||\mathbf{v}_{k'q}|\cos(\beta_{kq}^{k'q}). \tag{12}$$

  Invariance of the quantity $\mathbf{v}_{kq}\cdot\mathbf{v}_{k'q}$ under continuous symmetry transformations discussed in Section IV.A arises from the conservation of the "relative orientation" between the two vectors, i.e., the angle $\beta_{kq}^{k'q}$ between $\mathbf{v}_{kq}$ and $\mathbf{v}_{k'q}$, for each possible combination of the indices $(k,\, q)$ and (k',q) pertinent for a given symmetry case[20–22] (see below).

(c) The higher-(nth) order $(n>2)$ IC's exist for the cases that require solution of the characteristic equations of the order greater than two. The third $(n=3)$ and fourth-order $(n=4)$ IC's involve a great number of complicated combinations of the products of n number of independent CFP's, which have been identified for trigonal II (Ref. 21) and monoclinic[22] symmetries. The number of IC's and the degree of their complication increases with the order.

The properties of IC's defined above can be summarized as follows. The following vectors $\mathbf{v}_{kq}$ exist for a given symmetry case: $\mathbf{k}=2$: $|q|=2$ for a monoclinic $C_2\|Z$ case[22] (other monoclinic cases are discussed below); $\mathbf{k}=4$: $|q|=3$ for trigonal II,[21] $|q|=4$ for tetragonal II,[20] and $|q|=2$ and 4 for a monoclinic $C_2\|Z$ case;[22] and $\mathbf{k}=6$: $|q|=6$ for hexagonal II,[21] $|q|=3$ and 6 for trigonal II,[21] $|q|=4$ and 6 for tetragonal II,[20] and $|q|=2$, 4, and 6 for a monoclinic $C_2\|Z$ case.[22] Note that for triclinic symmetry all the pairs $(+q$ and $-q)$ for a given k are admissible. The admissible range and order of the IC's predicted by the algebraic symmetry considerations depend on the local site symmetry. For hexagonal II symmetry only three first-order IC's, B_2^0, B_4^0, and B_6^0, as well as one second-order IC, $|\mathbf{v}_{66}|$, exist.[21,53] For tetragonal II symmetry the determinants of the orders (2×2), (3×3), and (4×4) were analyzed algebraically.[20] It was proved[22] that the IC's of the first and second orders are fully sufficient for this case. For trigonal II symmetry,[21] in addition to the first- and second-order IC's, the existence of three IC's of the third order in B_k^q, denoted T_{46}^{36}, V_{466}^{336}, and

T_{66}^{36}, has been identified by explicit algebraic derivations. It may be expected that no higher-order IC's exist for trigonal II symmetry.[21] For the monoclinic symmetry $C_2 \| Z$ case,[22] in addition to the first-, second-, and several more third-order IC's, a large number of the fourth-order IC's has been identified by explicit algebraic derivations. Some of the third-order IC's for the monoclinic symmetry $C_2 \| Z$ case could be resolved into products of the first-order IC's (B_k^q with $q=0$) and second-order IC's [$|\mathbf{v}_{kq}|$ and $\mathbf{v}_{kq} \cdot \mathbf{v}_{k'q}$ defined in Eqs. (11) and (12), respectively]. Concerning the fourth-order IC's, their complexity for monoclinic symmetry is reflected,[22] e.g., in the fact that the IC's of the type $F\{B_k^{\pm 2} B_{k'}^{q'} B_{k''}^{q''} B_6^{\pm 6}\}$ only involve 116 terms of the fourth order in B_k^q's with k, k', $k''=2$, 4 and q', $q''=\pm 2$ and ± 4. Resolution of all higher-order IC's, which may appear in the characteristic equations of the monoclinic CF Hamiltonian, presents a formidable algebraic task. Several points are worth mentioning. First, it has been directly checked, using transformation relations[26] and algebraic calculations,[20–22] that each of the second-, third-, and fourth-order IC's explicitly identified is indeed invariant with respect to an arbitrary rotation ϕ/Oz. Second, only the quantities in Eq. (11) have been to a certain extent, utilized independently (see Sec. V), whereas neither those in Eq. (12) nor the higher-order IC's ($n>2$) have been considered in the literature since they were introduced in the literature.[20–22] Third, all IC's carry useful information,[20–22] which can be utilized for a more comprehensive description of transition ions at low-symmetry sites as illustrated by our recent studies. Here we exploit the canonical Noether's theorem (theorem 1) and the algebraic symmetry considerations discussed above to put forward the following statement.

b. Conjecture 1

The "invariant combinations" (IC's) revealed by the algebraic symmetry considerations and categorized above are the conserved quantities stipulated by the canonical Noether's theorem applied to the CF Hamiltonians in question (theorem 1).

The IC's identified in the course of the explicit algebraic symmetry considerations[20–22] as specific combinations of CFP's, i.e., equivalently the conserved quantities, arise naturally from the canonical Noether's theorem. Theorem 1 and conjecture 1 establish a direct link between Noether's theorem and the algebraic symmetry of CF Hamiltonians invariant under continuous rotational symmetry. Thus the major part of the main aims of this paper outlined in the Introduction has been achieved. Neither the specific features of continuous symmetry cases in question discussed in Sec. IV A nor their deeper meaning encapsulated in theorem 1 and conjecture 1 proposed above have been fully realized in the literature as yet. The same applies to their implications accounted for by corollaries 1–5 discussed in Sec. IV C. On the other hand, it may be expected that the conserved quantities algebraically determined for CF Hamiltonians invariant under continuous rotational symmetry should be somehow related to the rotational invariants and the moments of CF Hamiltonians. The latter quantities are defined for arbitrary symmetry and are also conserved under rotations of the coordinates. These ramifications of theorem 1 and conjecture 1 are considered in Sec. V.

