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LETTER TO THE EDITOR

A relativistic effective Hamiltonian for S-state ions

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Abstract. This paper uses the 'effective operator technique' to develop a relativistic formulation to describe the crystalline electric field splitting of an S-state ion. This formulation leads to an effective Hamiltonian which is capable of describing the ERP and ENDOR spectra observed from S-state ions such as Gd^{3+}. It replaces the traditional phenomenological spin Hamiltonian and reveals that all those total angular momentum tensor operators permitted by symmetry considerations are included. It is shown that Kramers' theorem which is valid only for spin states must be modified to apply to only the lowest degenerate level of the ground state of any ion since all tensor operators $T_q^k(J)$ where k is odd and $k \neq 1$ are allowed because J, and not S, is a good relativistic quantum number.

Elliott and Stevens [1] were probably the first to recognize that the degeneracy of the ground state for a pure S-state ion could not be decreased by the presence of a crystalline electric field. In fact, the Zeeman interaction is the only non-zero interaction for a pure S-state ion [2]. Consequently, it is remarkable that the EPR and ENDOR spectra of S-state impurity ions in diamagnetic host lattices exhibit well developed fine structure and hyperfine structure as well as shifts due to nuclear quadrupole interactions [1, 3]. A phenomenological spin Hamiltonian was developed to parameterize the observed spectra [1, 3]. The zero field splitting was described by spin angular momentum operators having the same transformation properties as the corresponding spherical harmonics required in the expansion of the potential due to a crystalline electric field of the appropriate symmetry [3]. The spin may be real or fictitious [1]. Odd rank terms were omitted because of Kramers' theorem [4] that invokes the time reversal properties of a pure spin system [3].

Smith *et al* [5] have summarized the various mechanisms that had been proposed to explain the observed zero field splittings in the EPR spectra of S-state ion gadolinium (Gd^{3+}). However these mechanisms are incapable of describing the observed splitting. The relativistic mechanism proposed by Wybourne [6] was the only mechanism successful in predicting splittings of the correct magnitude, but the sign was incorrect. He

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used the concept of an 'effective operator' introduced by Sandars and Beck [7] to show that the non-relativistic crystalline electric field Hamiltonian

$$H_{CEF}^{NR} = \sum A_q^k r^k C_q^k \tag{1}$$

where C_q^k is a Racah irreducible tensor operator [8, 9] can be replaced by

$$H_{CEF}^R = \sum_{k_s k_l} A_q^k b_k(k_s, k_l) W^{(k_s k_l)}{}_q^k(S, L) \tag{2}$$

where $W^{(k_s k_l)}{}_q^k(S, L)$ is an 'effective' double tensor operator [6].

The relativistic formulation requires the use of the total angular momentum $J = L + S$ because J is a constant of the motion or a good relativistic quantum number [2] and involves Russel–Saunders or LS coupling [7] whilst the orbital L and spin S angular momenta are not good relativistic quantum numbers.

This paper is the logical extension of the effective operator technique concepts introduced by Wybourne [6] and their generalization by Chatterjee and Buckmaster [10]. It is assumed that the matrix elements are such that

$$\langle n\tfrac{1}{2}ljm | A_q^k r^k C_q^k | n'\tfrac{1}{2}l'j'm' \rangle = A_q^k \langle n\tfrac{1}{2}ljm | b_k(k_s, k_l) W^{(k_s k_l)}{}_q^k | n'\tfrac{1}{2}l'j'm' \rangle. \tag{3}$$

The Wigner–Eckart theorem [8, 9, 11] can be used to reduce (3)

$$A^k \langle nl \| r^k \| n'l' \rangle \langle n\tfrac{1}{2}lj \| C^k \| n'\tfrac{1}{2}l'j' \rangle = b_k(k_s, k_l)\langle n\tfrac{1}{2}lj \| W^{(k_s k_l)k} \| n'\tfrac{1}{2}l'j \rangle. \tag{4}$$

