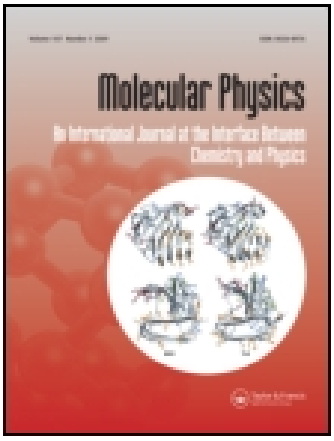

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Some investigations in the theory of open-shell ions

J.S. Griffith [a]

[a] Department of Theoretical Chemistry , University Chemical Laboratory , Lensfield Road, Cambridge

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Some investigations in the theory of open-shell ions

Part I. The spin-Hamiltonian

by J. S. GRIFFITH
Department of Theoretical Chemistry, University Chemical Laboratory, Lensfield Road, Cambridge

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It is shown that second-order perturbation theory leads to the usual quadratic and bilinear terms in the spin-Hamiltonian for a spatially non-degenerate state even when excited states differing in multiplicity from the ground states are included. The form of the spin-Hamiltonian adequate to represent arbitrary splittings of the ground manifold is considered and explicit results given for the fine structure and for those interactions with nucleus and external magnetic field which are linear in **I** and **H** respectively.

1. Introduction

The spin-Hamiltonian is by now a very well-known device, introduced originally in a particular form by Pryce [1]. The idea is to take an n-dimensional manifold of states, usually eigenstates of an approximate Hamiltonian, and regard it as the eigenmanifold for $\mathbf{S}^2$ with $S=\frac{1}{2}(n-1)$ of a spin vector **S**. The states are usually classified by writing a basis of the manifold as $|M\rangle$, where M is the S_z value of **S** and the $|M\rangle$ are correctly connected in phase [2]. Then the matrix elements of parts $\mathscr{H}_j$ of the true Hamiltonian are represented by operator equivalents, polynomial in the components of **S**, which have the same matrix elements as the $\mathscr{H}_j$ within the manifold. The coefficients in the polynomials involve quantities like the components of the external magnetic field **H** or even of the nuclear spin **I**. In the latter case we consider the direct product of the n-dimensional manifold for the electronic functions with a $(2I+1)$-dimensional manifold for the ground level of the nucleus and then **I** may be regarded as just a number within the electronic manifold.

We should be clear at once that in the general formulation of the concept there is no implication about the behaviour of **S** or the $|M\rangle$ under rotations. **S** should be regarded as something like the isotopic spin $\boldsymbol{\tau}$ which does not operate in ordinary space. For this reason it is often called a fictitious spin vector. However, there is a real danger of confusion here because **S** is often very closely related to the real spin vector. Unlike isotopic spin space, in practice fictitious spin space is usually chosen to approximate as closely as possible to real spin space.

There are two main approaches to the theoretical determination of a spin-Hamiltonian. The first uses an 'unperturbed' Hamiltonian which is diagonal within the ground manifold, calculates the actual splittings to a certain order in perturbation theory and finally represents these calculated splittings

by means of operator equivalents [1, 3]. The second is to express a general splitting of the ground manifold as a power series in external quantities such as the components of **H** and **I** and to determine operator equivalents for the coefficients in the power series which are adequate to represent any splitting [3–6]. Naturally the two approaches are complementary and an investigation of any particular problem usually uses both kinds of approach.

Pryce [1] took a spin-independent unperturbed Hamiltonian and calculated the form of spin-Hamiltonian with fictitious spin S for a spatially non-degenerate state with actual spin S by second-order perturbation theory. However, he assumed that the ground and excited manifolds in his calculation were each contained in the ground term of the free ion. Especially he neglected matrix elements to excited states differing in multiplicity from the ground states. It is the main purpose of this paper to rectify that neglect and to show that the general form

$$\mathscr{H}(S) = \sum(\beta g_{ij} H_i S_j + D_{ij} S_i S_j + A_{ij} S_i I_j) \tag{1}$$

that he obtained for the spin-Hamiltonian remains unchanged. The modification of his proof for the first-order terms is, of course, quite trivial. Therefore I merely consider that part of the calculation which is second-order in the spin–orbit coupling $\mathscr{H}_1$ or first-order in both $\mathscr{H}_1$ and either a nuclear moment or the external magnetic field. I use the methods introduced by Racah [7] into the theory of angular momenta because I think they give the required new results in the simplest and most straightforward way. I then show that my results are equivalent to Pryce's when we add his restrictive assumptions, although of course the method of this paper is rather a roundabout one in that particular case.

