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Rotation matrix elements and further decomposition functions of two-vector tesseral spherical tensor operators; their uses in electron paramagnetic resonance spectroscopy

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Abstract. Matrix elements, $A^{(k)}_{g,h}$ ($k = 1$–6), which describe a general Euler angle transformation of coordinates to which tesseral spherical tensor operators, $\mathfrak{I}_{k,q}$, are referred have been calculated and extended to include matrix elements for odd k. The matrix elements have been incorporated into a general axis-transformation computer program which relates to parameter sets in any one of the more commonly used tesseral forms, namely, conventional Stevens, normalized Stevens (Racah normalization) and normalized spherical tensor (Koster and Statz normalization) operators. Tables of decomposition functions of tesseral spherical tensor operators, $\mathfrak{I}_{k,q}(\boldsymbol{B}, \boldsymbol{J})$ ($\boldsymbol{J} = \boldsymbol{S}, \boldsymbol{I}$), are extended to detail decompositions for terms of dimension BJ^7 and, implicitly, for decomposition of any two vector operators $\mathfrak{I}_{k,q}(\boldsymbol{V}, \boldsymbol{W})$ to experimentally usable single vector forms where $V^{k_V} W^{k_W}$ (one of k_V, k_W unity) is the dimension of a general term in the decomposition. Tables detailing the symmetry-allowed terms under the 11 Laue (site) crystal classes are also extended to include tesseral tensorial sets up to rank 8, thus including the new terms. The use of these functions to describe electron paramagnetic resonance studies of high-spin nuclear Zeeman interactions is discussed.

1. Introduction

This paper is aimed in part at the EPR experimentalist who wishes to use spin operators in irreducible tesseral spherical tensor form, or to relate parameter sets, perhaps in non-irreducible form (second-rank Cartesian tensors or Stevens operators for example), to an irreducible set. We outline the procedures for obtaining the necessary matrix elements to effect such transformations. Tables of some of the matrix elements in explicit algebraic form, including previously unpublished elements for odd k, are given; complete tables are available from sources indicated. A computer program is described which uses the algebraic forms of the rotation matrix elements to effect general axis transformations and/or interconvert spin-Hamiltonian (SH) parameters in any one of the commonly used tesseral forms.

A second aim is to extend tensorial decompositions of two-vector tesseral tensor operators describing terms of dimension $J_1 J_2^7$ into experimentally usable single-vector forms. Tables of decompositions are included where the lowest site symmetry, $\bar{1}$ Laue class, is assumed. The production of such terms leads generally to eighth-rank tensors for which it is then required to know the site symmetry constraints which restrict the terms to be included in the SH. Tables of symmetry-allowed terms for eighth-rank irreducible tesseral tensors are listed for each of

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the 11 Laue crystal classes. In combination with earlier related listings, the tables of this paper can be used to analyse EPR spectra of transition ions with $S \leqslant 7/2$, $I \leqslant 7/2$ at sites of any symmetry. To our knowledge these tables have not appeared previously.

Since the appearance of a paper by Kikuchi and Matarrese [1] some four decades ago and generalizations by the Buckmaster group [2, 3], the use of spherical tensor spin operators has become relatively widespread in electron paramagnetic resonance (EPR) spectroscopy. Early in the historical development of an appropriate general SH, the utility of an expression with real coefficients, that is expressed as tesseral combinations of complex operator functions, was recognized. Pryce [4] and Abragam and Pryce [5] developed the SH using tesseral combinations of operator equivalents, derived earlier by Stevens [6] and Elliot and Stevens [7]. These operator equivalents have the same transformation properties as spherical harmonic polynomials $Y_{k,q}$ (q integral in the range $-k \leqslant q \leqslant k$). For $J \geqslant 2$ the Stevens nomenclature is still widely used, particularly for field-independent terms of dimension J^4, J^6, but there are a number of drawbacks:

(i) as with the Cartesian tensor nomenclature commonly used to represent second-rank tensor quantities, there are redundancies involved which become particularly evident when formulating some high-spin terms;
(ii) most early tabulations excluded operators with $q < 0$, necessary to describe all but a few high-symmetry point groups (we note that Rudowicz [8] refers to the full set of O_k^q ($-k \leqslant q \leqslant k$) as 'extended' Stevens operators); and
(iii) Stevens operator equivalents are not normalized, which has the effect that there is no simple function of the parameters (operator coefficients) by which to gauge their 'size'.

In 1960 Kikuchi and Matarrese [1] in their EPR study of Mn^{2+} in calcite remarked: 'An alternative procedure is suggested by the property that the spherical harmonics, $Y_{l,m}$, transform like Racah [9] spherical tensor operators, $T_m^{(l)}$, generated by ...'. The advantages for EPR of such a spherical tensor nomenclature have been documented extensively since that time [3, 8, 10, 11] and we shall only dwell briefly on a few of the more pertinent details. Principally, there need be no redundancy in the terms, the behaviour of the operators under axis transformation is easily obtained via tabulated functions and the resulting operators are normalized. Two normalizations have been used: (i) that of Racah spherical tensor operators [9] (alternatively Buckmaster $\tilde{O}_k^q$-operators [2]); and (ii) Koster and Statz $T_{k,\pm q}$-operators [12]. Buckmaster *et al* [3] first used the latter in EPR and detailed their behaviour under a polar axis transformation via listed $d^{(k)}_{q',q}(\beta)$ finite rotation matrix elements. A SH so formulated contained no redundancies and the resulting Hamiltonian matrix was Hermitian. However, the operator coefficients were still complex and, additionally, the 'size' as measured by the norm of the coefficients was not preserved under axis rotation. (This is a generalization for orthogonal tensors of a well-known theorem in vector analysis: the length (norm) of a vector is invariant under an orthogonal transformation.) Gaite and co-workers [13, 14] first utilized this important property via normalized (tesseral) combinations of either Racah (usually now, after [13, 14, 8], written as $O_k'^q$) or Koster and Statz spherical tensor operators. The tesseral form had been used already for many years to represent the real forms of the H-like p, d, f wavefunctions and was also widely used in crystal-field theory (see Prather [15] and Hutchings [16]) and in spin-operator form by Scherz [17].

Rudowicz [8] and, independently, two of the present authors [10] outlined the desirability of having a set of tabulated matrix elements to effect general axis transformations of coordinate frames to which either Stevens operators or tesseral combinations of spherical tensor operators are referred. The former dealt with both extended and normalized Stevens operators and produced matrix elements for a polar rotation $\mathbf{R}(\phi, \theta, 0)$; a general transformation of axes was

envisaged as a succession of polar rotations. Reference [10] outlined, for tesseral spherical tensor operators, the calculation of generalized rotation matrix elements, $A^{(k)}_{g,h}$ (actually labelled $A^{(l)}_{h,k}$ in that reference), in two different notations, $f(\alpha, \beta, \gamma)$ and $f(a_{ij})$, where α, β, γ are the usual Euler angles as defined by Edmonds [18] and the matrix **a** represents a general orthogonal transformation of the axis frame to which the components of the (real or fictitious) electron spin S are referred. Matrix elements for $k = 2$ [10] and for $k = 4, 6$ [19] were listed in both notations. The present paper extends these calculations and listings to odd-k matrix elements.

The second aim arises from the necessity of having as near a complete set of operators as possible with which to cover complicated high-spin systems. Buckmaster *et al* [3] outlined the process for obtaining experimentally usable single-vector spherical tensor spin operators from a two-vector form $T_{k,q}(\boldsymbol{B}, \boldsymbol{S})$; the most general form requires decomposition of three-vector operators $T_{k,q}(\boldsymbol{B}, \boldsymbol{S}, \boldsymbol{I})$ [11]. (It is noted that no unique decomposition of such a triple-vector tensor operator exists, just as there is no unique way of coupling three angular momentum vectors [18]. Different decomposition routes produce different, but equivalent, parameter sets [11].)

Reference [11] outlined the production of a maximally reduced SH (MRSH) obtained, implicitly (see also [20]), from a two-vector form $\mathfrak{I}_{k,q}(\boldsymbol{V}, \boldsymbol{W})$ where $\boldsymbol{V}, \boldsymbol{W}$ can represent any one of $\boldsymbol{B}, \boldsymbol{S}, \boldsymbol{I}$ and $V^{k_V} W^{k_W}$, with one or other of k_V, k_W unity, is the dimension of a general term in the decomposition. These functions have been utilized in the international program EPRNMR [21]. However, there are evidently missing functions. So far as we are aware, no general decompositions of $\mathfrak{I}_{k,q}(\boldsymbol{B}, \boldsymbol{S}, \boldsymbol{I})$ exist and, as found in a recent detailed study of hyperfine structure of ^{49}Ti in zircon [20], certain eighth-rank tensor decompositions were required but not available. This publication also seeks to remedy this latter deficiency. Production of eighth-rank single-vector tesseral tensor operators requires also an extension of table 4 of [10] detailing the symmetry-allowed tesseral operators for paramagnetic sites of a given Laue class.