Explicit forms of the IC's i.e., the conserved quantities in question, depend on the notations and conventions used to express CF Hamiltonians. In the above formulation we have employed, without the loss of generality, the ES operators[34,37] used in Eq. (1). Similar relations to Eqs. (11) and (12) apply for the CF Hamiltonians expressed in the Wybourne notation[11,34] employed in Eqs. (2) and (3) and are given in the Appendix. The conservation of the quantities defined in Eq. (11) reflects the fact that under the continuous symmetry operation, i.e., here a rotation about a special symmetry axis (or direction), the parameters with $+q$ and $-q$ for a given k transform only into combinations of themselves,[20–22] whereas the parameters B_k^0, $k=2$, 4, and 6, remain invariant as discussed in Sec. IV A. Equations (11) and (12) apply uniquely for tetragonal II (C_4, S_4, C_{4h}), trigonal II (C_3, S_6), and hexagonal II (C_6, C_{3h}, C_{6h}) symmetries, for which the choice of the special symmetry axis as the quantization z axis of the operators is a unique natural choice (see Refs. 17, 20, and 21). For monoclinic (C_2, C_{1h}, C_{2h}) symmetry, apart from the $C_2 \| Z$ case, two additional choices exist[22] for labeling the special symmetry axis (or direction), namely, $C_2 \| y$ and the $C_2 \| x$ axis of the ES operators[37] O_k^q. Hence, Eqs. (11) and (12) apply only for the choice of the special symmetry axis (or direction) as the quantization z axis: $C_2 \| Z$. For the other two choices, $C_2 \| y$ and $C_2 \| x$, more complicated forms of Eqs. (11) and (12) are required, which involve other combinations of the CFP's with the choice-specific values of q for a given k. However, the same meaning, i.e., the "*length of vectors*" and the "*angles between vectors*," can be ascribed to the conserved quantities of the second order for each monoclinic case.

An interesting question is whether any geometrical or topological meaning can be ascribed to the IC's (the conserved quantities) in question. A simple geometrical meaning can be ascribed to the second-order quantities defined in Eqs. (11) and (12) as illustrated in Figs. 1 and 2 using two- and three-dimensional representations in the CFP space, respectively. The planar representation in Fig. 1 is fully sufficient for hexagonal II (one vector, $\mathbf{v}_{66}$ only) and tetragonal II symmetry (two vectors, $\mathbf{v}_{44}$ and $\mathbf{v}_{64}$ only) cases. More involved diagrams, as, e.g., in Fig. 2, are needed for trigonal II symmetry, yielding three vectors ($\mathbf{v}_{43}, \mathbf{v}_{63}, \mathbf{v}_{66}$) and for monoclinic and triclinic symmetries, yielding even more such vectors. However, due to the complexity and large number of the IC's of the order higher than two, no adequate geometrical meaning could be ascribed in a straightforward way to the higher-order IC's identified so far.[21,22] A vexing question to be considered is if a single conservation law can sum up all the IC's (the conserved quantities) discussed above. For tetragonal II symmetry the area of the triangle span by vectors $\mathbf{v}_{44}$ and $\mathbf{v}_{64}$ in Fig. 1 or equivalently the volume of the two cones spanned by these vectors in Fig. 2 is a conserved quantity. An extension of such geometrical interpretations of the second-order conserved quantities presented in Figs. 1 and 2 as well as the concept of "constrained hypersurface" in the phase space of the Lagrangian[7] may provide a hint in a

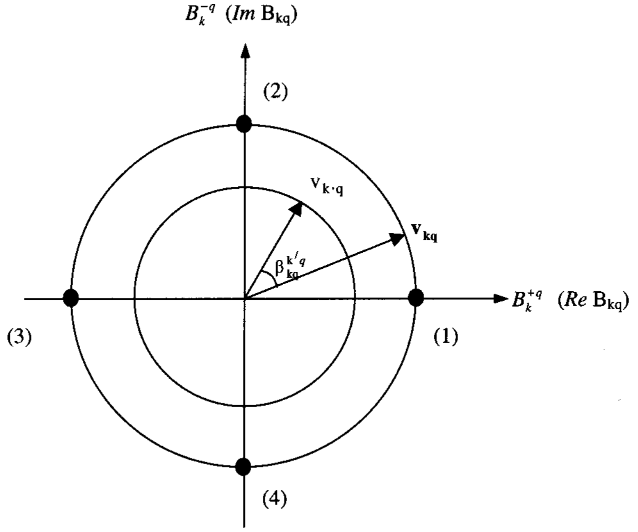

FIG. 1. Schematic planar representation of the second-order conserved quantities stipulated by Noether's theorem: type (i)—the length of vectors and type (ii)—the relative orientation, i.e., the angle between two respective vectors. Points (1)–(4) denoted by ● are discussed in text.

search for such a generalized conservation law. By analogy it may be expected that the conservation of a hyperstructural quantity, e.g., volume enclosed by a hypersurface in the CFP multidimensional space, shall also be obeyed for trigonal, monoclinic, and triclinic symmetries. However, the amount of work involved in explicit derivation of the necessary equations and their proof may be prohibitive. One may hope that by employing modern algebraic programming techniques and parallel computing it may be feasible to arrive at a general "conservation law" as a direct consequence of Noether's theorem, which shall encompass all the "primary" conserved quantities in question.