It can be shown following Yutsis *et al* [12] and Rotenberg *et al* [13] that

$$b_k(k_s, k_l) = \sum_{j,j'} \frac{(-1)^{j+1/2}}{(2k+1)} [(2k_s + 1)(2k_l + 1)]^{1/2}(2j+1)(2j'+1)x$$

$$\times \begin{pmatrix} j & k & j' \\ \tfrac{1}{2} & 0 & -\tfrac{1}{2} \end{pmatrix} \begin{Bmatrix} \tfrac{1}{2} & \tfrac{1}{2} & k_s \\ l & l' & k_l \\ j & j' & k \end{Bmatrix} R_{j,j'}^k \tag{5}$$

where

$$R_{j,j'}^k = \int_0^\infty r^k (F_j F_{j'} + G_j G_{j'})\, dr.$$

F and G are the large and small components of the Dirac eigenfunctions and $j, j' = l \pm \tfrac{1}{2}$ [14]. Note that k_s takes only integer values because $k_s = 2S$ and is limited to zero or one since $S = \tfrac{1}{2}$ for one-electron eigenstates. The spin-dependent terms $b_k(1k)$ are zero in the non-relativistic limit [14].

The application of this formalism can be demonstrated by the following example. The phenomenological spin Hamiltonian for the crystalline electric field of C_{3h} symmetry experienced by gadolinium (Gd^{3+}) impurity ions in the diamagnetic lanthanide ethyl sulphate nonahydrate lattice [5]

$$H_{CEF}^{NR} = \sum_{\substack{k=2,3,4,5,6,7 \\ r \neq 0, \pm 3, \pm 6}} A_q^r r^k C_q^k \tag{6}$$

where the allowed values of k and q are determined from the tables in Prather [15] and Tuszynski *et al* [16] of the allowed tesseral harmonics constrained by the various non-cubic point group symmetries. The odd terms with values of k that are not allowed since

they are not time reversal invariant [3] are included since it will be shown that the relativistic operators corresponding to them are allowed. The 'effective' Hamiltonian corresponding to (6) is constructed by replacing each of the terms in (6) by the corresponding relativistic effective operator,

$$H^{NR}_{CEF} = A^2_0 r^2 C^2_0(S) \tag{7a}$$

by

$$H^R_{CEF} = A^2_0[b_2(02)W^{(02)\,2}_{0} + b_2(11)W^{(11)\,2}_{0}$$
$$+ b_2(12)W^{(12)\,2}_{0} + b_2(13)W^{(13)\,2}_{0}] \tag{7b}$$

$$H^{NR}_{CEF} = A^3_{\pm3} r^3 C^3_{\pm}(s) \tag{8a}$$

by

$$H^R_{CEF} = A^3_{\pm3}[b_3(03)W^{(03)\,3}_{\pm} + b_3(12)W^{(12)\,3}_{\pm3}$$
$$+ b_3(13)W^{(13)\,3}_{\pm3} + b_3(14)W^{(14)\,3}_{\pm3}] \tag{8b}$$

$$H^{NR}_{CEF} = A^4_0 r^4 C^4_0(S) \tag{9a}$$

by

$$H^R_{CEF} = A^4_0[b_4(04)W^{(04)\,4}_{0} + b_4(13)W^{(13)\,4}_{0}$$
$$+ b_4(14)W^{(14)\,4}_{0} + b_4(15)W^{(15)\,4}_{0}] \tag{9b}$$

$$H^{NR}_{CEF} = A^5_3 r^5 C^5_3(S) \tag{10a}$$

by

$$H^R_{CEF} = A^5_{\pm3}[b_5(05)W^{(05)\,5}_{\pm3} + b_5(14)W^{(14)\,5}_{\pm3}$$
$$+ b_5(15)W^{(15)\,5}_{\pm3} + b_5(16)W^{(16)\,5}_{\pm3}] \tag{10b}$$

$$H^{NR}_{CEF} = A^6_0 r^6 C^6_0(S) \tag{11a}$$

by

$$H^R_{CEF} = A^6_0[b_6(06)W^{(06)\,6}_{0} + b_6(15)W^{(15)\,6}_{0}$$
$$+ b_6(16)W^{(16)\,6}_{0} + b_6(17)W^{(17)\,6}_{0}] \tag{11b}$$

$$H^{NR}_{CEF} = A^6_{\pm3} r^6 C^6_{\pm6}(S) \tag{12a}$$

by

$$H^R_{CEF} = A^6_{\pm6}[b_6(06)W^{(06)\,6}_{\pm6} + b_6(15)W^{(15)\,6}_{\pm6}$$
$$+ b_6(16)W^{(16)\,6}_{\pm6} + b_6(17)W^{(17)\,6}_{\pm6}] \tag{12b}$$

and

$$H^{NR}_{CEF} = A^7_{\pm3} r^7 C^7_{\pm3}(S) \tag{13a}$$

by

$$H^R_{CEF} = A^7_{\pm3}[b_7(07)W^{(07)\,7}_{\pm3} + b_7(16)W^{(16)\,7}_{\pm3}$$
$$+ b_7(17)W^{(17)\,7}_{\pm3} + b_7(18)W^{(18)\,7}_{\pm3}]. \tag{13b}$$