Finally I discuss the determination of a least general spin-Hamiltonian necessary to represent any splitting independent of **H** or **I** or linear in one of them. The treatment is general and simple and easily extensible to other terms in the power series. For convenience I break up the true Hamiltonian into three parts. $\mathscr{H}_1$ is the spin–orbit coupling energy. $\mathscr{H}_2$ is that part of the nuclear hyperfine interaction which is linear in both **I** and one of the spin vectors for the electrons. $\mathscr{H}_3$ is the sum of the remainder of the hyperfine interaction and the part $\beta\mathbf{H}.\mathbf{L}$ of the interaction with the external magnetic field. The other part $2\beta\mathbf{H}.\mathbf{S}$ causes no difficulty and we do not mention it again. $\mathscr{H}_3$ does not include any spin vector. Other small terms in the Hamiltonian are not discussed. The perturbation procedure adopted means we consider that part of the matrix.

$$-\sum_{j,\,M''} E_j^{-1} \langle MO|\sum \mathscr{H}_i|M''j\rangle\langle M''j|\sum \mathscr{H}_i|M'O\rangle \tag{2}$$

which is quadratic or linear in $\mathscr{H}_1$ (see Pryce [1]). The unperturbed energy E_0 is taken zero, M, M'', M' classify S_z values, O is the ground manifold and j numbers the $(2S'+1$ dimensional) excited manifolds.

2. Properties of the matrix elements

We have to show that our spin-Hamiltonian is real. For this and other reasons it is desirable to specify the corresponding properties for the kets occurring in the calculations. We use the operator introduced by Kramers [8] into the theory of magnetic properties (which is related also to time-reversal [9])

and denote its effect by an asterisk. It applies to kets and linear operators. I use a bar to denote the other type of conjugate. Thus $\bar{\mathbf{l}} = -\mathbf{l}^* = \mathbf{l}$, $\bar{\mathbf{s}} = -\mathbf{s}^* = \mathbf{s}$ for orbital and spin angular momentum vectors, while for any number c we always have $\bar{c} = c^*$. Our unperturbed kets are written $|Mj\rangle$ where $j = 0$ gives the ground states and otherwise Mj give the quantum numbers of excited states. M refers always to S_z and $|Mj\rangle$ for fixed j are correctly connected in phase. Finally, as is always possible, we define

$$|Mj\rangle^* = (-1)^M |-Mj\rangle \tag{3}$$

for all j. This implies also

$$\langle Mj|^* = (-1)^{-M} \langle -Mj|. \tag{4}$$

Clearly $\overline{\mathscr{H}}_1 = \mathscr{H}_1{}^* = \mathscr{H}_1$. However, we choose to suppose that neither spatial rotations nor the Kramers operator affect the kets referring to nuclear properties. So the nuclear moment $\mathbf{I}$ and the kets $|M_I\rangle$ are left unaltered. With this definition we have

$$\overline{\mathscr{H}}_2 = -\mathscr{H}_2{}^* = \mathscr{H}_2.$$

We now determine the dependence of the matrix elements of $\mathscr{H}_1$ and $\mathscr{H}_2$ on the spin quantum numbers. I depend heavily here on results in the general theory of angular momenta and use the notation of the book by Fano and Racah [7] (henceforth referred to as FR). However, I differ slightly in that I adopt Racah's earlier definition [10] of the phases of the components of a vector $\mathbf{a}$ when expressed as a tensor operator, writing

$$a_0 = a_z, \qquad a_{\pm 1} = \frac{1}{\sqrt{2}} (\mp a_x - i a_y). \tag{5}$$

This means that the reduced matrix element for the spin vector $\mathbf{S}$ is

$$\langle \alpha S \| S^{(1)} \| \alpha' S' \rangle = \delta_{\alpha\alpha'} \delta_{SS'} \{S(S+1)(2S+1)\}^{1/2} \tag{6}$$

in place of FR, equation (14.9).

The spin–orbit coupling is

$$\mathscr{H}_1 = \sum_{\kappa\nu} (-1)^\nu u_{\kappa\nu} s_{\kappa-\nu} \tag{7}$$

where κ numbers the electrons and ν the components†. Therefore

$$\begin{aligned} \langle MO|\mathscr{H}_1|M''j\rangle &= \sum_{\kappa\nu n} (-1)^\nu \langle MO|u_{\kappa\nu}|Mn\rangle \langle Mn|s_{\kappa-\nu}|M''j\rangle \\ &= \sum_\nu (-1)^{\nu+S-M} Y_\nu \bar{V} \begin{pmatrix} 1 & S' & S \\ -\nu & M'' & -M \end{pmatrix}, \end{aligned} \tag{8}$$

where the Y_ν are numbers independent of M and M'' (use FR, equation (14.4)). Therefore

