DERIVATION OF SPIN HAMILTONIAN BY TENSOR ALGEBRA IN PERTURBATION THEORY

By C. Rudowicz

Institute of Physics, A. Mickiewicz University, Poznań*

(Received July 5, 1972; Revised paper received October 18, 1972)

The direct adoption of tensor algebra in perturbation theory is proposed. Formulas for the recoupling of invariant products are established and applied in the derivation of spin Hamiltonian for $3d^n$ ions. The resulting Hamiltonians are expressed in the operator equivalents $\tilde{O}^{(k)}$, for which tabulated matrix elements are available. Expressions for spin Hamiltonian tensors up to the fourth order in spin variables and applicable to all symmetries are derived. A simple procedure for deriving higher-order Zeeman terms is outlined.

1. Introduction

It is well known that group theory [1] and tensor algebra [2] can be exploited in the construction of spin Hamiltonian strictly on symmetry arguments, but the systematic use of tensor algebraical methods in the derivation of spin Hamiltonian by means of perturbation theory appears novel.

Most authors deal separately with any particular paramagnetic ion of $3d^n$ configuration when using perturbation theory. Only a few attempts have been made to derive general formulas for spin Hamiltonian tensors.

The previous attempts have been carried out by standard perturbation theory [3] and by a more serious formalism of effective Hamiltonian [4], in both cases up to the third order of perturbation theory. Those results were limited in some sense. Firstly, spin Hamiltonian containing terms up to the third order in spin variables is insufficient for ions with spin $S \geqslant 2$ [5]. Secondly, using only vector algebra, the previous authors [3], [4] succeeded in obtaining final expressions only in the form $\hat{\vec{S}} \cdot D \cdot \hat{\vec{S}}$. Moreover, they were quite unable to derive the higher-order Zeeman terms, in general arising still from the third order of perturbation theory. Thirdly, they resorted to a simplyfing relation of rather limited validity (see discussion on Eq. (18)).

* Address: Instytut Fizyki, Uniwersytet im. A. Mickiewicza, Sekcja Fizyki Teoretycznej, Matejki 48/49, 60-769 Poznań, Poland.

In this paper, we propose a method of adopting tensor algebra directly in perturbation theory. On recoupling of the invariant products arising in crude perturbation expressions, we get highly compact final expressions without the usual amount of effort. We thus extend the derivation of spin Hamiltonian up, to the fourth order of perturbation theory to cover the cases of $3d^n$ ions with spin $S = 2$. The method proposed avoids the other above stated limitations.

The paper is conceived as follows. A model Hamiltonian is outlined in Section 2. In Section 3 we develop the necessary formulas of irreducible tensor algebra. In Sections 4, 5, and 6, we derive the relevant expressions from the second, third and fourth order of perturbation theory, respectively. Section 7 is devoted to symmetry considerations.

An advantage of our methods resides in the expressing of the general spin Hamiltonian directly in the operator equivalents $\tilde{O}^{(k)}$[6], for which matrix elements are tabulated in the literature [7].

2. Hamiltonian

In perturbational approach to the derivation of an effective Hamiltonian $\tilde{\mathscr{H}}$, the proper choice of a "real" Hamiltonian $\hat{\mathscr{H}} = \hat{\mathscr{H}}_0+\hat{V}$ plays the central role. The effective Hamiltonian $\tilde{\mathscr{H}}$ is constructed so as to operate in an arbitrarily choosen subspace Ω_0 of the vectorial space Ω of all eigenstates of $\hat{\mathscr{H}}_0$. The space Ω_0 is spanned by the eigenstates belonging to a specified eigenvalue ε_0. The eigenvalues of $\tilde{\mathscr{H}}$ have to be the same as those of $\hat{\mathscr{H}}$ inside the manifold Ω_0 and, in practice, are easier to obtain.

For an iron group ion in a crystalline environment, the Hamiltonian can be written in general as:

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0+\hat{\mathscr{H}}_{SO}+\hat{\mathscr{H}}_{Ze}+\hat{\mathscr{H}}'_{CF}+\hat{\mathscr{H}}_{SS}+\hat{\mathscr{H}}_n+\hat{\mathscr{H}}_{Zn}. \tag{1}$$

The terms in (1) are arranged in decreasing order of importance. $\hat{\mathscr{H}}_0$ represents the Hamiltonian of an isolated ion, including the strongest part of the crystal field, with symmetry of a point group G_0. Next, $\hat{\mathscr{H}}'_{CF}$ represents the remaining part of the crystal field, of lower symmetry. The other terms represent the effect of spin-orbit coupling $\hat{\mathscr{H}}_{SO}$, spin-spin $\hat{\mathscr{H}}_{SS}$, and hyperfine $\hat{\mathscr{H}}_n$ interactions. $\hat{\mathscr{H}}_Z$ is the Zeeman electronic (e) and nuclear (n) term.

The eigenstates of $\hat{\mathscr{H}}_0$ in (1) are tensorial products of the spin and orbital parts. The zero-order orbital parts $|v\Gamma_{\alpha j}]$ can be taken as appropriate linear combinations of eigenstates of the orbital angular momentum operator $\hat{\vec{L}}$[8]:

$$|v\Gamma_{\alpha j}] = \sum_m a^m_{\alpha j}|vLm], \tag{2}$$

where Γ_α labels an irreducible representation of the point group G_0, j labels a row of Γ_α, and v is an additional quantum number. The numerical coefficients $a^m_{\alpha j}$ are extensively tabulated in [9].

