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Higher-order Zeeman and spin terms in the electron paramagnetic resonance spin Hamiltonian; their description in irreducible form using Cartesian, tesseral spherical tensor and Stevens' operator expressions

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Abstract
In setting up a spin Hamiltonian (SH) to study high-spin Zeeman and high-spin nuclear and/or electronic interactions in electron paramagnetic resonance (EPR) experiments, it is argued that a maximally reduced SH (MRSH) framed in tesseral combinations of spherical tensor operators is necessary. Then, the SH contains only those terms that are necessary *and* sufficient to describe the particular spin system. The paper proceeds then to obtain interrelationships between the parameters of the MRSH and those of alternative SHs expressed in Cartesian tensor and Stevens operator-equivalent forms. The examples taken, initially, are those of Cartesian and Stevens' expressions for high-spin Zeeman terms of dimension BS^3 and BS^5. Starting from the well-known decomposition of the general Cartesian tensor of second rank to three irreducible tensors of ranks 0, 1 and 2, the decomposition of Cartesian tensors of ranks 4 and 6 are treated similarly. Next, following a generalization of the tesseral spherical tensor equations, the interrelationships amongst the parameters of the three kinds of expressions, as derived from equivalent SHs, are determined and detailed tables, including all redundancy equations, set out. In each of these cases the lowest symmetry, $\bar{1}$ Laue class, is assumed and then examples of relationships for specific higher symmetries derived therefrom. The validity of a spin Hamiltonian containing mixtures of terms from the three expressions is considered in some detail for several specific symmetries, including again the lowest symmetry. Finally, we address the application of some of the relationships derived here to seldom-observed low-symmetry effects in EPR spectra, when high-spin electronic and nuclear interactions are present.

1. Introduction

In this paper we wish to establish relationships amongst the three most commonly used 'tensorial' operator forms used in EPR spectroscopy with a view to describing how best to analyse high-spin Zeeman interactions, with terms of dimension $BJ^n (n = 3, 5)$, or higher-spin nuclear and/or electronic interactions, with terms of dimension $J_1J_2^n, J_1^nJ_2$ $(J_1, J_2 = S, I; n = 3, 5)$. We use the descriptor 'tensorial' rather loosely because the Stevens'

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operator equivalents for given J do not constitute a tensor. Nevertheless, for given J and $|m|$ these operators are related simply by a factor to the corresponding tesseral spherical tensor operator [1].

Our motives in setting out this work were several. Firstly, having set the proposition that a tesseral spherical tensor operator (TSTO) formalism is essential to handle the interactions that are the subject of this paper, we saw a need to detail the relationships to alternative formulations, the Cartesian and Stevens' forms. Although it is known [1, 2] that these two latter forms lead, for high-spin terms, to redundancies if used to set up the spin Hamiltonian (SH), the detailed redundancy equations have not to our knowledge been enunciated. We seek herein to remedy this and in so doing establish conditions under which a SH that may contain mixtures of TSTOs, Cartesian and Stevens operators is valid.

Over the last 3–4 decades various forms of irreducible spherical tensor operators have been used with increasing frequency in framing a very general SH with which to analyse electron paramagnetic spectra of centres with any specified spins, S and I. The reader interested in details of spin Hamiltonian formalisms is referred to the exhaustive review by Rudowicz and Misra [3]. For a brief historical survey of such developments the reader is referred to [2]. In a single sentence, the advantage of the spherical tensor notation is that one arrives at a theoretically correct expression that contains only those terms that are necessary *and* sufficient to describe the spin system at hand. Such a SH has been described as being maximally reduced [4] and there has been an inclination by some authors, ourselves included, to regard the maximally reduced SH (MRSH) as being something of a 'gold standard' without, perhaps, giving sufficient regard to the meanings of the parameters therein, or to their relations with those of earlier SHs. The earlier expressions are of two principal forms, the Cartesian tensor form as exemplified by a SH commonly used to frame the well-known second rank 'tensor' quantities $\mathbf{g}, \mathbf{A}, \mathbf{D}, \mathbf{P}$ and $\mathbf{g}_n$ and, the Stevens' operator forms [5, 6] used traditionally in expressions describing zero-field splitting (ZFS) terms when $J \geqslant 2 \quad (J = S, I)$.

If higher-spin Zeeman terms, $BJ^n (n = 3, 5)$ or higher-spin nuclear terms of dimensions $J_1 J_2^n, J_1^n J_2 \ (J_1, J_2 = S, I; n = 3, 5)$ are included in the SH, it is highly desirable (if not essential) to use an irreducible tesseral spherical tensor operator (TSTO) form because both the Cartesian and Stevens' expressions although deceptively compact, contain more (many more in the former case) terms than are necessary. One can, relatively simply, frame a SH in either of the Cartesian or Stevens' forms but, must in addition specify also the redundancy equations involved. References [1, 2] outlined in considerable detail the many advantages of the TSTO SH and specified the number of redundancies involved between this and the equivalent Stevens' expressions, but did not detail the redundancy equations. So far as we are aware, the very much more complicated case of comparison of the SHs in Cartesian tensor notation and TSTO notation has never been reported although detailed tables of all redundancies involved were calculated by one of us some 16 years ago [28].

Two potential problems arise from the above. Firstly, our 'gold standard' MRSH produces, in principle, an exact mathematical way of framing the SH and, combined with very precise measurements, can produce SH parameters that lead to principal directions of 'tensors' comparable in precision to bond-angle determination in x-ray diffractometry (see for example [7, 8]); but, what is the significance of the parameters produced in terms of electron–nuclear interactions? Secondly, as addressed in a recent paper [9], is it valid to frame a SH in, for example, a combination of Cartesian (for $\mathbf{g}, \mathbf{A}, \mathbf{D}, \mathbf{P}$ and $\mathbf{g}_n$), Stevens' (for ZFS terms $J \geqslant 2 (J = S, I)$) and TSTO forms? This is an option for example in the international programme EPR–NMR [10, 11] on the grounds that the Cartesian and Stevens' forms are most familiar to would-be users—but, is the SH thus framed valid when high-spin terms of the type described above are present? This is a particular question raised in [9]. We shall address this question later in the paper.

We shall order the consideration of TSTO, Cartesian and Stevens' tensorial (type) notations as follows. We start from the well-known decomposition of the general 2nd rank Cartesian tensor to three irreducible tensors of ranks 0, 1 and 2 [12, 13]. We consider next the general extension of this process and outline the reduction of 4th and 6th rank Cartesian tensors taking high-spin terms of dimension BS^3 and BS^5 respectively as examples. Next, the interrelationships amongst the parameters of the three types of expressions, as derived from equivalent SHs, are evaluated and detailed tables set out. In each of these cases the lowest symmetry, $\bar{1}$ Laue class, is considered and then examples of relationships for specific higher symmetries derived there from. The validity, or otherwise, of a SH containing mixtures of terms in the three notations is considered in some detail for several specific symmetries. Finally, the application of some of the relationships to seldom-observed low-symmetry effects in EPR spectra when high-spin electronic and nuclear interactions are present is addressed.

2. Theory section

2.1. Tesseral spherical tensor operators (TSTOs)—definitions

Throughout this paper we shall use the following definitions for the TSTOs

$$\begin{aligned}
\Im_{k,0}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) &= T_{k,0}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) \\
\Im_{k,q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) &= \frac{1}{\sqrt{2}}\{(-1)^q T_{k,q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) \\
&\quad + T_{k,-q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2)\} \qquad (1) \\
\Im_{k,-q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) &= \frac{\mathrm{i}}{\sqrt{2}}\{(-1)^{q+1} T_{k,q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2) \\
&\quad + T_{k,-q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2)\}.
\end{aligned}$$

In equation (1), the constituent $T_{k,q}^{k_1,k_2,k_3}(\mathbf{J}_1, \mathbf{J}_2)$ are Koster and Statz [14] normalized spherical tensor operators where, herein, one of k_1, k_2, k_3 will always be assumed zero so

Table 1. Single-vector decomposition products of TSTO SHs in the form of equations (9). Refer to section 2.4 for implicit relationships for other high-spin forms.

Term	Single-vector decomposition product
BS	$\frac{1}{\sqrt{3}}B_{0,0}^{1,1,0}\{-\hat{B}_x\Im_{1,1}(\mathbf{S})-\hat{B}_y\Im_{1,-1}(\mathbf{S})-\hat{B}_z\Im_{1,0}(\mathbf{S})\}$
	$\frac{1}{\sqrt{6}}B_{2,0}^{1,1,0}\{-\hat{B}_x\Im_{1,1}(\mathbf{S})-\hat{B}_y\Im_{1,-1}(\mathbf{S})+2\hat{B}_z\Im_{1,0}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{2,1}^{1,1,0}\{\hat{B}_z\Im_{1,1}(\mathbf{S})+\hat{B}_x\Im_{1,0}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{2,-1}^{1,1,0}\{\hat{B}_z\Im_{1,-1}(\mathbf{S})+\hat{B}_y\Im_{1,0}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{2,2}^{1,1,0}\{\hat{B}_x\Im_{1,1}(\mathbf{S})+\hat{B}_y\Im_{1,-1}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{2,-2}^{1,1,0}\{\hat{B}_y\Im_{1,1}(\mathbf{S})+\hat{B}_x\Im_{1,-1}(\mathbf{S})\}$
BS^3	$\frac{1}{\sqrt{7}}B_{2,0}^{1,3,0}\{-\sqrt{3}\hat{B}_z\Im_{3,0}(\mathbf{S})-\sqrt{2}[\hat{B}_x\Im_{3,1}(\mathbf{S})+\hat{B}_y\Im_{3,-1}(\mathbf{S})]\}$
	$\frac{1}{\sqrt{21}}B_{2,1}^{1,3,0}\{\sqrt{3}\hat{B}_x\Im_{3,0}(\mathbf{S})-2\sqrt{2}\hat{B}_z\Im_{3,1}-\sqrt{5}[\hat{B}_x\Im_{3,2}(\mathbf{S})+\hat{B}_y\Im_{3,-2}(\mathbf{S})]\}$
	$\frac{1}{\sqrt{21}}B_{2,-1}^{1,3,0}\{\sqrt{3}\hat{B}_y\Im_{3,0}(\mathbf{S})-2\sqrt{2}\hat{B}_z\Im_{3,-1}+\sqrt{5}[\hat{B}_y\Im_{3,2}(\mathbf{S})-\hat{B}_x\Im_{3,-2}(\mathbf{S})]\}$
	$\frac{1}{\sqrt{42}}B_{2,2}^{1,3,0}\{\hat{B}_x\Im_{3,1}(\mathbf{S})-\hat{B}_y\Im_{3,-1}(\mathbf{S})-\sqrt{10}\hat{B}_z\Im_{3,2}(\mathbf{S})-\sqrt{15}[\hat{B}_x\Im_{3,3}(\mathbf{S})-\hat{B}_y\Im_{3,-3}(\mathbf{S})]\}$
	$\frac{1}{\sqrt{42}}B_{2,-2}^{1,3,0}\{\hat{B}_y\Im_{3,1}(\mathbf{S})+\hat{B}_x\Im_{3,-1}(\mathbf{S})-\sqrt{10}\hat{B}_z\Im_{3,-2}(\mathbf{S})+\sqrt{15}[\hat{B}_y\Im_{3,3}(\mathbf{S})-\hat{B}_x\Im_{3,-3}(\mathbf{S})]\}$
	$\frac{1}{\sqrt{14}}B_{4,0}^{1,3,0}\{2\sqrt{2}\hat{B}_z\Im_{3,0}(\mathbf{S})-\sqrt{3}[\hat{B}_x\Im_{3,1}(\mathbf{S})+\hat{B}_y\Im_{3,-1}(\mathbf{S})]\}$
	$\frac{1}{2\sqrt{14}}B_{4,1}^{1,3,0}\{2\sqrt{5}\hat{B}_x\Im_{3,0}(\mathbf{S})+\sqrt{30}B_z\Im_{3,1}(\mathbf{S})-\sqrt{3}[\hat{B}_x\Im_{3,2}(\mathbf{S})+\hat{B}_y\Im_{3.-2}(\mathbf{S})]\}$
	$\frac{1}{2\sqrt{14}}B_{4,-1}^{1,3,0}\{2\sqrt{5}\hat{B}_y\Im_{3,0}(\mathbf{S})+\sqrt{30}B_z\Im_{3,-1}(\mathbf{S})+\sqrt{3}[\hat{B}_y\Im_{3,2}(\mathbf{S})-\hat{B}_x\Im_{3.-2}(\mathbf{S})]\}$
	$\frac{1}{2\sqrt{14}}B_{4,2}^{1,3,0}\{\sqrt{15}[\hat{B}_x\Im_{3,1}(\mathbf{S})-\hat{B}_y\Im_{3,-1}(\mathbf{S})]+2\sqrt{6}\hat{B}_z\Im_{3,2}(\mathbf{S})-[\hat{B}_x\Im_{3,3}(\mathbf{S})+\hat{B}_y\Im_{3,-3}(\mathbf{S})]\}$
	$\frac{1}{2\sqrt{14}}B_{4,-2}^{1,3,0}\{\sqrt{15}[\hat{B}_y\Im_{3,1}(\mathbf{S})-\hat{B}_x\Im_{3,-1}(\mathbf{S})]+2\sqrt{6}\hat{B}_z\Im_{3,-2}(\mathbf{S})+[\hat{B}_x\Im_{3,3}(\mathbf{S})-\hat{B}_y\Im_{3,-3}(\mathbf{S})]\}$
	$\frac{1}{2\sqrt{2}}B_{4,3}^{1,3,0}\{\sqrt{3}[\hat{B}_x\Im_{3,2}(\mathbf{S})-\hat{B}_y\Im_{3,-2}(\mathbf{S})]+\sqrt{2}\hat{B}_z\Im_{3,3}(\mathbf{S})\}$
	$\frac{1}{2\sqrt{2}}B_{4,-3}^{1,3,0}\{\sqrt{3}[\hat{B}_y\Im_{3,2}(\mathbf{S})+\hat{B}_x\Im_{3,-2}(\mathbf{S})]+\sqrt{2}\hat{B}_z\Im_{3,-3}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{4,4}^{1,3,0}\{\hat{B}_x\Im_{3,3}(\mathbf{S})-\hat{B}_y\Im_{3,-3}(\mathbf{S})\}$
	$\frac{1}{\sqrt{2}}B_{4,-4}^{1,3,0}\{\hat{B}_y\Im_{3,3}(\mathbf{S})+\hat{B}_x\Im_{3,-3}(\mathbf{S})\}$