The double tensors $W^{(k_s k_l)}{}^k_q$ can be transformed into the product of single tensors using

$$W^{(k_s k_l)}{}^k_q(S, L) = \sum_{q_s q_l} (-1)^{k_s + k_l - k}(2k + 1)^{1/2}\begin{pmatrix} k_s & k_l & k \\ q_s & q_l & -q \end{pmatrix} T^{k_s}_{q_s}(S) T^{k_l}_{q_l}(L) \tag{14}$$

where the triangle rule $\triangle(k_s k_l k)$ must be satisfied [2, 8, 9, 10]. $k + k_s + k_l = 0$ or $0 \leq k_s + k_l - k, 0 \leq k_s + k - k_l$ and $0 \leq k_l + k - k_s$ where $k_s + k_l + k$ is either an odd or even integer.

It is useful to collect those terms for which $k_s = 0$ since these terms correspond to those in (6) except that they are now total angular momentum rather than spin angular momentum operators i.e. $T^k_q(J)$ rather than $T^k_q(S)$.

The first term in (7b) reduces to

$$H^R_{CEF} = A^2_0 b_2(02) W^{(02)}{}^2_0 = A^2_0 b_2(02) T^2_0(J) \tag{15a}$$

where $b_2(02) = -(2\sqrt{42}/735)[25(R_{7/2,7/2})^2 + 18(R_{5/2,5/2})^2 + 6(R_{7/2,5/2})^2]$. Similarly for (8b):

$$H^R_{CEF} = A^3_{\pm3} b_3(03) W^{(03)}{}^3_{\pm3} = A^3_{\pm3} b_3(03) T^3_{\pm3}(J) \tag{15b}$$

where $b_3(03) = (12/7\sqrt{42})(R_{7/2,5/2})^3$.

For (9b)

$$H^R_{CEF} = A^4_0 b_4(04) W^{(04)}{}^4_0 = A^4_0 b_4(04) T^4_0(J) \tag{15c}$$

where $b_4(04) = (2\sqrt{77}/1617)[18(R_{7/2,7/2})^4 + 11(R_{5/2,5/2})^4 + 20(R_{7/2,5/2})^4]$.

For (10b)

$$H^R_{CEF} = A^5_{\pm3} b_5(05) W^{(05)}{}^5_{\pm3} = A^5_{\pm3} b_5(05) T^5_{\pm3}(J) \tag{15d}$$

where $b_5(05) = (4\sqrt{70}/539)(R_{7/2,5/2})^5$.

For (11b)

$$H^R_{CEF} = A^6_0 b_6(06) W^{(06)}{}^6_0 = A^6_0 b_6(06) T^6_0(J) \tag{15e}$$

where $b_6(06) = -(10\sqrt{462}/3003)[(R_{7/2,7/2})^6 + 6(R_{7/2,5/2})^6]$.

For (12b)

$$H^R_{CEF} = A^6_{\pm6} b_6(06) W^{(06)}{}^6_{\pm6} = A^6_{\pm6} b_6(06) T^6_{\pm6}(J) \tag{15f}$$

where $b_6(06) = -(10\sqrt{924}/3003)[(R_{7/2,7/2})^6 + 6(R_{7/2,5/2})^6]$.

For (13b)

$$H^R_{CEF} = A^7_{\pm3} b_7(07) W^{(07)}{}^7_{\pm3} = A^7_{\pm3} b_7(07) T^7_{\pm3}(J) \tag{15g}$$

where $b_7(07) = 0$.

Waber and Cromer [17] have computed self-consistent relativistic Dirac–Slater eigenfunctions for some ions and obtained $R_{7/2,7/2} = 0.824$ au and $R_{5/2,5/2} = 0.804$ au for Gd^{3+}. Wybourne [18] has suggested that since $R_{7/2,5/2}$ has not been computed, it can be estimated from $(R_{7/2,7/2} + R_{5/2,5/2})/2$.