Often, it is sufficient to confine $\hat{\mathscr{H}}_0$ to the manifold of states arising from the lowest ^{2S+1}L free-ion term. Within this manifold, one can rewrite the first terms of (1) in a simplified form:

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0+\hat{V}= \hat{\mathscr{H}}_0+\lambda\hat{\vec{L}}\cdot\hat{\vec{S}}+\mu_B(\hat{\vec{L}}+2\hat{\vec{S}})\cdot\vec{H}, \tag{3}$$

where L and S are the total orbital and spin angular momenta, H is an external magnetic field. Thus, here, the space Ω is of dimension $(2L+1)\cdot(2S+1)$.

In this paper we consider the derivation of general spin Hamiltonian on the basis of the 'model' Hamiltonian (3) when the ground orbital state of $\hat{\mathscr{H}}_0$ is nondegenerate. Then the subspace Ω_0, in which the spin Hamiltonian $\tilde{\mathscr{H}}$ operates, is of dimmension $(2S+1)$.

A similar simplification as in Eq. (3) is possible for the last three terms of Eq. (1) [10]. An extension of the presented tensorial method to treat situations when the term $\hat{\mathscr{H}}'_{CF}$ is relevant, *i.e.* of a magnitude comparable to $\hat{\mathscr{H}}_{SO}$ or $\hat{\mathscr{H}}_{Ze}$, is straightforward.

3. *Tensor algebra formulas*

In the problem under consideration, there occur various multiple products like $(\vec{A}\cdot\hat{\vec{S}})(\vec{B}\cdot\hat{\vec{S}})$ ..., up to the quadruple product in the fourth order of perturbation theory. $\vec{A}$, $\vec{B}$, ..., stand for a vector being a matrix element of the operator $\hat{\vec{L}}$, or for the magnetic field vector $\vec{H}$. A mathematical framework for the separation of variables $(\vec{A}, \vec{B}, ...,)$ on one side and $(\hat{\vec{S}}, \hat{\vec{S}}, ...,)$ on the another is provided by irreducible tensor algebra.

For the recoupling of a product of invariant products, we can use a specialized form of the general equation [11]:

$$(A^{(j_1)}\cdot S^{(j_1)})(A^{(j_2)}\cdot S^{(j_2)})(A^{(j_3)}\cdot S^{(j_3)})(A^{(j_4)}\cdot S^{(j_4)}) =$$
$$= \sum_{j_{34}j_{234}j}([A^{(j_1)}\times[A^{(j_2)}\times[A^{(j_3)}\times A^{(j_4)}]^{(j_{34})}]^{(j_{234})}]^{(j)}\times$$
$$\times[S^{(j_1)}\times[S^{(j_2)}\times[S^{(j_3)}\times S^{(j_4)}]^{(j_{34})}]^{(j_{234})}]^{(j)}). \tag{4}$$

The recoupling can be carried out as well in any other alternate coupling scheme, as *e.g.* $(j_{12}j_{123})$ instead of $(j_{34}j_{234})$.

In this paper, we adopt the basic definitions of tensor algebra in accordance with Ref. [12].

From Eq. (4) any desired product can be obtained by a stepwise procedure. The tensors involved in this procedure are defined in Appendix A.

We find the following recoupling expressions:

— double product:

$$(A^{(1)}\cdot S^{(1)})(B^{(1)}\cdot S^{(1)}) \equiv \tfrac{1}{3}(\vec{A}\cdot\vec{B})S(S+1)+$$
$$+\frac{i}{2}(\vec{A}\times\vec{B})\cdot\hat{S}+\beta T^{(2)}_{AB}\cdot\tilde{O}^{(2)}, \tag{5}$$

— triple product:

$$(A^{(1)}\cdot S^{(1)})(B^{(1)}\cdot S^{(1)})(C^{(1)}\cdot S^{(1)}) \equiv$$
$$\equiv \varepsilon_0\vec{A}\cdot(\vec{B}\times\vec{C})+\vec{R}_{ABC}\cdot\tilde{O}^{(1)}+\varepsilon_3 X^{(2)}_{ABC}\cdot\tilde{O}^{(2)}+\alpha_3 X^{(3)}_{ABC}\cdot\tilde{O}^{(3)}, \tag{6}$$

where

$$\vec{R}_{ABC} = \varepsilon_1((\vec{A}\cdot\vec{B})\,\vec{C}+\vec{A}(\vec{B}\cdot\vec{C}))+\varepsilon_2(\vec{A}\cdot\vec{C})\,\vec{B}$$

$$\varepsilon_1 = \tfrac{1}{5}\,S(S+1)+\tfrac{1}{10}; \qquad \varepsilon_0 = \frac{i}{6}\,S(S+1)$$

$$\varepsilon_2 = \tfrac{1}{5}\,S(S+1)-\tfrac{2}{5}; \qquad \varepsilon_3 = -i\left(1+\frac{1}{\sqrt{3}}\right) \tag{7}$$