that, as required, the number of non-zero superscripts and the number of vector arguments is equal. That is, we shall consider two-vector operators only and, frequently, we shall use shorthand versions of the operators such as $\Im_{k,q}$ or $T_{k,q}^{1,1}$ when no ambiguity is involved. Single-vector forms, $T_{k,q}(\mathbf{J})$, of these operators have been listed by Buckmaster *et al* [15] for $0 \leqslant k \leqslant 7$. In this paper, the Buckmaster *et al* compilation, that is known to be correct, will be regarded as the 'basis set' of spherical tensor operators. In EPR, the superscripts k_1, k_2, k_3 are written frequently as ℓ_B, ℓ_S, ℓ_I with $\ell_B + \ell_S + \ell_I = \ell =$ even to preserve time reversal invariance.

Equations such as (1) can be decomposed to useable single-vector form via

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

In (2) $\left(\begin{smallmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{smallmatrix}\right)$ is a Wigner $3j$ coefficient that is automatically zero unless both $q_1 + q_2 = -q$ and the triangle condition $|k_1 - k_2| \leqslant k \leqslant k_1 + k_2$ are satisfied [12].

As a simple example, we consider the SH comprising first-degree linear electronic Zeeman terms, $\mathbf{J}_1 = \mathbf{B}$; $\mathbf{J}_2 = \mathbf{S}$; $k_1 = k_2 = 1$ and $k_3 = 0$, that may be represented in irreducible TSTO form as

$$H_S^{1,1,0} = \mu_B B\left\{B_{0,0}^{1,1,0}\Im_{0,0}^{1,1,0}(\hat{\mathbf{B}},\mathbf{S}) + \sum_{m=-2}^{2} B_{2,m}^{1,1,0}\Im_{2,m}^{1,1,0}(\hat{\mathbf{B}},\mathbf{S})\right\}. \tag{3}$$

Equation (3) can be decomposed into single-vector form utilizing (2) [1] to give

$$H_S^{1,1,0} = \mu_B B\left\{B_{0,0}^{1,1,0}U_{1,0,0} + \sum_{m=-2}^{2}(B_{2,m}^{1,1,0}U_{1,2,m})\right\} \tag{4}$$

where the $U_{j,\ell,m}(j = 1)$ are linear functions of single-vector TSTOs. These linear functions have been tabulated [1] for $j = 1, 3, 5$ (and also for terms quadratic in magnetic field). For the convenience of readers these tables, for $j = 1, 3$ are reproduced, in slightly more explicit form, in table 1 of this paper.

2.2. *Decomposition of Cartesian tensors of rank 2*

These 'tensors', more correctly described as 3×3 parameter matrices, are those used commonly in expressions of the type

$$H_S = \mu_B\mathbf{B}^T\cdot\mathbf{g}\cdot\mathbf{S} + \mathbf{I}^T\cdot\mathbf{A}\cdot\mathbf{S} + \mathbf{S}^T\cdot\mathbf{D}\cdot\mathbf{S} + \mathbf{I}^T\cdot\mathbf{P}\cdot\mathbf{I} - \mu_n\mathbf{B}^T\cdot\mathbf{g}_n\cdot\mathbf{I} \tag{5}$$

where the terms have their customary meanings. The operators are column vectors and the superscript T indicates transpose, i.e., $\mathbf{B}^{\mathrm{T}}$, for example, is a row vector. In general one should consider the 3×3 parameter matrices as asymmetric and we shall write them, using the leading electronic Zeeman term as example, in Cartesian tensor form as

$$H_S^{1,1,0} = \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{\ell=x,y,z} g_{j,\ell} \hat{B}_j S_\ell. \tag{6}$$

It should be noted that in some references, for example [1, 2], the leading factor in equations like (4) has been written $g_e \mu_{\mathrm{B}} B$ rather than $\mu_{\mathrm{B}} B$ and this needs to be taken into account when considering the magnitudes of the derived parameters.

In equation (6), $\hat{\mathbf{B}}$ represents a unit vector, with components $\hat{B}_x, \hat{B}_y, \hat{B}_z$, along which the magnetic field is directed. It is well known that the 3×3 asymmetric Cartesian tensor of second rank is reducible to three irreducible tensors of ranks 0, 1 and 2, the latter being symmetric and traceless (see, for example, [12, 13]). The reduction corresponds to the operation

$$\mathcal{D}_1 \times \mathcal{D}_1 = \mathcal{D}_0 + \mathcal{D}_1 + \mathcal{D}_2 \tag{7}$$

in terms of the representations, $\mathcal{D}_j$, of the rotation group. Symmetry in the g matrix is imposed via 3 redundancy equations $g_{j,\ell} = g_{\ell,j} (j \neq \ell)$. The 1st rank anti-symmetric tensor (a vector) then disappears and the reduction is to a zero rank tensor and second rank symmetric and traceless tensor. There are other ways of describing this reduction but the above will be convenient in generalizing the process for Cartesian tensors of higher ranks.

Comparing coefficients of operators in (4) and (6), the following relations, with B parameters as subject, are obtained

$$B_{0,0}^{1,1,0} = -\frac{1}{\sqrt{3}}(g_{xx} + g_{yy} + g_{zz}) \tag{8a}$$

$$\begin{gathered} B_{2,0}^{1,1,0} = \frac{\sqrt{2}}{\sqrt{3}}\left\{-\frac{1}{2}(g_{xx} + g_{yy}) + g_{zz}\right\} \\ B_{2,2}^{1,1,0} = \frac{1}{\sqrt{2}}(g_{xx} - g_{yy}) \qquad B_{2,-2}^{1,1,0} = \sqrt{2} g_{xy} \\ B_{2,1}^{1,1,0} = \sqrt{2} g_{xz} \qquad B_{2,-1}^{1,1,0} = \sqrt{2} g_{yz}. \end{gathered} \tag{8b}$$

Equation (8*a*) is a zero rank tensor (a scalar) and (8*b*) a second rank tensor. In section 3.1 below, we shall show similarly that a 4th rank Cartesian tensor is expressible as a sum of two irreducible tensors of ranks 2 and 4 and a 6th rank Cartesian tensor as a sum of two irreducible tensors of ranks 4 and 6.

From equations (8*a*) and (8*b*) 6 B parameters of the irreducible TSTO form are related by linear equations to 6 only parameters of the symmetric Cartesian tensor, $\mathbf{g}$. The latter three terms in (8*b*) are zero for D_{2h} symmetry (i.e., diagonal g tensor) and, if uniaxial symmetry is imposed, we obtain simply

$$B_{0,0}^{1,1,0} = -\frac{1}{\sqrt{3}}(2g_\perp + g_\parallel) \qquad B_{2,0}^{1,1,0} = \frac{\sqrt{2}}{\sqrt{3}}(-g_\perp + g_\parallel). \tag{8c}$$

Each of the symmetric 3×3 matrices $\mathbf{g}$, $\mathbf{A}$, $\mathbf{D}$, $\mathbf{P}$ and $\mathbf{g}_n$ of (5) can be expressed similarly in terms of B parameters—see for example [16, 1, 2].

2.3. Extension to Cartesian tensors of ranks 4 and 6

In this section we shall continue to use, as examples, the linear and higher-order electronic Zeeman interactions. For completeness, and for use in section 2.4, we shall give expressions also for the corresponding terms expressed in Stevens' operators. The complete set of relations is

(i) in tesseral spherical tensor form

$$\begin{aligned} H_S^{1,1,0} &= \mu_{\mathrm{B}} B \left\{ B_{0,0}^{1,1,0} \Im_{0,0}(\hat{\mathbf{B}}, \mathbf{S}) + \sum_{m=-2}^{2} B_{2,m}^{1,1,0} \Im_{2,m}(\hat{\mathbf{B}}, \mathbf{S}) \right\} \\ H_S^{1,3,0} &= \mu_{\mathrm{B}} B \left\{ \sum_{m=-2}^{2} B_{2,m}^{1,3,0} \Im_{2,m}(\hat{\mathbf{B}}, \mathbf{S}) + \sum_{m=-4}^{4} B_{4,m}^{1,3,0} \Im_{4,m}(\hat{\mathbf{B}}, \mathbf{S}) \right\} \\ H_S^{1,5,0} &= \mu_{\mathrm{B}} B \left\{ \sum_{m=-4}^{4} B_{4,m}^{1,5,0} \Im_{4,m}(\hat{\mathbf{B}}, \mathbf{S}) + \sum_{m=-6}^{6} B_{6,m}^{1,5,0} \Im_{6,m}(\hat{\mathbf{B}}, \mathbf{S}) \right\} \end{aligned} \tag{9}$$

(ii) in Stevens' operator form

$$\begin{aligned} H_S^{1,1,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{q=-1}^{1} \hat{B}_j B_{1j}^q \bar{O}_1^q \\ H_S^{1,3,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{q=-3}^{3} \hat{B}_j B_{3j}^q \bar{O}_3^q \\ H_S^{1,5,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{q=-5}^{5} \hat{B}_j B_{5j}^q \bar{O}_5^q \end{aligned} \tag{10}$$

(iii) in Cartesian tensor form

$$\begin{aligned} H_S^{1,1,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{\ell=x,y,z} g_{j,\ell} \hat{B}_j S_\ell \\ H_S^{1,3,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{\ell=x,y,z} \times \sum_{m=x,y,z} \sum_{n=x,y,z} g_{j,\ell mn} \hat{B}_j S_\ell S_m S_n \\ H_S^{1,5,0} &= \mu_{\mathrm{B}} B \sum_{j=x,y,z} \sum_{\ell=x,y,z} \sum_{m=x,y,z} \sum_{n=x,y,z} \times \sum_{p=x,y,z} \sum_{r=x,y,z} g_{j,\ell mnpr} \hat{B}_j S_\ell S_m S_n S_p S_r. \end{aligned} \tag{11}$$

At first sight each of equations (10) and (11) appears a more compact way of expressing the SH for such terms but both are reducible. In equations (10), for example, 21 BS^3 terms reduce to 14 and 33 BS^5 terms reduce to 22, i.e., 7 and 11 redundancy equations respectively are required. These are results that we have stated earlier [1, 2], and shall return

Table 2. Redundancies amongst the $BJ^n(n=1,3,5;\ J=S,I)$ Cartesian parameters for electronic and nuclear Zeeman terms expressed in the form of equation (11). In the generic equations listed j, ℓ, m and n represent any one of x, y or z under the restrictions shown.