$$\overline{\langle MO|\mathscr{H}_1|M''j\rangle} = \sum_\nu (-1)^{\nu+S-M} \bar{Y}_\nu \bar{V} \begin{pmatrix} 1 & S' & S \\ -\nu & M'' & -M \end{pmatrix}$$

but this is just a number and so also equal to

$$\begin{aligned} \langle MO|\mathscr{H}_1|M''j\rangle^* &= (-1)^{M''-M} \langle -MO|\mathscr{H}_1|-M''j\rangle \\ &= \sum_\mu (-1)^{\mu+M''+S} Y_\mu \bar{V} \begin{pmatrix} 1 & S' & S \\ -\mu & -M'' & M \end{pmatrix} \\ &= \sum_\nu (-1)^{\nu+M''+1-S'} Y_{-\nu} \bar{V} \begin{pmatrix} 1 & S' & S \\ -\nu & M'' & -M \end{pmatrix} \end{aligned} \tag{9}$$

† We are not assuming that $\mathbf{u}$ is necessarily $\xi(r)\mathbf{1}$, see Stevens [11].

where we have used (8) and the symmetry properties of $\bar{V}$. It then follows from the orthonormality relations (FR equation (10.17)) for the $\bar{V}$ that

$$\bar{Y}_\nu = (-1)^{1+S'-S+\nu} Y_{-\nu}. \tag{10}$$

In just the same way we write

$$\langle MO|\mathscr{H}_2|M''j\rangle = \sum_\nu (-1)^{\nu+S-M} Y_\nu' \bar{V}\begin{pmatrix} 1 & S' & S \\ -\nu & M'' & -M \end{pmatrix} \tag{11}$$

and find

$$\bar{Y}_\nu' = (-1)^{S'-S+\nu} Y_{-\nu}'. \tag{12}$$

As in FR, equation (7.10), we now define the elements of irreducible product sets by writing

$$(S\times S)_\gamma^{(c)} = \sum_{\mu\nu} \langle 11\mu\nu|11c\gamma\rangle S_\mu S_\nu \tag{13}$$

and from (6) and FR, equation (15.15), have

$$\langle \alpha S||(S\times S)^{(c)}||\alpha S\rangle = (-1)^{c+2S} S(S+1)(2S+1)(2c+1)^{1/2} \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S \end{pmatrix}. \tag{14}$$

In a strictly analogous manner we define $(Y\times Y)_\gamma^{(c)}$, $(Y'\times Y')_\gamma^{(c)}$ and $(Y'\times Y)_\gamma^{(c)}$. It then follows from the properties of the Wigner coefficients that $(Y\times Y)_\gamma^{(1)}$ is identically zero, while $(Y\times Y')_\gamma^{(c)} - (Y'\times Y)_\gamma^{(c)}$ is identically zero for $c=0$ or 2. Finally $(Y'\times Y)_\gamma^{(1)} = -(Y\times Y')_\gamma^{(1)}$.

3. Derivation of the spin-Hamiltonian by perturbation theory

Considering $\mathscr{H}_1$ and $\mathscr{H}_2$, the matrix (2) has the two kinds of second-order parts

$$-\sum_{jM''} E_j^{-1} \langle MO|\mathscr{H}_1|M''j\rangle\langle M''j|\mathscr{H}_1|M'O\rangle \tag{15}$$

which gives the fine structure and

$$-\sum_{jM''} E_j^{-1}\{\langle MO|\mathscr{H}_1|M''j\rangle\langle M''j|\mathscr{H}_2|M'O\rangle + \langle MO|\mathscr{H}_2|M''j\rangle\langle M''j|\mathscr{H}_1|M'O\rangle\} \tag{16}$$

which gives the hyperfine structure. We abbreviate these to $-\sum_j E_j^{-1} X_{MM'}{}^j$ and $-\sum_j E_j^{-1} Z_{MM'}{}^j$ respectively.

Then using (8) and (10) and the symmetry properties of the $\bar{V}$ we find

$$\begin{aligned} X_{MM'}{}^j &= \sum_{M''} \langle MO|\mathscr{H}_1|M''j\rangle\langle M''j|\mathscr{H}_1|M'O\rangle \\ &= \sum_{M''\mu\nu} (-1)^{\nu+S-S'+1} Y_\mu Y_\nu \bar{V}\begin{pmatrix} 1 & S & S' \\ -\mu & -M & M'' \end{pmatrix} \bar{V}\begin{pmatrix} S & 1 & S' \\ M' & -\nu & -M'' \end{pmatrix}, \end{aligned}$$

and then with the help of FR, equation (11.18):

$$\begin{aligned} X_{MM'}{}^j &= \sum_{\mu\nu c\gamma} (-1)^{\gamma+S+1-M'}(2c+1)\bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S' \end{pmatrix} \bar{V}\begin{pmatrix} S & S & c \\ M' & -M & -\gamma \end{pmatrix} \bar{V}\begin{pmatrix} 1 & 1 & c \\ \mu & \nu & -\gamma \end{pmatrix} Y_\mu Y_\nu \\ &= \sum_{c\gamma} (-1)^{c+1+S-M'}(2c+1)^{1/2}\bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S' \end{pmatrix} \bar{V}\begin{pmatrix} S & S & c \\ M' & -M & -\gamma \end{pmatrix} (Y\times Y)_\gamma^{(c)}. \end{aligned} \tag{17}$$