— quadruple product:

$$(A^{(1)}\cdot S^{(1)})\,(B^{(1)}\cdot S^{(1)})\,(C^{(1)}\cdot S^{(1)})\,(D^{(1)}\cdot S^{(1)}) \equiv$$

$$\equiv -2i\varepsilon_0\vec{A}_0\vec{R}_{BCD}+\left\{\varepsilon_0\vec{A}(\vec{B}\cdot(\vec{C}\times\vec{D}))+\frac{i}{2}\,(\vec{A}\times\vec{R}_{BCD})+\varepsilon_3\alpha_1 Z^{(1)}_{ABCD}\right\}\cdot\tilde{O}^{(1)}+$$

$$\{\beta T^{(2)}_{AB}+\varepsilon_3\alpha_2 Z^{(2)}_{ABCD}+\alpha_\alpha\gamma_2 V^{(2)}_{A,\,BCD}\}\cdot\tilde{O}^{(2)}+$$

$$\{\varepsilon_3\alpha'_3 Z^{(3)}_{ABCD}+\alpha_3\gamma_3 V^{(3)}_{A,\,BCD}\}\cdot\tilde{O}^{(3)}+\alpha_3\gamma_4 V^{(4)}_{A,\,BCD}\cdot\tilde{O}^{(4)}. \tag{8}$$

It is easily verified that Eq. (5) yields the same vectorial identity as the one used in [4] when applied to its left hand term:

$$(\vec{A}\cdot\vec{S})\,(\vec{B}\cdot\vec{S})-(\vec{B}\cdot\vec{S})\,(\vec{A}\cdot\vec{S}) \equiv i(\vec{A}\times\vec{B})\cdot\vec{S}. \tag{9}$$

However, in perturbation theory calculations there also occur problems concerning a single $(\vec{A}\cdot\vec{S})\,(\vec{B}\cdot\vec{S})$.

Eqs (6) and (8) lie beyond the scope of vector algebra, and provide a method for extending perturbation theory and for dealing with related problems.

4. *Second order spin Hamiltonian*

For details of the perturbation theory formalism, we refer to [4]. An effective Hamiltonian up to second order in $\hat{V}$ is given by

$$\tilde{\mathscr{H}}^{(2)} = P_0VP_0-P_0VKVP_0. \tag{10}$$

The operators P_0 and K are defined as:

$$P_0 = \sum_a |a]\,[a|\,, \qquad K = \sum_\alpha \frac{|\alpha]\,[\alpha|}{\Delta_\alpha}\,, \tag{11}$$

where the states $|a]$ belong to the space Ω_0 and the $|\alpha]$'s to the space Ω' being the difference of Ω and Ω_0, whereas $\Delta_\alpha = \varepsilon_\alpha-\varepsilon_0$.

Considering the model outlined in Section 2, we have the set $\{|a]\}$ being the product $|v_1\Gamma_1]\otimes\{|S],\ldots,|-S]\}$, and the set $\{|\alpha]\}$ being $\{|v\Gamma_{\alpha j}]\}\otimes\{|S],\ldots,|-S]\}$, with $v\neq v_1$.

Inserting (3) into (10) and resorting to Eq. (5), we find:

$$\tilde{\mathscr{H}}^{(2)} = B^{(2)} \cdot \tilde{O}^{(2)} + \mu_B \vec{H} \cdot g \cdot \vec{S} + \{H^2\}, \tag{12}$$

where the constant terms are omitted, and

$$B^{(2)} = -\beta\lambda^2 \sum_{\alpha} \frac{1}{\Delta_\alpha} T_\alpha^{(2)} \tag{13}$$

$$g = 2 - \lambda \sum_{\alpha} \frac{1}{\Delta_\alpha} (\vec{L}_{0\alpha}\vec{L}_{\alpha 0} + \vec{L}_{\alpha 0}\vec{L}_{0\alpha}) \tag{14}$$

$$\{H^2\} = -\mu_B^2 \sum_{\alpha} \frac{1}{\Delta_\alpha} \{\tfrac{1}{3}(\vec{L}_{0\alpha} \cdot \vec{L}_{\alpha 0})\vec{H}^2 + T_\alpha^{(2)} \cdot H^{(2)}\}. \tag{15}$$

The second order tensors have the following meaning:

$$T_\alpha^{(2)} = [L_{0\alpha}^{(1)} \times L_{\alpha 0}^{(1)}]^{(2)}; \qquad H^{(2)} = [H^{(1)} \times H^{(1)}]^{(2)}. \tag{16}$$

Above, summation extends over all excited states $|v\Gamma_{\alpha j}]$ belonging to Ω', *i.e.* over the appropriate v, α, j.

The symbols $\vec{L}_{ij}$ will denote throughout this paper vectors which are matrix elements of the operator $\hat{\vec{L}}$,

$$[i|\hat{\vec{L}}|j] = \sum_q [i|\hat{L}_q^{(1)}|j]\vec{e}_q^{[1]} \equiv \vec{L}_{ij} = L_{ij}^{(1)}. \tag{17}$$

If the $|i]$ and $|j]$ are taken to be $|v\Gamma_{\alpha j}]$'s and the latter are chosen to be real then, since $\hat{\vec{L}}$ is an imaginary operator, we have [4]:

$$\vec{L}_{ij} = -\vec{L}_{ji} \quad \text{and} \quad \vec{L}_{ii} = 0. \tag{18}$$

But if the $|v\Gamma_{\alpha j}]$ are chosen as complex, then the first relation in Eq. (18) is no longer valid. Thus, in the derivation of spin Hamiltonian, we have not used it. For a proof, we consider a simpler example. Let us take the eigenstates of an operator $\hat{\vec{L}}$ to be $|m] = |i]$ and $|m'] = |j]$ in a complex basis. We have

$$[m|\hat{\vec{L}}|m'] = \sum_q [m|\hat{L}_q^{(1)}|m']\vec{e}_q^{[1]} = \sum_q A_q^{(1)}\vec{e}_q^{[1]} \tag{19}$$

$$[m'|\hat{\vec{L}}|m] = \sum_q [m'|\hat{L}_q^{(1)}|m]\vec{e}_q^{[1]} = \sum_q B_q^{(1)}\vec{e}_q^{[1]}. \tag{20}$$

From hermicity of $\hat{\vec{L}}$, one finds:

$$B_{-q}^{(1)} = (-1)^{1-q}(A_q^{(1)})^* \quad \text{or} \quad B_q^{(1)} = (-1)^{1+q}(A_{-q}^{(1)})^*. \tag{21}$$

Neither of the relations (21) reduces simply to the first relation of (18).