2. Theory

2.1. The tesseral spherical tensor operators

We shall utilize throughout the definitions (see also [10, 11])

$$\mathfrak{I}_{k,0} = T_{k,0} \tag{1a}$$

$$\mathfrak{I}_{k,q} = \frac{1}{\sqrt{2}} \left\{ (-1)^q T_{k,q} + T_{k,-q} \right\} \qquad 0 \leqslant q \leqslant k \tag{1b}$$

$$\mathfrak{I}_{k,-q} = \frac{\mathrm{i}}{\sqrt{2}} \left\{ (-1)^{q+1} T_{k,q} + T_{k,-q} \right\} \qquad 0 \leqslant q \leqslant k \tag{1c}$$

to define tesseral combinations of Koster and Statz spherical tensor operators (hereafter simply tesseral spherical tensor operators, TSTO) in the nomenclature of Edmonds [18] where, from [10], $\mathfrak{I}_{k,q}$ is written for the tesseral operator to distinguish it from the components $T_{k,q}$ (listed by Buckmaster *et al* [3] for k = 1–7). Shorthand notations, for example $T_{k,q} = T_{k,q}(\boldsymbol{J})$, have been used in equations (1) and will be used often throughout this paper. (We have followed Edmonds [18] and most recent publications (see for example [8, 22]) in using the subscripts k, q to define the tesseral operators while noting that many earlier publications used the more familiar l, m quantum numbers. The reader should note in particular the change in nomenclature from the two references [10, 11], which are widely referred to in this paper. The symbol $\mathfrak{I}$ is used throughout in place of the symbol $\mathcal{T}$ used in the text of references [10, 11].) The definitions of equations (1*a*)–(1*c*) lead naturally to coefficients of the $\mathfrak{I}_{k,q}$ being

written [10, 11] as $B_{k,q}$ (some care is required here, as this notation has also been used for the coefficients of $T_{k,q}$) as distinct from the widely used Stevens notation B_k^q. This notation also allows an easy progression to a more general coefficient $B_{k,q}^{k_1,k_2,k_3}$ (see particularly [11] for terms in a MRSH). It is readily shown [18] via the definition [9, 18]

$$T_{k,q}^{\dagger} = (-1)^q T_{k,-q} \tag{2}$$

that the operators $\mathfrak{I}_{k,q}$, as distinct from the constituent $T_{k,q}$, are Hermitian self-adjoint ($\mathfrak{I}_{k,q}^{\dagger} = \mathfrak{I}_{k,q}$ and $\mathfrak{I}_{k,-q}^{\dagger} = \mathfrak{I}_{k,-q}$) and the coefficients are now real. (We have followed the Racah [9] definition of the Hermitian adjoint of an operator, equation (2), while noting that mathematical texts frequently use the terms 'adjugate' or 'tranjugate' rather than Hermitian adjoint [23].) Using again the relation (2), equations (1*b*) and (1*c*) become

$$\mathfrak{I}_{k,q} = \frac{(-1)^q}{\sqrt{2}} \left\{ T_{k,q} + T_{k,q}^{\dagger} \right\} \tag{3a}$$

$$\mathfrak{I}_{k,-q} = \frac{\mathrm{i}(-1)^q}{\sqrt{2}} \left\{ -T_{k,q} + T_{k,q}^{\dagger} \right\}. \tag{3b}$$

Clearly equations (3*a*), (3*b*) may be used alternatively to (1*b*), (1*c*). They are related simply by a factor $\sqrt{2} \times (-1)^q$ to the tesseral functions used recently by Buckmaster and Chatterjee [22].

2.2. The spin Hamiltonian

The SH to be used is written in the notation outlined in [11], namely as

$$\mathcal{H}_S^{k_1,k_2} = G \left\{ \sum_{q=-|k_1-k_2|}^{|k_1-k_2|} B_{|k_1-k_2|,q}^{k_1,k_2} \mathfrak{I}_{|k_1-k_2|,q}^{k_1,k_2}(\boldsymbol{V}, \boldsymbol{W}) + \sum_{q=-(k_1+k_2)}^{k_1+k_2} B_{(k_1+k_2),q}^{k_1,k_2} \mathfrak{I}_{(k_1+k_2),q}^{k_1,k_2}(\boldsymbol{V}, \boldsymbol{W}) \right\} \tag{4}$$

where the vectors $\boldsymbol{V}, \boldsymbol{W}$ can represent any one of $\boldsymbol{B}, \boldsymbol{S}, \boldsymbol{I}$. In equation (4), k is constrained by the triangle condition $|k_1 - k_2| \leqslant k \leqslant k_1 + k_2$ and must be even to preserve time-reversal invariance. (In terms of the nomenclature of the previous section, k_1, k_2 could have been written as k_V, k_W.) Equation (4) is a generalization of the tesseral operator definitions of equations (1). The following two examples will illustrate its use. The equation

$$\mathcal{H}_S^{0,4} = \sum_{q=-4}^{4} B_{4,q}^{0,4} \mathfrak{I}_{4,q}^{0,4}(\hat{\boldsymbol{B}}, \boldsymbol{J})$$

with $k_1 = 0$, $k_2 = 4$, $G = \frac{1}{2}$ and $\boldsymbol{J} = \boldsymbol{S}, \boldsymbol{I}$ represents field-independent (zero-field) terms of dimension J^4; $\hat{\boldsymbol{B}}$ is a unit vector in an arbitrary direction and could be omitted. Similarly the superscripts can, without ambiguity, be omitted leading to more familiar expressions for zero-field terms of dimension S^4 or I^4 [11]. Similarly the equation

$$\mathcal{H}_S^{1,3} = G \left\{ \sum_{q=-2}^{2} B_{2,q}^{1,3} \mathfrak{I}_{2,q}^{1,3}(\hat{\boldsymbol{B}}, \boldsymbol{J}) + \sum_{q=-4}^{4} B_{4,q}^{1,3} \mathfrak{I}_{4,q}^{1,3}(\hat{\boldsymbol{B}}, \boldsymbol{J}) \right\}$$

with $k_1 = 1, k_2 = 3$ and $\boldsymbol{J} = \boldsymbol{S}, \boldsymbol{I}$, represents Zeeman terms of dimension BJ^3; in this instance $\hat{\boldsymbol{B}}$ is a unit vector in the direction of the magnetic field $\boldsymbol{B}$. The factor G takes values $g_e\beta_e B$, $-g_n\beta_n B$ when $\boldsymbol{J} = \boldsymbol{S}, \boldsymbol{I}$ respectively; g_e, β_e, g_n, β_n are the free-electron g, the Bohr magneton, the nuclear g and the nuclear magneton, respectively. (From [11], the factor G in equation (4) takes values $(g_e\beta_e B)^2$ or $(-g_n\beta_n B)^2$ for terms quadratic in field. The reader is referred to references [11, 20] for further detail on the formulation and detail of equation (4).)

Equation (4) seems at first sight to be a more cumbersome way of expressing the SH than the equivalent equation expressed in Stevens (or extended Stevens) operators but, as emphasized in

[11], equation (4) is maximally reduced and there are no redundancies as distinct from the case for the equivalent Stevens expression. In this latter regard, the reader is referred again to [11] for a more detailed discussion on the SH for terms of dimensions BJ^3, BJ^5. Decomposition of the two-vector operators of (4) to experimentally usable single-vector operators is outlined in subsection 3.3 below.

2.3. Coordinate rotations and derivation of the general rotation matrix elements, $A^{(k)}_{g,h}$

Generalized coordinate rotations in EPR have been discussed in some detail in [10]. The basis is the general orthogonal transformation

$$\boldsymbol{J} = \mathbf{a}\boldsymbol{J}' \tag{5}$$

where the prime refers to the components of the spin vector in the new coordinates. $\mathbf{a}$, constrained by the orthogonality relations $a_{ik}a_{jk} = \delta_{ij}, a_{ki}a_{kj} = \delta_{ij}$ and the condition $\mathrm{Det}(\mathbf{a}) = +1$, defines a ($3 \times 3$ in this case) proper rotation matrix. The SH must be invariant under such a transformation and so also must the SH parameters [10].

