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1972 J. Phys. A: Gen. Phys. 5 1649

(http://iopscience.iop.org/0022-3689/5/12/003)

J. Phys. A: Gen. Phys., Vol. 5, December 1972. Printed in Great Britain. 

# The spin hamiltonian

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MS received 16 June 1972

**Abstract.** We derive a spin hamiltonian $V(S)$ for the $g$ fold degenerate level of a system perturbed in first order by a physical perturbation $V$; the derivation explicitly relates the coefficients $a, b, c, \ldots$ of $V(S)$ to the matrix elements $V_{MM'}$ of $V$ between the zero order physical basis functions $\psi_M$. We show how the symmetry of $V$ and time reversal affect $V(S)$, and consider three often treated examples as an illustration of the power and unity of our method.

## 1. Introduction

The spin hamiltonian is an example of an equivalent operator, which is often used in quantum mechanics: one has a physical system and wishes to investigate an observable whose operator is $A$; $A$ is replaced by $A_{eq}$ which, when acting in a convenient 'fictitious' base $|i\rangle$, gives the information sought, for example, the energies and wavefunctions of the system. The spin hamiltonian is an operator equivalent to the physical hamiltonian of the system and is greatly used in solid state physics, particularly to describe paramagnetic ions in crystals (Abragam and Bleaney 1970, Griffith 1961, Koster and Statz 1959, Bleaney and Stevens 1953). The first explicit example is due to Pryce (1950) where the physical spin and the 'fictitious' spin in the spin hamiltonian were in fact identical (we shall explain what we mean by this later); since then its use has proliferated and has been implicitly generalized. In many spin hamiltonians in the literature the 'spin' bears no relation at all to the physical spin and, indeed, the system could be composed of spinless particles. As a result of this generalization it is often not at all obvious how to relate the coefficients $a, b, c, \ldots$ of the spin hamiltonian to the physical parameters of the problem (eg its matrix elements).

We shall show how to relate the spin hamiltonian coefficients to the physical problem for a system with a $g$ fold degenerate level acted on in first order by a perturbation $V$. In general $V$ splits the level and we want to find the resultant eigenvalues (energies) and eigenfunctions. In the absence of $V$ the level is spanned by a zero order base $\phi_1, \phi_2, \ldots \phi_g$; both $V$ and $\phi_i$ are functions of $\boldsymbol{r}_1, \boldsymbol{s}_1, \boldsymbol{r}_2, \boldsymbol{s}_2, \ldots \boldsymbol{r}_n, \boldsymbol{s}_n$, where $\boldsymbol{r}_j$ and $\boldsymbol{s}_j$ are the position and spin of the $j$th particle (electron) in the $n$ particle problem.

Let us relabel the $\phi_i$ as $\psi_{-S}, \psi_{-S+1}, \ldots \psi_M, \ldots \psi_S$, where $g = 2S+1$; this is merely a formal change of suffix and we have $\phi_i \equiv \psi_{i-S-1}$. The energies and eigenfunctions of $V$ are found by diagonalizing the $g \times g$ matrix with elements

$$V_{MM'} = \sum_{S_i} \int \psi_M(\boldsymbol{x})^* V(\boldsymbol{x}) \psi_{M'}(\boldsymbol{x}) \, \mathrm{d}\boldsymbol{r}$$

where $\boldsymbol{x} = \boldsymbol{r}_1, \boldsymbol{s}_1, \ldots \boldsymbol{r}_n, \boldsymbol{s}_n$. We remark in passing that the explicit evaluation of such an element may be difficult and tedious, and that the necessary physical understanding

and mathematical techniques may not be common to other systems studied. Now consider an operator $V(S)$ 'equivalent' to $V$ and a base we call $|SM\rangle$ which 'corresponds' to $|\psi_M\rangle$. If all the $g^2$ elements $\langle SM|V(S)|SM'\rangle$ are identical to the $V_{MM'}$ above, then it follows the energies and eigenfunctions of $V(S)$ in $|SM\rangle$ are the same as those of $V$ in $\psi_M$ (Stevens 1963, Griffith 1960). We call $V(S)$ the spin hamiltonian and define the $|SM\rangle$ to be standard angular momentum states:

$$S_z|SM\rangle = M|SM\rangle \qquad S_\pm|SM\rangle = \sqrt{\{(S\mp M)(S\pm M+1)\}}|S, M\pm 1\rangle$$

(Messiah 1961). Our $V(S)$ is a function of spin operators $S_z, S_\pm$ and our task is to find the form of this function such that

$$\langle SM|V(S)|SM'\rangle \equiv V_{MM'} \qquad \text{for all } M, M' = -S, \ldots +S. \tag{1}$$

We say that there is a correspondence between the real basis $\psi_M$ and the spin basis $|SM\rangle$ such that, if $\phi = \Sigma_M a_M\psi_M$ is an eigenfunction of the physical problem, then $|\phi\rangle = \Sigma_M a_M|SM\rangle$ is an eigenfunction of the spin hamiltonian $V(S)$.