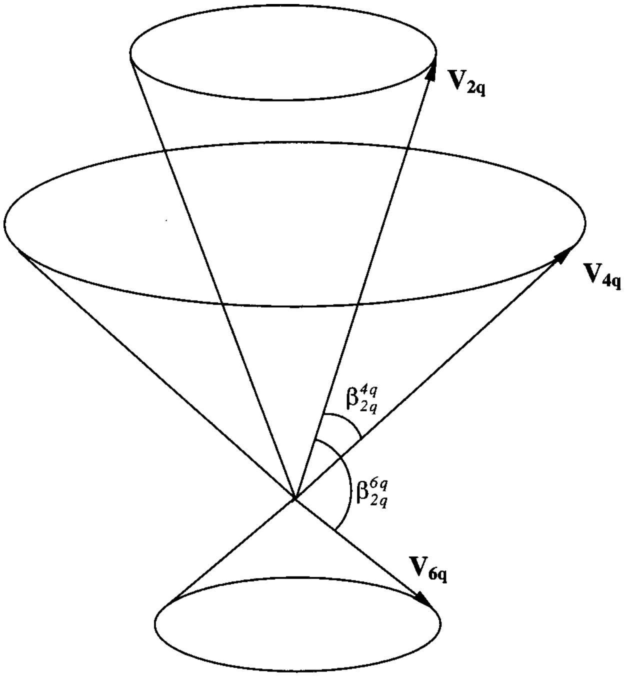

FIG. 2. Schematic three-dimensional representation of the second-order conserved quantities of the rank $k=2$, 4, and 6 stipulated by Noether's theorem: type (i)—the length of vectors and type (ii)—the relative orientations, i.e., the angles between two respective vectors.

C. Implications of the canonical Noether's theorem and the conserved quantities

Other aspects involved in the main aims of this paper concern application of the general constraints imposed by Noether's theorem on the CF Hamiltonians in question. It appears that the existence of the conserved quantities stipulated by theorem 1 and conjecture 1 put forward in Sec. IV B has profound practical implications for interpretation of experimental CFP data sets for the continuous symmetry cases in question. For example, it has been established earlier[20] that for tetragonal II symmetry only the "length of the vector," given in the ES notation as

$$|\mathbf{v}_{44}| = (\{B_4^4\}^2 + \{B_4^{-4}\}^2)^{1/2}, \tag{13}$$

can be experimentally determined. This contradicts the fitting strategy used in one of the existing CF approaches (the approach "C" defined below), which attempts to determine independently the values of both CFP's: B_4^4 and B_4^{-4}. It turns out that the limitation imposed by Eq. (13) is a direct implication of the canonical Noether's theorem, since the length of the vector $|\mathbf{v}_{44}|$ is nothing else but the conserved quantity stipulated by Noether's theorem for these continuous symmetry cases.

The properties of the conserved quantities and their implications are summarized in the following three corollaries, which are generalizations of the conclusions arising from the explicit algebraic symmetry considerations.[20–22] These implications apply, in general, to any Hamiltonian of the type in Eq. (10) invariant under continuous rotational symmetry.

a. Corollary 1

The coefficients of the characteristic equations of the CF Hamiltonians described by the theorem 1 are functions of the admissible conserved quantities defined by conjecture 1 only.

The validity of corollary 1 has been confirmed directly by using the algebraic programming language ALTRAN to derive the explicit functional dependence of the coefficients of the characteristic equations of the CF Hamiltonians for RE ions for each of the four symmetry cases in question.[20–22] It has been revealed that these coefficients are simple functions of the CFP's B_k^0, with $k=2$, 4, and 6 (i.e., the first-order conserved quantities), whereas they are complicated functions of the second- and higher-order $(n>2)$ conserved quantities only. In other words, the meaning of corollary 1 is that the algebraic symmetry of the CF Hamiltonians in question must reflect the conservation of the quantities stipulated by theorem 1 and conjecture 1. In the discussion that follows these quantities are referred to as "the conserved quantities."

b. Corollary 2

Only the conserved quantities can be directly and independently determined from fitting the experimental energy-level structure to the theoretical energy levels.

Corollary 2 points out that, contrary to the fitting strategy used implicitly by many authors (see, e.g., Refs. 20–22, 25, and 26), the CFP's admissible by group theory for a given symmetry cannot be directly and independently determined from fitting the experimental spectra. These are only the conserved quantities stipulated by Noether's theorem, which can be determined in this way. Moreover, knowledge of the conserved quantities does not enable independent determination of the full set of the CFP's admissible by group theory for a given symmetry case. This is due to the fact that the conserved quantities of the order higher than one, as, e.g., the type (i) second-order quantities in Eq. (11), always involve combinations of two interrelated CFP's. Hence, not each individual CF parameter belonging to a given pair ($+q$ and $-q$) can be independently determined from fitting the experimental energy-level structure.

c. Corollary 3

The conserved quantities of the order $n=1$ determine directly the magnitudes and the signs of the CFP's B_k^q with $q=0$, whereas those of the order $n\geqslant 2$ determine the magnitudes of the allowed combinations of the CFP's and the relative signs of B_k^q with $q\neq 0$.