Transformation relations of $T_{k,q}$-operators are formulated most conveniently in terms of the Euler angles α, β, γ (here we use the axis conventions detailed in Edmonds [18], including choice of phase, and used also by Buckmaster *et al* [3]) via the equation

$$T_{k,q}(\boldsymbol{J}) = \mathrm{e}^{\mathrm{i}q\alpha} \sum_{q'=-k}^{k} (-1)^{q'-q} d^{(k)}_{q',q}(\beta) T_{k,q'}(\boldsymbol{J}') \mathrm{e}^{\mathrm{i}q'\gamma} \tag{6}$$

for the particular case of spin operator $\boldsymbol{J}$. When the transformation (6) is applied to the SH (4), the relations between the parameters $B'_{k,q}$ in the new frame and the $B_{k,q}$ of the old frame may be written via equations (12) of reference [10] as

$$\underset{(2k+1)\times 1}{\left[B'_{k,q}\right]} = \underset{(2k+1)\times(2k+1)}{\left[A^{(k)}_{g,h}\right]} \times \underset{(2k+1)\times 1}{\left[B_{k,q}\right]} \tag{7}$$

where the integral subindices g, h relate to the quantum numbers q through

$$\begin{aligned} &g \text{ or } h \quad = 1,\ 2,\quad 3,\ 4,\quad 5,\ \ldots,\ 2k,\ 2k+1 \\ &\text{when } q = 0,\ 1,\ -1,\ 2,\ -2,\ \ldots,\ k,\ -k. \end{aligned}$$

(Again, the attention of the reader is drawn to the change in nomenclature from [10] where the symbol $A^{(l)}_{h,k}$ was used.) Equation (7) represents an orthogonal transformation and, as defined for the 3×3 matrix $\mathbf{a}$ in equation (5), $\mathbf{A}$ is a proper rotation matrix of dimension $2k + 1$. The axis rotation can however be more generally expressed, for reasons discussed below, in terms of the orthogonal rotation given by equation (5) (see reference [10]). The relations between the Euler and a_{ij} notations are given in equations (13) of reference [10] and detailed in table 1 below.

Table 1 also details the contracted notation to be used for the listed matrix elements $A^{(k)}_{g,h}$. The matrix elements for $k = 1$ are given simply by

$$\begin{pmatrix} A^{(1)}_{1,1} & A^{(1)}_{1,2} & A^{(1)}_{1,3} \\ A^{(1)}_{2,1} & A^{(1)}_{2,2} & A^{(1)}_{2,3} \\ A^{(1)}_{3,1} & A^{(1)}_{3,2} & A^{(1)}_{3,3} \end{pmatrix} = \begin{pmatrix} a_{33} & a_{13} & a_{23} \\ a_{31} & a_{11} & a_{21} \\ a_{32} & a_{12} & a_{22} \end{pmatrix}. \tag{8}$$

Those for $k = 2, 3$ are listed in table 2. (The $k = 2$ matrix elements are repeated from reference [10] but, for consistency, are listed here in the more compact notation of table 1.) Those for $k = 4, 5, 6$ are obtainable from the authors or via the program ROTSTO (see the appendix).

Table 1. Relations between the Euler notation, a_{ij} notation and contracted a_{ij} notation.

Euler angle notation	a_{ij} notation	Contracted notation
$(1+\cos\beta)\cos(\alpha+\gamma)$	$a_{11}+a_{22}$	a_{1+}
$-(1-\cos\beta)\cos(\alpha-\gamma)$	$a_{11}-a_{22}$	a_{1-}
$-(1+\cos\beta)\sin(\alpha+\gamma)$	$a_{12}-a_{21}$	a_{2-}
$-(1-\cos\beta)\sin(\alpha-\gamma)$	$a_{12}+a_{21}$	a_{2+}
$\sin\beta\,\mathrm{e}^{\mathrm{i}\alpha}$	$a_{13}+\mathrm{i}a_{23}$	—
$-\sin\beta\,\mathrm{e}^{-\mathrm{i}\gamma}$	$a_{31}+\mathrm{i}a_{32}$	—
$\sin\beta$	—	s
$\cos\beta$	a_{33}	c
$\sin^n\beta\,\mathrm{e}^{\mathrm{i}n\alpha}$	$(a_{13}+\mathrm{i}a_{23})^n$	$C_{n\alpha}+\mathrm{i}S_{n\alpha}$
$(-1)^n\sin^n\beta\,\mathrm{e}^{-\mathrm{i}n\gamma}$	$(a_{31}+\mathrm{i}a_{32})^n$	$C_{n\gamma}+\mathrm{i}S_{n\gamma}$
$(1+\cos\beta)^n\mathrm{e}^{-\mathrm{i}n(\alpha+\gamma)}$	$(a_{1+}+\mathrm{i}a_{2-})^n$	$C_{na}+\mathrm{i}S_{na}$
$(-1)^n(1-\cos\beta)^n\mathrm{e}^{\mathrm{i}n(\alpha-\gamma)}$	$(a_{1-}+\mathrm{i}a_{2+})^n$	$C_{nb}+\mathrm{i}S_{nb}$

The functions $f^{(k)}_{m',m}=f^{(k)}_{m',m}(\cos\beta)=f^{(k)}_{m',m}(a_{33})$ of table 2 are repetitively used parts of the $d^{(k)}_{m',m}(\beta)$ finite rotation matrix elements where $f^{(2)}_{1,\pm1}=2a_{33}\mp1$, $f^{(3)}_{1,\pm1}=3a_{33}\mp1$ and $f^{(3)}_{2,\pm1}=15a^2_{33}\mp10a_{33}-1$.

3. Discussion

3.1. Applications of the rotation matrix elements $A^{(k)}_{g,h}$

These have been detailed elsewhere [10] and we shall dwell only on a few more pertinent points. Most applications are effected via the program ROTSTO which can be used as a stand-alone procedure or called as a subroutine in more complicated calculations.

Firstly, the correctness of the matrix elements: it has been checked algebraically by independent replicate calculations by three of the authors (see reference [24] for the most recent), and numerically in the program ROTSTO (in each case to the precision of the input rotation matrix): (i) that the input rotation matrix and all generated rotation matrices are proper rotation matrices as defined earlier; and (ii) that invariance in the norm is ensured for tensorial sets of ranks 1–6 for a general rotation $\mathbf{R}(\alpha\beta\gamma)$ with each angle varied by small increments.

The simplest and most obvious application is that of comparison of SH parameters for different formulations of the SH and where different sets of reference axes may have been chosen. This application refers to input parameters from SHs expressed in one of the three tesseral forms outlined in the introduction and utilizes the interrelations expressed in equations (14), (15) of [10] and table 1 of [11] (see also references [8, 25]). Output is expressed in all three forms.

The advantage of the notation used in table 2 over a simple Euler angle notation [10] is that any change of basis can be carried through a series of calculations. Two examples involving perturbation approximations follow. The most common perturbation calculation is that involving a predominant electronic Zeeman term in the SH. Then a rotation of coordinates is required which diagonalizes the Zeeman term. The rotation is defined by equation (5) where the elements of $\mathbf{a}$ (or, equation (8), the elements of $\mathbf{A}$) are chosen such that $\beta_e\boldsymbol{B}\cdot\mathbf{g}\boldsymbol{S}$ becomes

Table 2. Matrix elements $A^{(k)}_{g,h}$, $k = 2, 3$, in the a_{ij} notation detailed in table 1.