5. *Third order contribution*

The third order contribution to an effective Hamiltonian is given by

$$\tilde{\mathscr{H}}^{(3)} = P_0VKVKVP_0 - \tfrac{1}{2}\{P_0VK^2VP_0VP_0 + P_0VP_0VK^2VP_0\}. \tag{22}$$

On inserting (3) into (22), one obtains terms of order λ^3, $\lambda^2\mu_B$, $\lambda\mu_B^2$, and μ_B^3. The last two terms will be omitted from our calculations, whereas we discuss the former two separately as $\tilde{\mathscr{H}}'_3$ and $\tilde{\mathscr{H}}''_3 + \tilde{\mathscr{H}}'''_3$.

The term of order λ^3 is:

$$\tilde{\mathscr{H}}'_3 = \lambda^3 \sum_{\alpha_1 \neq \beta} \frac{1}{\Delta_\alpha \Delta_\beta} (\vec{L}_{0\alpha} \cdot \hat{\vec{S}})(\vec{L}_{\alpha\beta} \cdot \hat{\vec{S}})(\vec{L}_{\beta 0} \cdot \hat{\vec{S}}). \tag{23}$$

Making use of Eq. (6), we can transform (23) into a sum of four terms like: a constants, $\tilde{O}^{(1)}$, $\tilde{O}^{(2)}$ and $\tilde{O}^{(3)}$. For reasons of symmetry $\tilde{O}^{(1)}$ and $\tilde{O}^{(3)}$ vanish (see Section 7). The only relevant term can be the one related with $\tilde{O}^{(2)}$; it constitutes the third order contribution to $B^{(2)}$.

Thus, we find:

$$\tilde{\mathscr{H}}'_3 = b^{(2)} \cdot \tilde{O}^{(2)} \tag{24}$$

and

$$b^{(2)} = \lambda^3 \varepsilon_3 \sum_{\alpha \neq \beta} \frac{1}{\Delta_\alpha \Delta_\beta} X^{(2)}_{A,BC}$$

where A, B, C, stand for $\vec{L}_{0\alpha}$, $\vec{L}_{\alpha\beta}$, $\vec{L}_{\beta 0}$, respectively.

The terms of order $\lambda^2\mu_B$ are of slightly more complicated form. There are two different types of single component terms, like:

$$(H \cdot A)(B \cdot S)(C \cdot S) \tag{25}$$

and

$$(H \cdot S)(A \cdot S)(B \cdot S). \tag{26}$$

Making use of Eq. (5) for terms like (25) and of Eq. (6) for ones like (26) when restricting ourselves to terms related with $\tilde{O}^{(1)}$, we find:

$$\tilde{\mathscr{H}}''_3 = \mu_B \vec{H} \cdot (g_3^a + g_3^b) \cdot \hat{\vec{S}}, \tag{27}$$

where

$$g_3^a = \frac{i}{2}\lambda^2 \sum_{\alpha_1 \neq \beta} \frac{1}{\Delta_\alpha \Delta_\beta} \{\vec{L}_{\beta 0}(\vec{L}_{0\alpha} \times \vec{L}_{\alpha\beta}) + \vec{L}_{\alpha\beta}(\vec{L}_{0\alpha} \times \vec{L}_{\beta 0}) + \vec{L}_{0\alpha}(\vec{L}_{\alpha\beta} \times \vec{L}_{\beta 0})\} \tag{28}$$

$$g_3^b = \frac{i}{2}\lambda^2 \sum_{\alpha} \frac{1}{\Delta_\alpha^2} \{(\vec{L}_{0\alpha}\vec{L}_{\alpha 0} + \vec{L}_{\alpha 0}\vec{L}_{0\alpha}) - 2(\vec{L}_{0\alpha} \cdot \vec{L}_{\alpha 0})\mathscr{I}\}. \tag{29}$$

By applying the identity (A18), we obtain g_3^a in a more compact form:

$$g_3^a = \frac{i}{2}\lambda^2 \sum_{\alpha\neq\beta} \frac{1}{\Delta_\alpha\Delta_\beta}\{2\vec{L}_{\alpha\beta}(\vec{L}_{0\alpha}\times\vec{L}_{\beta 0}) - \vec{L}_{\alpha\beta}\cdot(\vec{L}_{0\alpha}\times\vec{L}_{\beta 0})\mathscr{I}\}. \tag{30}$$

$\mathscr{I}$ in (29) and (30) is the unit dyadic; when defined in spherical coordinates, it is:

$$\mathscr{I} = \sum_q (-1)^{1-q} e_q^{[1]} e_{-q}^{[1]}. \tag{31}$$

The tensors g_3^a and g_3^b constitute the third order contribution to the usual g-tensor.