Corollary 3 has an important bearing on the feasibility of the experimental determination of the magnitudes and signs of the CFP's for very low-symmetry cases. For monoclinic and triclinic symmetries, since there exist more CFP's apart from the first- and second-order conserved quantities, one would need to establish all possible higher-order conserved quantities in order to account for all the interrelationships between the CFP's. In principle, one should be able to obtain all admissible conserved quantities by considering the algebraic symmetry of the characteristic equations as was done in Refs. 20–22, and hence construct all these interrelationships. Knowledge of these interrelationships could be utilized in a twofold way. *First*, it would enable independent determination of the magnitudes and relative signs of some but not all CFP's admissible by group theory for a given symmetry. *Second*, it would enable imposing sensible constraints on the fitting procedures. However, solving the whole set of the equations for the conserved quantities, which is required in order to obtain all interrelationships between CFP's, may be practically impossible. Hence, one would need to resort again to numerical fitting strategies without the knowledge of sensible constraints, as is the current practice, in spite of the often-unreliable outcomes.

Before putting forward the remaining two specific corollaries we shall first outline briefly the current situation concerning interpretation of experimental data for the continuous symmetry cases. There exist in the literature three approaches, denoted[20–22] "A," "R," and "C," to fitting the experimental spectra for RE ions at sites exhibiting one of the five symmetry types in question:[20–22,25,26,59–75]

The first is the approximated (A) approach, in which the actual point-symmetry group is approximated by a higher group, for which the CFP data set does not involve the negative q components in Eq. (1) [or equivalently the Im parts of CFP's in Eqs. (2) and (3)]. The major motivation for adopting the approach A is that it offers a significant computation simplification by neglecting of the "imaginary" terms, i.e., in fact the imaginary matrix elements. Truncation of the CF Hamiltonian, however, affects the selections rules and thus the assignments of the theoretical energy levels to those observed experimentally. Hence it may lead to incorrect values of the experimental energy levels being used in fittings. In spite of its drawbacks, the approach A combined with the descent in symmetry method (see, e.g., Refs. 16 and 17) may provide reliable, albeit approximate values of CFP's. Approach A is satisfactory especially if the distortions accounting for lowering the local site symmetry to the actual one can be considered as small in the crystallographic sense. Then, to a good approximation the effect of the corresponding low-symmetry CFP's on the observed spectra can be neglected.

The second is the reduced (R) approach, in which one component of a pair of CFP's with $+q$ and $-q$ is set to zero. In practice, usually the CFP [in the ES operator notation,[34,37] Eq. (1)] B_k^{-q}, with the highest q for the lowest k, is selected for reduction to zero, i.e., B_6^{-6} for hexagonal II, B_4^{-4} for tetragonal II, and B_4^{-3} for trigonal II, but B_2^{-2} for monoclinic symmetry. This approach has also an apparent computational advantage, since less CFP's are used in calculating the matrix elements and hence in carrying out the fittings.

The last is the complete (C) approach, in which all CFP's admissible by group theory for a given site symmetry are allowed in the fittings. On the face, this approach seems to be the most correct one from the point of view of group theory. However, it turns out that proponents of approach C as well as of approach R have overlooked some more subtle points, which bear on the interpretation of experimental data and the correctness of each approach.

On the basis of corollaries 1–3, which concern the general constraints imposed on the CF Hamiltonians invariant under continuous symmetry and arise from theorem 1 and conjecture 1, we put forward corollary 4 and 5, which concern implications specific for interpretation of approaches C and R. These corollaries account for the feasibility of determination of the magnitudes and signs of CFP's from spectral data and have a profound bearing on the interpretation of the CFP data sets experimentally determined using approach C or R. Reviews of such CFP data sets available in the literature are carried out in separate papers.[25,26]

d. Corollary 4

There exist one to many correspondences between the conserved quantities and the magnitudes of the CFP's with $q\neq 0$ determined in approach C.

According to corollary 4 the least-squares fitting using approach C turns out to yield CFP data sets, which at best correspond to one possible minimum from a continuous set of equivalent minima in the multidimensional CFP space, but at worst correspond to an ill-determined local minimum. Two important facts arise as a consequence of the inherent constraint stated in corollary 4. *First*, because of the continuous symmetry, there exists an infinite number of ‘‘full’’ CFP data sets, i.e., including all group-theory admissible CFP’s, which are used in approach C. Each equivalent CFP data set yields the same values of the energy levels. *Second*, approach C *apparently* offers experimental determination of the angle of rotation ϕ/Oz, which can bring one component of the pair of parameters with $+q$ and $-q$ to zero. This might have been a viable result only if the original x and y axes could have been defined with respect to the crystallographic axes. If one could define such an initial reference frame, an infinite number of physically equivalent yet distinct data sets could have been determined from fittings. Each such data set (i) should yield the same value, say, ϕ, of the angle of rotation ϕ_i/Oz required to set one component of the pair of parameters with $+q$ and $-q$ to zero. However, in fact, this is impossible, and no x and y axes can be defined for the symmetry cases under consideration. As our literature survey reveals, these facts are still not recognized by many experimentalists, especially those employing inelastic neutron-scattering measurements for determination of CFP’s. Concrete recent examples and their analyses are provided, e.g., for tetragonal II (Ref. 26) and monoclinic symmetries.[25,71] Even having reliable initial CFP data sets to start the fittings, which can be predicted, e.g., by the point-charge model or more advanced model calculations,[15–17] the final outcome of approach C fittings may be some artifacts rather than well-determined CFP data sets. This may be one of the reasons why the nonlinear least-squares fittings of 15 CFP’s required for RE ions at monoclinic symmetry sites are regarded as ‘‘*notoriously unreliable*.’’[53] Additional reasons for such unreliability are provided by the present considerations.