SH term	Generic equation		No. of equations
BS	$g_{j,\ell}=g_{\ell,j}$	$j\neq\ell$	3
		Total	3
BS^3	$g_{j,\ell mm}=g_{\ell,jmm}$	$j\neq\ell\neq m$	3
	$g_{j,\ell xx}+g_{j,\ell yy}+g_{j,\ell zz}=0$		9
	$g_{j,\ell\ell\ell}-g_{\ell,j\ell\ell}=2(g_{j,mm\ell}-g_{m,jm\ell})$	$j\neq\ell\neq m$	3
	$g_{x,xyy}+g_{y,yzz}+g_{z,zxx}=g_{y,yxx}+g_{x,xzz}+g_{z,zyy}=-\frac{1}{2}(g_{x,xxx}+g_{y,yyy}+g_{z,zzz})$		1
		Total	16
BS^5	$g_{j,\ell mmmm}=g_{\ell,jmmmm}$	$j\neq\ell\neq m$	3
	$g_{j,\ell mnxx}+g_{j,\ell mnyy}+g_{j,\ell mnzz}=0$		30
	$g_{j,\ell\ell\ell\ell\ell}-g_{\ell,j\ell\ell\ell\ell}=4(g_{j,mm\ell\ell\ell}-g_{m,jm\ell\ell\ell})$	$j\neq\ell\neq m$	6
	$(g_{j,jmmmm}+g_{m,mjjjj})-(g_{\ell,\ell mmmm}+g_{m,m\ell\ell\ell\ell})=3(g_{j,j\ell\ell mm}-g_{\ell,\ell jjmm})$	$j\neq\ell\neq m$	2
		Total	41

to in section 2.4. For the moment we are interested in the interrelations between (10) and (11).

The reduction according to equation (7) can be generalized [13] for Cartesian tensors of higher ranks to

$$\mathcal{D}_{j_1}\times\mathcal{D}_{j_2}=\sum_{j=|j_1-j_2|}^{j_1+j_2}\mathcal{D}_j. \tag{12}$$

Utilizing equation (12), a Cartesian tensor of rank 4 reduces as

$$3\mathcal{D}_0+6\mathcal{D}_1+6\mathcal{D}_2+3\mathcal{D}_3+\mathcal{D}_4$$

with $3\times1+6\times3+6\times5+3\times7+9=3^4$ components. Likewise, a Cartesian tensor of rank 6 reduces as

$$15\mathcal{D}_0+36\mathcal{D}_1+40\mathcal{D}_2+29\mathcal{D}_3+15\mathcal{D}_4+5\mathcal{D}_5+\mathcal{D}_6$$

with $15\times1+36\times3+40\times5+29\times7+15\times9+5\times11+13=3^6$ components.

Ideally, in order to match the number of independent parameters involved, we should like to be able to reduce the BS^3 Cartesian tensor of (11) to the sum of two irreducible tensors of ranks 2 and 4 and likewise the BS^5 Cartesian tensor to the sum of two irreducible tensors of ranks 4 and 6 where the parameters are related linearly to those of the TSTO form and where redundancies between the two formalisms can be stated. Since 81 and 729 components of the 4th and 6th rank tensors must be reduced to 14 and 22 respectively, the task is evidently reasonably formidable.

One can reduce greatly the number of independent parameters in the 4th and 6th rank Cartesian tensors using the permutation rule. By this rule the Cartesian tensor elements, $g_{j,\ell mn}$ for example from (11), are equal if they are related solely by a permutation of the subscripts associated with components of the same vector, the vector $\mathbf{S}$ in the example given. (The vector components themselves are of course still bound by their commutation relationships.) On applying the permutation rule, 81 parameters of the 4th rank tensor reduce to 30, and 729 parameters of the tensor of rank 6 reduce to 63. One must specify then 16 redundancy relationships for the 4th rank tensor and 41 redundancy relationships for the 6th rank tensor in order to match the parameter numbers in each case to the irreducible spherical tensor forms.

The relationships between the parameters in the TSTO notation of (9) and the Cartesian tensor notation of (11) are established as follows. First, the two-vector operators of equations (9) are decomposed into single-vector forms as outlined in [1] utilizing table 1. The single-vector tesseral operators, $\Im_{k,q}$, are converted to linear combinations of products of spin-vector components, S_x, S_y and S_z, thus producing expressions of the form of (11), but with coefficients $B^{1,k_2,0}_{k,q}$. Comparing coefficients of operators between (11) and the converted TSTO forms one obtains sets of simultaneous linear equations relating parameters in the two notations. By eliminating parameters $B^{1,k_2,0}_{k,q}$ from these simultaneous linear equations, linear equations relating the Cartesian parameters were found. These (generic) equations, listed in table 2, express the redundancies amongst the Cartesian parameters. The appropriate sets of simultaneous linear equations are listed in column three of table 3. These results, as summarized in tables 2 and 3, are for the most general case, that of the paramagnetic ion occupying a site of $\bar{1}$ Laue class. To our knowledge, these relationships have not appeared previously.

To make clear the procedure of the previous paragraph, we detail a simple example, that of BS^3 terms for a uniaxial case, D_{4h} (=$4/mmm$) symmetry. Then, from equations (9) and table 1, we obtain the following single-vector TSTO SH

$$\begin{aligned}H^{1,3,0}_S&=\frac{1}{\sqrt{7}}B^{1,3,0}_{2,0}\{-\sqrt{3}\hat{B}_z\Im_{3,0}(\mathbf{S})\\&\quad-\sqrt{2}[\hat{B}_x\Im_{3,1}(\mathbf{S})+\hat{B}_y\Im_{3,-1}(\mathbf{S})]\}\\&\quad+\frac{1}{\sqrt{14}}B^{1,3,0}_{4,0}\{2\sqrt{2}\hat{B}_z\Im_{3,0}(\mathbf{S})\\&\quad-\sqrt{3}[\hat{B}_x\Im_{3,1}(\mathbf{S})+\hat{B}_y\Im_{3,-1}(\mathbf{S})]\}\\&\quad+\frac{1}{\sqrt{2}}B^{1,3,0}_{4,4}\{\hat{B}_x\Im_{3,3}(\mathbf{S})-\hat{B}_y\Im_{3,-3}(\mathbf{S})\}.\end{aligned}\tag{13}$$

Table 3. Cartesian tensor elements as defined in equations (11) as linear functions of tesseral spherical tensor parameters as defined in equations (9).

SH term	Tensor element	Linear function of tesseral spherical tensor parameters
BS	$g_{x,x}$	$-\frac{1}{\sqrt{3}}B_{0,0}^{1,1,0}-\frac{1}{\sqrt{6}}B_{2,0}^{1,1,0}+\frac{1}{\sqrt{2}}B_{2,2}^{1,1,0}$
	$g_{x,y}$	$\frac{1}{\sqrt{2}}B_{2,-2}^{1,1,0}$
	$g_{x,z}$	$\frac{1}{\sqrt{2}}B_{2,1}^{1,1,0}$
	$g_{y,x}$	$\frac{1}{\sqrt{2}}B_{2,-2}^{1,1,0}$
	$g_{y,y}$	$-\frac{1}{\sqrt{3}}B_{0,0}^{1,1,0}-\frac{1}{\sqrt{6}}B_{2,0}^{1,1,0}-\frac{1}{\sqrt{2}}B_{2,2}^{1,1,0}$
	$g_{y,z}$	$\frac{1}{\sqrt{2}}B_{2,-1}^{1,1,0}$
	$g_{z,x}$	$\frac{1}{\sqrt{2}}B_{2,1}^{1,1,0}$
	$g_{z,y}$	$\frac{1}{\sqrt{2}}B_{2,-1}^{1,1,0}$
	$g_{z,z}$	$-\frac{1}{\sqrt{3}}B_{0,0}^{1,1,0}+\frac{\sqrt{2}}{\sqrt{3}}B_{2,0}^{1,1,0}$
BS^3	$g_{x,xxx}$	$\frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0}-\frac{1}{\sqrt{70}}B_{2,2}^{1,3,0}+\frac{3}{2\sqrt{70}}B_{4,0}^{1,3,0}-\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}+\frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0}$
	$g_{x,xxy}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,-2}^{1,3,0}-\frac{1}{2\sqrt{14}}B_{4,-2}^{1,3,0}+\frac{1}{2\sqrt{2}}B_{4,-4}^{1,3,0}$
	$g_{x,xxz}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,1}^{1,3,0}-\frac{3}{4\sqrt{7}}B_{4,1}^{1,3,0}+\frac{1}{4}B_{4,3}^{1,3,0}$
	$g_{x,xyy}$	$\frac{1}{\sqrt{210}}B_{2,0}^{1,3,0}+\frac{\sqrt{7}}{3\sqrt{10}}B_{2,2}^{1,3,0}+\frac{1}{2\sqrt{70}}B_{4,0}^{1,3,0}-\frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0}$
	$g_{x,xyz}$	$-\frac{\sqrt{5}}{3\sqrt{14}}B_{2,-1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,-1}^{1,3,0}+\frac{1}{4}B_{4,-3}^{1,3,0}$
	$g_{x,xzz}$	$-\frac{2\sqrt{2}}{\sqrt{105}}B_{2,0}^{1,3,0}+\frac{\sqrt{2}}{3\sqrt{35}}B_{2,2}^{1,3,0}-\frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}$
	$g_{x,yyy}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,-2}^{1,3,0}-\frac{1}{2\sqrt{14}}B_{4,-2}^{1,3,0}-\frac{1}{2\sqrt{2}}B_{4,-4}^{1,3,0}$
	$g_{x,yyz}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,1}^{1,3,0}-\frac{1}{4}B_{4,3}^{1,3,0}$
	$g_{x,yzz}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,-2}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,-2}^{1,3,0}$
	$g_{x,zzz}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,1}^{1,3,0}+\frac{1}{\sqrt{7}}B_{4,1}^{1,3,0}$
	$g_{y,xxx}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,-2}^{1,3,0}-\frac{1}{2\sqrt{14}}B_{4,-2}^{1,3,0}+\frac{1}{2\sqrt{2}}B_{4,-4}^{1,3,0}$
	$g_{y,xxy}$	$\frac{1}{\sqrt{210}}B_{2,0}^{1,3,0}-\frac{\sqrt{7}}{3\sqrt{10}}B_{2,2}^{1,3,0}+\frac{1}{2\sqrt{70}}B_{4,0}^{1,3,0}-\frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0}$
	$g_{y,xxz}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,-1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,-1}^{1,3,0}+\frac{1}{4}B_{4,-3}^{1,3,0}$
	$g_{y,xyy}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,-2}^{1,3,0}-\frac{1}{2\sqrt{14}}B_{4,-2}^{1,3,0}-\frac{1}{2\sqrt{2}}B_{4,-4}^{1,3,0}$
	$g_{y,xyz}$	$-\frac{\sqrt{5}}{3\sqrt{14}}B_{2,1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,1}^{1,3,0}-\frac{1}{4}B_{4,3}^{1,3,0}$
	$g_{y,xzz}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,-2}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,-2}^{1,3,0}$
	$g_{y,yyy}$	$\frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0}+\frac{3}{\sqrt{70}}B_{2,2}^{1,3,0}+\frac{3}{2\sqrt{70}}B_{4,0}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}+\frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0}$
	$g_{y,yyz}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,-1}^{1,3,0}-\frac{3}{4\sqrt{7}}B_{4,-1}^{1,3,0}-\frac{1}{4}B_{4,-3}^{1,3,0}$
	$g_{y,yzz}$	$-\frac{2\sqrt{2}}{\sqrt{105}}B_{2,0}^{1,3,0}-\frac{\sqrt{2}}{3\sqrt{35}}B_{2,2}^{1,3,0}-\frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}-\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}$
	$g_{y,zzz}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,-1}^{1,3,0}+\frac{1}{\sqrt{7}}B_{4,-1}^{1,3,0}$
	$g_{z,xxx}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,1}^{1,3,0}-\frac{3}{4\sqrt{7}}B_{4,1}^{1,3,0}+\frac{1}{4}B_{4,3}^{1,3,0}$
	$g_{z,xxy}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,-1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,-1}^{1,3,0}+\frac{1}{4}B_{4,-3}^{1,3,0}$
	$g_{z,xxz}$	$\frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0}-\frac{\sqrt{5}}{3\sqrt{14}}B_{2,2}^{1,3,0}-\frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}$
	$g_{z,xyy}$	$\frac{\sqrt{2}}{3\sqrt{35}}B_{2,1}^{1,3,0}-\frac{1}{4\sqrt{7}}B_{4,1}^{1,3,0}-\frac{1}{4}B_{4,3}^{1,3,0}$
	$g_{z,xyz}$	$-\frac{\sqrt{5}}{3\sqrt{14}}B_{2,-2}^{1,3,0}+\frac{1}{\sqrt{14}}B_{4,-2}^{1,3,0}$
	$g_{z,xzz}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,1}^{1,3,0}+\frac{1}{\sqrt{7}}B_{4,1}^{1,3,0}$
	$g_{z,yyy}$	$\frac{\sqrt{2}}{\sqrt{35}}B_{2,-1}^{1,3,0}-\frac{3}{4\sqrt{7}}B_{4,-1}^{1,3,0}-\frac{1}{4}B_{4,-3}^{1,3,0}$
	$g_{z,yyz}$	$\frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0}+\frac{\sqrt{5}}{3\sqrt{14}}B_{2,2}^{1,3,0}-\frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}-\frac{1}{\sqrt{14}}B_{4,2}^{1,3,0}$
	$g_{z,yzz}$	$-\frac{4\sqrt{2}}{3\sqrt{35}}B_{2,-1}^{1,3,0}+\frac{1}{\sqrt{7}}B_{4,-1}^{1,3,0}$
	$g_{z,zzz}$	$-\frac{\sqrt{6}}{\sqrt{35}}B_{2,0}^{1,3,0}+\frac{2\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}$