A typical term of $V(S)$ could be $cS_+S_z^2$; now the coefficient $c$ must be related to the $V_{MM'}$ defining the physical problem; in § 2 we shall state the relationship explicitly, which we believe has not been done before. This relationship between the basic $V_{MM'}$ and the coefficients $\{c\}$ is one between the physics of the system and the mathematical formalism of the spin hamiltonian.

## 2. Analysis

An operator 0 is 'abstract', and we can perform few calculations with it, until it is defined in the base $|i\rangle$ where it acts; then (Messiah 1961)

$$0(i) = \sum_{i'i''} |i'\rangle\langle i'|0|i''\rangle\langle i''| \qquad \text{where} \qquad \sum_{i'} |i'\rangle\langle i'| = 1.$$

This means that

$$V(S) = \sum_{MM'} |SM\rangle\langle SM|V|SM'\rangle\langle SM'| \qquad \text{and} \qquad \sum_M |SM\rangle\langle SM| = 1 \tag{2}$$

for the first order case we treat; we define the complex number $\langle SM|V|SM'\rangle \equiv V_{MM'}$. (Notation: we use blunt kets $|M) \equiv |\psi_M)$ for the physical problem and sharp ones $|M\rangle \equiv |SM\rangle$ for the fictitious spin kets; we also write $V_{MM'} \equiv (M|V|M')$ if this is more convenient.) Then (2) is

$$V(S) = \sum_{MM'} V_{MM'}|M\rangle\langle M'| \tag{3}$$

which, assuming $V$ to be hermitian, can be written as

$$V(S) = \sum_{M\geqslant M'} |M\rangle\langle M'|V_{MM'}(1-\tfrac{1}{2}\delta_{MM'}) + \text{HC}, \tag{4}$$

HC means hermitian conjugate and $(1-\frac{1}{2}\delta_{MM'})$ ensures that the real quantity $V_{MM}|M\rangle\langle M|$ is not counted twice. We now need to express the operator $|M\rangle\langle M'|$ of (4) in terms of the components of $\boldsymbol{S}$; firstly

$$|M\rangle = \left(\frac{(S-M)!(S+M')!}{(S+M)!(S-M')!}\right)^{1/2} S_+^{M-M'}|M'\rangle$$

since $M \geqslant M'$ (Messiah 1961); secondly, the projection operator $|M'\rangle\langle M'|$ is

$$|SM'\rangle\langle SM'| \equiv |M'\rangle\langle M'| = \prod_{\substack{M''=-S \\ M''\neq M'}}^{+S} \frac{S_z - M''}{M' - M''} \tag{5}$$

(Löwdin 1964). Using (5), equation (3) becomes

$$V(S) = \sum_{M \geqslant M'} V_{MM'}(1 - \tfrac{1}{2}\delta_{MM'})S_+^{M-M'} \prod_{M'' \neq M'} \frac{S_z - M''}{M' - M''} \left( \frac{(S-M)!(S+M')!}{(S+M)!(S-M')!} \right)^{1/2} + \text{HC}. \tag{6}$$

This is the form of the spin hamiltonian we require; (6) contains all necessary products, powers and permutations of $S_z$, $S_+$ and $S_-$, and its complex coefficients are defined directly in terms of the physical matrix elements $V_{MM'}$. We now give $V(S)$ for degeneracies of 2, 3 and 4 (ie $S = \frac{1}{2}, 1, \frac{3}{2}$), which are of particular use for the 32 point groups $\mathscr{G}$;