e. Corollary 5

There exists a one-to-one correspondence between the conserved quantities and the magnitudes of the CFP’s with $q\neq 0$ determined in approach R for each specific choice of the CF parameter reduced to zero.

According to corollary 5, the CFP sets with the specific choice of CF parameter reduced to zero can be determined experimentally using approach R. Each such set is selected out of an infinite number of CFP data sets by imposing the additional condition $B_k^{-q}\equiv 0$ (or equivalently $B_k^{+q}\equiv 0$). For hexagonal II symmetry, setting either B_6^{-6} or B_6^{+6} to zero is equivalent to a specific choice of the rotational invariant $|\mathbf{v}_{66}|=|B_6^{+6}|$ or $|\mathbf{v}_{66}|=|B_6^{-6}|$, respectively. However, since no more $(\pm q)$ pairs exist using this specific choice, this does not affect the values of other CFP’s, i.e., the first-order IC’s B_k^0, $k=2$, 4, and 6. For tetragonal II symmetry, there exist two pairs of the parameters B_k^{-q} and B_k^{+q} to use for a reduction of one component of one pair to zero, whereas both components of the other pair can be completely determined in approach R. In general, the CFP’s with $q\neq 0$ in the ES operator notation[34,37] (and the equivalent Re and Im parts of CFP’s in the Wybourne notation[11,34]) determined in approach R turn out to represent just one specific CFP data set out of an infinite number of such data sets. Each such CFP set satisfies the requirement of the conservation of the quantities accounted for by theorem 1 and conjecture 1. Taking into account that only the relative signs of some CFP’s can be determined experimentally, the CFP data sets with the same magnitude but different signs also satisfy the conservation criteria as shown in Fig. 1. The specific character of a particular CFP data set determined in approach R reside in the actual selection of one component of a pair of parameters (B_k^{+q},B_k^{-q}) that is reduced to zero, i.e., such a CFP data set is k and $\pm q$ specific.

In view of the above, three additional questions arise. The first question concerns the uniqueness of the ‘‘intrinsic’’ selection within a given pair (B_k^{+q},B_k^{-q}), since several ‘‘intrinsic’’ choices to reduce one parameter to zero exist, as depicted in Fig. 1. On the plane with the axes denoted as $\{B_k^{+q}\}$ and $\{B_k^{-q}\}$ all possible values of the two corresponding parameters for each pair $(k,|q|)$ can be represented by a circle with the radius given by $|\mathbf{v}_{kq}|$ (see Fig. 1). Although the magnitudes of B_k^{-q} $(\mathrm{Im}\,B_{kq})$ corresponding to points (2) and (4) are of the same value, they differ in sign. Hence points (2) and (4) represent alternative ‘‘intrinsic’’ choices $(B_k^{+q}\equiv 0$ and $B_k^{-q}>0)$ and $(B_k^{+q}\equiv 0$ and $B_k^{-q}<0)$, respectively. Similarly, points (1) and (3) correspond to the prevailing choice $B_k^{-q}\equiv 0$, but two alternative ‘‘intrinsic’’ choices exist, namely, $B_k^{+q}>0$ and $B_k^{+q}<0$, respectively. All alternative choices satisfy the conservation criteria. The *second* question concerns the uniqueness of the pair (B_k^{+q},B_k^{-q}) selected for the reduction of one component to zero. In the cases in which more than one pair (B_k^{q},B_k^{-q}) exists, more ‘‘extrinsic’’ choices of the rank k is available for reduction of the parameter B_k^{-q} (or B_k^{+q}—as an ‘‘intrinsic’’ choice) to zero. This is the case for trigonal II (two pairs), monoclinic (six pairs), and triclinic symmetries (12 pairs). What criteria are to be adopted in selecting a particular pair? Each particular choice results in a physically equivalent CFP data set, yet the values of CFP’s are completely different. Examples of such correlated CFP data sets may be found, e.g., in Refs. 22 and 25. The current practice in this regard is an arbitrary choice of $B_k^{-q}\equiv 0$ with the lowest k. This is the most widely used choice, although no specific justification or advantage is offered. The *third* question concerns the mutual correlation between the alternative data sets obtained in approach R. Are the nonzero CFP’s obtained from fitting using approach R properly mutually correlated or do various parameters belong to disparate (i.e., uncorrelated) areas in the multidimensional CFP space, each of which corresponding to a specific choice of the CF parameter reduced to zero? A possible way to verify that the values in a given fitted CFP data set are properly correlated would be to carry out a number of fittings (say, $i=1-N$) including all CFP’s, as in approach C, and check the mutual correlation between data sets by proper transformations[37] ϕ_i/Oz. The *rotational invariants* and *norms* defined in Eqs. (4)–(7) are then helpful to assess the likelihood of the nonzero CFP’s being properly mutually correlated within a given CFP data set as well as with other data sets.