We then require the TSTOs of (13) expressed in terms of spin operators, S_x, S_y and S_z, namely

$$\begin{aligned}
\Im_{3,0}(\mathbf{S}) &= \frac{1}{\sqrt{10}}\{5S_z^3 + [1-3S(S+1)]S_z\} \\
&= \frac{1}{\sqrt{10}}\{5S_z^3 + (\hbar^2 - 3\mathbf{S}^2)S_z\} \\
&= \frac{1}{\sqrt{10}}\{2S_z^3 - 3S_x^2S_z - 3S_y^2S_z + \hbar^2 S_z\} \\
\Im_{3,1}(\mathbf{S}) &= \frac{\sqrt{3}}{4\sqrt{5}}\left\{S_x\left[4S_z^2 - S_x^2 - S_y^2 - \frac{\hbar^2}{2}\right]\right. \\
&\quad \left. + \left[4S_z^2 - S_x^2 - S_y^2 - \frac{\hbar^2}{2}\right]S_x\right\} \\
\Im_{3,-1}(\mathbf{S}) &= \frac{\sqrt{3}}{4\sqrt{5}}\left\{S_y\left[4S_z^2 - S_x^2 - S_y^2 - \frac{\hbar^2}{2}\right]\right. \\
&\quad \left. + \left[4S_z^2 - S_x^2 - S_y^2 - \frac{\hbar^2}{2}\right]S_y\right\} \\
\Im_{3,3}(\mathbf{S}) &= \tfrac{1}{2}\{S_x^3 - S_xS_y^2 - S_yS_xS_y - S_y^2S_x\} \\
\Im_{3,-3}(\mathbf{S}) &= -\tfrac{1}{2}\{S_y^3 - S_yS_x^2 - S_xS_yS_x - S_x^2S_y\}.
\end{aligned} \tag{14}$$

Next, we require the expansion of the second equation of equation (11), applying the permutation rule to reduce 81 terms to 30, but retaining all operator combinations to preserve the non-commutativity of the operators S_x, S_y and S_z. Comparing coefficients, $g_{j,\ell mn}$, of operators in this expansion with the three $B_{k,q}^{1,3,0}(k = 2, 4;\ q = 0, 4)$ coefficients of equations (13) of the same operators in equations (14), we obtain the following set of simultaneous linear equations

$$\begin{aligned}
g_{x,xxx} &= \frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0} + \frac{3}{2\sqrt{70}}B_{4,0}^{1,3,0} + \frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0} \\
g_{x,xyy} &= \frac{1}{\sqrt{210}}B_{2,0}^{1,3,0} + \frac{1}{2\sqrt{70}}B_{4,0}^{1,3,0} - \frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0} \\
g_{x,xzz} &= -\frac{2\sqrt{2}}{\sqrt{105}}B_{2,0}^{1,3,0} - \frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0} \\
g_{y,yxx} &= \frac{1}{\sqrt{210}}B_{2,0}^{1,3,0} + \frac{1}{2\sqrt{70}}B_{4,0}^{1,3,0} - \frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0} \\
g_{y,yyy} &= \frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0} + \frac{3}{2\sqrt{70}}B_{4,0}^{1,3,0} + \frac{1}{2\sqrt{2}}B_{4,4}^{1,3,0} \\
g_{y,yzz} &= -\frac{2\sqrt{2}}{\sqrt{105}}B_{2,0}^{1,3,0} - \frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0} \\
g_{z,zxx} &= \frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0} - \frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0} \\
g_{z,zyy} &= \frac{\sqrt{3}}{\sqrt{70}}B_{2,0}^{1,3,0} - \frac{\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0} \\
g_{z,zzz} &= -\frac{\sqrt{6}}{\sqrt{35}}B_{2,0}^{1,3,0} + \frac{2\sqrt{2}}{\sqrt{35}}B_{4,0}^{1,3,0}.
\end{aligned} \tag{15}$$

By eliminating the $B_{k,q}^{1,3,0}$ parameters from equations (15) we obtain the following set of redundancy equations amongst the $g_{j,\ell mn}$ parameters.

$$\begin{aligned}
g_{x,xxx} &= g_{y,yyy} \qquad & g_{x,xyy} &= g_{y,yxx} \\
g_{x,xzz} &= g_{y,yzz} \qquad & g_{z,zxx} &= g_{z,zyy}
\end{aligned} \tag{16a}$$

and

$$\begin{aligned}
g_{x,xxx} + g_{x,xyy} + g_{x,xzz} &= 0 \\
g_{y,yxx} + g_{y,yyy} + g_{y,yzz} &= 0 \\
g_{z,zxx} + g_{z,zyy} + g_{z,zzz} &= 0.
\end{aligned} \tag{16b}$$

Equations (16) allow the reduction from 9 parameters in (15) to three only independent parameters, for example

$$g_{z,zzz} = g_{\parallel} \qquad g_{x,xxx} = g_{y,yyy} = g_{\perp} \qquad g_{x,xyy} \tag{17}$$

thus matching in number and type (coefficients of 2nd and 4th rank tensors respectively) the three B parameters of (13). It can be verified easily that the relationships (15)–(17) are obtained from the general relationships for $\bar{1}$ Laue class in table 2 after making appropriate symmetry assumptions.

2.4. Generalization of the TSTO equations

So far we have treated only the case of electronic and nuclear Zeeman higher-order terms. The TSTO forms utilized in equations (8) can, however, be generalized to [2]

$$\begin{aligned}
H_S^{k_1,k_2} &= G\left\{\sum_{q=-|k_1-k_2|}^{k_1+k_2} B_{|k_1-k_2|,q}^{k_1,k_2}\Im_{|k_1-k_2|,q}^{k_1,k_2}(\mathbf{V},\mathbf{W})\right. \\
&\quad \left. + \sum_{q=-|k_1-k_2|}^{k_1+k_2} B_{|k_1+k_2|,q}^{k_1,k_2}\Im_{|k_1+k_2|,q}^{k_1,k_2}(\mathbf{V},\mathbf{W})\right\}
\end{aligned} \tag{18}$$

where the vectors $\mathbf{V}, \mathbf{W}$ can represent any one of $\mathbf{B}, \mathbf{S}, \mathbf{I}$. For Zeeman terms, $\mathbf{V} = \hat{\mathbf{B}}$ (a unit vector along which the magnetic field is directed), $\mathbf{W} = \mathbf{J}$ ($\mathbf{J} = \mathbf{S}, \mathbf{I}$) and $G = \mu_B B$ or $-\mu_n B$ according as $\mathbf{J} = \mathbf{S}, \mathbf{I}$ respectively. Equations of the form of (9) are generated thereby with dimensionless parameters, $B_{k,q}^{1,k_2,0}$, that are properties of the paramagnetic centre, independent of the applied magnetic field.

Taking $G = 1/2$, the equation

$$H_S^{0,k_2,0} = \sum_{q=-k_2}^{k_2} B_{k_2,q}^{0,k_2,0}\Im_{k_2,q}^{0,k_2,0}(\hat{\mathbf{B}},\mathbf{J}) \tag{19}$$

represents ZFS electronic terms of dimension S^{k_2} ($k_2 = 2, 4$ or 6); In this case, $\hat{\mathbf{B}}$ is a unit vector in an arbitrary direction and can be omitted. Similarly the superscripts in (19) can, without ambiguity, be omitted leading to more familiar expressions for zero-field terms of dimension S^{k_2}. Similar expressions for ZFS terms of dimension I^{k_3} are obtained by writing the third superscript as k_3. As in section 2.3, equation (19) can be compared to the equivalent expressions in Cartesian notation, namely

$$\begin{aligned}
H_S^{0,2,0} &= \sum_{j=x,y,z}\sum_{\ell=x,y,z} D_{j\ell}J_jJ_\ell \\
H_S^{0,4,0} &= \sum_{j=x,y,z}\sum_{\ell=x,y,z}\sum_{m=x,y,z}\sum_{n=x,y,z} D_{j\ell mn}J_jJ_\ell J_mJ_n
\end{aligned} \tag{20}$$

and linear relationships between the D parameters and the $B_{k_2,q}$ parameters obtained. These parameters are listed in table 3 and have dimensions of energy. Clearly the process is extended readily to tensors of rank 6 and higher.

Finally, the unit vector $\hat{\mathbf{B}}$ in equations (9) has components

$$\hat{B}_z = \Im_{1,0}(\hat{\mathbf{B}}) \qquad \hat{B}_x = \Im_{1,1}(\hat{\mathbf{B}}) \qquad \hat{B}_y = \Im_{1,-1}(\hat{\mathbf{B}}). \tag{21a}$$

It follows, on replacing equations (21*a*) with equations (21*b*)

$$\begin{aligned} J_z &= \Im_{1,0}(\mathbf{J}) \qquad J_x = \Im_{1,1}(\mathbf{J}) \\ J_y &= \Im_{1,-1}(\mathbf{J}) \qquad (\mathbf{J} = \mathbf{S}, \mathbf{I}) \end{aligned} \tag{21b}$$

and $G = 1$ in equation (18) that, implicitly covered in (18) and in the single-vector decompositions of table 1, are terms of dimension SI^n and $S^nI\,(n = 1, 3, 5)$. The corresponding tesseral spherical tensor parameters, $B_{k,q}^{0,k_2,k_3}$, have dimensions of energy. (In [1] we considered also terms of dimension $B^2S^{k_2}$ with parameters $B_{k,q}^{2,k_2,0}$ (dimensions, (energy)$^{-1}$). Such terms, quadratic in magnetic field may well become important in the analysis of high-field spectra, W-band for example, but we shall not be considering them further in this paper.) We shall be treating all terms, outlined in this section, in a later section of the paper.