$$\left.\begin{aligned}
V(\tfrac{1}{2}) &= \tfrac{1}{2}(S_z + \tfrac{1}{2})(\tfrac{1}{2}|V|\tfrac{1}{2}) - \tfrac{1}{2}(S_z - \tfrac{1}{2})(-\tfrac{1}{2}|V|-\tfrac{1}{2}) - S_+(S_z - \tfrac{1}{2})(\tfrac{1}{2}|V|-\tfrac{1}{2}) + \text{HC} \\
V(1) &= \tfrac{1}{4}S_z(S_z+1)(1|V|1) - \tfrac{1}{2}(S_z^2 - 1)(0|V|0) + \tfrac{1}{4}S_z(S_z-1)(-1|V|-1) \\
&\quad - \frac{1}{\sqrt{2}}S_+(S_z^2-1)(1|V|0) + \frac{1}{2\sqrt{2}}S_+S_z(S_z-1)(0|V|-1) \\
&\quad + \tfrac{1}{4}S_+^2S_z(S_z-1)(1|V|-1) + \text{HC} \\
64V(\tfrac{3}{2}) &= \tfrac{2}{3}(2S_z+3)(4S_z^2-1)(\tfrac{3}{2}|V|\tfrac{3}{2}) - 2(2S_z+1)(4S_z^2-9)(\tfrac{1}{2}|V|\tfrac{1}{2}) \\
&\quad + 2(2S_z-1)(4S_z^2-9)(-\tfrac{1}{2}|V|-\tfrac{1}{2}) - \tfrac{2}{3}(2S_z-3)(4S_z^2-1)(-\tfrac{3}{2}|V|-\tfrac{3}{2}) \\
&\quad - \frac{4}{\sqrt{3}}S_+(2S_z+1)(4S_z^2-9)(\tfrac{3}{2}|V|\tfrac{1}{2}) + 2S_+(2S_z-1)(4S_z^2-9)(\tfrac{1}{2}|V|-\tfrac{1}{2}) \\
&\quad - \frac{4}{3\sqrt{3}}S_+(2S_z-3)(4S_z^2-1)(-\tfrac{1}{2}|V|-\tfrac{3}{2}) \\
&\quad + \frac{4}{\sqrt{6}}S_+^2(2S_z-1)(4S_z^2-9)(\tfrac{3}{2}|V|-\tfrac{1}{2}) \\
&\quad - \frac{4}{3\sqrt{6}}S_+^2(2S_z-3)(4S_z^2-1)(\tfrac{1}{2}|V|-\tfrac{3}{2}) \\
&\quad - \tfrac{2}{9}S_+^3(2S_z-3)(4S_z^2-1)(\tfrac{3}{2}|V|-\tfrac{3}{2}) + \text{HC}
\end{aligned}\right\}. \tag{7}$$

Equations (7) may be algebraically simplified, but we have not done so since they show the form of the operators $|M\rangle\langle M'|$.

We have so far considered one degenerate level $|M)$ of the physical system; call it $|\alpha_0 M) \equiv |M)$ to distinguish it from other levels $|\alpha' M')$ with different unperturbed energy $E_{\alpha'} \neq E_{\alpha_0}$. Suppose we now wish to find the perturbed energies of $\alpha_0$ to second order in perturbation $V$; this is done by diagonalizing the spin hamiltonian

$$V^{(2)}(S) = \sum_{MM'} V^{(2)}_{MM'}|M\rangle\langle M'|$$

in the usual base $|M\rangle \equiv |\alpha_0 M\rangle$, where

$$V^{(2)}_{MM'} = (\alpha_0 M|V|\alpha_0 M') + \sum_{\alpha''(\neq\alpha_0)M''} \frac{(\alpha_0 M|V|\alpha'' M'')(\alpha'' M''|V|\alpha_0 M')}{E_{\alpha_0} - E_{\alpha''}}.$$

Thus to obtain $V^{(2)}(S)$ we replace $V_{MM'}$ by $V^{(2)}_{MM'}$ in (6). Extension to higher order perturbation involves $V^{(n)}(S)$ and $V^{(n)}_{MM'}$ (Messiah 1961).

## 3. The effect of symmetry

The spin hamiltonian is extensively used for paramagnetic impurities in crystals; thus $V$ has the often high symmetry of one of the 32 point groups $\mathcal{G}$, and symmetry considerations are important. The symmetry imposes relationships amongst the $V_{MM'}$, some being necessarily zero and the rest being known multiples of each other. Our spin hamiltonian (6) is perfectly general since it contains $g^2$ arbitrary real numbers, and it can thus apply to any of the 32 point groups.

In deriving $V(S)$ we used the zero-order base $\psi_M$; as is well known in first-order degenerate perturbation theory, any other base $\psi_{\bar{M}}$ related to $\psi_M$ by a unitary transformation $U$ is equally valid:

$$\psi_{\bar{M}} = U\psi_M = \sum_{M'} U_{\bar{M}M'}|M'),$$

where $\bar{M}, \bar{M}' = -S, \ldots +S$ as before. The spin hamiltonian can equally well be written in the base $\psi_{\bar{M}}$, when we shall call it $\bar{V}(S)$; (6) is altered only by replacing the $V_{MM'}$ by the $V_{\bar{M}\bar{M}'}$, and these are related by:

$$V_{\bar{M}\bar{M}'} = (\bar{M}|V|\bar{M}') = (M|U^+VU|M') = (UVU^+)_{MM'},$$

which, calling $\bar{V}$ the matrix with elements $V_{\bar{M}\bar{M}'}$, is

$$\bar{V} = UVU^+ \tag{8}$$

as is normal for the matrix representation of an operator. We note in particular that a group operation $U = R \subset \mathcal{G}$ affects only the coefficients $V_{MM'}$ and does *not* act on the states $|SM\rangle$; this illustrates the fictitious nature of the spin: if $\boldsymbol{S}$ were a real spin, a group operation $R$ would act on the $|SM\rangle$ according to the rotation matrices $D^{(S)}_{MM'}(\alpha\beta\gamma)$ (Messiah 1961). Equation (8) tells us how the form of $V(S)$ changes when we change the zero-order base functions; there is thus an infinity of spin hamiltonians for a given problem, each corresponding to the infinity of unitary transformations $U$. This should be borne in mind when reading the literature, where the nature of the $\psi_M$ is often ignored or only implied, and apparently different spin hamiltonians may in fact describe the same system.