k	g	h	m_g	m_h	Matrix elements $A^{(2)}_{g,h}$
2	1	1	0	0	$\frac{1}{2}(3a_{33}^2 - 1)$
2	1	2	0	1	$\sqrt{3}a_{13}a_{33}$
2	1	3	0	−1	$\sqrt{3}a_{23}a_{33}$
2	1	4	0	2	$\frac{\sqrt{3}}{2}C_{2\alpha}$
2	1	5	0	−2	$\frac{\sqrt{3}}{2}S_{2\alpha}$
2	2	1	1	0	$\sqrt{3}a_{31}a_{33}$
2	2	2	1	1	$\frac{1}{2}(a_{1+}f^{(2)}_{1,1} + a_{1-}f^{(2)}_{1,-1})$
2	2	3	1	−1	$\frac{1}{2}(-a_{2-}f^{(2)}_{1,1} + a_{2+}f^{(2)}_{1,-1})$
2	2	4	1	2	$\frac{1}{2}\{a_{13}(a_{1+} + a_{1-}) + a_{23}(a_{2-} - a_{2+})\}$
2	2	5	1	−2	$\frac{1}{2}\{a_{23}(a_{1+} + a_{1-}) + a_{13}(a_{2+} - a_{2-})\}$
2	3	1	−1	0	$\sqrt{3}a_{32}a_{33}$
2	3	2	−1	1	$\frac{1}{2}(a_{2-}f^{(2)}_{1,1} + a_{2+}f^{(2)}_{1,-1})$
2	3	3	−1	−1	$\frac{1}{2}(a_{1+}f^{(2)}_{1,1} - a_{1-}f^{(2)}_{1,-1})$
2	3	4	−1	2	$\frac{1}{2}\{a_{23}(a_{1-} - a_{1+}) + a_{13}(a_{2+} + a_{2-})\}$
2	3	5	−1	−2	$\frac{1}{2}\{a_{13}(a_{1+} - a_{1-}) + a_{23}(a_{2+} + a_{2-})\}$
2	4	1	2	0	$\frac{\sqrt{3}}{2}C_{2\gamma}$
2	4	2	2	1	$\frac{1}{2}\{a_{31}(a_{1+} + a_{1-}) - a_{32}(a_{2+} + a_{2-})\}$
2	4	3	2	−1	$\frac{1}{2}\{a_{32}(a_{1-} - a_{1+}) + a_{31}(a_{2+} - a_{2-})\}$
2	4	4	2	2	$\frac{1}{4}(C_{2a} + C_{2b})$
2	4	5	2	−2	$\frac{1}{4}(S_{2b} - S_{2a})$
2	5	1	−2	0	$\frac{\sqrt{3}}{2}S_{2\gamma}$
2	5	2	−2	1	$\frac{1}{2}\{a_{32}(a_{1+} + a_{1-}) + a_{31}(a_{2+} + a_{2-})\}$
2	5	3	−2	−1	$\frac{1}{2}\{a_{31}(a_{1+} - a_{1-}) + a_{32}(a_{2+} - a_{2-})\}$
2	5	4	−2	2	$\frac{1}{4}(S_{2a} + S_{2b})$
2	5	5	−2	−2	$\frac{1}{4}(C_{2a} - C_{2b})$

$g\beta_e B S'_z$ in the rotated coordinate frame. For symmetric $\mathbf{g}$ the conditions are [26, 27]

$$a_{i3} = \frac{1}{g}(e_i \cdot \mathbf{g}\boldsymbol{\eta}) \qquad (i = 1, 2, 3) \tag{9}$$

where e_i are the unit vectors in the original directions $\boldsymbol{x}, \boldsymbol{y}, \boldsymbol{z}$ respectively and $\boldsymbol{\eta}$ is a unit vector along which the magnetic field is directed, and the factor g of equation (9) is given by $g = (\tilde{\eta} \cdot \tilde{\mathbf{g}} \cdot \mathbf{g} \cdot \eta)^{1/2}$; $\mathbf{g}$ is the g-parameter matrix ('tensor'). This fixes three elements of $\mathbf{a}$ (or $\mathbf{A}$), the others being arbitrary within the constraint that $\mathbf{a}$ represent a proper rotation. The continuing details of the perturbation procedures incorporating matrix elements $A^{(k)}_{g,h}$ are given in [10]. The chief advantage is that complicated perturbation calculations can be effected to the desired order of approximation by computer, drawing on tabulated functions and the coordinate rotation program ROTSTO, rather than via lengthy and often unwieldy formulae.

For a predominant second-degree fine-structure term, one is restricted generally to numerical procedures. One might wish for example, as detailed by Buckmaster *et al* [3],

Table 2. (Continued)

k	g	h	m_g	m_h	Matrix elements $A^{(3)}_{g,h}$
3	1	1	0	0	$\frac{1}{2}a_{33}(5a_{33}^2-3)$
3	1	2	0	1	$\frac{\sqrt{6}}{4}a_{13}(5a_{33}^2-1)$
3	1	3	0	−1	$\frac{\sqrt{6}}{4}a_{23}(5a_{33}^2-1)$
3	1	4	0	2	$\frac{\sqrt{15}}{2}a_{33}C_{2\alpha}$
3	1	5	0	−2	$\frac{\sqrt{15}}{2}a_{33}S_{2\alpha}$
3	1	6	0	3	$\frac{\sqrt{10}}{4}C_{3\alpha}$
3	1	7	0	−3	$\frac{\sqrt{10}}{4}S_{3\alpha}$
3	2	1	1	0	$\frac{\sqrt{6}}{4}a_{31}(5a_{33}^2-1)$
3	2	2	1	1	$\frac{1}{8}(a_{1+}f^{(3)}_{1,1}+a_{1-}f^{(3)}_{1,-1})$
3	2	3	1	−1	$\frac{1}{8}(-a_{2-}f^{(3)}_{1,1}+a_{2+}f^{(3)}_{1,-1})$
3	2	4	1	2	$\frac{\sqrt{10}}{8}\{(a_{13}a_{1+}+a_{23}a_{2-})f^{(3)}_{2,1}+(a_{13}a_{1-}-a_{23}a_{2+})f^{(3)}_{2,-1}\}$
3	2	5	1	−2	$\frac{\sqrt{10}}{8}\{(a_{23}a_{1+}-a_{13}a_{2-})f^{(3)}_{2,1}+(a_{23}a_{1-}+a_{13}a_{2+})f^{(3)}_{2,-1}\}$
3	2	6	1	3	$\frac{\sqrt{15}}{8}\{(a_{1+}C_{2\alpha}+a_{2-}S_{2\alpha})+(a_{1-}C_{2\alpha}-a_{2+}S_{2\alpha})\}$
3	2	7	1	−3	$\frac{\sqrt{15}}{8}\{+(a_{1+}S_{2\alpha}-a_{2-}C_{2\alpha})+(a_{1-}S_{2\alpha}+a_{2+}C_{2\alpha})\}$
3	3	1	−1	0	$\frac{\sqrt{6}}{4}a_{32}(5a_{33}^2-1)$
3	3	2	−1	1	$\frac{1}{8}(a_{2-}f^{(3)}_{1,1}+a_{2+}f^{(3)}_{1,-1})$
3	3	3	−1	−1	$\frac{1}{8}(a_{1+}f^{(3)}_{1,1}-a_{1-}f^{(3)}_{1,-1})$
3	3	4	−1	2	$-\frac{\sqrt{10}}{8}\{(a_{23}a_{1+}-a_{13}a_{2-})f^{(3)}_{2,1}-(a_{23}a_{1-}+a_{13}a_{2+})f^{(3)}_{2,-1}\}$
3	3	5	−1	−2	$\frac{\sqrt{10}}{8}\{(a_{13}a_{1+}+a_{23}a_{2-})f^{(3)}_{2,1}+(-a_{13}a_{1-}+a_{23}a_{2+})f^{(3)}_{2,-1}\}$
3	3	6	−1	3	$-\frac{\sqrt{15}}{8}\{(a_{1+}S_{2\alpha}-a_{2-}C_{2\alpha})-(a_{1-}S_{2\alpha}+a_{2+}C_{2\alpha})\}$
3	3	7	−1	−3	$\frac{\sqrt{15}}{8}\{(a_{1+}C_{2\alpha}+a_{2-}S_{2\alpha})+(-a_{1-}C_{2\alpha}+a_{2+}S_{2\alpha})\}$
3	4	1	2	0	$\frac{\sqrt{15}}{2}a_{33}C_{2\gamma}$
3	4	2	2	1	$\frac{\sqrt{10}}{8}\{(a_{31}a_{1+}-a_{32}a_{2-})f^{(3)}_{2,1}+(a_{31}a_{1-}-a_{32}a_{2+})f^{(3)}_{2,-1}\}$
3	4	3	2	−1	$-\frac{\sqrt{10}}{8}\{(a_{31}a_{2-}+a_{32}a_{1+})f^{(3)}_{2,1}-(a_{31}a_{2+}+a_{32}a_{1-})f^{(3)}_{2,-1}\}$
3	4	4	2	2	$\frac{1}{4}(C_{2a}f^{(3)}_{2,2}+C_{2b}f^{(3)}_{2,-2})$
3	4	5	2	−2	$\frac{1}{4}(-S_{2a}f^{(3)}_{2,2}+S_{2b}f^{(3)}_{2,-2})$
3	4	6	2	3	$\frac{\sqrt{6}}{8}\{(a_{13}C_{2a}+a_{23}S_{2a})+(a_{13}C_{2b}-a_{23}S_{2b})\}$
3	4	7	2	−3	$\frac{\sqrt{6}}{8}\{(a_{23}C_{2a}-a_{13}S_{2a})+(a_{23}C_{2b}+a_{13}S_{2b})\}$

to transform a set of EPR parameters to coordinates which diagonalize the second-degree fine-structure term, the D-matrix in the conventional SH, or, perhaps in the case of relatively high site point group symmetry, refer the SH parameters to a threefold (or pseudo-threefold) or fourfold (or pseudo-fourfold) symmetry axis. In this latter example one might use the pseudo-symmetry search options of the program ROTSTO to find the pseudo-cubic axes and then the normal coordinate rotation option to obtain all of the SH parameters in the 'new' (pseudo-cube) coordinate frame. Reference [28] gives such an example: Fe^{3+}/α-quartz. The relevant equations for the pseudo-symmetry options of program ROTSTO are given in the next section.