We now show that the $X_{MM'}{}^j$ are the matrix elements in a spin-Hamiltonian of the quantity

$$R = \sum_{c\gamma} (-1)^\gamma T_\gamma^{(c)} (S\times S)_{-\gamma}^{(c)} \tag{18}$$

for suitable $T_\gamma^{(c)}$. Clearly, using (14):

$$\langle MO|R|M'O\rangle = \sum_{c\gamma} (-1)^{\gamma+S-M} T_\gamma^{(c)} S(S+1)(2S+1)(2c+1)^{1/2} \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S \end{pmatrix} \bar{V}\begin{pmatrix} S & S & c \\ M' & -M & -\gamma \end{pmatrix}, \quad (19)$$

which is identical with (17) providing we put

$$T_\gamma^{(c)} = (-1)^{c+1}\alpha\{S(S+1)(2S+1)\}^{-1}(Y\times Y)_\gamma^{(c)}$$

where

$$\alpha = \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S' \end{pmatrix} \Big/ \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S \end{pmatrix}$$

is easily deduced from the known expressions for $\bar{W}$ for the relevant values of S' and c [12]. It is given in the table. $T_\gamma^{(c)} = 0$ for $c = 1$ so R gives the usual symmetrical quadratic expression in the spin-Hamiltonian when we multiply by $-E_j^{-1}$ and sum over j. Further, using (10) and $\bar{S}_i = (-1)^i S_{-i}$, we easily deduce that R is real. This concludes the derivation for the fine structure. I mention here the obvious fact that the term with $c = 0$ only shifts the centre of gravity (downward, use (10)); that with $c = 2$ does not affect it.

		S'		
	α	$S-1$	S	$S+1$
c	0	-1	1	-1
	1	$-(S+1)$	1	S
	2	$(S+1)/(2S-1)$	1	$S/(2S+3)$

The quantity $\alpha = \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S' \end{pmatrix} \Big/ \bar{W}\begin{pmatrix} S & S & c \\ 1 & 1 & S \end{pmatrix}$ as a function of S for the relevant values of S', c.

For the case $S' = S$ we use the identity

$$\sum_{c\gamma} (-1)^\gamma (Y\times Y)_\gamma^{(c)} (S\times S)_{-\gamma}^{(c)} = (\mathbf{Y}\,.\,\mathbf{S})^2$$

to deduce

$$R = -\{S(S+1)(2S+1)\}^{-1}(\mathbf{Y}\,.\,\mathbf{S})^2.$$

If the spin–orbit coupling can be correctly represented as $\lambda \mathbf{L}\,.\,\mathbf{S}$ then (8) gives

$$\mathbf{Y} = (-1)^{2S+1}\lambda\{S(S+1)(2S+1)\}^{1/2}\langle 0|\mathbf{L}|n\rangle \quad (20)$$

so, remembering that for $S' = S$ we have $\bar{\mathbf{Y}} = -\mathbf{Y}$, the fine structure Hamiltonian becomes $-\lambda^2 \sum_{ij} \Lambda_{ij} S_i S_j$ where i and j now refer to the x, y and z components and

$$\Lambda_{ij} = \sum_n E_n^{-1} \langle 0|L_i|n\rangle\langle n|L_j|0\rangle$$

is real and symmetric. Thus we have recovered the expression derived by Pryce [1] under these particular restrictions.

The expression for R in terms of $\mathbf{Y}$ and $\mathbf{S}$ simplifies also for $S' = S \pm 1$. We have

$$S' = S+1: \quad R = \{S(S+1)(2S+1)(2S+3)\}^{-1}[(S+1)\mathbf{Y}^2\mathbf{S}^2 - S(\mathbf{Y}\,.\,\mathbf{S})^2]$$

$$S' = S-1: \quad R = \{S(S+1)(4S^2-1)\}^{-1}[S\mathbf{Y}^2\mathbf{S}^2 - (S+1)(\mathbf{Y}\,.\,\mathbf{S})^2]$$

with the vector **Y** now real. The reader who is familiar with the theory of invariants of the orthogonal group will recognize that the fact that R is in each case linearly dependent on the products $(\mathbf{Y}.\mathbf{S})^2$ and $\mathbf{Y}^2\mathbf{S}^2$ of scalar products is not accidental but is a necessary consequence of one of the central theorems of that subject (see Weyl [13], Theorem $T_m{}^n$, page 53). The expression (21) including the ϵ_{jlm} for the hyperfine energy is to be related also to that theorem, the quantity $\sum u_{jk}S_jI_k$ corresponding to an odd orthogonal invariant because the five constituent vectors are actually all pseudo-vectors.