## 4. Time reversal

We shall now show how a satisfactory and consistent time-reversal operator $K$ can be defined for $V(S)$. If the physical perturbation $V$ is time invariant ($KVK^+ = V$) then $K$ also must leave $V(S)$ invariant and is a symmetry operator of its group $\mathcal{G}$. This antiunitary operator $K$, like the other operators in § 3, acts on the physical states $|M)$ and the time-reversal $\bar{V}(S) = KV(S)K^+$ of $V(S)$ is by definition

$$\bar{V}(S) = \sum_{M\bar{M}'} (\bar{M}|V|\bar{M}')|\bar{M}\rangle\langle\bar{M}'| = \sum_{M\bar{M}'} (M|V|M')^*|\bar{M}\rangle\langle\bar{M}'|$$

where $|\bar{M}) = K|M)$. The physical system is either Kramers (odd number of electrons) or non-Kramers (even number), and it is always possible to choose the physical states $|M)$ such that either: (i) $|\bar{M}) \equiv K|M) = |M)$ for a non-Kramers system, or (ii) $|\bar{M}) \equiv K|M) = (-1)^{S-M}|-M)$ for a Kramers system (Abragam and Bleaney 1970, Jahn 1938). Thus

$$\bar{V}(S) = \sum (M|V|M')^*|M\rangle\langle M'| \qquad \text{(non-Kramers)}$$

and

$$\bar{V}(S) = \sum (M|V|M')^*(-1)^{2S-M-M'}|-M\rangle\langle -M'| \qquad \text{(Kramers)}.$$

These last two equations show that $V(S)$ is invariant, $\bar{V}(S) = V(S)$: in the first $(M|V|M')^* = (M|V|M')$ for 'real' states $|M)$, and in the second

$$(M|V|M')^* = (-1)^{2S-M-M'}(-M|V|-M')$$

for a Kramers system (Jahn 1938). Let the operator $|M\rangle\langle M'| \equiv F_{MM'}(S_\pm, S_z)$; then we can show from (6) that $(-1)^{2S-M-M'}|-M\rangle\langle -M'| = F_{MM'}(-S_\mp, -S_z)$. Thus the spin hamiltonian

$$V(S) = \sum V_{MM'}F_{MM'}(S_\pm, S_z)$$

has time reversal

$$\bar{V}(S) = \sum V^*_{MM'}F_{MM'}(S_\pm, S_z) \qquad \text{(non-Kramers)} \tag{9a}$$

$$\bar{V}(S) = \sum V^*_{MM'}F_{MM'}(-S_\mp, -S_z) \qquad \text{(Kramers)}. \tag{9b}$$

Equations (9) show that only for a Kramers system do we reverse the spin $\boldsymbol{S}$ under time-reversal $K$; in a non-Kramers system the spin $\boldsymbol{S}$ is invariant under $K$.

We think that (9a) has not been derived before and that our $K$ is not the same as the conventional time-reversal operator $k$, that is, as found in the literature. It is difficult to find an explicit consensus on how the conventional $k$ acts on $V(S)$ but we think it is as follows: $kck^+ = c^*$ for a constant $c$, $kAk^+ = \pm A^+ = \pm A$ for a time-even/odd hermitian operator $A$ and $k|M\rangle = (-1)^{S-M}|-M\rangle$ for the *fictitious* spin states $|M\rangle$, this last entailing spin reversal $k\boldsymbol{S}k^+ = -\boldsymbol{S}$ (Abragam and Bleaney 1970). Thus the conventional time-reversal of $V(S)$ for both Kramers *and* non-Kramers systems is

$$\begin{aligned}\bar{V}(S) \equiv kV(S)k^+ &= \sum k(M|V|M')k^+k|M\rangle\langle M'|k^+ \\ &= \sum (M|V|M')^*(-1)^{2S-M-M'}|-M\rangle\langle -M'| \\ &= \sum (M|V|M')^*F_{MM'}(-S_\mp, -S_z),\end{aligned}$$

from which we conclude that $V(S)$ is invariant only if

$$(M|V|M')^* = (-1)^{2S-M-M'}(-M|V|-M').$$

But this holds only for a Kramers system (Jahn 1938) and the conventional $k$ is thus incorrect for a non-Kramers system: our $K$ and the conventional $k$ agree for a Kramers system and our (9*a*) using $K$ gives the correct time-reversal for a non-Kramers system. We see that the conventional $k$ acts only on fictitious spin states $|M\rangle$, whereas the correct $K$ acts on physical states $|M)$.