Table 2. (Continued)

k	g	h	m_g	m_h	Matrix elements $A^{(3)}_{g,h}$
3	5	1	−2	0	$\frac{\sqrt{15}}{2}a_{33}S_{2\gamma}$
3	5	2	−2	1	$\frac{\sqrt{10}}{8}\{(a_{31}a_{2-}+a_{32}a_{1+})f^{(3)}_{2,1}+(a_{31}a_{2+}+a_{32}a_{1-})f^{(3)}_{2,-1}\}$
3	5	3	−2	−1	$-\frac{\sqrt{10}}{8}\{(-a_{31}a_{1+}+a_{32}a_{2-})f^{(3)}_{2,1}+(a_{31}a_{1-}-a_{32}a_{2+})f^{(3)}_{2,-1}\}$
3	5	4	−2	2	$\frac{1}{4}(S_{2a}f^{(3)}_{2,2}+S_{2b}f^{(3)}_{2,-2})$
3	5	5	−2	−2	$\frac{1}{4}(C_{2a}f^{(3)}_{2,2}-C_{2b}f^{(3)}_{2,-2})$
3	5	6	−2	3	$-\frac{\sqrt{6}}{8}\{(a_{23}C_{2a}-a_{13}S_{2a})-(a_{23}C_{2b}+a_{13}S_{2b})\}$
3	5	7	−2	−3	$\frac{\sqrt{6}}{8}\{(a_{13}C_{2a}+a_{23}S_{2a})-(a_{13}C_{2b}-a_{23}S_{2b})\}$
3	6	1	3	0	$\frac{\sqrt{10}}{4}C_{3\gamma}$
3	6	2	3	1	$\frac{\sqrt{15}}{8}\{(a_{1+}C_{2\gamma}-a_{2-}S_{2\gamma})+(a_{1-}C_{2\gamma}-a_{2+}S_{2\gamma})\}$
3	6	3	3	−1	$\frac{\sqrt{15}}{8}\{-(a_{2-}C_{2\gamma}+a_{1+}S_{2\gamma})+(a_{2+}C_{2\gamma}+a_{1-}S_{2\gamma})\}$
3	6	4	3	2	$-\frac{\sqrt{6}}{8}\{(-a_{31}C_{2a}+a_{32}S_{2a})+(-a_{31}C_{2b}+a_{32}S_{2b})\}$
3	6	5	3	−2	$-\frac{\sqrt{6}}{8}\{(a_{31}S_{2a}+a_{32}C_{2a})-(a_{31}S_{2b}+a_{32}C_{2b})\}$
3	6	6	3	3	$\frac{1}{8}(C_{3a}+C_{3b})$
3	6	7	3	−3	$\frac{1}{8}(-S_{3a}+S_{3b})$
3	7	1	−3	0	$\frac{\sqrt{10}}{4}S_{3\gamma}$
3	7	2	−3	1	$\frac{\sqrt{15}}{8}\{(a_{2-}C_{2\gamma}+a_{1+}S_{2\gamma})+(a_{2+}C_{2\gamma}+a_{1-}S_{2\gamma})\}$
3	7	3	−3	−1	$\frac{\sqrt{15}}{8}\{(a_{1+}C_{2\gamma}-a_{2-}S_{2\gamma})+(-a_{1-}C_{2\gamma}+a_{2+}S_{2\gamma})\}$
3	7	4	−3	2	$\frac{\sqrt{6}}{8}\{(a_{31}S_{2a}+a_{32}C_{2a})+(a_{31}S_{2b}+a_{32}C_{2b})\}$
3	7	5	−3	−2	$\frac{\sqrt{6}}{8}\{(a_{31}C_{2a}-a_{32}S_{2a})+(-a_{31}C_{2b}+a_{32}S_{2b})\}$
3	7	6	−3	3	$\frac{1}{8}(S_{3a}+S_{3b})$
3	7	7	−3	−3	$\frac{1}{8}(C_{3a}-C_{3b})$

3.2. Equations for pseudo-cube analysis

This work is detailed in papers by Gaite and co-workers (see references [13, 14]). Here we shall be content to give the relevant equations for tensors of ranks 4 and 6 (the latter, so far as we are aware, have not appeared previously). The criteria for threefold and fourfold axes of cubic pseudo-symmetry in a set of parameters of dimension S^4 have been set out by Gaite and Michoulier [13] and in somewhat modified form by Mombourquette *et al* [28]. Since, as noted above, the transformation properties of irreducible tensors under axis transformation depend only on their rank, k, we may use the simpler form, $B_{k,q}$, for $B^{k_1,k_2,k_3}_{k,q}$ and the formulae which follow refer to any irreducible tensors of ranks 4 and 6. We define, for $k = 4, 6$ throughout,

$$N_k = \sum_q (B_{k,q})^2 \qquad (-k \leqslant q \leqslant k)$$

where $(N_k)^{1/2}$ is the norm of the set.

3.2.1. Fourfold axes.

$$\varepsilon_4^{(k)} = \sum_q{}' (B_{k,q})^2/N_k \qquad (q \neq 0, \pm 4) \tag{10}$$

$$\gamma_4^{(k)} = \left[(B_{k,4})^2 + (B_{k,-4})^2\right]^{1/2} \Big/ \left|B_{k,0}\right| \tag{11}$$

$$\delta_4^{(k)} = 1 - \left(\frac{a'_k}{a^*_k}\right)^2 \tag{12}$$

where

$$a'_4 = \frac{7}{12}\left\{\left|B_{4,0}\right| + \frac{\sqrt{5}}{\sqrt{7}}\left[(B_{4,4})^2 + (B_{4,-4})^2\right]^{1/2}\right\}$$

$$a^*_4 = \left[\frac{7}{12}N_4\right]^{1/2}$$

$$a'_6 = \frac{1}{8}\left\{\left|B_{6,0}\right| + \sqrt{7}\left[(B_{6,4})^2 + (B_{6,-4})^2\right]^{1/2}\right\}$$

$$a^*_6 = \left[\frac{1}{6}N_6\right]^{1/2}.$$

3.2.2. Threefold axes.

$$\varepsilon_3^{(k)} = {\sum_q}' (B_{k,q})^2/N_k \qquad (q \neq 0, \pm 3, \pm 6) \tag{13}$$

$$\gamma_3^{(4)} = \left[(B_{4,3})^2 + (B_{4,-3})^2\right]^{1/2} \Big/ \left|B_{4,0}\right| \tag{14}$$

$$\gamma_3^{(6)} = \left\{\left[(B_{6,3})^2 + (B_{6,-3})^2\right]^{1/2} + \left[(B_{6,6})^2 + (B_{6,-6})^2\right]^{1/2}\right\} \Big/ \left|B_{6,0}\right| \tag{15}$$

$$\delta_3^{(k)} = 1 - \left(\frac{b'_k}{b^*_k}\right)^2 \tag{16}$$

where

$$b'_4 = \frac{7}{27}\left\{\left|B_{4,0}\right| + \frac{2\sqrt{5}}{\sqrt{7}}\left[(B_{4,3})^2 + (B_{4,-3})^2\right]^{1/2}\right\}$$

$$b^*_4 = \left[\frac{7}{27}N_4\right]^{1/2}$$

$$b'_6 = \frac{32}{81}\left\{\left|B_{6,0}\right| + \frac{35\sqrt{3}}{12}\left[(B_{6,3})^2 + (B_{6,-3})^2\right]^{1/2} + \frac{\sqrt{462}}{24}\left[(B_{6,6})^2 + (B_{6,-6})^2\right]^{1/2}\right\}$$

$$b^*_6 = \left[\frac{32}{81}N_6\right]^{1/2}.$$

The primed summation symbol in equations (10), (13) signifies that the summation includes only the specified values of q.