The calculation for the nuclear magnetic hyperfine interaction is a trivial modification of the preceding one. Remembering the difference of sign between (10) and (12), we have merely to replace $Y_\mu Y_\nu$ in the first line of (17) by $Y_\mu' Y_\nu - Y_\mu Y_\nu'$. We remarked earlier that $(Y' \times Y)_\gamma^{(c)} - (Y \times Y')_\gamma^{(c)}$ is zero unless $c=1$ when it is equal to $2(Y' \times Y)_\gamma^{(c)}$. Hence we now have

$$T_\gamma^{(1)} = 2\alpha\{S(S+1)(2S+1)\}^{-1}(Y' \times Y)_\gamma^{(1)}$$

with α in the table as before. One soon verifies, using (10), (12) and the definition of $(Y' \times Y)^{(1)}$ that R satisfies $R = \bar{R} = -\bar{R}^*$ as it should. Also

$$(S \times S)_\gamma^{(1)} = -\frac{1}{\sqrt{2}} S_\gamma$$

and so R is homogeneous and linear in each of **S** and **I** which completes the derivation. The part of the nuclear hyperfine interaction which commutes with **S** was incorporated in $\mathscr{H}_3$ and will be discussed shortly.

If we calculate only within states arising from a ground 1^n term of the ion and write

$$\mathscr{L}_\gamma^{(2)} = (\mathbf{L} \times \mathbf{L})_\gamma^{(2)}$$

where **L** is the total orbital angular momentum vector, we have

$$\mathscr{H}_2 = -P\kappa \mathbf{S}.\mathbf{I} - 3\sqrt{5}\xi P(I \times \mathscr{L}^{(2)} \times S)^{(0)}$$

according to FR, formula (10.5), and Abragam and Pryce [1]. The latter authors showed the second-order effects of the last term in $\mathscr{H}_2$ to give $3P\lambda\xi\sum_{jk} u_{jk}S_jI_k$ in the spin-Hamiltonian (there is a misprint in their equation (3.4) but not (3.7)) where

$$u_{jk} = -\tfrac{1}{2}i \sum_{lmn} \epsilon_{jlm} E_n^{-1} \langle 0|L_m|n\rangle\langle n|(L_kL_l + L_lL_k)|0\rangle, \tag{21}$$

with the j, k, l, m referring to Cartesian coordinates and $n \neq 0$. ϵ_{jlm} is the usual alternating tensor. We have

$$Y_\nu' = \sqrt{(15)}P\xi\{S(S+1)(2S+1)\}^{1/2}(-1)^{2S+1}(I \times \langle 0|\mathscr{L}^{(2)}|n\rangle)_\nu^{(1)}$$

and a corresponding spin-Hamiltonian

$$\mathscr{H}(S) = \sqrt{(30)}P\xi\lambda \sum_{n\gamma} E_n^{-1}(-1)^\gamma((I \times \langle 0|\mathscr{L}^{(2)}|n\rangle)^{(1)} \times \langle 0|L|n\rangle)_\gamma^{(1)} S_{-\gamma}.$$

This is easily shown to be the same as Abragam and Pryce's expression by using the identity

$$\sum_\gamma (-1)^\gamma (a \times b)_\gamma^{(1)} c_{-\gamma} = \tfrac{1}{2}i\sqrt{2} \sum_{lmj} \epsilon_{jlm} a_l b_m c_j$$

for the three vectors $a^{(1)} = (I \times \langle 0|\mathscr{L}^{(2)}|n\rangle)^{(1)}$, $\mathbf{b} = \langle 0|\mathbf{L}|n\rangle$ and $\mathbf{c} = \mathbf{S}$. In making this comparison, note that their $L_kL_l + L_lL_k$ is not a multiple of the irreducible tensorial quantity $\mathscr{L}^{(2)}$ but has a non-zero trace whose matrix elements between $|0\rangle$ and $|n\rangle$ are always zero with their assumptions.