We now show how our $K$ operates on the often-treated example of a non-Kramers doublet perturbed by a crystal field (which can split the doublet) and a magnetic field $\boldsymbol{H}$; the perturbation is $V = V_c + \boldsymbol{T}.\boldsymbol{H}$ where $\boldsymbol{T} = \Sigma_{i=1}^n \beta(\boldsymbol{l}_i + 2\boldsymbol{s}_i)$ and $\boldsymbol{H}$ are time-odd vectors under $K$. Dropping constant terms, (7) gives

$$V(\tfrac{1}{2}) = S_z\{(\tfrac{1}{2}|V|\tfrac{1}{2}) - (-\tfrac{1}{2}|V|-\tfrac{1}{2})\} + S_+(\tfrac{1}{2}|V|-\tfrac{1}{2}) + S_-(-\tfrac{1}{2}|V|\tfrac{1}{2}).$$

Choosing $|\bar{M}) = |M)$ and using the consequent forms of $(M|\boldsymbol{T}|M')$ and $(M|V_c|M')$ gives

$$V(\tfrac{1}{2}) = S_z\{(\tfrac{1}{2}|V_c|\tfrac{1}{2}) - (-\tfrac{1}{2}|V_c|-\tfrac{1}{2})\} + (S_+ + S_-)(\tfrac{1}{2}|V_c|-\tfrac{1}{2}) + (S_+ - S_-)\sum_{j=x'y'z}(\tfrac{1}{2}|T_j|-\tfrac{1}{2})H_j.$$

We now use (9a) to find the time-reversal of $V(\frac{1}{2})$, which gives $\bar{V}(\frac{1}{2}) = V(\frac{1}{2})$: the spin hamiltonian of this perturbed non-Kramers doublet *is* invariant under time-reversal $K$,

and we consider that our treatment illuminates the discussion found in the literature, where the conventional time-reversal operator is considered (Griffith 1963, Williams 1967, Mueller 1968, Washimiya *et al* 1970).

## 5. Examples

We now give three further examples which have been extensively studied and which show the utility of equation (6). Each also contains a Zeeman perturbation $\boldsymbol{T}\cdot\boldsymbol{H}$, where $\boldsymbol{T}=\beta\sum_{i=1}^{n}(\boldsymbol{l}_i+2\boldsymbol{s}_i)$.

### *5.1. A Kramers Doublet*

Pryce (1959) shows in a physically intuitive way that the relative signs of the components of the g tensor depend on the choice of physical states $|M\rangle$, and that neglect of this had led to interpretative error. We show the same using our formalism for $V(S)$. Omitting constant terms, (7) gives

$$V(\tfrac{1}{2})=S_z\{(\tfrac{1}{2}|V|\tfrac{1}{2})-(-\tfrac{1}{2}|V|-\tfrac{1}{2})\}+S_x\{(\tfrac{1}{2}|V|-\tfrac{1}{2})+(-\tfrac{1}{2}|V|\tfrac{1}{2})\}+\mathrm{i}S_y\{(\tfrac{1}{2}|V|-\tfrac{1}{2})-(-\tfrac{1}{2}|V|\tfrac{1}{2})\}.$$

With $\boldsymbol{H}=(H_{x'},H_{y'},H_{z'})$ and Zeeman perturbation $V=\boldsymbol{H}\cdot\boldsymbol{T}$ this becomes

$$\begin{aligned}V(\tfrac{1}{2})=S_z&\sum_{i=x',y',z'}\{(\tfrac{1}{2}|T_i|\tfrac{1}{2})-(-\tfrac{1}{2}|T_i|-\tfrac{1}{2})\}H_i\\&+S_x\sum_i\{(\tfrac{1}{2}|T_i|-\tfrac{1}{2})+(-\tfrac{1}{2}|T_i|\tfrac{1}{2})\}H_i+\mathrm{i}S_y\sum_i\{(\tfrac{1}{2}|T_i|-\tfrac{1}{2})-(-\tfrac{1}{2}|T_i|\tfrac{1}{2})\}H_i.\end{aligned}$$