The details of the application of equations (10)–(16) have been given elsewhere [13, 14, 28]. In summary, one varies the angular coordinates over a grid on the unit-sphere surface to find the polar and azimuthal angles, θ, ϕ respectively, with respect to the original coordinate frame, for which the 'search' parameter, $\varepsilon_n^{(k)}$ of equations (10), (13) ($n = 3, 4$; $k = 4, 6$), is minimized, in order to find the polar coordinates of the pseudo-threefold and fourfold axes respectively of the experimental $B_{k,q}$-tensor. Equations (10)–(16) together with the rotation matrix elements $A_{g,h}^{(k)}$ enable the pseudo-cube procedures in program ROTSTO. As in the axis rotation options, input can be in any one of the three tesseral forms described in the theory section above. As a check, the 'distortion' parameters $\gamma_n^{(k)}$ (equations (11), (14),

(15)) and $\delta_n^{(k)}$ (equations (12), (16)) are also computed at each angular interval. For exact cubic symmetry the search parameter ε and the distortion parameters γ, δ take the values shown in table 3.

Table 3. Values of the search parameter $\varepsilon_n^{(k)}$ and the distortion parameters $\gamma_n^{(k)}$, $\delta_n^{(k)}$ in exact cubic symmetry

	Fourfold axes			Threefold axes		
	$\varepsilon_4^{(k)}$	$\gamma_4^{(k)}$	$\delta_4^{(k)}$	$\varepsilon_3^{(k)}$	$\gamma_3^{(k)}$	$\delta_3^{(k)}$
$l=4$	0	$\sqrt{5}/\sqrt{7}$	0	0	$2\sqrt{5}/\sqrt{7}$	0
$l=6$	0	$\sqrt{7}$	0	0	$\sqrt{7}(2\sqrt{5}+\sqrt{22})/8\sqrt{3}$	0

3.3. $J_1 J_2^7$ terms in the SH.

As outlined in [3], and detailed for the case $\boldsymbol{V}=\boldsymbol{B}$, $\boldsymbol{W}=\boldsymbol{S}$ in [11], the two-vector operators of equation (4) are decomposed to experimentally usable single-vector operators via

$$T_{k,q}^{k_1,k_2}=\sum_{q_1=-k_1}^{k_1}\sum_{q_2=-k_2}^{k_2}(-1)^{k_1+k_2+q}(2k+1)^{1/2}\begin{pmatrix}k_1 & k_2 & k\\ q_1 & q_2 & -q\end{pmatrix}T_{k_1,q_1}T_{k_2,q_2}. \tag{17}$$

The principles involved are essentially those used by Grant and Strandberg [29] for a paramagnetic ion in cubic symmetry and by Buckmaster and Chatterjee [30] for Eu^{2+} in tetragonal symmetry, with the two important exceptions that here we consider the more general case of TSTO and assume the lowest possible site symmetry, $\bar{1}$ Laue class. The symmetry restrictions on the terms to be included in the SH for various site symmetries are considered in the next section. For the tensor decompositions to be now outlined we consider the particular cases $V=B=1$, $W=J=7/2$ ($J=S, I$) but note (see also [20]) that implicitly covered are all cases where V, W can be any one of B, S, I ($B\leqslant 1$). The $B_{k,q}^{k_1,k_2}$ of equation (4) are components of irreducible tensors of rank k.

The tensor decompositions required are defined generally by equations (4), (17). Here we shall give results for the particular example for terms of dimension BJ^7 when [11] the SH may be written as

$$\mathcal{H}_S^{(1,7)}=G\left\{\sum_{m=-6}^{6}(B_{6,m}^{1,7}U_{7,6,m})+\sum_{m=-8}^{8}(B_{8,m}^{1,7}U_{7,8,m})\right\} \tag{18}$$

where the $U_{l_J,l,m}$ (functions of $\mathfrak{I}_{l,m}(\boldsymbol{J})$, $\boldsymbol{J}=\boldsymbol{S},\boldsymbol{I}$; $I_J=7$, $l=l_J+1=8$, $l=l_J-1=6$ and $-l\leqslant m\leqslant l$) are listed in tables 4(a), 4(b). As earlier, $G=g_e\beta_e B$ or $-g_n\beta_n B$ according as $\boldsymbol{J}=\boldsymbol{S},\boldsymbol{I}$ respectively. These tables are formatted precisely as for the BJ^3, BJ^5 decompositions of table 3 of [11] for consistency. It is noted that in equation (18) and in tables 4(a), (b) we have replaced k, q by the quantum numbers l, m throughout, again for consistency with [11].

In tables 4(a), 4(b), $\hat{B}_x$, $\hat{B}_y$, $\hat{B}_z$ are components of the unit vector $\hat{\boldsymbol{B}}$ along which the magnetic field is directed and [11]

$$\hat{B}_z=\mathfrak{I}_{1,0}(\hat{\boldsymbol{B}})\qquad \hat{B}_x=\mathfrak{I}_{1,1}(\hat{\boldsymbol{B}})\qquad \hat{B}_y=\mathfrak{I}_{1,-1}(\hat{\boldsymbol{B}}). \tag{19}$$

It follows, on replacing equations (19) with equations (20):

$$J_z=\mathfrak{I}_{1,0}(\boldsymbol{J})\qquad J_x=\mathfrak{I}_{1,1}(\boldsymbol{J})\qquad J_y=\mathfrak{I}_{1,-1}(\boldsymbol{J})\qquad (\boldsymbol{J}=\boldsymbol{S},\boldsymbol{I}) \tag{20}$$

Table 4. (a) $U_{l_J,l,m}$ of equation (18) for $l_J = 7$; $l = l_J + 1$; $-l \leqslant m \leqslant l$. (b) $U_{l_J,l,m}$ of equation (18) for $l_J = 7$; $l = l_J + 1$; $-l \leqslant m \leqslant l$.