On the other hand, taking in the above procedure the part related with $\tilde{O}^{(3)}$ in (26), one can directly obtains other terms like $(\vec{H}\tilde{O}^{(3)})$, for example:

$$\tilde{\mathscr{H}}_3''' \propto X_{H,AB}^{(3)} \cdot \tilde{O}^{(3)}. \tag{32}$$

These terms (32) give rise to a higher-order Zeeman term of spin Hamiltonian. However, the transformation of (32) to the form derived strictly by symmetry arguments [1], [13] is less straightforward.

6. *Fourth order spin Hamiltonian*

The fourth order contribution to an effective Hamiltonian is given by:

$$\begin{aligned}\tilde{\mathscr{H}}_4 = & -P_0VKVKVKVP_0 + \tfrac{1}{2}\{P_0VKVK^2VP_0VP_0 + \\ & + P_0VK^2VP_0VKVP_0 + P_0VK^2VKVP_0VP_0 - \\ & - P_0VK^3VP_0VP_0VP_0 + \text{h.a.}\},\end{aligned} \tag{33}$$

where h.a. stands for the Hermitian adjoint of the preceding terms.

By inserting (3) into (33), one obtains terms of order λ^4, $\lambda^3\mu_B$, $\lambda^2\mu_B^2$, $\lambda\mu_B^3$, and μ_B^4. The last three terms will be omitted from our calculations, whereas the former two will be discussed separately as $\tilde{\mathscr{H}}_4'$ and $\tilde{\mathscr{H}}_4'' + \tilde{\mathscr{H}}_4'''$.

From Eq. (8), one notes that $\tilde{\mathscr{H}}_4'$ can be further decomposed into two relevant parts, namely a fourth order contribution to the parameters $B^{(2)}$, and a fourth order term $B^{(4)} \cdot \tilde{O}^{(4)}$. We assume a negligible role of the former part of $\tilde{\mathscr{H}}_4'$ and consider only the latter part. This assumption has been confirmed by numerical calculations of the magnitude of the parameters in question for some concrete situations [3], [14].

The fourth order spin Hamiltonian is finally found to be:

$$\tilde{\mathscr{H}}^{(4)} = B^{(4)} \cdot \tilde{O}^{(4)}, \tag{34}$$

where the parameter $B^{(4)}$ is of the following general form:

$$\begin{aligned}B^{(4)} = \alpha_3\gamma_4\lambda^4 \Bigg\{ & \sum_{\alpha} \frac{1}{\Delta_\alpha^3} V_a^{(4)} - \sum_{\alpha\neq\beta} \frac{1}{\Delta_\alpha^2\Delta_\beta} V_b^{(4)} + \\ & + \tfrac{1}{2}\sum_{\alpha\neq\beta}\left(\frac{1}{\Delta_\alpha^2\Delta_\beta} + \frac{1}{\Delta_\alpha\Delta_\beta^2}\right) V_c^{(4)} - \sum_{\alpha\neq\beta\neq\gamma} \frac{1}{\Delta_\alpha\Delta_\beta\Delta_\gamma} V_d^{(4)} \Bigg\}.\end{aligned} \tag{35}$$

The fourth rank tensors are the $V^{(4)}_{A,BCD}$'s defined in Appendix A, where $A, B, C, D,$ stand for $\vec{L}_{ij}$'s, respectively, as follows:

$$V^{(4)}_a : \vec{L}_{0\alpha}, \vec{L}_{\alpha 0}, \vec{L}_{0\alpha}, \vec{L}_{\alpha 0}$$
$$V^{(4)}_b : \vec{L}_{0\alpha}, \vec{L}_{\alpha\beta}, \vec{L}_{\beta\alpha}, L_{\alpha 0}$$
$$V^{(4)}_c : \vec{L}_{0\alpha}, \vec{L}_{\alpha 0}, \vec{L}_{0\beta}, \vec{L}_{\beta 0}$$
$$V^{(4)}_d : \vec{L}_{0\alpha}, \vec{L}_{\alpha\beta}, \vec{L}_{\beta\gamma}, \vec{L}_{\gamma 0}. \tag{36}$$

As to the terms of order $\lambda^3\mu_B$, we have to deal with two different types of single component terms, like:

$$(H \cdot A)(B \cdot S)(C \cdot S)(D \cdot S) \tag{37}$$

and

$$(H \cdot S)(A \cdot S)(B \cdot S)(C \cdot S). \tag{38}$$

Both (37) and (38) give rise to a fourth order contribution to the usual g-tensor. We assume its role as negligible in experimental situations [14].

However, the terms like (38) give rise to another relevant part of $\tilde{\mathscr{H}}'''_4$. The part related with $\tilde{O}^{(3)}$ constitutes a higher-order Zeeman like term:

$$\tilde{\mathscr{H}}'''_4 \propto \{\alpha_3\varepsilon_3 Z^{(3)}_{ABCD} + \alpha_3\gamma_3 V^{(3)}_{ABCD}\} \cdot \tilde{O}^{(3)} \tag{39}$$

where one of the vectors $\{A, B, C, D,\}$ is the $\vec{H}$-vector.

For Fe^{3+} ion in cubic symmetry, the higher-order Zeeman terms arising from the fourth order of perturbation theory have been shown to be experimentally negligible [15].

7. *Symmetry*

The part $\hat{\mathscr{H}}' = \hat{\mathscr{H}}_0 + \lambda\hat{\vec{L}} \cdot \hat{\vec{S}}$ in Eq. (3) has symmetry given by a point group G_0. Inclusion of the Zeeman term further reduces the point symmetry, as the magnetic field H is of symmetry $C_{\infty v}$. Then the purely spin part of an effective Hamiltonian $\tilde{\mathscr{H}}'$ has to be invariant under operation of all elements of the group G_0.