The part $\mathscr{H}_3$ of the Hamiltonian is easier to deal with because it commutes with **S**. Therefore the only excited states which contribute have the same multiplicity as the ground manifold and hence the matrix elements of $\mathscr{H}_1$ are proportional to those of **S**. Symbolically

$$\langle MO|\mathscr{H}_1|M''j\rangle = \langle MO|\mathbf{Z}.\mathbf{S}|M''j\rangle$$

for some **Z** depending on j but independent of M, M''. The matrix elements of $\mathscr{H}_3$ are diagonal in M and independent of it. Hence we arrive immediately at the appropriate terms in equation (1), the only difference from Pryce's derivation lying in the details of the formulae for the g_{ij} and this contribution to the A_{ij}.

4. The general spin-Hamiltonian

We now consider the following problem. Given a set of $2S+1$ states ψ_i for an n-electron system with $n+2S$ even, such that

$$\psi_i^* = \sum_{j=1}^{2S+1} a_{ij}\psi_j$$

for some matrix A, to construct a spin-Hamiltonian adequate to express completely arbitrary matrices of zero-field splitting, magnetic field energy and hyperfine energy within the set ψ_i. This has been discussed in particular cases by several authors [3–5] and with some generality by Koster and Statz [6]. However, the extreme simplicity of the general problem does not seem to have been fully appreciated. This has been obscured somewhat by the tendency to introduce group-theoretic considerations too early in the discussion. We suppose at first no restrictions of this kind on the real Hamiltonian and therefore the only conditions upon the matrix elements are those implied by the use of the Kramers operator.

It follows from the usual properties of the Kramers operator that we can find linear combinations of the ψ_i, which we write in ket notation, satisfying

$$|M\rangle^* = (-1)^M|-M\rangle,$$

where M runs from $-S$ to S. Our spin-Hamiltonian will have fictitious spin S and these basic states as eigenstates of the fictitious spin vector, which we write **S** because there is no danger of confusion with the real **S**.

Suppose now that we have an operator ρ whose matrix elements within the $|M\rangle$ are given. It follows from the usual decomposition of tensors of rank two under the orthogonal group that the quantity

$$X = \sum_{c\gamma} (-1)^\gamma Q_\gamma^{(c)} S_{-\gamma}^{(c)} \tag{22}$$

is adequate to represent the $(2S+1)^2$ matrix elements of ρ for suitable choices of the numbers $Q_\gamma^{(c)}$ providing the reduced matrix elements of the $S_{-\gamma}^{(c)}$ are all non-zero (generalizing the method of reference [4]). Here c runs through the integers from 0 to $2S$ and the $Q_\gamma^{(c)}$ are uniquely determined by ρ for a given choice of the $S_{-\gamma}^{(c)}$. The $S_{-\gamma}^{(c)}$ are irreducible tensor operators of degree c and the simplest choice for each is to take the irreducible product of degree c of c spin vectors S_i. Then $\overline{S_\gamma^{(c)}} = (-1)^c S_\gamma^{(c)*} = (-1)^\gamma S_{-\gamma}^{(c)}$ and we assume this. It is usual to take $\mathbf{S}^2$ rather than 1 for $S_0^{(0)}$ and then to combine it with the term of degree 2 to give a homogeneous quadratic expression.

Because of the crucial importance of the expansion (22) for our argument it is perhaps desirable to give a straightforward proof of its validity. We do this by observing that (FR, equation (14.4)):

$$\langle M|S_{-\gamma}^{(c)}|M'\rangle = \alpha(c)(-1)^{S-M}\bar{V}\begin{pmatrix} S & S & c \\ -M & M' & -\gamma \end{pmatrix}.$$

Therefore a typical matrix element of X is

$$\langle M|X|M'\rangle = \sum_{c\gamma} \alpha(c)(-1)^{S-M'}Q_{\gamma}^{(c)}\bar{V}\begin{pmatrix} S & S & c \\ -M & M' & -\gamma \end{pmatrix}$$

and therefore the matrix elements of X considered as a set of $(2S+1)^2$ quantities are a non-singular transform of the set of $(2S+1)^2$ quantities $\alpha(c)Q_{\gamma}^{(c)}$. (The minus signs do not affect this.) Provided, therefore, that $\alpha(c)$ is non-zero for each c, either set determines the other uniquely. This establishes (22).

We only need the case in which $\rho = \bar{\rho} = \epsilon\rho^*$ for $\epsilon = \pm 1$. This introduces the restrictions $\overline{Q_{\gamma}^{(c)}} = (-1)^{\gamma}Q_{-\gamma}^{(c)}$ always, and also $Q_{\gamma}^{(c)} = 0$ for $\epsilon = +1$ and c odd or $\epsilon = -1$ and c even as one readily sees. Expressed in a different notation these properties are well known.

Let us consider what this means, first for the fine structure Hamiltonian. The sum (22) now extends over even c from 0 to $2S$. Therefore for $S \leqslant 1\frac{1}{2}$ a symmetrical quadratic form in S_x, S_y and S_z with real coefficients is always adequate. For $S = 2$ or $2\frac{1}{2}$ the addition of a quartic term is sufficient, while for $S = 3$ or $3\frac{1}{2}$ we may need a sextic term. In these particular cases at least these results are known [3, 4, 14].