2.5. Relations between TSTO parameters and Stevens' parameters

The relationships between these two forms are established readily because each is proportional to tesseral combinations of operators that transform like spherical harmonic functions. Thus, from [17, 1] we obtain

$$\bar{O}_k^q = A_k^q \Im_{k,q}. \tag{22}$$

An extensive listing of the factors $A_k^q (q \leqslant 8)$ has been given in [1]. It is necessary to point out that the $\bar{O}_k^q$ functions refer to the 'complete' or, after Rudowicz [18], 'extended' set of Stevens' operators, $-q \leqslant k \leqslant q$, and not merely those for $q \geqslant 0$ as in many earlier listings.

We shall now outline briefly the establishment of the redundancy equations between the forms (9) and (10) where, again, we use as example the electronic Zeeman interaction for terms of dimension BS^3. Expanding (10) we obtain

$$\begin{aligned} H_S^{1,3} = \mu_B B \sum_{j=1}^{j\leqslant 2S} \{ & \hat{B}_x (B_{3x}^0 \bar{O}_3^0 + B_{3x}^1 \bar{O}_3^1 + B_{3x}^{-1} \bar{O}_3^{-1} + \cdots \\ & + B_{3x}^3 \bar{O}_3^3 + B_{3x}^{-3} \bar{O}_3^{-3}) + \hat{B}_y (B_{3y}^0 + \cdots) \\ & + \hat{B}_z (B_{3z}^0 + \cdots)\} \end{aligned} \tag{23}$$

i.e., $3 \times 7 = 21$ terms. Then, from equation (23) of [1] and table 1 we have terms

$$\hat{B}_x \left(\frac{1}{\sqrt{7}} B_{2,1} + \frac{\sqrt{5}}{\sqrt{14}} B_{4,1} \right) \Im_{3,0}$$

$$\hat{B}_x \left(-\frac{\sqrt{2}}{\sqrt{7}} B_{2,0} + \frac{1}{\sqrt{42}} B_{2,2} - \frac{\sqrt{3}}{\sqrt{14}} B_{4,0} + \frac{\sqrt{15}}{2\sqrt{14}} B_{4,2} \right) \Im_{3,1}$$

- -

$$\hat{B}_x \left(-\frac{\sqrt{5}}{\sqrt{14}} B_{2,-2} - \frac{1}{2\sqrt{14}} B_{4,-2} + \frac{1}{\sqrt{2}} B_{4,-4} \right) \Im_{3,-3}$$

i.e., seven relationships. Then, for example, $\bar{O}_3^0 = \sqrt{10}\Im_{3,0}$ (equation (2) and table 1 of [1]), so that on equating operator coefficients we obtain

$$\hat{B}_x \left(\frac{1}{\sqrt{7}} B_{2,1} + \frac{\sqrt{5}}{\sqrt{14}} B_{4,1} \right) \Im_{3,0} = \hat{B}_x B_{3x} \bar{O}_3^0 = \hat{B}_x B_{3x}^0 \sqrt{10} \Im_{3,0}$$

leading to $B_{3x}^0 = \frac{1}{\sqrt{70}} B_{2,1} + \frac{1}{2\sqrt{7}} B_{4,1}$ and, similarly, six other equations, $\hat{B}_{3x}(-3 \leqslant m \leqslant 3)$. We must repeat the same process for terms in $\hat{B}_y \Im_{3,m}$ and $\hat{B}_z \Im_{3,m}$ and obtain finally 21 expressions giving Stevens' parameters in terms of the spherical tensor coefficients, $B_{2,m}^{1,3}$ and $B_{4,m}^{1,3}$. These relationships along with those for terms of dimension S^2, S^4, BS, BS^3 and BS^5 are listed in table 5. The tensor parameters $B_{2,m}^{1,3} and B_{4,m}^{1,3}$ are members of irreducible tensors of ranks 2 (5 components) and 4 (9 components) respectively and hence it is clear that the 21 expressions for Stevens' parameters must be reducible. Solving the Stevens' expressions simultaneously leads to 14 (non-unique) linear relationships with the tensor components as subject. Consideration of the alternatives leads to seven redundancy relationships amongst the Stevens' parameters. These are listed in table 6 along with the 3 redundancy relationships for terms of dimension BS, (7 for terms of dimension BS^3) and the 11 for terms of dimension BS^5. The redundancy equations of table 6 have been independently calculated and verified by Kliava [29].

3. Discussion

3.1. Symmetry considerations

In deriving the relationships of tables 3–6 we have not assumed any symmetry constraints, with the exception that the SH must be invariant to the inversion operation. Hence, the tables produced are those appropriate to $\bar{1}$ Laue class—that is, triclinic ($1 = C_1$) point-group symmetry + the (space) inversion operation. By imposing appropriate symmetry constraints we can then, from the general tables 3–6 obtain the relationships for any of the other 10 Laue classes or, alternatively, for the lowest-symmetry member of a given Laue class, the corresponding rotation point group. The Laue class of the site of a paramagnetic centre is intuitively the more useful because, in the absence of extra intelligence on a particular problem, the EPR experiment alone does not distinguish the point-group symmetries of the members (point groups) of a given Laue class. In the following therefore we shall restrict ourselves to specific choices from the 11 Laue crystal classes.

The tables that we have appended each list expressions where the Cartesian tensor element or Stevens' parameter is given as a linear function of irreducible spherical tensor components, $B_{k,q}^{k_1,k_2,k_3}$ with one of k_1, k_2, k_3 zero. It is often more useful however to have the equivalent expression with the spherical tensor parameter as subject and we now do this for Laue class $\bar{1}$ restricting attention to the TSTO and Cartesian forms, equations (9) and (11). We shall make use also of some of the relationships of section 2.4 above.

Table 4. Cartesian tensor elements defined in equations (20) as linear functions of tesseral tensor parameters defined in equations (18) and (19) for ZFS terms of dimension S^{k_2} ($k_2 = 2, 4$). The same linear functions of parameters for terms of dimension I^{k_2} are obtained except that the superscripts are $0, 0, k_2$.

SH term	Tensor element	Linear function of tesseral tensor parameters
S^2	D_{xx}	$-\frac{1}{\sqrt{6}}B^{0,2,0}_{2,0} + \frac{1}{\sqrt{2}}B^{0,2,0}_{2,2}$
	D_{xy}	$\frac{1}{\sqrt{2}}B^{0,2,0}_{2,-2}$
	D_{xz}	$\frac{1}{\sqrt{2}}B^{0,2,0}_{2,1}$
	D_{yy}	$-\frac{1}{\sqrt{6}}B^{0,2,0}_{2,0} - \frac{1}{\sqrt{2}}B^{0,2,0}_{2,2}$
	D_{yz}	$\frac{1}{\sqrt{2}}B^{0,2,0}_{2,-1}$
	D_{zz}	$\frac{\sqrt{2}}{\sqrt{3}}B^{0,2,0}_{2,0}$
S^4	D_{xxxx}	$\frac{3}{2\sqrt{70}}B^{0,4,0}_{4,0} - \frac{1}{\sqrt{14}}B^{0,4,0}_{4,2} + \frac{1}{2\sqrt{2}}B^{0,4,0}_{4,4}$
	D_{xxxy}	$-\frac{1}{2\sqrt{14}}B^{0,4,0}_{4,-2} + \frac{1}{2\sqrt{2}}B^{0,4,0}_{4,-4}$
	D_{xxxz}	$-\frac{3}{4\sqrt{7}}B^{0,4,0}_{4,1} + \frac{1}{4}B^{0,4,0}_{4,3}$
	D_{xxyy}	$\frac{1}{2\sqrt{70}}B^{0,4,0}_{4,0} - \frac{1}{2\sqrt{2}}B^{0,4,0}_{4,4}$
	D_{xxyz}	$-\frac{1}{4\sqrt{7}}B^{0,4,0}_{4,-1} + \frac{1}{4}B^{0,4,0}_{4,-3}$
	D_{xxzz}	$-\frac{\sqrt{2}}{\sqrt{35}}B^{0,4,0}_{4,0} + \frac{1}{\sqrt{14}}B^{0,4,0}_{4,2}$
	D_{xyyy}	$-\frac{1}{2\sqrt{14}}B^{0,4,0}_{4,-2} - \frac{1}{2\sqrt{2}}B^{0,4,0}_{4,-4}$
	D_{xyyz}	$-\frac{1}{4\sqrt{7}}B^{0,4,0}_{4,1} - \frac{1}{4}B^{0,4,0}_{4,3}$
	D_{xyzz}	$\frac{1}{\sqrt{14}}B^{0,4,0}_{4,-2}$
	D_{xzzz}	$\frac{1}{\sqrt{7}}B^{0,4,0}_{4,1}$
	D_{yyyy}	$\frac{3}{2\sqrt{70}}B^{0,4,0}_{4,0} + \frac{1}{\sqrt{14}}B^{0,4,0}_{4,2} + \frac{1}{2\sqrt{2}}B^{0,4,0}_{4,4}$
	D_{yyyz}	$-\frac{3}{4\sqrt{7}}B^{0,4,0}_{4,-1} - \frac{1}{4}B^{0,4,0}_{4,-3}$
	D_{yyzz}	$-\frac{\sqrt{2}}{\sqrt{35}}B^{0,4,0}_{4,0} - \frac{1}{\sqrt{14}}B^{0,4,0}_{4,2}$
	D_{yzzz}	$\frac{1}{\sqrt{7}}B^{0,4,0}_{4,-1}$
	D_{zzzz}	$\frac{2\sqrt{2}}{\sqrt{35}}B^{0,4,0}_{4,0}$

In this instance, we shall consider a SH for high-spin terms of dimension SI^3 (refer to equations (21)) in a site of $\bar{1}$ Laue class where the Cartesian parameters may be labelled $C_{j,\ell mn}$ and the related TSTO parameters, $B^{0,1,3}_{2,m}$ and $B^{0,1,3}_{4,m}$. We wish to make the Bs subjects of linear relationships and, utilizing the redundancy relationships of table 2, ensure that there are equal numbers of B and C parameters. It turns out that the calculation is relatively straightforward. Inspection of the relationships of table 3 reveals that there are

- 9 equations containing at least two of $B^{0,1,3}_{2,0}$, $B^{0,1,3}_{2,2}$, $B^{0,1,3}_{4,0}$, $B^{0,1,3}_{4,2}$, $B^{0,1,3}_{4,4}$ and no other,
- 7 equations containing at least two of $B^{0,1,3}_{2,-2}$, $B^{0,1,3}_{4,-2}$, $B^{0,1,3}_{4,-4}$ and no other,
- 7 equations containing at least two of $B^{0,1,3}_{2,1}$, $B^{0,1,3}_{4,1}$, $B^{0,1,3}_{4,3}$ and no other and,
- 7 equations containing at least two of $B^{0,1,3}_{2,-1}$, $B^{0,1,3}_{4,-1}$, $B^{0,1,3}_{4,-3}$ and no other.

That is, we obtain a total of 30 equations containing $9 + 5 = 14$ $B^{0,1,3}_{j,m}$ parameters and, as already noted, 16 redundancy equations. Utilizing the latter, from table 2, we

Table 5. Stevens' parameters defined in equations (10) as linear functions of tesseral tensor parameters defined in equations (9) and (19).