Any perturbation theory-derived Hamiltonian has to possess the same general invariance properties as the corresponding one constructed strictly on symmetry arguments. This invariance is implicitly ensured in the constituents of the Hamiltonian's tensors. The results given in Sections 4, 5 and 6 contain only the relevant parts of the appropriate expressions.

At first sight, one might be inclined to conclude that every component of $B^{(2)}$ and $B^{(4)}$ is allowed. However, if the symmetry axis is taken to be the axis of quantization for the states $|v\Gamma_{\alpha j}]$, only some of the components can be nonzero in order to maintain the whole Hamiltonian invariant.

Below, we write the symmetry-allowed components of spin Hamiltonian tensors, for certain symmetries. The axes of quantization are chosen as in [9], [13] *i.e.* for the cases (a) and (b) — the axis of rotation $\hat{C}_4$, for (c) — the trigonal axis, and for (d) — the $\hat{C}_2$ axis.

a) cubic symmetry:

$$B^{(4)}_{\pm 4} = \sqrt{\tfrac{5}{14}}\, B^{(4)}_0 \text{ and } g \tag{40}$$

b) tetragonal symmetry:

$$B^{(2)}_0;\ B^{(4)}_0,\ B^{(4)}_{\pm 4} \text{ and } g_{\|},\ g_{\perp} \tag{41}$$

c) trigonal symmetry:

$$B^{(2)}_0;\ B^{(4)}_0,\ B^{(4)}_{\pm 3} \text{ and } g_{\|},\ g_{\perp} \tag{42}$$

d) rhombic symmetry:

$$B^{(2)}_0,\ B^{(2)}_{\pm 2};\ B^{(4)}_0,\ B^{(4)}_{\pm 2},\ B^{(4)}_{\pm 4} \text{ and } g_1,\ g_2,\ g_3. \tag{43}$$

From Wigner-Eckart theorem, we have [5] that the $B^{(2)}_q$ are relevant for spin $S \geqslant 1$, $B^{(4)}_q$ for $S \geqslant 2$, and the ordinary Zeeman terms for $S \geqslant 1/2$. Explicite formulas for the relevant components listed above are given in Appendix B.

The above derived expressions together with the results of Appendix B form a compact set of equations from which one ran directly "read out" any desired contribution to spin Hamiltonian for any symmetry.

It is worthwhile to determine the relations between our $B^{(2)}_q$, $B^{(4)}_q$ and the conventional parameters D, E, a, F. We refer to the formulation of [16] and [17].

A k-th order part of spin Hamiltonian, by the definition of a scalar product, is explicitly:

$$B^{(k)} \cdot \tilde{O}^{(k)} = \sum_q (-1)^{k-q} B^{(k)}_q \tilde{O}^{(k)}_{-q}. \tag{44}$$

On comparing the corresponding expressions (ours from Eq. (44) and that of [16], [17]), we find correspondingly for the symmetries (a) to (d). Below, a brief notation is used

$$B^{(k)}_{|q|} \equiv B^{(k)}_{+q} = B^{(k)}_{-q}$$

a)
$$\frac{a}{6} = \tfrac{5}{2} B^{(4)}_0. \tag{45}$$

b) On making use of the relation (4–128) in [8], we find:

$$\frac{a}{6} = \tfrac{1}{2}\sqrt{70}\, B^{(4)}_4 \tag{46}$$

$$\frac{F}{180} = \tfrac{1}{8}\left(B^{(4)}_0 - \tfrac{1}{5}\sqrt{70}\, B^{(4)}_4\right). \tag{47}$$

c) To avoid an introducing two different coordination systems, *i.e.* a cubic one $\{\xi, \eta, \zeta\}$ and a trigonal one $\{x, y. z\}$ as *e.g.* in [17], we simply leave the parameters $B^{(4)}_0$, $B^{(4)}_{\pm 3}$. In other words, we work in a coordinate system where the z-axis is the trigonal axis, as defined for Eq. (42).

d) In the cases (a)–(d), we have:

$$D = -\tfrac{3}{2} B_0^{(2)}. \tag{48}$$

The rhombic second order term:

$$E = -\sqrt{\tfrac{3}{2}}\, B_2^{(2)}. \tag{49}$$

For the $B_0^{(4)}$, $B_4^{(4)}$, Eqs (46) and (47) hold, whereas $B_{\pm 2}^{(4)}$ constitutes a fourth order rhombic term not used in conventional spin Hamiltonians.

8. *Conclusions*

We have proposed, in this paper, the direct adoption of tensor algebra in perturbation theory. The method rests on recoupling of invariant products arising in the earliest steps of perturbation theory calculations.

A word should be said about the approach of Grant and Strandberg [2] to spin Hamiltonian. These authors constructed spin Hamiltonian by tensor decomposition as a sum of symmetry-allowed invariant terms of variables $\hat{\vec{S}}$ and $\vec{H}$. Thus, the main idea of [2] is identical with that of Koster and Statz [1]who achieved the same goal by formal group theory. These results of [1] and [2] are equivalent [18]. However, neither of the "constructional" approaches can provide any information about the strenghth of the parameters involved, in contradistinction to the perturbation approach.

The adopting of tensor algebra in the manner proposed above permits the obtainment of compact expressions for tensor of spin Hamiltonian applicable to any particular symmetry. The relevant expressions are derived up to the fourth order of perturbation theory. The final form of spin Hamiltonian is expressed directly in the convenient operators $\tilde{O}^{(k)}$.