In view of the properties discussed above, the widespread interpretations of the CF parameter sets obtained using approach R, which imply, e.g., that the ‘‘*parameters* (are) *given* *in the axis system with one component of the pair of parameters with* $+q$ *and* $-q$ *(usually* $-q$*) set to zero" or that "a rotation has been carried out to bring one CF parameter to zero,"* are, in fact, incorrect. This interpretation assumes implicitly that such a transformation can be done, i.e., the angle of rotation around the symmetry axis, for which the latter condition is satisfied, can be determined. In fact, however, this angle cannot be determined from fitting the experimental energy levels. No particular orientation of the coordinate axes can be assigned to the CFP's determined in approach R, since as stated in corollary 2 the quantities that can be experimentally measured are the conserved quantities, i.e., the first-order quantities (B_k^0), the second-order quantities defined in Eqs. (11) and (12), and higher-order quantities (see theorem 1 and conjecture 1). For monoclinic (and triclinic) symmetry cases more such circles such as those in Fig. 1 or cones such as those in Fig. 2 are needed to represent the magnitudes and the relative signs of the CF parameters. Hence, more equivalent points such (1) and (3) as well as (2) and (4) can be found in the "*circles*" (Fig. 1) or "*cones*" (Fig. 2) corresponding to approach R for these very low-symmetry cases. A similar "*circular*" phenomenon has been encountered in the CF analysis within the ^5D approximation for $3d^4$ and $3d^6$ ions[81] for axial type-II symmetry cases without the deeper realization that it is a consequence of Noether's theorem. The ground-state phase diagrams[81] for tetragonal II and trigonal II symmetries indicate definite circles for the corresponding wave functions, thus satisfying the relationships between the CFP's stipulated by Noether's theorem.

Extension of the considerations of the algebraic symmetry, carried out so far for the four cases of CF Hamiltonians invariant under continuous rotational symmetry about a specific axis,[20–22] to triclinic symmetry requires computation of a horrendously large number of complicated higher-order invariant combinations appearing in the characteristic equation of a CF Hamiltonian. If one resorts to these involved computations then perhaps the algebraic symmetry approach can also provide additional invariants to those identified for the higher-symmetry cases. Nevertheless all general aspects and conclusions discussed in Sec. IV apply also triclinic symmetry. Additional aspects specific for CF Hamiltonians of triclinic symmetry are discussed in the next section.

V. CONSERVED QUANTITIES VS ROTATIONAL INVARIANTS AND MOMENTS OF CF HAMILTONIANS

As discussed in Sec. IV Noether's theorem (theorem 1) asserts that there must exist conserved quantities for triclinic symmetry cases as well. Unlike in the case of higher-symmetry CF Hamiltonians invariant only under continuous rotational symmetry about a specific axis, triclinic CF Hamiltonians are invariant under an arbitrary rotation of the coordinate system, which, in general, can be given by the three Euler angles (α, β, γ). The second-order rotational invariants, namely, the CF invariants S_k and the norms N_k of the ZFS parameters[34–40] defined in Sec. III for triclinic symmetry, as well as the related quantities, i.e., the CF strength parameters,[29–33,41–53] acquire deeper meaning in view of Noether's theorem. These quantities are nothing else but combinations of the conserved quantities of the first-order (B_k^0) and second-order (B_k^q) ones of type (i). Since the nth moments of CF Hamiltonians, Eq. (8), can be expressed[42,53] in terms of the second-order (S_k) and higher-order rotational invariants, hence, in turn, the former quantities are also related to the conserved quantities stipulated by Noether's theorem. The first-order moment in Eq. (9) is itself a conserved quantity, which ensures the conservation of the CFP's B_k^0 as stipulated by Noether's theorem stated in Sec. IV B.

Another way of looking at the rotational invariants S_k and the norms N_k for triclinic symmetry defined in Eqs. (4)–(7) is to consider the CFP's for a given $k=2$, 4, and 6, as a multidimensional vector $\mathbf{B_k}=\{B_k^{-k},\ldots,B_k^0,\ldots,B_k^k\}$, i.e., $(2k+1)=5$, 9, and 13, respectively. In analogy to the interpretation used for a limited (two-dimensional) subspace in Eq. (11), the quantities N_k as well as S_k [apart from the numerical constant used in Eq. (6)] thus have the meaning of the length of the vector $\mathbf{B_k}$.

Due to the ascent in symmetry method, the second-order rotational invariants and the CF strength parameters as well as the norms of the ZFS parameters, defined in Eqs. (4)–(7) for triclinic symmetry, can be generalized to the cases for which some CF (or ZFS) parameters must be exactly zero, as required for higher symmetries than triclinic. Thus, one obtains similarly these second-order quantities as the sums of the squares of the individual first- and second-order [type (i)] conserved quantities. Hence, the quantities S_k and N_k can be also applied to any higher-symmetry case and not only to triclinic symmetry.