The interaction with the magnetic field requires the specification of three matrices, one for each component of **H**, and with $\epsilon = -1$. Therefore we must put

$$V_1 = \sum_{c\gamma\delta} (-1)^{\gamma}Q_{\gamma}^{(c)}(\delta)S_{-\gamma}^{(c)}H_{\delta} \tag{23}$$

into the spin-Hamiltonian with $c \leqslant 2S$ and odd. Therefore the usual term $g_{ij}H_iS_j$ is always adequate for $S \leqslant 1$ but not, in general, for higher S. Similar remarks apply to the nuclear hyperfine interaction (there we have one matrix for each component of **I**).

Having dealt with the general problem, the restrictions imposed by a site symmetry group G are easily derived. First we remark that the classification symbols in the kets $|M\rangle$ do not necessarily give any indication of the behaviour of those kets under the operations of G. If a set of states with true spin S breaks up into the irreducible representations $\sum\Gamma_i$ under G there is no need for our set of $(2S+1)$ states to span the same set of Γ_i. They often do however, or at least the sets of matrix elements of any operator ρ have the same transformation properties as if they did†, so we consider that case now. We also suppose the elements of G operate also on the nuclear moment vector **I** and the external magnetic field **H**. Then the terms $\mathscr{H}_j$ in the Hamiltonian may be regarded as belonging to the unit representation of G.

Let the transformation matrix between an SM and an $S\Gamma_1M_1$ scheme for eigenkets of the true spin vector be $\langle SM|S\beta\Gamma_iM_i\rangle$, where β is inserted if Γ_i is

† i.e. like ${}^{2S+1}\Gamma$ with Γ a representation of degree one. When Γ is not the unit representation the argument given in the text is only trivially modified. Another kind of set of states is one related to a level of the free ion, e.g. in the rare earth series.

repeated. Then, by hypothesis, there exist linear combinations of our $(2S+1)$ states which may be written $|a\beta\Gamma_i M_i\rangle$, one for each choice of $\beta\Gamma_i M_i$, and having the indicated behaviour under G. Then write

$$|M\rangle = \sum_{\beta\Gamma_i M_i} \langle S\beta\Gamma_i M_i|SM\rangle |a\beta\Gamma_i M_i\rangle \tag{24}$$

for the states of the spin-Hamiltonian with M classifying the eigenstates of the fictitious spin. The $\mathscr{H}_j$ now satisfy

$$\langle a\beta\Gamma_i M_i|\mathscr{H}_j|a\beta'\Gamma_i' M_i'\rangle = f(\beta\beta')\delta(\Gamma_i\Gamma_i')\delta(M_i M_i'). \tag{25}$$

Let g belong to G. Then because g effects an orthonormal transformation on $|a\beta\Gamma_i M_i\rangle$ but does not alter β or Γ_i, and the spin-Hamiltonian $\mathscr{H}(S)$ must satisfy (25) in place of $\mathscr{H}_j$, we find

$$\langle a\beta\Gamma_i M_i|g\mathscr{H}(S)|a\beta'\Gamma_i' M_i'\rangle = f(\beta\beta')\delta(\Gamma_i\Gamma_i')\delta(M_i M_i'),$$

where g now operates only on $\mathscr{H}(S)$. From the orthogonality properties for group representations (see Weyl [13], especially section IV.1.2) it follows that if ϵ is an irreducible idempotent referring to any component other than that of the unit representation then $\epsilon\mathscr{H}(S)$ has all its matrix elements zero. Therefore the only non-zero matrix elements of $\mathscr{H}(S)$ arise from that part which is invariant under G and therefore the most general spin-Hamiltonian that we need take is that part of our previous spin-Hamiltonian which belongs to the unit representation of G.

We have established our result without using the relation (24). However, we need (24) to be true if we go on to determine the precise form of $\mathscr{H}(S)$ as a function of the fictitious spin **S**, because then we must know how **S** behaves under the elements of G and (24) assures us that we may without inconsistency define it to behave in the same way as a real vector would. This can be proved in the following way.

If the $|M\rangle$ and the $|a\beta\Gamma_i M_i\rangle$ are connected according to (24) then the matrix of any element of G within the $|M\rangle$ uniquely defines its matrix within the $|a\beta\Gamma_i M_i\rangle$ and conversely. The same is true for the matrix of the Kramers operator. Therefore providing we can choose the $|a\beta\Gamma_i M_i\rangle$ so that they give the right matrices for all these operators simultaneously, the same will be true for the $|M\rangle$ and we may define $\mathbf{S}^* = -\mathbf{S}$ and **S** to transform under G (but not necessarily under any larger group) in the same way as the true spin vector.