The utility of the general spin Hamiltonian expressions will be proven in a forthcoming publication [14].

The general method proposed by us permits moreover the deriving of perturbation theory relations for the parameters of higher order Zeeman terms, as outlined above.

The author wishes to express his deep indebtedness to Docent Dr L. Kowalewski for profitable discussions and for critically reading the manuscript, and to Dr T. Lulek for helpful comments. The author is also strongly indebted to Professor A. P. Jucys for his helpful letters on tensor methods.

APPENDIX A

1. Let us define some neccessary tensors, used in the stepwise procedure (see text). From Eq. (4) we find,

$$(A^{(1)} \cdot \hat{S}^{(1)})(B^{(1)} \cdot \hat{S}^{(1)}) = \sum_{l=0}^{2} (T^{(l)} \cdot \hat{U}^{(l)}) \tag{A1}$$

$$(A^{(1)} \cdot \hat{S}^{(1)})(T^{(2)} \cdot \hat{U}^{(2)}) = \sum_{l=1}^{3} (X^{(l)} \cdot \hat{Y}^{(l)}) \tag{A2}$$

$$(A^{(1)} \cdot \hat{S}^{(1)})(X^{(3)} \cdot \hat{Y}^{(3)}) = \sum_{l=2}^{4} (V^{(l)} \cdot \hat{Q}^{(l)}) \tag{A3}$$

where the tensors on the right are defined as:

$$T^{(l)} = [A^{(1)} \times B^{(1)}]^{(l)}; \quad \hat{U}^{(l)} = [\hat{S}^{(1)} \times \hat{S}^{(1)}]^{(l)} \tag{A4}$$

$$X^{(l)} = [A^{(1)} \times T^{(2)}]^{(l)}; \quad \hat{Y}^{(l)} = [S^{(1)} \times U^{(2)}]^{(l)} \tag{A5}$$

$$V^{(l)} = [A^{(1)} \times X^{(3)}]^{(l)}; \quad \hat{Q}^{(l)} = [\hat{S}^{(1)} \times \hat{Y}^{(3)}]^{(l)}. \tag{A6}$$

We also define a tensor $Z^{(l)}$ as:

$$Z^{(l)} = [A^{(1)} \times X^{(2)}]^{(l)}. \tag{A7}$$

2. The operators $\hat{U}^{(l)}$, $\hat{Y}^{(l)}$, $\hat{Q}^{(l)}$ are at the same time spherical tensor operators of the variables $(\hat{S}_0, \hat{S}_{\pm 1})$ [12]. Writing down explicitly their components [19] and making use of commutation relations [12], we can transform them to other angular momentum tensor operators, found in the literature. We have chosen, among all the others, those tabulated in [6], *i.e.* $O_q^{(k)}(j_z, j_\pm)$ because Tables of their matrix elements are available, as well (*e.g.* [7]).

Now, the $O_q^{(k)}$'s transform under conjugation operation as follows:

$$(O_q^{(k)})^* = (-1)^q O_{-q}^{(k)}. \tag{A8}$$

In order to maintain the same phase factor as in [12] and [9], we introduce new operators, defined as:

$$\tilde{O}_q^{(k)} = i^k O_q^{(k)}. \tag{A9}$$

The $\tilde{O}_q^{(k)}$'s have the desired property:

$$(\tilde{O}_q^{(k)})^* = (-1)^{k-q} \tilde{O}_{-q}^{(k)}. \tag{A10}$$

We have established the following relations and numerical coefficients:

$$\tilde{S}^{(1)} = \tilde{O}^{(1)} \tag{A11}$$

$$\hat{U}^{(0)} = \frac{1}{\sqrt{3}} (\hat{\vec{S}} \cdot \hat{\vec{S}}) = \frac{1}{\sqrt{3}} S(S+1) \tag{A12}$$

$$\hat{U}^{(1)} = -\frac{1}{\sqrt{2}} (\hat{\vec{S}} \times \hat{\vec{S}}) = -\frac{1}{\sqrt{2}} i\hat{\vec{S}} \tag{A13}$$

$$\hat{U}^{(2)} = \sqrt{\tfrac{2}{3}}\, \tilde{O}^{(2)} = \beta \tilde{O}^{(2)} \tag{A14}$$

$$\hat{Y}^{(l)} = \alpha_l \tilde{O}^{(l)} \tag{A15}$$

$$\hat{Q}^{(l)} = \gamma_l \tilde{O}^{(l)} \tag{A16}$$

and

$$\alpha_1 = \tfrac{1}{2}\sqrt{\tfrac{3}{5}}\{\tfrac{4}{3}S(S+1)-1\}; \quad \gamma_2 = \sqrt{\tfrac{3}{70}}\{2S(S+1)+1\}$$

$$\alpha_2 = -i; \quad \gamma_3 = -i\sqrt{\tfrac{6}{5}}$$

$$\alpha_3 = \sqrt{\tfrac{2}{5}}; \quad \gamma_4 = 2\sqrt{\tfrac{2}{35}}. \tag{A17}$$

3. The following vectorial identity holds

$$\vec{A}(\vec{B}\times\vec{C}) + \vec{C}(\vec{A}\times\vec{B}) \equiv \vec{B}(\vec{A}\times\vec{C}) - \vec{B}\cdot(\vec{A}\times\vec{C})\mathscr{I}.$$

APPENDIX B

1. The relevant components of a second rank tensor $T^{(2)}_{AB}$ are

$$T^{(2)}_0 = \frac{1}{\sqrt{6}}\{2A^{(1)}_0 B^{(1)}_0 + A^{(1)}_{-1}B^{(1)}_1 + A^{(1)}_1 B^{(1)}_{-1}\} \tag{B1}$$

$$T^{(2)}_{\pm 2} = A^{(1)}_{\pm 1}B^{(1)}_{\pm 1}. \tag{B2}$$

For brevity we define the following symbol

$$t^{(2)}_{AB} \equiv \sqrt{6}\, T^{(2)}_0. \tag{B3}$$

Henceforth we shall be omitting the index of rank in standard basis components [12] of the vectors.