To illustrate the relationship between the CF rotational invariants and the conserved quantities stipulated by Noether's theorem, we consider hexagonal (types II and I) and cubic symmetries dealt with in Ref. 53. For hexagonal II symmetry, the z axis is along the hexagonal axis or direction, while the x and y axes are in the plane perpendicular to the z axis with the direction of the x (y) axis arbitrary in this plane. With this choice of the z-axis direction, there are in total five CFP's permissible by group theory, i.e., using the compact form in the Wybourne notation, Eq. (2), we have the nonzero CFP's:[53] B_{20}, B_{40}, B_{60} (real ones), and B_{66} and $B_{6\text{-}6}$ (complex ones). The arbitrariness of the direction of the x and y axes will induce the existence of an infinite number of CFP data sets corresponding to an arbitrary rotation around the z axis. Hence, the invariance of certain combinations of CFP's exists. In view of the findings presented in Sec. IV, the results given for hexagonal symmetry[53] need reinterpretation. The second-order rotational invariants of the second, fourth, and sixth rank for hexagonal symmetry were given[53] (in the notation used here), respectively, as

$$(S_2)^2=(B_{20})^2/5, \quad (S_4)^2=(B_{40})^2/9,$$

$$(S_6)^2=\{|B_{60}|^2+2|B_{66}|^2\}/13. \tag{14}$$

On the other hand, as discussed in Sec. IV for this continuous symmetry case the following conserved quantities exist: the first-order ones, B_{20}, B_{40}, and B_{60}, and only one second-order one, which has the meaning of the length of the vector $\mathbf{v}_{66}=\{2|B_{66}|^2\}^{1/2}\equiv\{2(\mathrm{Re}\,B_{66})^2+2(\mathrm{Im}\,B_{66})^2\}^{1/2}$. Only these conserved quantities can be determined by fitting the experimental energy-level structure. In approach R, $\mathrm{Im}\,B_{66}$ is set to zero and the second-order conserved quantity becomes $|\mathbf{v}_{66}|=\{2(\mathrm{Re}\,B_{66})^2\}^{1/2}$. Comparing the second-order rotational invariants in Eq. (14) with the conserved quantities (the IC's) defined in Sec. IV B, it turns out that the second- and fourth-rank rotational invariants in Ref. 53 are equivalent, to, within a multiplicative factor, the first-order conserved quantities stipulated by Noether's theorem. The second-order rotational invariant[53] of the sixth rank in Eq. (14) is a sum of the squares of the individual first-order conserved quantity and the second-order type-i conserved quantity defined in Sec. IV. Obviously a sum as well as a product of conserved quantities are themselves conserved quantities.

One important invariant quantity has not yet been accounted for in the approach used in Ref. 53, namely, B_{60}. Taking this into account, it turns out that all nine third-order rotational invariants $v_k(k_1k_2k_3)$ derived for hexagonal symmetry[53] can be resolved into simple combinations of primary invariants. A question arises as to which, if any, of such combinations carry a piece of information that may be useful for fitting and interpretation of CF spectra. Assuming that, in principle, both magnitudes and signs of the first-order conserved quantities B_{20}, B_{40}, and B_{60}, can be independently determined, none of the third-order rotational invariants[53] $v_k(k_1k_2k_3)$ carries a piece of such information. In practice, however, it may be useful to incorporate into the fitting procedure a constraint arising from one of the third-order rotational invariants[53] $v_k(k_1k_2k_3)$, namely, $v_k(246)=\mathrm{sq\,rt}(5/143)B_{20}B_{40}B_{60}$, since it fixes the relative signs of the three CFP's each being independently a first-order conserved quantity. All other eight quantities $v_k(k_1k_2k_3)$ in Ref. 53 can be resolved into simple combinations of primary invariants and appear to play no useful role.

A similar reinterpretation applies also to the rotational invariants derived in Ref. 53 for cubic symmetry. All the "quadratic moments," i.e., the second-order rotational invariants, as well as the third- and fourth-order rotational invariants, are functions of only three first-order conserved quantities B_{20}, B_{40}, and B_{60}. It should be emphasized that it does not matter which numerical coefficients are associated with the combinations, either sums or products, of primary invariants. Hence, the painstaking derivation[53] of the involved numerical coefficients, e.g., of the type $d_k(k_1k_2k_3k_4)$ in the expressions for the fourth-order rotational invariants $v_4(k_1k_2k_3k_4;k)=d_k(k_1k_2k_3k_4)(B_{40})^m(B_{60})^n$ could be avoided since they do not introduce any new physical information.

VI. SUMMARY AND CONCLUSIONS

To the best of our knowledge, we have provided the first application of Noether's theorem in the area of the crystal- (ligand-) field (CF/LF) theory. The present considerations can be also applied to any generic Hamiltonian of the form $H=\Sigma\, A_{\mathrm{lm}}\chi_{\mathrm{lm}}(\mathbf{X})$, representing among others, also the zero-field splitting (ZFS) Hamiltonians. Noether's theorem applies to Hamiltonians invariant under continuous rotational symmetry, i.e., for the following cases: hexagonal II (C_6,C_{3h},C_{6h}), tetragonal II (C_4,S_4,C_{4h}), trigonal II (C_3,S_6), monoclinic (C_2,C_{1h},C_{2h}), and triclinic (C_i,C_1) symmetries. The interrelationships between Noether's theorem and the algebraic symmetry of CF Hamiltonians for these symmetry cases have been investigated. This has enabled formulation of two important statements: Theorem 1 and conjecture 1, which establish a direct link between the two concepts. Theorem 1 stipulates the existence of several conserved quantities, which by conjecture 1 are equivalent to the invariant combinations revealed by the algebraic symmetry considerations. Explicit forms of the conserved quantities, of the first and up to fourth order in CFP's, have been discussed for the CF Hamiltonians in question. Consequently, several corollaries based on theorem 1 and conjecture 1 have been proposed. Corollary 1 establishes the link between the coefficients of the characteristic equations of the CF Hamiltonians and the conserved quantities. The consequences of the invariance of CF Hamiltonians under continuous rotational symmetry, as stipulated by Noether's theorem, are encapsulated in corollaries 2–5.