We now transform to principal axes, where the natural crystal axes, the magnetic field axes and the spin axes are coincident, and finally have

$$\begin{aligned}V(\tfrac{1}{2})&=S_zH_z\{(\tfrac{1}{2}|T_z|\tfrac{1}{2})-(-\tfrac{1}{2}|T_z|-\tfrac{1}{2})\}\\&\quad+S_xH_x\{(\tfrac{1}{2}|T_x|-\tfrac{1}{2})+(-\tfrac{1}{2}|T_x|\tfrac{1}{2})\}+\mathrm{i}S_yH_y\{(\tfrac{1}{2}|T_y|-\tfrac{1}{2})-(-\tfrac{1}{2}|T_y|\tfrac{1}{2})\}\qquad(10)\\&\equiv g_xS_xH_x+g_yS_yH_y+g_zS_zH_z.\end{aligned}$$

We can now perform Pryce's unitary transformations $U$, giving $\bar{V}(S)$: (*a*) change the sign of one component: $U=\left[\begin{smallmatrix}1&0\\0&-1\end{smallmatrix}\right]$, that is, $|\bar{\tfrac{1}{2}})=|\tfrac{1}{2})$ and $|-\bar{\tfrac{1}{2}})=-|-\tfrac{1}{2})$.

$$\begin{aligned}\bar{V}(\tfrac{1}{2})&=S_xH_x\{(\bar{\tfrac{1}{2}}|T_x|-\bar{\tfrac{1}{2}})+(-\bar{\tfrac{1}{2}}|T_x|\bar{\tfrac{1}{2}})\}+\mathrm{i}S_yH_y\{(\bar{\tfrac{1}{2}}|T_y|-\bar{\tfrac{1}{2}})-(-\bar{\tfrac{1}{2}}|T_y|\bar{\tfrac{1}{2}})\}\\&\quad+S_zH_z\{(\bar{\tfrac{1}{2}}|T_z|\bar{\tfrac{1}{2}})-(-\bar{\tfrac{1}{2}}|T_z|-\bar{\tfrac{1}{2}})\}\\&=-S_xH_x\{(\tfrac{1}{2}|T_x|-\tfrac{1}{2})+(-\tfrac{1}{2}|T_x|\tfrac{1}{2})\}-\mathrm{i}S_yH_y\{(\tfrac{1}{2}|T_y|-\tfrac{1}{2})-(-\tfrac{1}{2}|T_y|\tfrac{1}{2})\}\\&\quad+S_zH_z\{(\tfrac{1}{2}|T_z|\tfrac{1}{2})-(-\tfrac{1}{2}|T_z|-\tfrac{1}{2})\}\\&=-g_xS_xH_x-g_yS_yH_y+g_zS_zH_z,\end{aligned}$$

that is,

$$\bar{g}_x=-g_x,\qquad\bar{g}_y=-g_y\qquad\text{and}\qquad\bar{g}_z=g_z.$$

(*b*) Interchange components: $U=\left[\begin{smallmatrix}0&1\\1&0\end{smallmatrix}\right]$, that is, $|\bar{\tfrac{1}{2}})=|-\tfrac{1}{2})$ and $|-\bar{\tfrac{1}{2}})=|\tfrac{1}{2})$.

$$\begin{aligned}\bar{V}(\tfrac{1}{2})&=S_xH_x\{(\tfrac{1}{2}|T_x|-\tfrac{1}{2})+(-\tfrac{1}{2}|T_x|\tfrac{1}{2})\}+\mathrm{i}S_yH_y\{(-\tfrac{1}{2}|T_y|\tfrac{1}{2})-(\tfrac{1}{2}|T_y|-\tfrac{1}{2})\}\\&\quad+S_zH_z\{(-\tfrac{1}{2}|T_z|-\tfrac{1}{2})-(\tfrac{1}{2}|T_z|\tfrac{1}{2})\}\\&=g_xS_xH_x-g_yS_yH_y-g_zS_zH_z,\end{aligned}$$

that is,

$$\bar{g}_x = g_x, \qquad \bar{g}_y = -g_y \qquad \text{and} \qquad \bar{g}_z = -g_z.$$

Results (*a*) and (*b*) agree with Pryce, but we cannot see with him that (*b*) is not an allowed physical transformation.

### 5.2. *Fourfold degeneracy in cubic symmetry*

This $\Gamma_8$ level in $O_h$ symmetry has degeneracy four and can be found in an odd-electron system (Bleaney 1959). It is always possible to find a unitary transformation $U$ giving states $\psi_M$ which transform under group $R \subset \mathscr{G}$ like a spin $|\frac{3}{2}M\rangle$. (This last sentence illustrates the confusion that can arise between any 'real' spin the system has and the fictitious spin $\boldsymbol{S}$ of $V(S)$; and it does not contradict our assertion in § 3 that $R$ acts on the physical states $\psi_M$, not on the spin states $|M\rangle$.) We assume that this is done and can then use tables of coupling coefficients for $\bar{\Gamma}_8 \times \Gamma_8 = \bar{U}' \times U'$ (Koster *et al* 1963, Griffith 1961). These give the relations between the $V_{MM'}$ for a Zeeman perturbation $V = \boldsymbol{H}.\boldsymbol{T}$ where $\boldsymbol{T}$ transforms like $\Gamma_4$ of $O_h$. Using the table for $\Gamma_4$ in $\bar{\Gamma}_8 \times \Gamma_8$ our equation (7) becomes