(a)	l_J	l	m	$U_{l_J,l,m}$
	7	6	0	$\frac{1}{\sqrt{15}}\left\{-\sqrt{7}\hat{B}_z\mathfrak{I}_{7,0} - 2\hat{B}_x\mathfrak{I}_{7,1} - 2\hat{B}_y\mathfrak{I}_{7,-1}\right\}$
	7	6	1	$\frac{1}{\sqrt{35}}\left\{\sqrt{7}\hat{B}_x\mathfrak{I}_{7,0} - 4\hat{B}_z\mathfrak{I}_{7,1} - \sqrt{6}\left[\hat{B}_x\mathfrak{I}_{7,2} + \hat{B}_y\mathfrak{I}_{7,-2}\right]\right\}$
	7	6	−1	$\frac{1}{\sqrt{35}}\left\{\sqrt{7}\hat{B}_y\mathfrak{I}_{7,0} - 4\hat{B}_z\mathfrak{I}_{7,-1} + \sqrt{6}\left[\hat{B}_y\mathfrak{I}_{7,2} - \hat{B}_x\mathfrak{I}_{7,-2}\right]\right\}$
	7	6	2	$\frac{1}{\sqrt{14}}\left\{\hat{B}_x\mathfrak{I}_{7,1} - \hat{B}_y\mathfrak{I}_{7,-1} - \sqrt{6}\hat{B}_z\mathfrak{I}_{7,2} - \sqrt{3}\left[\hat{B}_x\mathfrak{I}_{7,3} + \hat{B}_y\mathfrak{I}_{7,-3}\right]\right\}$
	7	6	−2	$\frac{1}{\sqrt{14}}\left\{\hat{B}_x\mathfrak{I}_{7,-1} + \hat{B}_y\mathfrak{I}_{7,1} - \sqrt{6}\hat{B}_z\mathfrak{I}_{7,-2} + \sqrt{3}\left[\hat{B}_y\mathfrak{I}_{7,3} - \hat{B}_x\mathfrak{I}_{7,-3}\right]\right\}$
	7	6	3	$\frac{1}{\sqrt{42}}\left\{\sqrt{2}\left[\hat{B}_x\mathfrak{I}_{7,2} - \hat{B}_y\mathfrak{I}_{7,-2}\right] - 4\hat{B}_z\mathfrak{I}_{7,3} - \sqrt{11}\left[\hat{B}_x\mathfrak{I}_{7,4} + \hat{B}_y\mathfrak{I}_{7,-4}\right]\right\}$
	7	6	−3	$\frac{1}{\sqrt{42}}\left\{\sqrt{2}\left[\hat{B}_x\mathfrak{I}_{7,-2} + \hat{B}_y\mathfrak{I}_{7,2}\right] - 4\hat{B}_z\mathfrak{I}_{7,-3} + \sqrt{11}\left[\hat{B}_y\mathfrak{I}_{7,4} - \hat{B}_x\mathfrak{I}_{7,-4}\right]\right\}$
	7	6	4	$\frac{1}{\sqrt{35}}\left\{\hat{B}_x\mathfrak{I}_{7,3} - \hat{B}_y\mathfrak{I}_{7,-3} - \sqrt{11}\left[\hat{B}_z\mathfrak{I}_{7,4} + \hat{B}_x\mathfrak{I}_{7,5} + \hat{B}_y\mathfrak{I}_{7,-5}\right]\right\}$
	7	6	−4	$\frac{1}{\sqrt{35}}\left\{\hat{B}_x\mathfrak{I}_{7,-3} + \hat{B}_y\mathfrak{I}_{7,3} + \sqrt{11}\left[-\hat{B}_z\mathfrak{I}_{7,-4} + \hat{B}_y\mathfrak{I}_{7,5} - \hat{B}_x\mathfrak{I}_{7,-5}\right]\right\}$
	7	6	5	$\frac{1}{2\sqrt{70}}\left\{\hat{B}_x\mathfrak{I}_{7,4} - \hat{B}_y\mathfrak{I}_{7,-4} - 2\sqrt{2}\hat{B}_z\mathfrak{I}_{7,5} - \sqrt{26}\left[\hat{B}_x\mathfrak{I}_{7,6} + \hat{B}_y\mathfrak{I}_{7,-6}\right]\right\}$
	7	6	−5	$\frac{1}{2\sqrt{70}}\left\{\hat{B}_y\mathfrak{I}_{7,4} + \hat{B}_x\mathfrak{I}_{7,-4} - 2\sqrt{2}\hat{B}_z\mathfrak{I}_{7,-5} + \sqrt{26}\left[\hat{B}_y\mathfrak{I}_{7,6} - \hat{B}_x\mathfrak{I}_{7,-6}\right]\right\}$
	7	6	6	$\frac{1}{\sqrt{210}}\left\{\hat{B}_x\mathfrak{I}_{7,5} - \hat{B}_y\mathfrak{I}_{7,-5} - \sqrt{26}\hat{B}_z\mathfrak{I}_{7,6} - \sqrt{91}\left[\hat{B}_x\mathfrak{I}_{7,7} + \hat{B}_y\mathfrak{I}_{7,-7}\right]\right\}$
	7	6	−6	$\frac{1}{\sqrt{210}}\left\{\hat{B}_y\mathfrak{I}_{7,5} + \hat{B}_x\mathfrak{I}_{7,-5} - \sqrt{26}\hat{B}_z\mathfrak{I}_{7,-6} + \sqrt{91}\left[\hat{B}_y\mathfrak{I}_{7,7} - \hat{B}_x\mathfrak{I}_{7,-7}\right]\right\}$
(b)	l_J	l	m	$U_{l_J,l,m}$
	7	8	0	$\frac{1}{\sqrt{30}}\left\{4\hat{B}_z\mathfrak{I}_{7,0} - \sqrt{7}\left[\hat{B}_x\mathfrak{I}_{7,1} + \hat{B}_y\mathfrak{I}_{7,-1}\right]\right\}$
	7	8	1	$\frac{1}{4\sqrt{5}}\left\{2\sqrt{6}\hat{B}_x\mathfrak{I}_{7,0} + \sqrt{42}\hat{B}_z\mathfrak{I}_{7,1} - \sqrt{7}\left[\hat{B}_x\mathfrak{I}_{7,2} + \hat{B}_y\mathfrak{I}_{7,-2}\right]\right\}$
	7	8	−1	$\frac{1}{4\sqrt{5}}\left\{2\sqrt{6}\hat{B}_y\mathfrak{I}_{7,0} + \sqrt{42}\hat{B}_z\mathfrak{I}_{7,-1} + \sqrt{7}\left[\hat{B}_y\mathfrak{I}_{7,2} - \hat{B}_x\mathfrak{I}_{7,-2}\right]\right\}$
	7	8	2	$\frac{1}{4}\left\{\sqrt{3}\left[\hat{B}_x\mathfrak{I}_{7,1} - \hat{B}_y\mathfrak{I}_{7,-1}\right] + 2\sqrt{2}\hat{B}_z\mathfrak{I}_{7,2} - \hat{B}_x\mathfrak{I}_{7,3} - \hat{B}_y\mathfrak{I}_{7,-3}\right\}$
	7	8	−2	$\frac{1}{4}\left\{\sqrt{3}\left[\hat{B}_y\mathfrak{I}_{7,1} + \hat{B}_x\mathfrak{I}_{7,-1}\right] + 2\sqrt{2}\hat{B}_z\mathfrak{I}_{7,-2} + \hat{B}_y\mathfrak{I}_{7,3} - \hat{B}_x\mathfrak{I}_{7,-3}\right\}$
	7	8	3	$\frac{1}{4\sqrt{3}}\left\{\sqrt{11}\left[\hat{B}_x\mathfrak{I}_{7,2} - \hat{B}_y\mathfrak{I}_{7,-2}\right] + \sqrt{22}\hat{B}_z\mathfrak{I}_{7,3} - \sqrt{2}\left[\hat{B}_x\mathfrak{I}_{7,4} + \hat{B}_y\mathfrak{I}_{7,-4}\right]\right\}$
	7	8	−3	$\frac{1}{4\sqrt{3}}\left\{\sqrt{11}\left[\hat{B}_y\mathfrak{I}_{7,2} + \hat{B}_x\mathfrak{I}_{7,-2}\right] + \sqrt{22}\hat{B}_z\mathfrak{I}_{7,-3} + \sqrt{2}\left[\hat{B}_y\mathfrak{I}_{7,4} - \hat{B}_x\mathfrak{I}_{7,-4}\right]\right\}$
	7	8	4	$\frac{1}{2\sqrt{10}}\left\{\sqrt{11}\left[\hat{B}_x\mathfrak{I}_{7,3} - \hat{B}_y\mathfrak{I}_{7,-3}\right] + 4\hat{B}_z\mathfrak{I}_{7,4} - \hat{B}_x\mathfrak{I}_{7,5} - \hat{B}_y\mathfrak{I}_{7,-5}\right\}$
	7	8	−4	$\frac{1}{2\sqrt{10}}\left\{\sqrt{11}\left[\hat{B}_y\mathfrak{I}_{7,3} + \hat{B}_x\mathfrak{I}_{7,-3}\right] + 4\hat{B}_z\mathfrak{I}_{7,-4} + \hat{B}_y\mathfrak{I}_{7,5} - \hat{B}_x\mathfrak{I}_{7,-5}\right\}$
	7	8	5	$\frac{1}{4\sqrt{5}}\left\{\sqrt{26}\left[\hat{B}_x\mathfrak{I}_{7,4} - \hat{B}_y\mathfrak{I}_{7,-4} + \hat{B}_z\mathfrak{I}_{7,5}\right] - \hat{B}_x\mathfrak{I}_{7,6} - \hat{B}_y\mathfrak{I}_{7,-6}\right\}$
	7	8	−5	$\frac{1}{4\sqrt{5}}\left\{\sqrt{26}\left[\hat{B}_y\mathfrak{I}_{7,4} + \hat{B}_x\mathfrak{I}_{7,-4} + \hat{B}_z\mathfrak{I}_{7,-5}\right] + \hat{B}_y\mathfrak{I}_{7,6} - \hat{B}_x\mathfrak{I}_{7,-6}\right\}$
	7	8	6	$\frac{1}{4\sqrt{15}}\left\{\sqrt{91}\left[\hat{B}_x\mathfrak{I}_{7,5} - \hat{B}_y\mathfrak{I}_{7,-5}\right] + 2\sqrt{14}\hat{B}_z\mathfrak{I}_{7,6} - \hat{B}_x\mathfrak{I}_{7,7} - \hat{B}_y\mathfrak{I}_{7,-7}\right\}$
	7	8	−6	$\frac{1}{4\sqrt{15}}\left\{\sqrt{91}\left[\hat{B}_y\mathfrak{I}_{7,5} + \hat{B}_x\mathfrak{I}_{7,-5}\right] + 2\sqrt{14}\hat{B}_z\mathfrak{I}_{7,-6} + \hat{B}_y\mathfrak{I}_{7,7} - \hat{B}_x\mathfrak{I}_{7,-7}\right\}$
	7	8	7	$\frac{1}{4}\left\{\sqrt{7}\left[\hat{B}_x\mathfrak{I}_{7,6} - \hat{B}_y\mathfrak{I}_{7,-6}\right] + \sqrt{2}\hat{B}_z\mathfrak{I}_{7,7}\right\}$
	7	8	−7	$\frac{1}{4}\left\{\sqrt{7}\left[\hat{B}_y\mathfrak{I}_{7,6} + \hat{B}_x\mathfrak{I}_{7,-6}\right] + \sqrt{2}\hat{B}_z\mathfrak{I}_{7,-7}\right\}$
	7	8	8	$\frac{1}{\sqrt{2}}\left\{\hat{B}_x\mathfrak{I}_{7,7} - \hat{B}_y\mathfrak{I}_{7,-7}\right\}$
	7	8	−8	$\frac{1}{\sqrt{2}}\left\{\hat{B}_y\mathfrak{I}_{7,7} + \hat{B}_x\mathfrak{I}_{7,-7}\right\}$