SH term	Stevens, parameter	Linear function of tesseral tensor parameters
S^2	B^0_2	$\frac{1}{\sqrt{6}}B^{0,2,0}_{2,0}$
	B^1_2	$\sqrt{2}B^{0,2,0}_{2,1}$
	B^{-1}_2	$\sqrt{2}B^{0,2,0}_{2,-1}$
	B^2_2	$\frac{1}{\sqrt{2}}B^{0,2,0}_{2,2}$
	B^{-2}_2	$\frac{1}{\sqrt{2}}B^{0,2,0}_{2,-2}$
S^4	B^0_4	$\frac{1}{2\sqrt{70}}B^{0,4,0}_{4,0}$
	B^1_4	$\frac{1}{\sqrt{7}}B^{0,4,0}_{4,1}$
	B^{-1}_4	$\frac{1}{\sqrt{7}}B^{0,4,0}_{4,-1}$
	B^2_4	$\frac{1}{\sqrt{14}}B^{0,4,0}_{4,2}$
	B^{-2}_4	$\frac{1}{\sqrt{14}}B^{0,4,0}_{4,-2}$
	B^3_4	$B^{0,4,0}_{4,3}$
	B^{-3}_4	$B^{0,4,0}_{4,-3}$
	B^4_4	$\frac{1}{2\sqrt{2}}B^{0,4,0}_{4,4}$
	B^{-4}_4	$\frac{1}{2\sqrt{2}}B^{0,4,0}_{4,-4}$
BS	B^0_{1x}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,1}$
	B^1_{1x}	$-\frac{1}{\sqrt{3}}B^{1,1,0}_{0,0} - \frac{1}{\sqrt{6}}B^{1,1,0}_{2,0} + \frac{1}{\sqrt{2}}B^{1,1,0}_{2,2}$
	B^{-1}_{1x}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,-2}$
	B^0_{1y}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,-1}$
	B^1_{1y}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,-2}$
	B^{-1}_{1y}	$-\frac{1}{\sqrt{3}}B^{1,1,0}_{0,0} - \frac{1}{\sqrt{6}}B^{1,1,0}_{2,0} - \frac{1}{\sqrt{2}}B^{1,1,0}_{2,2}$
	B^0_{1z}	$-\frac{1}{\sqrt{2}}B^{1,1,0}_{0,0} + \frac{\sqrt{2}}{\sqrt{3}}B^{1,1,0}_{2,0}$
	B^1_{1z}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,1}$
	B^{-1}_{1z}	$\frac{1}{\sqrt{2}}B^{1,1,0}_{2,-1}$
BS^3	B^0_{3x}	$\frac{1}{\sqrt{70}}B^{1,3,0}_{2,1} + \frac{1}{2\sqrt{7}}B^{1,3,0}_{4,1}$
	B^1_{3x}	$-\frac{\sqrt{3}}{\sqrt{70}}B^{1,3,0}_{2,0} + \frac{1}{2\sqrt{70}}B^{1,3,0}_{2,2} - \frac{3}{2\sqrt{70}}B^{1,3,0}_{4,0}$ $+ \frac{3}{4\sqrt{14}}B^{1,3,0}_{4,2}$
	B^{-1}_{3x}	$\frac{1}{2\sqrt{70}}B^{1,3,0}_{2,-2} + \frac{3}{4\sqrt{14}}B^{1,3,0}_{4,-2}$
	B^2_{3x}	$-\frac{\sqrt{5}}{\sqrt{14}}B^{1,3,0}_{2,1} - \frac{3}{4\sqrt{7}}B^{1,3,0}_{4,1} + \frac{3}{4}B^{1,3,0}_{4,3}$
	B^{-2}_{3x}	$-\frac{\sqrt{5}}{\sqrt{14}}B^{1,3,0}_{2,-1} - \frac{3}{4\sqrt{7}}B^{1,3,0}_{4,-1} + \frac{3}{4}B^{1,3,0}_{4,-3}$
	B^3_{3x}	$-\frac{\sqrt{5}}{2\sqrt{14}}B^{1,3,0}_{2,2} - \frac{1}{4\sqrt{14}}B^{1,3,0}_{4,2} + \frac{1}{2\sqrt{2}}B^{1,3,0}_{4,4}$
	B^{-3}_{3x}	$-\frac{\sqrt{5}}{2\sqrt{14}}B^{1,3,0}_{2,-2} - \frac{1}{4\sqrt{14}}B^{1,3,0}_{4,-2} + \frac{1}{2\sqrt{2}}B^{1,3,0}_{4,-4}$
	B^0_{3y}	$\frac{1}{\sqrt{70}}B^{1,3,0}_{2,-1} + \frac{1}{2\sqrt{7}}B^{1,3,0}_{4,-1}$
	B^1_{3y}	$\frac{1}{2\sqrt{70}}B^{1,3,0}_{2,-2} + \frac{3}{4\sqrt{14}}B^{1,3,0}_{4,-2}$
	B^{-1}_{3y}	$-\frac{\sqrt{3}}{\sqrt{70}}B^{1,3,0}_{2,0} - \frac{1}{2\sqrt{70}}B^{1,3,0}_{2,2} - \frac{3}{2\sqrt{70}}B^{1,3,0}_{4,0}$ $- \frac{3}{4\sqrt{14}}B^{1,3,0}_{4,2}$
	B^2_{3y}	$\frac{\sqrt{5}}{\sqrt{14}}B^{1,3,0}_{2,-1} + \frac{3}{4\sqrt{7}}B^{1,3,0}_{4,-1} + \frac{3}{4}B^{1,3,0}_{4,-3}$
	B^{-2}_{3y}	$-\frac{\sqrt{5}}{\sqrt{14}}B^{1,3,0}_{2,1} - \frac{3}{4\sqrt{7}}B^{1,3,0}_{4,1} - \frac{3}{4}B^{1,3,0}_{4,3}$
	B^3_{3y}	$\frac{\sqrt{5}}{2\sqrt{14}}B^{1,3,0}_{2,-2} + \frac{1}{4\sqrt{14}}B^{1,3,0}_{4,-2} + \frac{1}{2\sqrt{2}}B^{1,3,0}_{4,-4}$
	B^{-3}_{3y}	$-\frac{\sqrt{5}}{2\sqrt{14}}B^{1,3,0}_{2,2} - \frac{1}{4\sqrt{14}}B^{1,3,0}_{4,2} - \frac{1}{2\sqrt{2}}B^{1,3,0}_{4,4}$
	B^0_{3z}	$-\frac{\sqrt{3}}{\sqrt{70}}B^{1,3,0}_{2,0} + \frac{\sqrt{2}}{\sqrt{35}}B^{1,3,0}_{4,0}$

Table 5. (Continued.)

SH term	Stevens, parameter	Linear function of tesseral tensor parameters
	B_{3z}^{1}	$-\frac{\sqrt{2}}{\sqrt{35}}B_{2,1}^{1,3,0}+\frac{3}{4\sqrt{7}}B_{4,1}^{1,3,0}$
	B_{3z}^{-1}	$-\frac{\sqrt{2}}{\sqrt{35}}B_{2,-1}^{1,3,0}+\frac{3}{4\sqrt{7}}B_{4,-1}^{1,3,0}$
	B_{3z}^{2}	$-\frac{\sqrt{5}}{\sqrt{14}}B_{2,2}^{1,3,0}+\frac{3}{\sqrt{14}}B_{4,2}^{1,3,0}$
	B_{3z}^{-2}	$-\frac{\sqrt{5}}{\sqrt{14}}B_{2,-2}^{1,3,0}+\frac{3}{\sqrt{14}}B_{4,-2}^{1,3,0}$
	B_{3z}^{3}	$\frac{1}{4}B_{4,3}^{1,3,0}$
	B_{3z}^{-3}	$\frac{1}{4}B_{4,-3}^{1,3,0}$
BS^5	B_{5y}^{-1}	$-\frac{\sqrt{5}}{2\sqrt{154}}B_{4,0}^{1,5,0}-\frac{1}{2\sqrt{154}}B_{4,2}^{1,5,0}-\frac{5}{4\sqrt{231}}B_{6,0}^{1,5,0}-\frac{\sqrt{5}}{6\sqrt{22}}B_{6,2}^{1,5,0}$
	B_{5y}^{2}	$\frac{\sqrt{7}}{2\sqrt{11}}B_{4,-1}^{1,5,0}+\frac{1}{2\sqrt{11}}B_{4,-3}^{1,5,0}+\frac{5}{6\sqrt{11}}B_{6,-1}^{1,5,0}+\frac{\sqrt{5}}{\sqrt{22}}B_{6,-3}^{1,5,0}$
	B_{5y}^{-2}	$-\frac{\sqrt{7}}{2\sqrt{11}}B_{4,1}^{1,5,0}-\frac{1}{2\sqrt{11}}B_{4,3}^{1,5,0}-\frac{5}{6\sqrt{11}}B_{6,1}^{1,5,0}-\frac{\sqrt{5}}{\sqrt{22}}B_{6,3}^{1,5,0}$
	B_{5y}^{3}	$\frac{\sqrt{7}}{6\sqrt{22}}B_{4,-2}^{1,5,0}+\frac{1}{12\sqrt{22}}B_{4,-4}^{1,5,0}+\frac{\sqrt{5}}{12\sqrt{22}}B_{6,-2}^{1,5,0}+\frac{5}{8\sqrt{35}}B_{6,-4}^{1,5,0}$
	B_{5y}^{-3}	$-\frac{\sqrt{7}}{6\sqrt{22}}B_{4,2}^{1,5,0}-\frac{1}{12\sqrt{22}}B_{4,4}^{1,5,0}-\frac{\sqrt{5}}{12\sqrt{22}}B_{6,2}^{1,5,0}-\frac{5}{8\sqrt{35}}B_{6,4}^{1,5,0}$
	B_{5y}^{4}	$\frac{3}{2\sqrt{11}}B_{4,-3}^{1,5,0}+\frac{\sqrt{5}}{4\sqrt{22}}B_{6,-3}^{1,5,0}+\frac{5}{4\sqrt{6}}B_{6,-5}^{1,5,0}$
	B_{5y}^{-4}	$-\frac{3}{2\sqrt{11}}B_{4,3}^{1,5,0}-\frac{\sqrt{5}}{4\sqrt{22}}B_{6,3}^{1,5,0}-\frac{5}{4\sqrt{6}}B_{6,5}^{1,5,0}$
	B_{5y}^{5}	$\frac{3}{4\sqrt{22}}B_{4,-4}^{1,5,0}+\frac{1}{8\sqrt{35}}B_{6,-4}^{1,5,0}+\frac{1}{4\sqrt{2}}B_{6,-6}^{1,5,0}$
	B_{5y}^{-5}	$-\frac{3}{4\sqrt{22}}B_{4,4}^{1,5,0}-\frac{1}{8\sqrt{35}}B_{6,4}^{1,5,0}-\frac{1}{4\sqrt{2}}B_{6,6}^{1,5,0}$
	B_{5z}^{0}	$-\frac{\sqrt{5}}{6\sqrt{154}}B_{4,0}^{1,5,0}+\frac{1}{2\sqrt{231}}B_{6,0}^{1,5,0}$
	B_{5z}^{1}	$-\frac{1}{\sqrt{77}}B_{4,1}^{1,5,0}+\frac{5}{12\sqrt{11}}B_{6,1}^{1,5,0}$
	B_{5z}^{-1}	$-\frac{1}{\sqrt{77}}B_{4,-1}^{1,5,0}+\frac{5}{12\sqrt{11}}B_{6,-1}^{1,5,0}$
	B_{5z}^{2}	$-\frac{\sqrt{7}}{\sqrt{22}}B_{4,2}^{1,5,0}+\frac{2\sqrt{10}}{3\sqrt{11}}B_{6,2}^{1,5,0}$
	B_{5z}^{-2}	$-\frac{\sqrt{7}}{\sqrt{22}}B_{4,-2}^{1,5,0}+\frac{2\sqrt{10}}{3\sqrt{11}}B_{6,-2}^{1,5,0}$
	B_{5z}^{3}	$-\frac{1}{3\sqrt{11}}B_{4,3}^{1,5,0}+\frac{\sqrt{5}}{4\sqrt{22}}B_{6,3}^{1,5,0}$
	B_{5z}^{-3}	$-\frac{1}{3\sqrt{11}}B_{4,-3}^{1,5,0}+\frac{\sqrt{5}}{4\sqrt{22}}B_{6,-3}^{1,5,0}$
	B_{5z}^{4}	$-\frac{3}{2\sqrt{22}}B_{4,4}^{1,5,0}+\frac{5}{2\sqrt{35}}B_{6,4}^{1,5,0}$
	B_{5z}^{-4}	$-\frac{3}{2\sqrt{22}}B_{4,-4}^{1,5,0}+\frac{5}{2\sqrt{35}}B_{6,-4}^{1,5,0}$
	B_{5z}^{5}	$\frac{1}{4\sqrt{6}}B_{6,5}^{1,5,0}$
	B_{5z}^{-5}	$\frac{1}{4\sqrt{6}}B_{6,-5}^{1,5,0}$

obtain the following full set of 14 required relationships, (24*a*) and (24*a*), where the groupings highlight the division into two irreducible tensorial sets of ranks 2 and 4. There are 14, and only 14, C parameters but the equations are not unique—there are other, equally valid, reductions of the C parameters possible.