2. Relevant components of a fourth rank tensor $V^{(4)}_{A,BCD}$ are

$$V^{(4)}_0 = \frac{1}{\sqrt{70}}\{(t^{(2)}_{AB})(t^{(2)}_{CD}) + (t^{(2)}_{AD})(t^{(2)}_{BC}) + (t^{(2)}_{AC})(t^{(2)}_{BD}) -$$

$$-(A_1B_{-1}+A_{-1}B_1)C_1D_{-1} - (A_1C_{-1}+A_{-1}C_1)B_{-1}D_1 -$$

$$-(A_1D_{-1}+A_{-1}D_1)B_1C_{-1} - 8A_0B_0C_0D_0\} \tag{B4}$$

$$V^{(4)}_{\pm 2} = \frac{1}{\sqrt{28}}\{A_{\pm 1}B_{\pm 1}(t^{(2)}_{CD}) + (t^{(2)}_{AB})C_{\pm 1}D_{\pm 1} +$$

$$+2(A_{\pm 1}+A_0)(B_0C_0D_{\pm 1} + B_0C_{\pm 1}D_0)\} \tag{B5}$$

$$V^{(4)}_{\pm 3} = \tfrac{1}{2}\{A_0B_{\pm 1}C_{\pm 1}D_{\pm 1} + A_{\pm 1}B_0C_{\pm 1}D_{\pm 1} + A_{\pm 1}B_{\pm 1}C_0D_{\pm 1} +$$

$$+A_{\pm 1}B_{\pm 1}C_{\pm 1}D_0\} \tag{B6}$$

$$V^{(4)}_{\pm 4} = A_{\pm 1}B_{\pm 1}C_{\pm 1}D_{\pm 1} \tag{B7}$$

3. Relevant components of a second rank tensor $X^{(2)}_{A,BC}$ are

$$X^{(2)} = -\tfrac{1}{2}\{(A_{-1}B_1 - A_1B_{-1})C_0 + B_0(A_{-1}C_1 - A_1C_{-1})\} \tag{B8}$$

$$X^{(2)}_{\pm 2} = \mp \frac{1}{\sqrt{6}}\{(A_0B_{\pm 1} - A_{\pm 1}B_0)C_{\pm 1} + B_{\pm 1}(A_0C_{\pm 1} - A_{\pm 1}C_0)\}. \tag{B9}$$

The above expressions were obtained by a stepwise procedure using the Tables for decomposition of products $D^{(l)} \otimes D^{(k)}$ found in [19].

REFERENCES

[1] G. F. Koster, M. Statz, *Phys. Rev.*, **113**, 445 (1959).
[2] W. J. C. Grant, M. P. W. Strandberg, *J. Phys. Chem. Solids*, **25**, 635 (1964).
[3] H. H. Tippins, *Phys. Rev.*, **160**, 343 (1967).
[4] C. E. Soliverez, *J. Phys.* C, **2**, 2161 (1969).
[5] W. Hauser, in *Paramagnetic Resonance*, Ed. by W. Low, vol. I, Academic Press 1963.
[6] D. Smith, J. H. M. Thornley, *Proc. Phys. Soc.*, **89**, 779 (1966).
[7] R. J. Birgeneau, *Canad. J. Phys.*, **45**, 3761 (1967).
[8] C. J. Ballhausen, *Introduction to Ligand Field Theory*, McCraw-Hill Comp., New York 1962.
[9] A. M. Leushin, *Tables of Functions Transforming According to the Irreducible Representations of the Crystallographical Point Groups*, Nauka, Moskva 1968, in Russian.
[10] A. S. Woodward, R. Chatterjee, *J. Phys.* C, **4**, 1378 (1971).
[11] U. Fano, G. Racach, *Irreducible Tensorial Sets*, Academic Press, New York 1959 (second edition 1967).
[12] A. P. Jucys, A. A. Bandzaitis, *Theory of Angular Momentum in Quantum Mechanics*, Leidykla Mintis, Vilnius 1965, in Russian.
[13] A. M. Leushin, in *Paramagnetic Resonance* (sbornik statey), Kazan 1964, in Russian.
[14] C. Rudowicz, *Acta Phys. Polon.*, **A43**, 565 (1973).
[15] R. Lacroix, J. Weber, *Helv. Phys. Acta*, **44**, 172 (1971).
[16] B. Bleaney, K. W. H. Stevens, *Rep. Progr. Phys.*, **16**, 108 (1953).
[17] B. Bleaney, R. S. Trenam, *Proc. Roy. Soc.*, **A223**, 1 (1954).
[18] J. S. M. Havrey, H. Kiefte, *J. Phys.* B, **3**, 1326 (1970).
[19] V. Heine, *Group Theory in Quantum Mechanics*, Pergamon Press 1960.