and $G = 1$ in equation (18) that, implicitly covered in the decompositions of tables 4(a), 4(b) are terms of dimension SI^7 and S^7I. In the nomenclature of [11] the following irreducible tensorial sets, $B_{l,m}^{l_B,l_S,l_I}$ ($-l \leqslant m \leqslant l$ with one of l_B, l_S, l_I necessarily zero), arise, explicitly or implicitly, from the decompositions listed in tables 4(a), 4(b). Terms linear in magnetic field, BJ^7, give rise to irreducible tensorial sets $B_{6,m}^{1,7,0}$, $B_{6,m}^{1,0,7}$ of rank 6 and $B_{8,m}^{1,7,0}$, $B_{8,m}^{1,0,7}$ of rank 8; the tensor components are unitless. Terms of dimension SI^7 and S^7I, independent of the magnetic field, give rise to irreducible tensorial sets $B_{6,m}^{0,1,7}$, $B_{6,m}^{0,7,1}$ of rank 6 and $B_{8,m}^{0,1,7}$, $B_{8,m}^{0,7,1}$ of rank 8; the tensor components have units of energy. As noted earlier and in [11], the transformation of these tensors under rotation depends only on their rank.

As part of this project the above terms have been incorporated into the program EPRNMR [21] and applied in a recent EPR study of high-spin nuclear Zeeman terms which are required to explain the hyperfine structure of ^{49}Ti ($I = 7/2$) in a Ti^{3+} ion in zircon [20, 24]. Within error, terms of dimension BI^7 were found to be zero, although those of dimension BI^3, BI^5 had been found [20] to be relatively large and statistically significant. This mirrors the relative magnitudes of terms of dimension J^4, J^6, the former being large and the latter, within error, zero. The contribution of terms of dimension SI^7 has yet to be examined.

3.4. Site symmetry constraints on terms of dimension $J_1 J_2^7$ in the SH.

The combined requirements of time-reversal invariance and inversion symmetry invariance restrict the terms in the SH, equation (4), according to equation (21):

$$\xi \mathfrak{T}_{k,q} \xi^{-1} = (-1)^k \mathfrak{T}_{k,q} \qquad (\xi = \theta \text{ or } \boldsymbol{I}_v) \tag{21}$$

to terms with k even [10]. In equation (21), θ is the time-inversion operator as defined by Brink and Satchler [31] and $\boldsymbol{I}_v$ is the inversion operator. Furthermore (see for example Rae [32] and Weil *et al* [33]), only sites conforming to one of the 11 Laue crystal classes (point group symmetry + a centre of inversion) need be considered. Prather [15] has detailed the procedures for obtaining the tesseral harmonics which transform as the totally symmetric irreducible representation under the symmetry operations of the 27 non-cubic crystal point groups. These results have been used by various authors (see for example [10, 23, 34]) to obtain tables pertinent to the EPR experiment. Here we list in table 5 in the format of table 4 of [10] the non-zero $B_{8,q}$-parameters (the transformation properties depend only on subscripts k, q and are independent of superscripts k_1, k_2) required in the SH for sites of each of the 11 Laue crystal classes. Following Prather [15] and [10] the axis system is chosen such that $\boldsymbol{z}$ corresponds to the highest-fold rotation axis (C_n) and $\boldsymbol{y}$ corresponds to a C_2' axis if one exists (consult references [10, 34] for further details).

As an application of the principles involved, we draw on the example of references [10, 11], namely, a paramagnetic ion in a C_2 (Laue class $2/m$) site of α-quartz. For $k = 8$ the non-vanishing $B_{k,q}$ are, in addition to those for $k = 2, 4$ given in [10], and those for $k = 6$ given in [11], the following:

$$k = 8 \qquad q = 0, \pm 2, \pm 4, \pm 6, \pm 8.$$

As a final comment, it is noted that we have not addressed the possibility that terms of odd k may exist in the SH—that is, terms which violate time-reversal invariance. We shall be content to note, following Grachëv [35], that it is always possible, via a unitary transformation, to eliminate terms with odd k. Restriction of the terms of the SH to those with k even does not restrict the useful rotation matrix elements $A_{g,h}^{(k)}$ to those with k even. One can readily envisage cases where one might wish to effect an axis transformation for tensor operators $\mathfrak{T}_{k,q}$ or Stevens operators O_k^q where k may be odd. An example might be an axis transformation of the expressions of table 4. A similar example is given in reference [11], namely, an axis

Table 5. Non-zero $B_{l,m}$ ($l = 8$) coefficients of equation (4) for site symmetries of the 11 Laue crystal classes. Notation: $+ \equiv B_{l,|m|}$ non-zero; $- \equiv B_{l,-|m|}$ non-zero (see reference [10] for further details). Abbreviations: PGS: point group symmetry; LC: Laue class; Tri: Triclinic; Mono: Monoclinic; Ortho: Orthorhombic; Int: International; Sch: Schoenflies.

		Tri	Mono	Ortho	Tetragonal		Trigonal		Hexagonal		Cubic	
PGS:					422				622			
			2	222	4	$4mm$		32	6	$6mm$		432
	Int.:[a]	1	m	$mm2$	$\bar{4}$	$\bar{4}2m$	3	$3m$	$\bar{6}$	$\bar{6}m2$	23	$\bar{4}3m$
LC:		$\bar{1}$	$2/m$	mmm	$4/m$	$4/mmm$	$\bar{3}$	$\bar{3}m$	$6/m$	$6/mmm$	$m3$	$m3m$
	Sch.:[b]	C_i (S_2)	C_{2h}	D_{2h}	C_{4h}	D_{4h}	C_{3i} (S_6)	D_{3d}	C_{6h}	D_{6h}	T_h	O_h
$l =$	$\lvert m\rvert =$											
8	8	+ −	+ −	+							+	+
	7	+ −										
	6	+ −	+ −	+			+ −	+	+ −	+	+	
	5	+ −										
	4	+ −	+ −	+	+ −	+					+	+
	3	+ −					+ −	+				
	2	+ −	+ −	+							+	
	1	+ −										
	0	+	+	+	+	+	+	+	+	+	+	+

[a] The final point group entry in each column indicates also the Laue class (LC).
[b] The Laue class is also given in Schoenflies notation (Sch.).

transformation of a general expression (equation [27] of [11]) for terms linear in the magnetic field expressed in Stevens operators.

Appendix

The following are available from the authors or from the sources outlined.

(i) *Program ROTSTO together with test data files and a help file.* The program is written in standard FORTRAN specifically for a VAX system with an ALPHA processor. It will be available without charge directly from the authors or via the shareware facilities of the International EPR Society (refer to the *EPR Newsletter* for details).

(ii) *Algebraic tables of matrix elements $A^{(k)}_{g,h}$ for $k = 1$–6 prepared in Scientific Workplace in TEX format.* Alternatively these matrix elements can be extracted in algebraic form directly from the appropriate subroutines of the program ROTSTO; the matrix elements in the program are formatted precisely as indicated in tables 1, 2 above to facilitate this extraction. (Reference [19], which detailed many of the calculations in [10] and listed matrix elements $A^{(k)}_{g,h}$ for $k = 2, 4, 6$, is no longer available. Substantially the same information and updated tables are included in [24]. The authors undertake to make the relevant sections of this reference available to interested readers via e-mail.)

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