$$\begin{aligned} 64V(\tfrac{3}{2}) = {} & \tfrac{32}{3}H_zS_z(12\alpha_1 + 41\alpha_2 - 20\alpha_2 S_z^2) \\ & - 8(2\alpha_1 + \alpha_2)H_-S_+(2S_z - 3)(2S_z + 1)^2 + 2(4\alpha_1 - 3\alpha_2)H_-S_+(2S_z - 1)(4S_z^2 - 9) \\ & + \tfrac{10}{9}\alpha_2 H_+ S_+^3(2S_z - 3)(4S_z^2 - 1) + \text{HC}, \end{aligned} \tag{11}$$

where $\alpha_1$ and $\alpha_2$ are constants depending on the ion in question. Note that (7) allows us to write (11) in a form immediately suitable for calculations; previous arguments, which invoke terms like $H_x(aS_x + bS_x^3)$ have to be tediously converted into terms containing operators $S_+$ and $S_-$.

### 5.3. *An $S = \frac{5}{2}$ level in a cubic plus Zeeman field*

By an $S = \frac{5}{2}$ level we mean here an ion having sixfold degeneracy in spherical symmetry, this degeneracy being lifted by $V = V_{\text{cub}} + V_{\text{Zeem}} \equiv V_c + \boldsymbol{H}.\boldsymbol{T}$ (Koster and Statz 1959, Grant and Strandberg 1964, Abragam and Bleaney 1970).

We shall choose our physical basis $|\psi_M)$ as

| $\lvert\psi_M)$ | $\lvert U'\nu)$ | $\lvert U'\mu)$ | $\lvert U'\lambda)$ | $\lvert U'\kappa)$ | $\lvert E''\alpha'')$ | $\lvert E''\beta'')$ |
|---|---|---|---|---|---|---|
| $\lvert M\rangle$ | $\lvert -\frac{5}{2}\rangle$ | $\lvert -\frac{3}{2}\rangle$ | $\lvert -\frac{1}{2}\rangle$ | $\lvert \frac{1}{2}\rangle$ | $\lvert \frac{3}{2}\rangle$ | $\lvert \frac{5}{2}\rangle$ |

(12)

(we could have chosen the $|\psi_M)$ as the $|\frac{5}{2}M)$ of the unperturbed $S = \frac{5}{2}$ level, that is,

$$|M) = |\tfrac{5}{2}), |\tfrac{3}{2}), |\tfrac{1}{2}), \ldots$$

$$|M\rangle = |\tfrac{5}{2}\rangle, |\tfrac{3}{2}\rangle, |\tfrac{1}{2}\rangle, \ldots$$

but this is not diagonal in $V_c$; (12) is, and this is more convenient). Then

$$\begin{aligned} V(\tfrac{5}{2}) &= \sum_{MM'} (M|V|M')|M\rangle\langle M'| \\ &= \sum (M|V_c|M')\delta_{MM'}|M\rangle\langle M'| + \boldsymbol{H}.\sum (M|\boldsymbol{T}|M')|M\rangle\langle M'|. \end{aligned}$$

We call $\Delta E = E(U') - E(E'')$ the energy splitting in zero magnetic field, let $E(U') = 0$ and put $\boldsymbol{H} = H_z(0, 0, 1)$ for comparison with other treatments:

$$V(\tfrac{5}{2}) = \Delta E(|\tfrac{5}{2}\rangle\langle\tfrac{5}{2}| + |\tfrac{3}{2}\rangle\langle\tfrac{3}{2}|) + H_z \sum_{MM'} (M|T_z|M')|M\rangle\langle M'|.$$

We use tables of coupling coefficients for $\bar{U}' \times U'$, $\bar{E}'' \times E''$ and $\bar{E}'' \times U'$ to find the elements $(\mathrm{M}|T_z|M')$, whence

$$\begin{aligned} 1024V(\tfrac{5}{2}) = & -\tfrac{4}{15}\Delta E(4S_z^2 - 1)(2S_z + 3)(2S_z + 5)(4S_z - 11) \\ & + \boldsymbol{H}_z\Big\{\alpha_1(4S_z^2 - 9)(2S_z - 5)(2S_z + 1)(22S_z + 49) \\ & + \alpha_2(4S_z^2 - 25)(2S_z - 1)(2S_z - 3)(6S_z + 7) \\ & + \alpha_3(4S_z^2 - 1)(2S_z + 3)(2S_z + 5)(3S_z - 7) \\ & + \alpha_4\left(\frac{4}{3\sqrt{2}}S_+(2S_z + 5) - \frac{1}{4500}S_+^5(2S_z - 1)\right)(4S_z^2 - 9)(2S_z - 5)(2S_z + 1)\Big\} + \mathrm{HC}, \end{aligned} \tag{13}$$

the constants $\alpha_i$ and $\Delta E$ depending on the ion in question. We think that our derivation of (13) is simpler than that of the above authors; in general they use tensor decomposition (Grant and Strandberg 1964, Koster and Statz 1959, Hauser 1963).