Insight has been gained by looking at the canonical Noether's theorem from the point of view of the algebraic symmetry. The ramifications of the present considerations provide a solid basis for interpretation of experimental CF parameter data sets appearing in the literature. The existing three approaches to fitting experimental data, namely, complete (C—all CF parameters), reduced (R—one CF parameter set to zero), and approximate (A—all imaginary components of CF parameter neglected), have been reconsidered from the point of view of the conserved quantities stipulated by Noether's theorem. The considerations enable also to solve the longstanding problem, i.e., choosing the CF parameters that can be determined from fitting the experimental energy-level structure to the theoretical energy levels. The rotational invariants and norms as well as the moments of CF Hamiltonians used in the CF studies are discussed from the point of view of the conserved quantities stipulated by Noether's theorem. In order to illustrate the implications of Noether's theorem and to provide practical applications of theorem 1, conjecture 1, and the resulting corollaries, two specific cases are considered in detail. In this paper the rotational invariants for hexagonal (types II and I) and cubic symmetries are discussed. Their deeper meaning, hitherto, not realized in the literature, is elucidated. In a separate paper[26] the interpretation of CFP data sets for rare-earth ions in $\mathrm{LiYF_4}$ and structurally similar systems with tetragonal type-II (S_4) symmetry are thoroughly reviewed and discussed. A detailed survey of the relevant examples taken from the recent CF and superposition models as well as ZF-EPR studies for various symmetry cases will be presented elsewhere in the future.

ACKNOWLEDGMENTS

Thanks are due to Joseph H. T. Lau and Dr. A. Galeev for providing Refs. 2 and 5 and Refs. 30 and 31, respectively. This work was supported by the City University of Hong Kong through a doctoral studentship to Ms. Qin.

APPENDIX

The forms of the conserved quantities stipulated by Noether's theorem (Sec. IV B) expressed in terms of the CF parameters in the Wybourne notation[11,34] are as follows:
first order: B_{20}, B_{40}, B_{60}, second order: (i) $|\mathbf{v}_{kq}| = (2\{\mathrm{Re}\, B_{kq}\}^2 + 2\{\mathrm{Im}\, B_{kq}\}^2)^{1/2}$ $q>0$, (ii) $\mathbf{v}_{kq}\cdot\mathbf{v}_{k'q} = |\mathbf{v}_{kq}||\mathbf{v}_{k'q}|\cos(\beta_{kq}^{k'q})$ q, $q'>0$.
Explicitly, the second-order conserved quantities of type (ii) (Sec. IV B) are given by

$$\begin{aligned}\mathbf{v}_{kq}\cdot\mathbf{v}_{k'q} &= (\mathrm{Re}\, B_{kq}\mathrm{Re}\, B_{k'q} + \mathrm{Im}\, B_{kq}\, \mathrm{Im}\, B_{k'q})\\ &= (\{\mathrm{Re}\, B_{kq}\}^2 + \{\mathrm{Im}\, B_{kq}\}^2)^{1/2}(\{\mathrm{Re}\, B_{k'q}\}^2\\ &\quad + \{\mathrm{Im}\, B_{k'q}\}^2)^{1/2}\cos(\beta_{kq}^{k'q})\end{aligned}$$

or, alternatively, by the angle

$$\beta_{kq}^{k'q} = \arccos\{(\mathbf{v}_{kq}\cdot\mathbf{v}_{k'q})/(|\mathbf{v}_{kq}||\mathbf{v}_{k'q}|)\}.$$

Specifically, for tetragonal type-II symmetry we obtain

$$|\mathbf{v}_4| = [2(\{\mathrm{Re}\, B_{44}\}^2 + [\mathrm{Im}\, B_{44}]^2)]^{1/2},$$

$$|\mathbf{v}_{64}| = [2(\{\mathrm{Re}\, B_{64}\}^2 + \{\mathrm{Im}\, B_{64}\}^2)]^{1/2},$$

$$\begin{aligned}\beta_{44}^{64} = \arccos\big((&\mathrm{Re}\, B_{44}\,\mathrm{Re}\, B_{64} + \mathrm{Im}\, B_{44}\,\mathrm{Im}\, B_{64})/\{[(\mathrm{Re}\, B_{44})^2\\ &+ (\mathrm{Im}\, B_{44})^2]^{1/2}[(\mathrm{Re}\, B_{64})^2 + (\mathrm{Im}\, B_{64})^2]^{1/2}\}\big).\end{aligned}$$

In the approach R, $\mathrm{Im}\, B_{44} \equiv 0$. In the approach A, $\mathrm{Im}\, B_{44} \equiv 0$, $\mathrm{Im}\, B_{64} \equiv 0$.

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