$$B_{2,0}^{0,1,3}=\frac{\sqrt{15}}{\sqrt{14}}\{C_{x,xxx}+C_{y,yyy}-C_{z,zzz}+C_{x,xyy}+C_{y,yxx}\}$$
$$B_{2,1}^{0,1,3}=\frac{3\sqrt{5}}{\sqrt{14}}\{C_{x,zzz}-C_{z,xxx}\}$$
$$B_{2,-1}^{0,1,3}=\frac{3\sqrt{5}}{\sqrt{14}}\{C_{y,zzz}-C_{z,yzz}\} \tag{24a}$$
$$B_{2,2}^{0,1,3}=\frac{3\sqrt{10}}{2\sqrt{7}}\{C_{x,xyy}-C_{y,yxx}\}$$
$$B_{2,-2}^{0,1,3}=\frac{3\sqrt{10}}{2\sqrt{7}}\{C_{x,yyy}-C_{y,xyy}\}$$

$$\begin{aligned}
B_{4,0}^{0,1,3}&=\frac{3\sqrt{5}}{2\sqrt{14}}\{C_{x,xxx}+C_{y,yyy}\\
&\quad+\tfrac{4}{3}C_{z,zzz}+C_{x,xyy}+C_{y,yxx}\}\\
B_{4,1}^{0,1,3}&=\frac{1}{\sqrt{7}}\{4C_{x,zzz}+3C_{z,xzz}\}\\
B_{4,-1}^{0,1,3}&=\{4C_{y,zzz}+3C_{z,yzz}\}\\
B_{4,2}^{0,1,3}&=-\frac{1}{\sqrt{14}}\{7(C_{x,xxx}-C_{y,yyy})+9(C_{x,xyy}-C_{y,yxx})\}\\
B_{4,-2}^{0,1,3}&=-\frac{2}{\sqrt{14}}\{6C_{y,xyy}+7C_{y,xxx}+C_{x,yyy}\}\\
B_{4,3}^{0,1,3}&=4C_{z,xxx}+3C_{z,xzz}\\
B_{4,-3}^{0,1,3}&=-\{4C_{z,yyy}+3C_{z,yzz}\}\\
B_{4,4}^{0,1,3}&=\frac{1}{2\sqrt{2}}\{C_{x,xxx}+C_{y,yyy}-3(C_{x,xyy}+C_{y,yxx})\}\\
B_{4,-4}^{0,1,3}&=\sqrt{2}\{C_{y,xxx}-C_{x,yyy}\}.
\end{aligned} \tag{24b}$$

Table 6. Redundancies among Stevens' parameters defined in equations (10).

SH term	Redundancy equations among Stevens' parameters
BS	$B_{1y}^{1}=B_{1x}^{-1}$
	$B_{1z}^{1}=B_{1x}^{0}$
	$B_{1z}^{-1}=B_{1y}^{0}$
BS^3	$B_{3y}^{1}=B_{3x}^{-1}$
	$2B_{3z}^{1}=6B_{3x}^{0}+(B_{3x}^{2}+B_{3y}^{-2})$
	$2B_{3z}^{-1}=6B_{3y}^{0}+(B_{3x}^{-2}-B_{3y}^{2})$
	$2B_{3z}^{2}=5(B_{3x}^{1}-B_{3y}^{-1})+3(B_{3x}^{3}+B_{3y}^{-3})$
	$2B_{3z}^{-2}=10B_{3x}^{-1}+3(B_{3x}^{-3}-B_{3y}^{3})$
	$6B_{3z}^{3}=B_{3x}^{2}-B_{3y}^{-2}$
	$6B_{3z}^{-3}=B_{3x}^{-2}+B_{3y}^{2}$
BS^5	$B_{5y}^{1}=B_{5x}^{-1}$
	$2B_{5z}^{1}=30B_{5x}^{0}+(B_{5x}^{2}+B_{5y}^{-2})$
	$2B_{5z}^{-1}=30B_{3y}^{0}+(B_{5x}^{-2}-B_{5y}^{2})$
	$2B_{5z}^{2}=7(B_{5x}^{1}-B_{5y}^{-1})+6(B_{5x}^{3}+B_{5y}^{-3})$
	$2B_{5z}^{-2}=14B_{5x}^{-1}+6(B_{5x}^{-3}-B_{5y}^{3})$
	$6B_{5z}^{3}=(B_{5x}^{2}-B_{5y}^{-2})+(B_{5x}^{4}+B_{5y}^{-4})$
	$6B_{5z}^{-3}=(B_{5x}^{-2}+B_{5y}^{2})+(B_{5x}^{-4}-B_{5y}^{4})$
	$4B_{5z}^{4}=9(B_{5x}^{3}-B_{5y}^{-3})+5(B_{5x}^{5}+B_{5y}^{-5})$
	$4B_{5z}^{-4}=9(B_{5x}^{-3}+B_{5y}^{3})+5(B_{5x}^{-5}-B_{5y}^{5})$
	$10B_{5z}^{5}=B_{5x}^{4}-B_{5y}^{-4}$
	$10B_{5z}^{-5}=B_{5x}^{-4}+B_{5y}^{4}$

From equations (24) the appropriate expressions for specific higher-symmetry Laue classes can be written down from knowledge of the TSTOs that transform as the totally-symmetric irreducible representation under the symmetry operations of the class [17, 19, 2]; these transformation properties depend only on the subscripts k, q and are independent of superscripts k_1, k_2 and k_3. For example, the expression for orthorhombic symmetry (D_{2h} or mmm Laue class) is, from (24), just the sum of those terms that contain $B_{2,0}$, $B_{2,2}$, $B_{4,0}$, $B_{4,2}$ and $B_{4,4}$ only. These terms are

$$\begin{aligned}
B_{2,0}^{0,1,3} &= \frac{\sqrt{15}}{\sqrt{14}}\{C_{x,xxx} + C_{y,yyy} - C_{z,zzz} + C_{x,xyy} + C_{y,yxx}\}\\
B_{2,2}^{0,1,3} &= \frac{3\sqrt{10}}{2\sqrt{7}}\{C_{x,xyy} - C_{y,yxx}\}\\
B_{4,0}^{0,1,3} &= \frac{3\sqrt{5}}{2\sqrt{14}}\{C_{x,xxx} + C_{y,yyy}\\
&\quad + \tfrac{4}{3}C_{z,zzz} + C_{x,xyy} + C_{y,yxx}\}\\
B_{4,2}^{0,1,3} &= -\frac{1}{\sqrt{14}}\{7(C_{x,xxx} - C_{y,yyy}) + 9(C_{x,xyy} - C_{y,yxx})\}\\
B_{4,4}^{0,1,3} &= \frac{1}{2\sqrt{2}}\{C_{x,xxx} + C_{y,yyy} - 3(C_{x,xyy} + C_{y,yxx})\}.
\end{aligned} \qquad (25a)$$

Equations (25a) contain, as required 5 (and only 5) C parameters that are related linearly to the 5 tesseral B parameters. It must be emphasized that these equations are not unique; they are one of many equivalent combinations of C parameters themselves related by the redundancy equations of table 2. Concomitantly, a SH for SI^3 terms expressed in Cartesian tensor form will not be unique. We have not indeed, at this stage, attempted to specify a Cartesian SH for SI^3 terms but, as for the tensors of rank 2 considered in section 2.2, it is clear, utilizing the relationships of (25a), that the TSTO SH for mmm Laue class from table 1, namely

$$\begin{aligned}
H_S^{0,1,3} &= \frac{1}{\sqrt{7}}B_{2,0}^{0,1,3}\{-\sqrt{3}S_z\Im_{3,0}^{0,1,3}(\mathbf{I})\\
&\quad - \sqrt{2}[S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{\sqrt{42}}B_{2,2}^{0,1,3}\{S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) - S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})\\
&\quad - \sqrt{10}S_z\Im_{3,2}^{0,1,3}(\mathbf{I}) - \sqrt{15}[S_x\Im_{3,3}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-3}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{\sqrt{14}}B_{4,0}^{0,1,3}\{2\sqrt{2}S_z\Im_{3,0}^{0,1,3}(\mathbf{I})\\
&\quad - \sqrt{3}[S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{2\sqrt{14}}B_{4,2}^{0,1,3}\{\sqrt{15}[S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) - S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})]\\
&\quad + 2\sqrt{6}S_z\Im_{3,2}^{0,1,3}(\mathbf{I}) - [S_x\Im_{3,3}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-3}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{\sqrt{2}}B_{4,4}^{0,1,3}\{S_x\Im_{3,3}^{0,1,3}(\mathbf{I}) - S_y\Im_{3,-3}^{0,1,3}(\mathbf{I})\}
\end{aligned} \qquad (25b)$$

is sufficient to cover both cases. The equations appropriate to D_{4h} or $4/mmm$ Laue class may be obtained similarly or, from (25a), taking $C_\perp = C_{x,xxx} = C_{y,yyy}$, $C_\parallel = C_{z,zzz}$ and $C_{y,yxx} = C_{x,xyy}$. Then, we obtain

$$\begin{aligned}
B_{2,0}^{0,1,3} &= \frac{\sqrt{15}}{\sqrt{14}}\{2C_\perp - C_\parallel + 2C_{x,xyy}\}\\
B_{4,0}^{0,1,3} &= \frac{3\sqrt{5}}{\sqrt{14}}\left\{C_\perp + \frac{2}{3}C_\parallel + C_{x,xyy}\right\}\\
B_{4,4}^{0,1,3} &= \frac{1}{\sqrt{2}}\{C_\perp - 3C_{x,xyy}\}
\end{aligned} \qquad (26a)$$

where the three B parameters are related linearly to 3 (and 3 only) Cartesian C parameters and the TSTO equation (26b) (cf equations (13)) appropriate to uniaxial (tetragonal, D_{4h}) symmetry is sufficient to cover both cases.

$$\begin{aligned}
H_S^{0,1,3} &= \frac{1}{\sqrt{7}}B_{2,0}^{0,1,3}\{-\sqrt{3}S_z\Im_{3,0}^{0,1,3}(\mathbf{I})\\
&\quad - \sqrt{2}[S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{\sqrt{14}}B_{4,0}^{0,1,3}\{2\sqrt{2}S_z\Im_{3,0}^{0,1,3}(\mathbf{I})\\
&\quad - \sqrt{3}[S_x\Im_{3,1}^{0,1,3}(\mathbf{I}) + S_y\Im_{3,-1}^{0,1,3}(\mathbf{I})]\}\\
&\quad + \frac{1}{\sqrt{2}}B_{4,4}^{0,1,3}\{S_x\Im_{3,3}^{0,1,3}(\mathbf{I}) - S_y\Im_{3,-3}^{0,1,3}(\mathbf{I})\}.
\end{aligned} \qquad (26b)$$

Again, the relationships of equations (26a) are *not* unique.

Although the reduction algebra involved is considerably more tedious, the sixth rank tensors of dimension SI^5 can be handled similarly.