Consequently, it has been shown that the relativistic effective operator formulation leads to relativistic effective Hamiltonians that involves all those total angular momentum tensor operators specified by the symmetry constraints determined by the crystalline electric field symmetery. The relativistic operators $W^{(k_s k_l)}{}^k_q$ have been shown by Chatterjee and Buckmaster [10] to be Hermitian provided that the definition

$W^{(k,k_l)}{}_{q}^{k}(J)\dagger = (-1)^{k-q}W^{(k,k_l)}{}^{k}_{-q}$, which is the double tensor generalization of $T_q^k(J)\dagger = (-1)^{k-q}T^k_{-q}(J)$, is used [8, 19]. The terms $T^3_{\pm 3}(J)$ and $T^3_{\pm 3}(J)$, which split the $J = \pm\frac{3}{2}$ energy level, originate only from terms in the relativistic effective Hamiltonian for which the spin is zero. Consequently, other higher order terms are included in this relativistic effective Hamiltonian, which are not present in the zero-field splitting crystalline electric field terms of a phenomenological spin Hamiltonian. This splitting may be referred to as a relativistic splitting since it involves total angular momentum eigenfunctions rather than as a Kramers' splitting that involves only spin angular momentum eigenfunctions. It should be noted that a $J = \pm\frac{1}{2}$ ground state will not be split by a relativistic effective operator $W^{(01)}{}_{\frac{1}{2}}$ because this term is not permitted for a crystalline electric field of any symmetry [15, 16] in agreement with the statement of Abragam and Bleaney [3] that the ground state of any Kramers' ion cannot be split by an electric field. This demonstrates that crystal field symmetry concepts and the restricted version of Kramers' theorem are consistent. It is not necessary to discuss the question of whether the 'effective' Hamiltonian is time reversal invariant [8, 9] because this constraint was introduced only to ensure that non-relativistic phenomenological spin Hamiltonians satisfy Kramers' theorem. It should be noted that although the total angular momentum tensor operators $T_q^{(k)}(J)$ are not time reversal invariant since $\theta T_q^k(J)\theta^{-1} = (-1)^{k-q}T^k_{-q}(J)$ [8, 9]. However, the introduction of tesseral total angular momentum operators [16]:

$$C_q^k(J) = [T_q^k(J) + (-1)^{k-q}T^k_{-q}(J)]/2 \tag{16a}$$

and

$$S_q^k(J) = [T_q^k(J) - (-1)^{k-q}T^k_{-q}(J)]/2i \tag{16b}$$

where $C_0^k(J) = T_0^k(J)$ and $S_0^k(J) = 0$ for $k = 2$ resolves this deficiency, since

$$\theta C_q^k(J)\theta^{-1} = C_q^k(J) \tag{17a}$$

and

$$\theta S_q^k(J)\theta^{-1} = S_q^k(J). \tag{17b}$$

It is notationally awkward and inconvenient to introduce double tesseral operators, so the more traditional approach has been followed for simplicity.

It should also be recalled that the ground state in the example of the gadolinium Gd^{3+} ($4f^7$, ^8S) is not a pure S-state. Wybourne [18] has shown that the ground state eigenfunction is $0.986\,66|^8S_7\rangle + 0.1618|^6P_5\rangle - 0.0123|^6D_7\rangle$. It is probable that this deviation from a pure S-state combined with the fact that 4f electrons should be described by relativistic eigenfunctions is the reason that the eight-fold degeneracy of the free-ion ground state for Gd^{3+} is partially lifted resulting in three doubly degenerate and two singly degenerate eigenstates with the $|\pm\frac{1}{2}\rangle$ level lowest. Finally, it is noted that this paper has demonstrated that the H^{NR}_{CEF} given by Buckmaster *et al* [19] has the correct form relativistically although the derivation was flawed because it used spin (S) rather than total angular momentum (J) and, consequently, violated Kramers' theorem, although the tesseral spin angular momentum operators were time reversal invariant [16].

In conclusion, it has been demonstrated by using a relativistic rather than a non-relativistic formulation of the Hamiltonian for the crystalline electric field that all those total angular momentum tensor operators permitted by symmetry considerations should be included in an effective rather than a spin Hamiltonian.

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