We choose our $|a\beta\Gamma_i M_i\rangle$ to transform correctly under G, as of course we may because of the definition of irreducible representation. Write $|a\beta\Gamma_i M_i\rangle$ as a row vector ψ. Then if ψT also transforms correctly under G we have

$$\psi TR = \psi RT$$

for all matrices of the representation. Therefore by Schur's lemma T is a multiple ϵ of the unit matrix. $|\epsilon| = 1$ because ψ and ψT are normalized. We now consider the effect of the Kramers operator on ψ. The transformed vector ψ^* forms a basis for the irreducible representation $\bar{\Gamma}_i$ having matrices $\bar{R}$ which are the complex conjugates of the R. It is well known that there are three possible types of relationship of $\bar{\Gamma}_i$ to Γ_i and the representations Γ_i can be divided accordingly into three categories [16]. In the first category R can be taken always real and by choosing ϵ appropriately we can always take the row vector ψT

to be real. This shows that the functions of any representation Γ_i of this category can be chosen to conform simultaneously to a standard behaviour under G and the Kramers operator.

In the second category $\bar{\Gamma}_i$ is equivalent to Γ_i but the matrices R cannot be chosen wholly real. Here we insist that $\psi^* = \psi S$ for some S. It can be shown that this is always possible if one accepts the corresponding assumption at the beginning of the section [17]. Suppose now φ with $\varphi^* = \varphi U$ defines the standard behaviour of Γ_i under the various operators. We assume ψ behaves under G in the same way as φ and prove that there is a number $\epsilon = \exp(i\alpha)$ such that $(\epsilon\psi)^* = (\epsilon\psi)U$. First we note that $\varphi^* \bar{R} = \phi R U = \varphi U \bar{R}$ and so we have both

$$RU = U\bar{R} \quad \text{and} \quad RS = S\bar{R}.$$

Hence

$$RSU^{-1} = S\bar{R}U^{-1} = SU^{-1}R$$

for all R and so $S = \lambda U$ for some number λ. Because φ and ψ are normalized we have $|\lambda| = 1$, so $\lambda = \exp(i\beta)$. Therefore

$$(\epsilon\psi)^* = \exp(-i\alpha)\psi \exp(i\beta)U = \exp[i(\beta - 2\alpha)](\epsilon\psi)U$$

and we put $\beta = 2\alpha$ to give our result.

Finally in the third category Γ_i and $\bar{\Gamma}_i$ are inequivalent so there is no difficulty. Again we require that ψ^* is among our set of kets when ψ is.

For G the octahedral group we now deduce that as the total magnetic field operator and the total nuclear hyperfine operator transform as A_1, the electronic parts must transform as T_1. It then follows from the known breakdown of irreducible representations of the three dimensional rotation group under G [15] that, in the most general case, we need $(\lambda+1)^2$ parameters for each of these operators when $S = 2\lambda + \frac{1}{2}$ or $2\lambda + 1$ and $\lambda(\lambda+1)$ when $S = 2\lambda$ or $2\lambda - \frac{1}{2}$. In particular we need two for $S = 1\frac{1}{2}$, four for $S = 2\frac{1}{2}$ and six for $S = 3\frac{1}{2}$ as has been remarked, in part, elsewhere [5, 6]. The general solution for the fine structure is equally easy to obtain but does not give quite such a succinct formula. For $S \leqslant 1\frac{1}{2}$ we need one parameter, i.e. merely a choice of energy zero which would usually be taken to be zero. For $S = \lambda$ or $\lambda + \frac{1}{2}$, greater than $\frac{1}{2}$ and less than six, we need λ parameters. Thus we need two for $S = 2\frac{1}{2}$ and three for $S = 3\frac{1}{2}$ as is well known [3].

I conclude by remarking that in calculating the spin-Hamiltonian $\mathscr{H}(S)$ by the second-order perturbation treatment of § 3 we can again assume that $\mathscr{H}(S)$ belongs to the unit representation of the site spinor symmetry group G. This is because we can take our states as $|a\Gamma_i M_i\rangle$ where Γ_i is an irreducible representation of G and M_i a component. Then allowing G to operate also on $\mathbf{H}$ and $\mathbf{I}$ we have equation (25) for a part $\mathscr{H}_j$ of $\mathscr{H}$, i.e. the perturbation matrix is diagonal in Γ_i, M_i and independent of M_i. It follows immediately that among our ground set of states $\mathscr{H}(S)$ is diagonal in Γ_i and M_i and, for fixed a, Γ_i, independent of M_i. Therefore we may assume $\mathscr{H}(S)$ belongs to the unit representation of G.

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