## 6. Discussion

Our spin hamiltonian (6) is the most general one possible which describes a $g$ fold degenerate level split by a perturbation $V$ in first order. It has the advantage of giving the coefficients of the conventional spin hamiltonian directly in terms of the physical matrix elements $V_{MM'}$; for example, the coefficient $c$ of $cS_z^3$ in $V(\frac{3}{2})$ of (7) is

$$64c = \tfrac{16}{3}(\tfrac{3}{2}|V|\tfrac{3}{2}) - 8(\tfrac{1}{2}|V|\tfrac{1}{2}) + 8(-\tfrac{1}{2}|V|-\tfrac{1}{2}) + \tfrac{16}{3}(-\tfrac{3}{2}|V|-\tfrac{3}{2}).$$

Thus experimental determination of enough conventional coefficients $a, b, \ldots$ should allow us to find the $V_{MM'}$. The spin hamiltonian (6) is not the only satisfactory one; due to the commutation relations $[S_z, S_\pm] = \pm S_\pm$ and $[S_+, S_-] = 2S_z$ we can change (6) so that it looks different in form. Because of this and other factors it would often be difficult to correlate the $V_{MM'}$ with the $a, b, c, \ldots$ unless the author is quite explicit as to his base $\psi_M$.

We have derived $V(S)$ in what we consider its most convenient form—maximum use is made of $S_z$ and only the lowest powers $p$ in $S_\pm^p$ are used. There are alternative derivations (which could all be shown the same by use of the commutation relations); one is to write

$$V(S) = \sum_{MM'} V_{MM'}|M\rangle\langle M'| = \sum V_{MM'}f(M)f(M')S_-^{S-M}|S\rangle\langle S|S_+^{S-M'} \tag{14}$$

where $f(M) = \{(2S)!(S-M)!/(S+M)!\}^{1/2}$ (Messiah 1961). The operator $|S\rangle\langle S|$ can be found by iteration from

$$|S\rangle\langle S| = 1 - \sum_{M \neq S} |M\rangle\langle M| = 1 - \sum_{M \neq S} f(M)^2 S_-^{S-M}|S\rangle\langle S|S_+^{S-M}. \tag{15}$$

Iteration of (15) gives $|S\rangle\langle S|$ in powers $S_-^n S_+^n$; explicit values for degeneracies 2, 3, and 4 are

$$|\tfrac{1}{2}\rangle\langle\tfrac{1}{2}| = 1 - S_- S_+$$

$$|1\rangle\langle 1| = 1 - \tfrac{1}{2} S_- S_+$$

$$|\tfrac{3}{2}\rangle\langle\tfrac{3}{2}| = 1 - \tfrac{1}{3} S_- S_+ + \tfrac{1}{36} S_-^2 S_+^2 - \tfrac{1}{108} S_-^3 S_+^3 .$$

Substitution of $|S\rangle\langle S|$ in (14) gives a spin hamiltonian

$$V(S) = \sum_{MM'M''} V_{MM'} a_{MM'M''} S_-^{2S-M-M''} S_+^{2S-M'-M''} \tag{16}$$

where the $a_{MM'M''}$ are known. The $V(S)$ of (16) has a certain pleasing symmetry in that only terms $S_-^m S_+^n$ occur.

The spin hamiltonian is said to be of great use to the experimentalist since the only knowledge needed to use it is that of the spin operators,

$$S_z|SM\rangle = M|SM\rangle \qquad S_\pm|SM\rangle = \sqrt{\{(S \mp M)(S \pm M + 1)\}}|S, M \pm 1\rangle.$$

The conventional coefficients $a, b, c, \ldots$ are what are measured experimentally and are often quoted as fundamental data in their own right; in this sense the spin hamiltonian can be said to unite disparate problems, since they all involve calculations with $\boldsymbol{S}$ only, whereas the $V_{MM'}$ of the basic physical problems may involve specialist physics and mathematics. This unity can tend to obscure the fact that the $a, b, c, \ldots$ must be related to the more basic $V_{MM'}$: our equation (6) shows this relationship explicitly.

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