3.2. The SH for higher-order spin terms expressed in Cartesian tensor form

As noted in section 3.1, it is not possible to write a unique SH for such terms in Cartesian tensor form. It is, nevertheless, instructive to construct such a SH and we now do this for the three Laue classes, $\bar{1}$, mmm and $4/mmm$, of section 3.1. We start by considering first the lowest symmetry, $\bar{1}$, and write the Cartesian SH (again) for terms of dimension SI^3, taking into account contractions arising from the permutation of coefficients but retaining all operator permutations to allow for non-commutativity of the operators I_x, I_y and I_z in the functions $\hat{S}_j I_\ell I_m I_n$. After applying *all* 16 of the redundancy equations of table 2 we arrive at a SH expression containing 14 only C parameters. This expression is rather cumbersome and we shall not reproduce it here. For orthorhombic, D_{2h} symmetry, the further contraction is relatively simple and we obtained the following equation

$$\begin{aligned}
H_S^{0.1.3} &= C_{x,xxx}\hat{S}_x\{I_x^3 - [I_z^2 I_x + I_z I_x I_z + I_x I_z^2]\}\\
&\quad + C_{y,yyy}\hat{S}_y\{I_y^3 - [I_x^2 I_y + I_x I_y I_x + I_y I_x^2]\}\\
&\quad + C_{z,zzz}\hat{S}_z\{I_z^3 - [I_y^2 I_z + I_y I_z I_y + I_z I_y^2]\}\\
&\quad + C_{x,xyy}\hat{S}_x\{[I_y^2 I_x + I_y I_x I_y + I_x I_y^2]\\
&\quad - [I_z^2 I_x + I_z I_x I_z + I_x I_z^2]\}\\
&\quad + C_{y,yzz}\hat{S}_z\{[I_z^2 I_y + I_z I_y I_z + I_y I_z^2]\\
&\quad - [I_x^2 I_y + I_x I_y I_x + I_y I_x^2]\}\\
&\quad + C_{z,zxx}\hat{S}_z\{[I_x^2 I_z + I_x I_z I_x + I_z I_x^2]\\
&\quad - [I_y^2 I_z + I_y I_z I_y + I_z I_y^2]\}
\end{aligned} \qquad (27)$$

in terms of 6 parameters. Equations (27) can be reduced to the required 5 parameters by the substitutions $C_{y,yzz} = -C_{y,yxx} - C_{y,yyy}$ and $C_{z,zxx} = -\frac{1}{2}(C_{x,xxx} - C_{y,yyy} + C_{z,zzz}) - C_{x,xyy} + C_{y,yxx}$ utilizing the second and fourth $BS^3(IS^3)$ redundancy equations respectively of table 2. Thus (27) is a Cartesian equation of 5 independent parameters, $C_{x,xxx}$, $C_{y,yyy}$, $C_{z,zzz}$, $C_{x,xyy}$ and $C_{y,yxx}$. The equation is, of course, not unique but the choices made enable to match the same 5 C parameters that are related linearly to 5 tesseral B parameters of equations (25*a*). The corresponding equation for tetragonal, D_{4h} symmetry, may be obtained similarly or, simply by writing $C_{x,xxx} = C_{y,yyy} = C_{\perp}$, $C_{z,zzz} = C_{\parallel}$ and $C_{y,yxx} = C_{x,xyy}$ where the resulting equation matches in number and type the three independent C parameters of equations (26*a*).

3.3. A consideration of SHs containing mixed TSTO, Cartesian and Stevens' forms

A good place to start is a consideration of a recent paper [20] that measured and analysed the complex hyperfine structure of ^{47}Ti and ^{49}Ti isotopes in 15 K X-band spectra of a Ti^{3+} centre in tetragonal zircon. In this study, in addition to the standard second rank 'tensor' terms of equation (5), all terms of the types BI^3, BI^5, SI^3, SI^5 and I^4 were found necessary to describe adequately the hyperfine structure. A feature of the observed spectra was a marked angular dependence of the titanium hyperfine lines in the perpendicular, *ab* crystal plane, even although the Ti^{3+} ion was clearly from the observed g and A matrices in a site of tetragonal symmetry. The spectra were analysed with international programme EPR-NMR [10] where equation (5) is used to describe second rank 'tensor' quantities, Stevens' operators to describe ZFS terms of dimension I^4 (actually EPR-NMR allows ZFS terms to be expressed optionally in TSTO form) and TSTOs to describe higher-spin terms, BI^n, SI^n $(n = 3, 5)$. It has been suggested [9] that such a mixed SH is invalid when the higher-order terms are present and could, depending on relative magnitudes of derived parameters, lead to false values of, for example, g and A principal values.

In section 2.2 we showed that equation (5) can be replaced by an equivalent expression framed in TSTOs since the parameters of the two forms are related linearly to one another. For any specific site symmetry there are equal numbers of independent Cartesian parameters and independent TSTO coefficients. This information is relatively well known already [16, 1]. Similarly, the parameters of Cartesian and STSO forms for higher-order terms of dimensions BJ^n, $J_1J_2^n$, $J_1^nJ_2$ $(n = 3, 5)$ are, from sections 2.3 and 2.4, also linearly related. It follows that there is no more difficulty in relating the parameters in the two nomenclatures for such higher-order terms than there is for the second rank tensors of equation (5)—*provided one compares equivalent SHs*. The generation of equivalent Hamiltonians for any Laue class is outlined in section 3.2 above.

That use of a mixed Hamiltonian might lead to erroneous values of principal values of g and/or A (see again [9]) does not seem to be correct. It is true, taking electronic Zeeman terms as example, that inclusion of higher-order terms, BS^3, BS^5, ..., will influence the g principal values to a minor extent because the operators involved span the same ket vectors and there will be matrix elements containing parameters from all three electronic Zeeman-type terms. The effect is to make the g parameter matrix slightly more anisotropic than it would be in the absence of the higher-spin terms. This, from the preceding discussion, is independent of whether one utilizes a mixed SH or one framed completely in TSTOs.

What is the significance of the parameters produced in terms of electron–nuclear interactions? So far as terms in equation (5) are concerned, the relationships between a theoretical Hamiltonian, in terms of electron–nuclear interactions, and the experimental, or *spin* Hamiltonian are well established—see, in particular, Bleaney and Stevens [21]. It follows immediately from equations (8) that relationships are easily established between theory and a SH expressed in TSTO form. The same is true of ZFS terms of dimension J^n $(n = 2, 4, 6\ldots)$, traditionally set up from the theory of the crystalline electric field, in terms of Stevens' operator equivalents. The equivalent relationships to the TSTO ZFS SH are, from section 2.4 and table 5, also easily established.

It can, thus, be stated unequivocally, that use of a mixed SH of Cartesian second rank (symmetric) 'tensors', Stevens' operator ZFS terms and TSTO higher-spin nuclear and/or electronic terms is perfectly valid, and there are no redundancies involved. Using the equations and tables of this paper, one can convert the parameters of any one of the forms to those of any other. This can be done, moreover, for any specified Laue class.

3.4. The importance (or otherwise) of higher-spin Zeeman and nuclear terms in EPR of ions with $S \geqslant 3/2$; $I > 0$

Since a large portion of this paper is devoted to the analytical forms of higher-spin electronic and nuclear terms in the SH we should discuss, albeit briefly, their significance (or otherwise) in EPR studies in EPR of transition ions. Let it be said at the outset that such interest has been at best spasmodic and restricted to small groups of experimentalists. There are, however, sufficient points of interest that would warrant the time and effort spent in calculating the appropriate analytical forms of the terms and including them in a general matrix-diagonalization-refinement programme—for example [11].

Bleaney [22] and Koster and Statz [14] first pointed out that acceptance of symmetry-allowed SH terms of the form $B^{\ell_B}S^{\ell_S}I^{\ell_I}(\ell_B + \ell_S + \ell_I = \ell = \text{even})$ where $\ell_S \leqslant 2S, \ell_I \leqslant 2I$ could include, generally, higher-degree Zeeman terms of dimensions $BJ^n (n = 3, 5)$ and/or higher-spin terms of dimensions $J_1J_2^n$, $J_1^nJ_2$ $(J_1, J_2 = S, I; n = 3, 5)$. Considerable interest followed almost immediately thereafter, particularly for studies of Co^{2+} in sites of cubic symmetry in certain crystals [23] (see also [1] for brief summary with further references). Reference [1] pointed out that one should be sceptical of claimed detection of such terms if the SH utilized does not contain *all* terms required for a given site symmetry or, furthermore, may have used a perturbation approach in which some higher-order terms were neglected.

A couple of studies in which the present authors were involved will illustrate some of the consequences of appearance of some high-spin terms.

In a 10 K X-band study of Fe^{3+} in $\bar{1}$ sites in $CaWO_4$ [24] evidence was found for rather large magnitude terms of dimension BS^3 and BS^5, these being necessary to obtain a good fit to the data using EPR-NMR [10]. The main features observed that were attributable to the inclusion of the high-spin terms: a 20-fold diminution in the RMSD between observed and calculated line positions; a marked increase in the anisotropy of the g principal values; a fitted $\cos 4\theta$ angular dependence of $g_{\mathrm{eff}} = 4.3$ lines that is dependent on the inclusion of high-spin Zeeman terms in the SH; a set of four three-fold pseudo-symmetry axes [25, 26] that are, within error, common to the tensor sets $B_{4,m}^{1,3}$, $B_{4,m}^{1,5}$ and $B_{6,m}^{1,5}$.

The second study [20, 27] (see section 3.3) involved 10 K X-band measurements on a Ti^{3+} d^1 centre in tetragonal zircon; the site symmetry of Ti^{3+} is $\bar{4}2m(D_{2d})$ tetragonal. (It should be noted that the dimensioned high-spin parameters of table 2 of [20] are in units $1/g_e\mu_B$ Gauss and *not* mT as stated. The conclusions of the paper are not affected thereby.) To account for all of the features of the spin system(s) $S = 1/2, I = 5/2$ (^{47}Ti isotope) and $S = 1/2, I = 7/2$ (^{49}Ti isotope) it was necessary to include terms of the following types: $BI^n(n = 3, 5)$, $SI^n(n = 3, 5)$ and I^4. The effects of the terms on the observed EPR spectra were rather subtle but certainly not trivial: (i) a marked $\cos 4\theta$ angular dependence of both line positions and line intensities in the perpendicular (*ab* plane) crystal orientation that can arise only from operators $\Im_{k,m}(\mathbf{I})(k = 4, 6; m = 0, 4)$ and would be absent in the conventional uniaxial SH; (ii) an apparent anisotropy in the nuclear Zeeman interaction that was identified with anisotropy in the chemical-shielding tensor, $\boldsymbol{\sigma}$; (iii) an experimental ratio $^{47}P_\parallel/^{49}P_\parallel$ that is in very good agreement with that calculated from the corresponding nuclear quadrupole moments—the agreement in the absence of high-spin terms is rather poor.

We might conclude from these two studies the following. Firstly, for some transition ion systems, provided the measurements are precise enough, the electronic and nuclear Zeeman interactions are described by all three types of terms, BS, BS^3 and BS^5 and BI, BI^3 and BI^5 respectively and *not* simply the traditional linear magnetic-field term of first degree, This raises the question: do the two tensors (parameter sets) from BS^3 and BS^5 terms have pseudo-2-fold axes related to the principal directions of $\mathbf{g}$? Secondly *all* so-called second rank 'tensor' quantities of equation (1) can be influenced to some extent by inclusion of higher-order spin terms. As noted in section 3.3, inclusion of high-spin Zeeman terms in the SH leads to the result that the g and/or g_n matrices appear more anisotropic than in the absence of such terms. The inclusion can also, for the A parameter matrix lead to a so-called 'hyperfine anomaly' and for the nuclear electric quadrupole and nuclear g matrices to so-called pseudo-quadrupole and pseudo-nuclear Zeeman interactions respectively.

The two studies above both utilized 'mixed' SHs. From section 2.3, this would seem not to be an erroneous procedure. Whatever then may be the shortcomings of the two analyses, the use of an incorrect SH is, we believe, not one of them. We concede, however, that a SH framed completely in TSTO form might be more satisfying.

A few concluding remarks regarding occurrence of high-spin terms are pertinent. In order to establish that the parameters determined for the, usually, small interactions that are the subject of this paper are meaningful, one needs to show that they are statistically significant and can, ideally, be related to other known physical quantities. The first of these would, generally, demand a large number of very precise data points collected in a three-dimensional single-crystal study [7, 8, 16, 20, 24], with parameter refinement by matrix diagonalization procedures [11]. A couple of examples of the second criterion, the relationships of quadrupole terms to nuclear quadrupole moments, and relationship of an anisotropic nuclear g interaction to the chemical-shielding tensor are given in the Ti^{3+}/zircon study above [20]. Although one might perhaps regard such effects as being low symmetry related, we note that in the Fe^{3+}/scheelite study [24] the site symmetry was indeed low, namely $\bar{1}$, but in the second study [20] the site symmetry was D_{2d} tetragonal.

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Appendix

The tables in this paper have been restricted, in the interests of brevity, to those, in the main, giving relationships for tensors of ranks $\leqslant 4$. We have, however, full tables including tensors of ranks 6. The authors undertake to make the full set of tables available as PDF files to interested readers.

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